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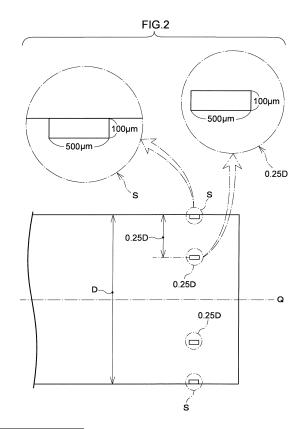
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#### (54) HIGH STRENGTH STEEL WIRE

(57) A high-strength steel wire includes a predetermined chemical composition. In the high-strength steel wire, a metallographic microstructure includes a pearlite structure of not less than 95% by area, an average aspect ratio R of a pearlite block, measured in a surface layer in a cross section in an axial direction including an axis of the steel wire, is 2.0 or more, assuming that a diameter of the steel wire is D, a ratio of an average aspect ratio measured in the surface layer to an average aspect ratio measured at a position of 0.25D is 1.1 or more in the cross section in the axial direction including the axis of the steel wire, and a tensile strength of the steel wire is 1,800 MPa or more.



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#### Description

Technical Field

5 **[0001]** The present disclosure relates to a high-strength steel wire.

**Background Art** 

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**[0002]** Steel wires have been applied to, for example, civil engineering and building structure applications such as wires for ropes and wires for bridges. The wires for ropes and the wires for bridges have been produced using, for example, a steel wire obtained by performing patenting treatment of a piano wire rod to have a pearlite structure, followed by wire drawing and aging treatment of the piano wire.

**[0003]** Patent Document 1 proposes a high-strength steel wire in which the average aspect ratio of plate-shaped cementite in pearlite is set to 30 or less in a region having a depth of at least 1/10 d of the surface layer of the steel wire (d represents the radius of the steel wire).

[0004] Patent Document 2 proposes a high-strength steel wire in which the hardness of a region from a surface to 0.1 D is set to not more than 1.1 times internal hardness assuming that the wire diameter of the steel wire is D. [0005]

Patent Document 1: Japanese Patent Application Laid-Open (JP-A) No. 2004-360005

Patent Document 2: JP-A No. 2009-280836

#### SUMMARY OF INVENTION

#### 25 Technical Problem

**[0006]** In recent years, for example, high-strength steel wires having a tensile strength of 1,800 MPa or more have been demanded for the purpose of, e.g., reducing construction costs and reducing the weights of structures in the case of applying the steel wires to civil engineering and building structure applications.

[0007] However, the hydrogen embrittlement resistance of a steel wire may be deteriorated with increasing the strength of the steel wire. Accordingly, further improvement in the hydrogen embrittlement resistance of high-strength steel wires has been demanded.

[0008] An object of the present disclosure is to provide a high-strength steel wire having high strength and excellent hydrogen embrittlement resistance.

Solution to Problem

[0009] Means for solving the problem described above includes the following aspects.

- (1) A high-strength steel wire including a chemical composition including, in terms of % by mass: C : from 0.70 to 1.20%, Si : from 0.10 to 2.00%, Mn : from 0.20 to 1.00%, P : 0.030% or less, S : 0.030% or less, N : from 0.0010 to 0.0100%, Al : from 0 to 0.100%, Cr : from 0 to 2.00%, V : from 0 to 0.30%, B : from 0 to 0.0050%, Ti : from 0 to 0.050%, Nb : from 0 to 0.050%, Zr : from 0 to 0.050%, Ni : from 0 to 2.00%, Cu : from 0 to 1.00%, Sn : from 0 to 0.50%, Mg : from 0 to 0.010%, and Ca : from 0 to 0.010%, the balance being Fe and impurities, wherein: a metallographic microstructure includes a pearlite structure having an area ratio of 95% or more, an average aspect ratio R of a pearlite block, measured in a surface layer in a cross section in an axial direction including an axis of the steel wire, is 2.0 or more, assuming that a diameter of the steel wire is D, a ratio of an average aspect ratio of pearlite block, measured in the surface layer, to an average aspect ratio of pearlite block, measured at a position of 0.25D, is 1.1 or more in the cross section in the axial direction including the axis of the steel wire, and a tensile strength of the steel wire is 1,800 MPa or more.
  - (2) The high-strength steel wire according to the above (1), wherein the chemical composition includes, in terms of % by mass, one or more of: Al: from 0.005 to 0.100%, Cr: from 0.01 to 2.00%, V: from 0.01 to 0.30%, B: from 0.0001 to 0.0050%, Ti: from 0.001 to 0.050%, Nb: from 0.001 to 0.050%, Zr: from 0.001 to 0.050%, or Ni: from 0.01 to 2.00%.
  - (3) The high-strength steel wire according to the above (1) or (2), wherein a content of Al in the chemical composition is, in terms of % by mass, from more than 0.005 to 0.100%.
    - (4) The high-strength steel wire according to any one of the above (1) to (3), wherein the steel wire has a diameter of from 2.5 mm to 9.5 mm.

#### Advantageous Effects of Invention

[0010] According to the present disclosure, a high-strength steel wire having high strength and excellent hydrogen embrittlement resistance can be provided.

#### BRIEF DESCRIPTION OF DRAWINGS

#### [0011]

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Fig. 1 is a schematic view illustrating a cross section orthogonal to the direction of an axis including the axis of a steel wire which is a high-strength steel wire of the present disclosure.

Fig. 2 is a schematic view illustrating a cross section in the direction of an axis including the axis of a steel wire which is a high-strength steel wire of the present disclosure.

#### **DESCRIPTION OF EMBODIMENTS**

[0012] For suppressing the deterioration of the hