



(11) **EP 2 980 240 A1**

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

(43) Date of publication:
03.02.2016 Bulletin 2016/05

(21) Application number: **14773951.0**

(22) Date of filing: **10.03.2014**

(51) Int Cl.:
C22C 38/00 ^(2006.01) **C22C 38/14** ^(2006.01)
C22C 38/54 ^(2006.01) **C21D 8/06** ^(2006.01)
C21D 9/52 ^(2006.01)

(86) International application number:
PCT/JP2014/056103

(87) International publication number:
WO 2014/156573 (02.10.2014 Gazette 2014/40)

(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

(30) Priority: **27.03.2013 JP 2013067465**

(71) Applicant: **Kabushiki Kaisha Kobe Seiko Sho
(Kobe Steel, Ltd.)
Kobe-shi, Hyogo 651-8585 (JP)**

(72) Inventors:
• **ISHIDA, Tomonobu
Hyogo 657-0863 (JP)**
• **YOSHIHARA, Nao
Hyogo 657-0863 (JP)**

(74) Representative: **Müller-Boré & Partner
Patentanwälte PartG mbB
Friedenheimer Brücke 21
80639 München (DE)**

(54) **HIGH-STRENGTH STEEL WIRE MATERIAL EXHIBITING EXCELLENT COLD-DRAWING PROPERTIES, AND HIGH-STRENGTH STEEL WIRE**

(57) Provided are: a high-strength steel wire material which exhibits excellent cold-drawing properties and a high prescribed strength; a high-strength steel wire produced from this high-strength steel wire material; and a zinc-plated high-strength steel wire. This high-strength steel wire material is characterized by respectively including 0.80-1.3% of C, 0.1-1.5% of Si, 0.1-1.5% of Mn, more than 0% but not more than 0.03% of P, more than 0% but not more than 0.03% of S, 0.02-0.2% of Ti,

0.01-0.10% of Al, and 0.001-0.006% of N, the remainder comprising iron and unavoidable impurities. The high-strength steel wire material is further characterized in that the relationship in formula (1), namely $0.05\% \geq [\text{Ti}^*] \geq (0.0023 [\text{C}])$ (with the caveat that $[\text{Ti}^*] = (\text{the total amount of Ti - the total amount of Ti in compounds having a size of at least } 0.1 \mu\text{m})$, and $[\text{C}]$ represents the carbon content (in mass%)), is satisfied.

EP 2 980 240 A1

Description

Technical Field

5 **[0001]** The present invention relates to a high-strength steel wire that is useful as a material for a galvanized steel wire for use in a rope for a bridge or the like, and a high-strength steel wire rod to produce such a high-strength steel wire. In particular, the invention relates to a high-strength steel wire rod having good workability for wire-drawing without heat treatment after rolling.

10 Background Art

[0002] A steel wire or a steel wire strand, which is subjected to hot-dip galvanization to improve corrosion resistance, is used for a rope for use in a bridge. As a material for such a steel wire, for example, JIS G 3548 describes a steel wire having a wire diameter of 5 mm and a tensile strength TS of about 1500 to 1700 MPa. A carbon steel described in JIS G 3506 is mainly used as a material steel for the steel wire.

15 **[0003]** A steel wire as a material for the hot-dip galvanized steel wire is demanded to be reduced in manufacturing cost, and demanded to be advantageously reduced in steel usage and improved in the degree of freedom of bridge design by increasing strength of the steel wire. In other words, development of a steel wire, which has high strength and is manufactured at low cost, is demanded.

20 **[0004]** The galvanized steel wire is typically manufactured in the following manner. First, a wire rod (steel wire rod) fabricated through hot rolling is placed in a ring shape on a cooling conveyer for pearlite transformation, and is then wound up into a coil to yield a wire rod coil. Subsequently, the wire rod coil is subjected to patenting treatment for higher strength and uniform microstructure. The patenting treatment is a type of heat treatment, in which a wire rod is typically heated to about 950°C using a continuous furnace for austenization, and is then dipped in a refrigerant such as a lead bath maintained at about 500°C to produce a fine and homogeneous pearlite phase.

25 **[0005]** Subsequently, the wire rod is subjected to cold wire-drawing, so that a steel wire having a predetermined strength is produced through a work hardening function of pearlite steel. Subsequently, the steel wire is dipped in a galvanizing bath maintained at about 450°C for galvanization, so that a galvanized steel wire is produced. The galvanized steel wire may be further subjected to finish drawing. A parallel wire strand (PWS) as a bundle of such steel wires or a galvanized steel wire strand as a strand of such steel wires is used as a cable for a bridge.

30 **[0006]** In such a series of manufacturing steps, the patenting treatment causes an increase in manufacturing cost. Although the patenting treatment is effective in increasing strength of a wire rod and providing uniform quality thereof, it is disadvantageous not only in increasing manufacturing cost but also in environmental issues such as CO₂ emission and use of an environment-load substance. The hot-rolled wire rod could be advantageously drawn to be formed into a product (i.e., a steel wire) without heat treatment. Drawing the hot-rolled wire rod without heat treatment is called "rod drawing".

35 **[0007]** To achieve high strength of a wire rod subjected to rod drawing, hypereutectoid steel having a large C content must be used to compensate strength reduction caused by omitting the patenting treatment. However, proeutectoid cementite is gradually precipitated with an increase in C content, which disadvantageously reduces wire-drawability. It is therefore desired to achieve a wire rod having a good property that enables rod drawing with reduced influence of the proeutectoid cementite even if the C content is increased to increase strength (such a property is referred to as "rod drawability").

40 **[0008]** There have been provided various techniques for improving wire-drawability. For example, PTL 1 provides a technique for improving wire-drawability through cooling in a molten salt bath after hot rolling. Such a technique is referred to as direct patenting treatment. However, the direct patenting treatment using the molten salt bath leads to higher manufacturing cost and worse maintainability of equipment than air blast cooling. In addition, wire-drawability of the produced steel is low, about 80% in area reduction ratio, and a strength level of the wire (steel wire) is only about 180 to 190 kgf/mm² (1764 to 1862 MPa).

45 **[0009]** PTL 2 discloses a technique for increasing strength of a wire rod by controlling a cooling condition after hot rolling so that the patenting treatment is omitted. However, the steel produced by such a technique has a low wire-drawability, about 50% in area reduction ratio, and the wire has a considerably low strength level, about 1350 to 1500 MPa.

Citation List

55 Patent Literature

[0010]

PTL 1: Japanese Unexamined Patent Application Publication No. Hei 4(1992)-289128.

PTL 2: Japanese Unexamined Patent Application Publication No. Hei 5(1993)-287451.

Summary of Invention

Technical Problem

[0011] An object of the invention, which has been achieved in light of such circumstances, is to provide a high-strength steel wire rod having good rod drawability and predetermined high strength, and a high-strength steel wire produced of such a high-strength steel wire rod, and a high-strength galvanized steel wire.

Solution to Problem

[0012] The high-strength steel wire rod of the invention, by which the above-described object is achieved, contains C: 0.80 to 1.3% (by mass percent (the same applies to the following for the components)), Si: 0.1 to 1.5%, Mn: 0.1 to 1.5%, P: more than 0% and 0.03% or less, S: more than 0% and 0.03% or less, Ti: 0.02 to 0.2%, Al: 0.01 to 0.10%, and N: 0.001 to 0.006%, the remainder consisting of iron and inevitable impurities, where the relationship of Formula (1) is satisfied.

$$0.05\% \geq [\text{Ti}^*] \geq (0.0023 \times [\text{C}]) \cdots (1)$$

where $[\text{Ti}^*]$ represents "the total amount of Ti the amount of Ti in compounds having a size of 0.1 μm or more", and $[\text{C}]$ represents the carbon content (by mass percent)).

[0013] The amount of Ti in compounds having a size of 0.1 μm or more refers to the amount of Ti in compounds in the residue collected through filtration with a mesh having an opening of 0.1 μm .

[0014] In the high-strength steel wire rod of the invention, it is preferred that its microstructure includes a pearlite phase in an area ratio of 90% or more, and proeutectoid cementite has a maximum length of 15 μm or less. It is further preferred that the amount of dissolved N in the wire rod is more than 0% and 0.0005% or less.

[0015] The chemical composition of the high-strength steel wire rod further effectively contains, as necessary, (a) B: more than 0% and 0.010% or less, (b) Cr: more than 0% and 0.5% or less, (c) V: more than 0% and 0.2% or less, and (d) at least one element selected from the group consisting of Ni: more than 0% and 0.5% or less, Cu: more than 0% and 0.5% or less, Mo: more than 0% and 0.5% or less, Co: more than 0% and 1.0% or less, and Nb: more than 0% and 0.5% or less. The properties of the wire rod are further improved depending on a type of the component to be contained.

[0016] The invention also includes a high-strength steel wire produced through wire-drawing (for example, a drawing process) of the high-strength steel wire rod as described above. A high-strength galvanized steel wire, which is produced by performing hot-dip galvanization on the high-strength steel wire, preferably has a tensile strength TS equal to or higher than the tensile strength TS^* defined by Formula (2).

$$\text{TS}^* = -87.3D + 2234 \text{ (MPa)} \cdots (2)$$

where D represents wire diameter (mm) of the high-strength galvanized steel wire.

Advantageous Effects of Invention

[0017] According to the invention, a high-strength steel wire rod having good rod drawability and high strength is provided by strictly defining the chemical composition of the wire rod in consideration of a precipitation state of fine TiC . The steel wire produced of such a high-strength steel wire rod is greatly useful as a material for a hot-dip galvanized steel wire or a steel wire strand as a material for a rope for use in a bridge and the like.

Description of Embodiments

[0018] To solve the above-described problems, the inventors have made investigations on a relationship between a microstructure of a wire rod and wire-drawability. In particular, the inventors also have made investigations on a precipitation mechanism of proeutectoid cementite in hypereutectoid steel. As a result, it has been found that precipitation of proeutectoid cementite can be suppressed by precipitating fine TiC in the vicinity of a grain boundary. In particular, a

fine TiC having a size of 0.1 μm or less is most effective, and a sufficient amount of such fine TiC must be precipitated. As the C content in steel increases, cementite is more readily precipitated, and thus a larger amount of fine TiC is required. Such an effect is less likely to be given by coarse TiC; hence, the fine TiC is necessary to be precipitated as much as possible. It is therefore extremely important to appropriately control the precipitated amount and size distribution of TiC.

[0019] The fine TiC having a size of 0.1 μm or less is precipitated in the vicinity of an austenite grain boundary as described above. This makes it possible to decrease grain boundary energy and thus suppress precipitation of proeutectoid cementite. Although great effort and cost are required to directly determine the fine TiC, such determination can be made in a simplified manner by using electroextraction residue measurement. Specifically, while the entire amount of Ti exists in steel in a form of compounds such as TiC and TiN, TiN has a size of about 5 to 10 μm . Hence, the amount of Ti in compounds having a size of 0.1 μm or more, more specifically the amount of Ti in compounds in the residue collected through filtration with a mesh having an opening of 0.1 μm is measured and subtracted from the total amount of Ti in steel. The value obtained from such a subtraction is denoted as $[\text{Ti}^*]$, which represents the amount of fine TiC passing through the mesh. The Ti in compounds means Ti that exists in a form of a compound.

[0020] As the C content in steel increases, the proeutectoid cementite is more readily precipitated, and thus a larger amount of fine TiC is required. Based on such a relationship, the $[\text{Ti}^*]$ is required in the amount of $0.0023 \times [\text{C}]$ or more, preferably $0.0023 \times [\text{C}] + 0.001\%$ or more, and more preferably $0.0023 \times [\text{C}] + 0.005\%$ or more, where $[\text{C}]$ represents the C content. On the other hand, if a large amount of fine TiC is precipitated, grain boundaries become brittle, and toughness of the wire rod is degraded, causing longitudinal cracking during wire-drawing. From such a point, the upper limit of $[\text{Ti}^*]$ is 0.05% or less, preferably 0.03% or less, and more preferably 0.01% or less.

[0021] The steel wire rod of the invention must satisfy the basic composition of the wire rod. In addition, the chemical composition of the steel wire rod must be appropriately adjusted to appropriately control a precipitation state of TiC. From such a point, the range of each chemical component of the wire rod is determined based on the following reason.

(C: 0.80 to 1.3%)

[0022] C is an element that is effective in increasing strength. Increased C content increases strength of a cold-rolled steel wire. The C content must be 0.80% or more to ensure the target strength level of the invention. However, if the C content is excessive, proeutectoid cementite is precipitated in grain boundaries, which impairs wire-drawability. From such a point, the C content must be 1.3% or less. The lower limit of the C content is preferably 0.84% or more, and more preferably 0.90% or more. The upper limit thereof is preferably 1.2% or less, and more preferably 1.1% or less.

(Si: 0.1 to 1.5%)

[0023] Si is an effective deoxidizer, and exhibits an effect of decreasing the amount of oxide-based inclusion in steel. In addition, Si increases strength of the wire rod, and exhibits an effect of suppressing cementite granulation along with thermal history during hot-dip galvanization, and thus suppressing a reduction in strength. Si must be contained 0.1% or more so as to effectively exhibit such effects. However, an excessive Si content degrades toughness of the wire rod; hence, the Si content must be 1.5% or less. The lower limit of the Si content is preferably 0.15% or more, and more preferably 0.20% or more. The upper limit thereof is preferably 1.4% or less, and more preferably 1.3% or less.

(Mn: 0.1 to 1.5%)

[0024] Mn greatly improves hardenability of steel, and thus exhibits an effect of lowering a transformation temperature during air blast cooling, and increasing strength of a pearlite phase. Mn must be contained 0.1% or more so as to effectively exhibit such effects. However, Mn is an element that is easily segregated, and if Mn is excessively contained, hardenability of a portion, in which Mn is segregated, is excessively enhanced, and a supercooled phase such as martensite may be formed. In consideration of such influences, the upper limit of the Mn content is 1.5% or less. The lower limit of the Mn content is preferably 0.2% or more, and more preferably 0.3% or more. The upper limit thereof is preferably 1.4% or less, and more preferably 1.3% or less.

(P: more than 0% and 0.03% or less, S: more than 0% and 0.03% or less)

[0025] P and S are each segregated in prior austenite grain boundaries and thus make the grain boundaries brittle, leading to a degradation in fatigue characteristics. It is therefore basically preferred that the content of each of P and S is as low as possible, but the upper limit of the content is defined to be 0.03% or less in terms of industrial production. Each content is preferably 0.02% or less, and more preferably 0.01% or less. P and S are each an impurity that is inevitably contained in steel, and it is difficult to decrease the content thereof to 0% in terms of industrial production.

(Ti: 0.02 to 0.2%)

[0026] Ti is an element that is extremely important for the wire rod of the invention, which finely precipitates in a form of TiC in the vicinity of a grain boundary, and thus exhibits an effect of suppressing precipitation of proeutectoid cementite. The effect is due to a function of fixing C in a form of TiC in the vicinity of a grain boundary, and a function of relaxing grain boundary energy to hinder cementite nucleation by the fine TiC of 0.1 μm or less in size. In addition, as with Al, Ti exhibits an effect of refining crystal grains and an effect of improving toughness through nitride formation. Ti must be contained 0.02% or more so as to effectively exhibit such effects. However, if the Ti content is excessive, TiC is excessively precipitated, which makes the grain boundary brittle, leading to degradation in toughness. From such a point, the Ti content must be 0.2% or less. The lower limit of the Ti content is preferably 0.03% or more, and more preferably 0.04% or more. The upper limit thereof is preferably 0.18% or less, and more preferably 0.16% or less.

(Al: 0.01 to 0.10%)

[0027] Al has a strong deoxidizing function, and exhibits an effect of decreasing the amount of oxide-based inclusion in steel. In addition, Al promisingly exhibits an effect of refining crystal grains due to pinning of nitride and an effect of decreasing the amount of dissolved N. Al must be contained 0.01% or more so as to exhibit such effects. However, if the Al content is excessive, the amount of Al-based inclusion such as Al_2O_3 increases, which disadvantageously increases wire breaking rate during wire-drawing. The Al content must be 0.10% or less in order to prevent such a disadvantage. The lower limit of the Al content is preferably 0.02% or more, and more preferably 0.03% or more. The upper limit thereof is preferably 0.08% or less, and more preferably 0.06% or less.

(N: 0.001 to 0.006%)

[0028] N is dissolved in steel as an interstitial element and induces embrittlement due to strain aging, which degrades toughness of the wire rod. The upper limit of the N content (total N) in steel is therefore 0.006% or less. However, such a disadvantage is provided only by dissolved N that is dissolved in steel. A nitrogen precipitate that is precipitated in a form of nitride, i.e., N in compounds has no bad influence on toughness. Hence, the amount of dissolved N that is dissolved in steel is desirably controlled separately from N in steel (total N). The amount of dissolved N is preferably 0.0005% or less, and more preferably 0.0003% or less. On the other hand, it is difficult to decrease the amount of dissolved N in steel to less than 0.001% in terms of industrial production; hence, the lower limit of the N content in steel is 0.001% or more. The upper limit of the N content in steel is preferably 0.004% or less, and more preferably 0.003% or less.

[0029] The components defined in the invention are as described above. The remainder consists of iron and inevitable impurities. The inevitable impurities may include elements that are introduced depending on starting materials, other materials, and situations of production facilities, etc. The wire rod further effectively contains the following elements singly or in appropriate combination as necessary: (a) B: more than 0% and 0.010% or less, (b) Cr: more than 0% and 0.5% or less, (c) V: more than 0% and 0.2% or less, and (d) at least one element selected from the group consisting of Ni: more than 0% and 0.5% or less, Cu: more than 0% and 0.5% or less, Mo: more than 0% and 0.5% or less, Co: more than 0% and 1.0% or less, and Nb: more than 0% and 0.5% or less. The properties of the wire rod are further improved depending on a type of the component to be contained. The reason for defining the range of each of the elements to be contained is as follows.

(B: more than 0% and 0.010% or less)

[0030] B hinders formation of proeutectoid ferrite or proeutectoid cementite, and thus exhibits an effect of facilitating control of a microstructure to be formed into a homogeneous pearlite phase. In addition, B fixes N in steel in a form of BN, and thereby suppresses strain aging and improves toughness of the wire rod. B is preferably contained 0.0003% or more so as to effectively exhibit such effects. The B content is more preferably 0.0005% or more, and further preferably 0.0008% or more. However, if the B content is excessive, a compound with iron (B-constituent) is precipitated, which induces cracking during hot rolling; hence, the upper limit of the B content is preferably 0.010% or less. The upper limit of the B content is more preferably 0.008% or less, and further preferably 0.006% or less.

(Cr: more than 0% and 0.5% or less)

[0031] Cr reduces the lamellar spacing of pearlite, and thus exhibits an effect of improving strength or toughness of the wire rod. In addition, as with Si, Cr exhibits an effect of suppressing reduction in strength of the wire rod during galvanization. However, when the Cr content is excessive, the effects wastefully reach saturation; hence, the appropriate

Cr content is preferably 0.5% or less. The Cr content is preferably 0.001% or more and more preferably 0.05% or more so that the effects of Cr are effectively exhibited. The upper limit of the Cr content is more preferably 0.4% or less, and further preferably 0.3% or less.

5 (V: more than 0% and 0.2% or less)

10 **[0032]** V forms fine carbide/nitride (carbide, nitride, and carbonitride) and thus exhibits an effect of increasing strength and an effect of refining crystal grains. In addition, V fixes dissolved N and thus promisingly suppresses aging embrittlement. The V content is preferably 0.001% or more and more preferably 0.05% or more so that the effects of V are effectively exhibited. However, when the V content is excessive, the effects wastefully reach saturation; hence, the appropriate V content is preferably 0.2% or less. The V content is more preferably 0.18% or less, and further preferably 0.15% or less.

15 (At least one element selected from the group consisting of Ni: more than 0% and 0.5% or less, Cu: more than 0% and 0.5% or less, Mo: more than 0% and 0.5% or less, Co: more than 0% and 1.0% or less, and Nb: more than 0% and 0.5% or less)

20 **[0033]** Ni is an element that is effective in improving toughness of the steel wire subjected to wire-drawing. The Ni content is preferably 0.05% or more and more preferably 0.1% or more so that the effect of Ni is effectively exhibited. However, when the Ni content is excessive, the effect wastefully reaches saturation; hence, the appropriate Ni content is preferably 0.5% or less, more preferably 0.4% or less, and further preferably 0.3% or less.

25 **[0034]** Cu and Mo are each an element that is effective in improving corrosion resistance of the steel wire. The content of each of Cu and Mo is preferably 0.01% or more and more preferably 0.05% or more so that such an effect is effectively exhibited. However, if the Cu content is excessive, Cu reacts with S and forms CuS that is segregated in grain boundaries, causing flaws during a wire-rod manufacturing process. Hence, the upper limit of the Cu content is preferably 0.5% or less, more preferably 0.4% or less, and further preferably 0.3% or less.

30 **[0035]** Mo is also an element that is effective in improving corrosion resistance of the steel wire as with Cu. However, if the Mo content is excessive, a supercooled phase is readily formed during hot rolling, and ductility is degraded. Consequently, the upper limit of the Mo content is preferably 0.5% or less, more preferably 0.4% or less, and further preferably 0.3% or less.

35 **[0036]** Co reduces the amount of proeutectoid cementite, and thus exhibits an effect of facilitating control of a microstructure to be formed into a homogeneous pearlite phase. However, when Co is excessively contained, the effect wastefully reaches saturation. The upper limit of the Co content is therefore preferably 1.0% or less, more preferably 0.8% or less, and further preferably 0.5% or less. The Co content is preferably 0.05% or more, more preferably 0.1% or more, and further preferably 0.2% or more so that the effect of Co is effectively exhibited.

40 **[0037]** As with Ti, Nb forms nitride and thus contributes to refining crystal grains. In addition, Nb fixes dissolved N and thus promisingly suppresses aging embrittlement. However, when Nb is excessively contained, the effects wastefully reaches saturation. The upper limit of the Nb content is therefore preferably 0.5% or less, more preferably 0.4% or less, and further preferably 0.3% or less. The Nb content is preferably 0.05% or more, more preferably 0.1% or more, and further preferably 0.2% or more so that the effects of Nb are effectively exhibited.

[0038] The high-strength steel wire rod of the invention preferably has a microstructure mainly including a pearlite phase (for example, 90% or more in area ratio), but is allowed to partially (10% or less in area ratio) contain another phase (for example, proeutectoid ferrite or bainite).

45 **[0039]** In the invention, length of the proeutectoid cementite is further preferably controlled. The proeutectoid cementite, which is precipitated on a side near the center with reference to a position of D/4 (D: diameter of the wire rod) of the wire rod, causes cracking during wire-drawing, and thus causes cuppy break. The cementite (lamellar cementite) that forms a lamellar structure of pearlite has a property of rotating in response to wire-drawing and orienting in a longitudinal direction of the wire rod. However, the proeutectoid cementite cannot rotate in synchronization with a surrounding phase, and cracking occurs at an interface between the phases. The dominant factor of such rotation is the length of the proeutectoid cementite. If the length (maximum length) of the proeutectoid cementite exceeds 15 μm , the cementite is less likely to rotate, causing cracking. However, a short proeutectoid cementite easily rotates, and does not significantly impair the wire-drawability. From such a point, the length (maximum length) of the proeutectoid cementite is preferably 15 μm or less, more preferably 13 μm or less, and further preferably 10 μm or less. The lower limit of the length of the proeutectoid cementite may be, for example, but not limited to, about 0.1 μm .

55 **[0040]** The high-strength steel wire rod of the invention has good rod drawability and high strength. For example, the wire rod of the invention is allowed to have a tensile strength of 1100 MPa or more, and preferably 1200 MPa or more. The upper limit of the tensile strength is typically, but not limited to, about 1500 MPa.

[0041] The high-strength steel wire rod of the invention should be manufactured according to a usual manufacturing

condition while a billet having a chemical composition adjusted as described above is used. However, as described below, there is a preferred manufacturing condition to appropriately adjust the microstructure or the like of the wire rod.

[0042] In a typical manufacturing process of a high-carbon steel wire rod, a billet having a predetermined chemical composition is heated and austenized. The austenized billet is hot-rolled into a wire rod having a predetermined wire diameter, and is then cooled on a cooling conveyor, during which the austenite phase is transformed into a pearlite phase. In this process, a fine austenite phase is produced along with dynamic recrystallization during the hot rolling, and when TiC is precipitated concurrently with such recrystallization, the TiC can be finely dispersed in the vicinity of a grain boundary. Last four passes (four passes from the last pass to the last pass but three) of rolling most greatly affect the crystal grain size, and the area reduction strain over the last four passes is denoted as ε . When the area reduction strain ε is adjusted to be 0.4 or more, the crystal grains can be sufficiently refined, and TiC can be finely dispersed. The area reduction strain ε is represented by $\varepsilon = \ln (S_1 / S_2)$ (S_1 : cross section of a wire rod on an inlet side of a mill roll, S_2 : cross section of a wire rod on an outlet side thereof). The lower limit of the area reduction strain ε is preferably 0.42 or more, and more preferably 0.45 or more. The upper limit thereof is preferably 0.8 or less, and more preferably 0.6 or less.

[0043] The finely precipitated TiC is progressively coarsened during the cooling step after rolling. At this time, an important requirement is placing temperature of the wire rod. The placing temperature is controlled at 850 to 950°C, thereby a desired precipitation state of TiC is preferably provided. If the placing temperature exceeds 950°C, TiC is coarsened. If the placing temperature is lower than 850°C, TiC is excessively fine. The upper limit of the placing temperature is more preferably 940°C or lower, and further preferably 930°C or lower. The lower limit of the placing temperature is more preferably 870°C or higher, and further preferably 880°C or higher.

[0044] The wire rod is cooled by air blast cooling in the cooling step after rolling. At this time, if cooling rate (average cooling rate) is too high, bainite or the like is easily contained, which prevents formation of a microstructure mainly including a pearlite phase. From such a point, average cooling rate in a range of the placing temperature is preferably 20 °C/sec or less, more preferably 18 °C/sec or less, and further preferably 14 °C/sec or less. In light of reducing precipitation of the proeutectoid cementite, the lower limit of the average cooling rate is preferably 3 °C/sec or more, more preferably 4 °C/sec or more, and further preferably 5 °C/sec or more.

[0045] The high-carbon steel wire rod (high-strength steel wire rod) of the invention is good in rod drawability, and thus provides a high-strength steel wire, which exhibits desired properties such as strength and a torsion value, through wire-drawing. Such a high-strength steel wire is typically used as a high-strength galvanized steel wire after its surface is subjected to hot-dip galvanization. The wire rod of the invention is good in rod drawability, and thus can be drawn without wire breaking even if an area reduction ratio is, for example, but not limited to, more than 80%, and furthermore 83% or more. The upper limit of the area reduction ratio is, for example, but not limited to, 95% or less. The hot-dip galvanization of the steel wire should be performed for about 15 sec to 1 min in a hot-dip galvanization bath at, for example, 350°C or higher (preferably 400°C or higher) and 550°C or lower (preferably 500°C or lower). The steel wire subjected to wire-drawing such as a drawing process has higher strength with a smaller wire diameter thereof. The tensile strength TS of the high-strength galvanized steel wire is preferably equal to or higher than the tensile strength TS* defined by Formula (2), more preferably equal to or higher than TS* + 50 (MPa), and further preferably equal to or higher than TS* + 100 (MPa). The relationship of the Formula (2) is experimentally obtained.

$$TS^* = -87.3D + 2234 \text{ (MPa)} \cdots (2)$$

where D represents wire diameter (mm) of the high-strength galvanized steel wire.

[0046] This application claims the benefit of Japanese Priority Patent Application JP 2013-67465 filed on March 27, 2013, the entire contents of which are incorporated herein by reference.

[0047] Although the invention is now described in detail with an example, the invention should not be limited thereto, and modifications or alterations thereof may be made within the scope without departing from the gist described before and later, all of which are included in the technical scope of the invention.

Example

[0048] Billets (cross section 155 × 155 mm in size) having chemical compositions (steel types A to S) listed in Table 1 were prepared. The billets were each hot-rolled into a predetermined wire diameter, placed in a ring shape on a cooling conveyor, subjected to control cooling with air blast cooling for pearlite transformation, and wound in a coil shape, so that hot-rolled wire rod coils were produced. In Table 1, "-" represents "not contained".

Table 1

Steel type	Chemical composition (mass%)															
	C	Si	Mn	Al	P	S	N	Ti	Cr	V	B	Mo	Cu	Co	Ni	Nb
A	1.05	0.40	0.30	0.035	0.010	0.010	0.0042	0.06	-	-	-	-	-	-	-	-
B	0.92	0.90	0.50	0.040	0.011	0.006	0.0037	0.02	-	-	-	-	-	-	-	-
C	0.98	0.60	0.70	0.030	0.008	0.008	0.0053	0.08	0.15	-	-	-	-	-	-	-
D	0.88	0.60	0.70	0.033	0.010	0.010	0.0044	0.07	0.20	-	0.0015	-	-	-	-	-
E	1.05	0.70	0.85	0.070	0.010	0.011	0.0032	0.13	-	0.07	-	-	-	-	-	-
F	0.97	0.62	0.51	0.060	0.007	0.010	0.0046	0.08	-	-	0.0020	-	-	-	-	-
G	0.84	0.43	1.20	0.040	0.010	0.020	0.0051	0.10	-	-	-	-	-	-	-	-
H	1.02	0.60	0.70	0.030	0.020	0.008	0.0048	0.09	0.20	-	0.0022	-	-	-	-	-
I	0.90	0.50	0.81	0.090	0.007	0.010	0.0052	0.09	-	-	-	-	0.07	-	-	-
J	1.20	0.40	0.60	0.050	0.008	0.012	0.0031	0.05	-	-	-	-	-	-	0.20	-
K	0.85	0.24	0.61	0.020	0.006	0.008	0.0042	0.16	0.15	0.20	-	-	-	0.20	-	-
L	1.30	0.69	0.51	0.080	0.010	0.007	0.0058	0.18	0.20	-	-	-	-	-	-	0.21
M	0.80	0.25	0.50	0.020	0.015	0.011	0.0036	0.08	-	-	0.0012	-	-	-	-	-
N	0.93	1.43	1.50	0.030	0.010	0.010	0.0052	0.13	-	-	-	0.20	-	-	-	-
O	1.10	0.20	0.80	0.050	0.008	0.013	0.0047	0.07	0.30	-	-	-	-	-	-	-
P	0.72	0.39	0.68	0.070	0.010	0.010	0.0018	0.05	-	-	-	-	-	-	-	0.10
Q	1.40	0.40	0.58	0.060	0.008	0.011	0.0037	0.03	-	-	-	-	-	-	-	0.10
R	0.96	0.61	0.59	0.050	0.008	0.011	0.0044	0.01	-	-	-	-	-	-	-	-
S	0.89	0.69	0.70	0.080	0.008	0.010	0.0053	0.25	-	-	-	-	-	-	-	-
* The remainder: iron and inevitable impurities other than P and S																

[0049] For each of the produced hot-rolled wire rods, an unsteady portion of an edge (i.e., an end of the hot-rolled wire rod) was cut off, and then a good edge was sampled for evaluation of the hot-rolled wire rod. Specifically, the hot-rolled wire rod was evaluated in the following manner on wire diameter, $[Ti^*]$, amount of dissolved N, maximum length of proeutectoid cementite, microstructure, and tensile strength TS. In Table 2, "heating temperature" represents furnace temperature before hot rolling, and area reduction strain ε represents the total area reduction strain ε over the last four passes (four passes from the last pass to the last pass but three) of rolling. In addition, "average cooling rate" represents an average cooling rate from start of placing to a point of 800°C. For test No. 5, however, an average cooling rate from start of placing to a point of 750°C was obtained.

(Evaluation of Distribution State of Tic and Amount of Dissolved N)

[0050] $[Ti^*]$ and the amount of dissolved N were evaluated with electroextraction residue measurement. In this measurement, a 10% acetylacetone solution was used for extraction while a 0.1 μm mesh was used. The amount of Ti in compounds in a residue was measured by inductively coupled plasma (ICP) emission spectrometry, the amount of N in compounds and the amount of B in compounds therein were measured by absorption photometry, and the amount of AlN therein was measured by a bromoester method. The sample amount was 3 g for the bromoester method, and 0.5 g for each of the emission spectrometry and the absorption photometry. Since the precipitation state of TiC is changed only after heating treatment at 1000°C or higher, the precipitation state may be determined for a steel wire subjected to a drawing process or hot-dip galvanization. Using such values, the amount of $[Ti^*]$ was determined based on " $[Ti^*]$ = total Ti amount - amount of Ti in compounds having a size 0.1 μm or more", and the amount of dissolved N was determined based on "amount of dissolved N = total N amount - amount of N in compounds".

(Evaluation of Tensile Strength TS and Microstructure of Hot-Rolled Wire Rod)

[0051] An edge sample of each hot-rolled wire rod was subjected to a tensile test to determine the tensile strength TS of the hot-rolled wire rod. At this time, the average for three tests ($n = 3$) was obtained. A similar edge sample was buried in a resin and observed by a scanning electron microscope (SEM) to evaluate a state of the proeutectoid cementite. The sample was observed along a section (cross section) perpendicular to a longitudinal direction of the wire rod. The proeutectoid cementite was observed on a side near the center with reference to a position of $D/4$ (D: diameter of the wire rod) in the section, and the maximum length of the proeutectoid cementite was measured. When an end of the proeutectoid cementite was split into a plurality of branches, a value of the sum of the lengths of the branches was obtained.

[0052] Table 2 shows the fabrication conditions of the samples and evaluation results. Table 2 also shows a value of $0.0023 \times [C]$ of each hot-rolled wire rod (C is the C content of the hot-rolled wire rod).

Table 2

Test No.	Steel type	Hot-rolling condition				Hot-rolled wire rod						
		Heating temperature (°C)	Area reduction strain ε (-)	Placing temperature (°C)	Average cooling rate (°C/sec)	Wire diameter of hot-rolled wire rod (mm)	[Ti*] (mass%)	$0.0023 \times [C]$ (mass%)	Amount of dissolved N (mass%)	Maximum length of proeutectoid cementite (μm)	Microstructure	TS (MPa)
1	A	1100	0.41	900	8	14.0	0.0070	0.0024	0.0003	10	P	1293
2	B	1050	0.47	850	8	13.0	0.0040	0.0021	0.0003	8	P	1266
3	C	1100	0.43	900	8	13.5	0.0102	0.0023	0.0002	7	P	1306
4	C	1100	0.47	1000	8	13.0	0.0017	0.0023	0.0005	18	P	1267
5	C	1100	0.43	800	8	13.5	0.0600	0.0023	0.0003	10	P	1306
6	C	1100	0.27	870	8	13.0	0.0018	0.0023	0.0003	17	P	1287
7	C	1100	0.60	870	25	13.0	0.0014	0.0023	0.0003	7	P+B	1341
8	D	1000	0.51	850	14	8.0	0.0041	0.0020	0.0004	3	P	1251
9	E	1000	0.46	900	11	10.0	0.0103	0.0024	0.0002	7	P	1421
10	F	1150	0.51	920	14	80	0.0064	0.0022	0.0004	7	P	1383
11	G	1150	0.51	850	14	8.0	0.0035	0.0019	0.0002	1	P	1277
12	H	1000	0.47	880	8	13.0	0.0321	0.0023	0.0005	11	P	1321
13	I	1000	0.46	856	12	9.0	0.0261	0.0021	0.0001	5	P	1259
14	J	1150	0.45	900	17	6.4	0.0037	0.0028	0.0003	13	P	1423
15	K	1100	0.46	900	18	6.0	0.0076	0.0020	0.0001	4	P	1279
16	L	1100	0.46	900	18	6.0	0.0042	0.0030	0.0011	13	P	1463
17	M	1100	0.43	870	7	16.0	0.0037	0.0018	0.0002	1	P	1216
18	N	1150	0.47	880	8	13.0	0.0079	0.0021	0.0001	6	P	1237
19	O	1150	0.48	940	14	8.0	0.0206	0.0025	0.0015	11	P	1357
20	P	1100	0.42	820	8	13.0	0.0102	0.0017	0.0005	0	P	1067
21	Q	1100	0.54	820	8	13.0	0.0201	0.0032	0.0004	22	P	1403

(continued)

Test No.	Steel type	Hot-rolling condition				Hot-rolled wire rod						
		Heating temperature (°C)	Area reduction strain ε (-)	Placing temperature (°C)	Average cooling rate (°C/sec)	Wire diameter of hot-rolled wire rod (mm)	[Ti*] (mass%)	$0.0023 \times [C]$ (mass%)	Amount of dissolved N (mass%)	Maximum length of proeutectoid cementite (μm)	Microstructure	TS (MPa)
22	R	1100	0.43	850	8	13.0	0.0014	0.0022	0.0004	18	P	1256
23	S	1100	0.42	880	14	8.0	0.0700	0.0020	0.0001	2	P	1121

[0053] Each of the hot-rolled wire rods produced as above was formed into a predetermined wire diameter by cold wire-drawing, and was then dipped for about 30 sec in a hot-dip galvanization bath at about 440 to 460°C to yield a hot-dip galvanized steel wire. The tensile strength TS of the wire (hot-dip galvanized steel wire) was evaluated by a tensile test. At this time, the average for three tests (n = 3) was obtained. In addition, a torsion value was measured by a torsion test, and presence of longitudinal cracking was determined from observation of a fracture pattern. For the torsion value, the number of times of torsion before break was normalized with a chuck-to-chuck distance of 100 mm, and the average for three tests (n = 3) was calculated. In the three torsion tests, a sample showing at least one longitudinal crack was determined to be sample with longitudinal cracking.

[0054] Table 3 shows the results of evaluation of the hot-dip galvanized steel wire, the evaluation being made on wire diameter, an area reduction ratio after cold wire-drawing, tensile strength TS, tensile strength TS* obtained by the Formula (2), and presence of longitudinal cracking.

Table 3

Test No.	Steel type	Galvanized steel wire					
		Wire diameter (mm)	Area reduction ratio (%)	TS (MPa)	TS* (MPa)	Torsion value (the number of times)	Presence of longitudinal cracking
1	A	5.2	86.2	2103	1780	34	Not present
2	B	5.1	84.6	2034	1789	34	Not present
3	C	5.2	85.2	2140	1780	32	Not present
4	C	Wire breaking					
5	C	5.2	85.2	2104	1780	13	Present
6	C	Wire breaking					
7		Wire breaking					
8	D	2.9	86.9	2203	1981	42	Not present
9	E	3.7	86.3	2274	1911	31	Not present
10	F	2.8	87.8	2301	1990	46	Not present
11	G	2.9	86.9	2206	1981	36	Not present
12	H	5.1	84.6	2140	1789	44	Not present
13	I	3.3	86.6	2168	1946	32	Not present
14	J	2.3	87.1	2301	2033	31	Not present
15	K	2.4	84.0	2268	2024	33	Not present
16	L	2.2	86.6	2311	2042	22	Not present
17	M	5.8	86.9	2312	1728	43	Not present
18	N	5.2	84.0	2097	1780	37	Not present
19	O	3.2	84.0	2234	1955	21	Not present
20	P	4.5	88.0	1890	1841	34	Not present
21	Q	Wire breaking					
22	R	Wire breaking					
23	S	3.2	84.0	2031	1955	11	Present

[0055] The following consideration can be made from such results. Specifically, Test Nos. 1 to 3 and 8 to 19 each satisfy all the requirements defined in the invention, in which a pearlite phase occupies at least 90% (by area percent) of the microstructure thereof. In addition, any defect such as wire breaking is not found during wire-drawing, and good wire strength and good torsion characteristics are shown after hot-dip galvanization treatment. Among them, each of Test Nos. 16 and 19 has a slightly large amount of dissolved N and a slightly low torsion value.

[0056] In contrast, Test Nos. 4 to 7 and 20 to 23 are examples that each do not satisfy one of the requirements defined in the invention (or do not satisfy a further preferred requirement), in which a defect such as wire breaking is found during wire-drawing, or wire strength or torsion characteristics is/are bad after hot-dip galvanization treatment.

[0057] Among them, for Test No. 4, the placing temperature is as high as 1000°C, and the amount of [Ti*] is small (i.e., TiC is coarsened, and the maximum length of the proeutectoid cementite exceeds 15 μm.); hence, the proeutectoid cementite cannot be suppressed, and wire breaking occurs during wire-drawing. For Test No. 5, the placing temperature is as low as 800°C, and the amount of [Ti*] is excessively large (i.e., TiC is excessively refined); hence, grain boundaries become brittle, and longitudinal cracking occurs.

[0058] For Test No. 6, the area reduction strain ϵ over the last four passes is small, and crystal grains are not sufficiently refined, and thus the amount of [Ti*] is small (i.e., TiC is not refined. Furthermore, the maximum length of the proeutectoid cementite exceeds 15 μm.); hence, the proeutectoid cementite cannot be suppressed, and wire breaking occurs during wire-drawing. For Test No. 7, cooling rate is high, and the microstructure includes a mixed phase of pearlite and bainite (area ratio of bainite: 40%); hence, drawability is degraded, and wire breaking occurs during wire-drawing.

[0059] Test No. 20 is an example using steel (steel type P) having a low C content, for which strength is low. Test No. 21 is an example using steel (steel type Q) having an excessively high C content, for which the proeutectoid cementite cannot be suppressed, and wire breaking occurs.

[0060] Test No. 22 is an example using steel (steel type R) having a low Ti content, for which the proeutectoid cementite cannot be suppressed, and wire breaking occurs. Test No. 23 is an example using steel (steel type S) having an excessively high Ti content, for which the amount of [Ti*] is excessive, and longitudinal cracking occurs.

Industrial Applicability

[0061] The wire rod of the invention has good rod drawability and high strength. Hence, the wire rod is preferred as a material for a hot-dip galvanized steel wire or a steel wire strand as a material for a rope for use in a bridge and the like, which is thus extremely useful in industry.

Claims

1. A high-strength steel wire rod having good rod drawability, comprising:

C: 0.80 to 1.3% (by mass percent (the same applies to the following for the components));

Si: 0.1 to 1.5%;

Mn: 0.1 to 1.5%;

P: more than 0% and 0.03% or less;

S: more than 0% and 0.03% or less;

Ti: 0.02 to 0.2%;

Al: 0.01 to 0.10%; and

N: 0.001 to 0.006%,

the remainder consisting of iron and inevitable impurities,

wherein a relationship of Formula (1) is satisfied

$$0.05\% \geq [\text{Ti}^*] \geq (0.0023 \times [\text{C}]) \cdots (1)$$

where [Ti*] represents "the total amount of Ti - the amount of Ti in compounds having a size of 0.1 μm or more", and [C] represents the carbon content (by mass percent)).

2. The high-strength steel wire rod according to claim 1, wherein a microstructure includes a pearlite phase having an area ratio of 90% or more, and proeutectoid cementite has a maximum length of 15 μm or less.

3. The high-strength steel wire rod according to claim 1, wherein the amount of dissolved N is more than 0% and 0.0005% or less.

4. The high-strength steel wire rod according to claim 2, wherein the amount of dissolved N is more than 0% and 0.0005% or less.

5. The high-strength steel wire rod according to any one of claims 1 to 4, further comprising one or more of B, Cr, V, and M, M representing at least one element selected from the group consisting of Ni, Cu, Mo, Co, and Nb, in the proportions of B: more than 0% and 0.010% or less, Cr: more than 0% and 0.5% or less, V: more than 0% and 0.2% or less, Ni: more than 0% and 0.5% or less, Cu: more than 0% and 0.5% or less, Mo: more than 0% and 0.5% or less, Co: more than 0% and 1.0% or less, and Nb: more than 0% and 0.5% or less.
6. A high-strength steel wire that is produced through wire-drawing of the high-strength steel wire rod according to any one of claims 1 to 4.
7. A high-strength steel wire that is produced through wire-drawing of the high-strength steel wire rod according to claim 5.
8. A high-strength galvanized steel wire produced by performing hot-dip galvanization on the high-strength steel wire according to claim 6, wherein the high-strength galvanized steel wire has a tensile strength TS equal to or higher than tensile strength TS* defined by Formula (2)

$$TS^* = -87.3D + 2234 \text{ (MPa)} \cdots (2)$$

where D represents wire diameter (mm) of the high-strength galvanized steel wire.

9. A high-strength galvanized steel wire produced by performing hot-dip galvanization on the high-strength steel wire according to claim 7, wherein the high-strength galvanized steel wire has a tensile strength TS equal to or higher than tensile strength TS* defined by Formula (2)

$$TS^* = -87.3D + 2234 \text{ (MPa)} \cdots (2)$$

where D represents wire diameter (mm) of the high-strength galvanized steel wire.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/056103

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/00(2006.01)i, C22C38/14(2006.01)i, C22C38/54(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)
C22C38/00, C22C38/14, C22C38/54, 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 1996-2014
Kokai Jitsuyo Shinan Koho 1971-2014 Toroku Jitsuyo Shinan Koho 1994-2014

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.
X Y A	JP 2012-97300 A (Kobe Steel, Ltd.), 24 May 2012 (24.05.2012), claims; paragraph [0037], table 1, steel types G, L, P; paragraphs [0040] to [0044]; paragraph [0047], table 3, test no.7, 12, 16; paragraph [0055], table 6, test no.7, 12, 16 & US 2013/0216423 A1 & EP 2634280 A1 & WO 2012/057070 A1 & CA 2812469 A & KR 10-2013-0058075 A	5, 7 9 1-4, 6, 8
Y A	JP 8-296022 A (Nippon Steel Corp.), 12 November 1996 (12.11.1996), claims (Family: none)	9 1-8

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

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"&" document member of the same patent family
"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	

Date of the actual completion of the international search
08 May, 2014 (08.05.14)

Date of mailing of the international search report
20 May, 2014 (20.05.14)

Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/056103

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	JP 2003-96544 A (Nippon Steel Corp.), 03 April 2003 (03.04.2003), claims; paragraph [0040] (Family: none)	9 1-8
A	JP 2010-270391 A (Nippon Steel Corp.), 02 December 2010 (02.12.2010), entire text & US 2012/0014831 A1 & EP 2532764 A1 & WO 2011/092905 A & KR 10-2011-0101231 A & CN 102301024 A & MX 2011008034 A	1-9
A	JP 2007-39799 A (Nippon Steel Corp.), 15 February 2007 (15.02.2007), entire text & US 2009/0151824 A1 & EP 1900837 A1 & WO 2007/001054 A1 & KR 10-2008-0017464 A & CN 101208445 A	1-9
A	JP 2000-192148 A (Kobe Steel, Ltd.), 11 July 2000 (11.07.2000), entire text (Family: none)	1-9

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP HEI41992289128 A [0010]
- JP HEI51993287451 A [0010]
- JP 2013067465 A [0046]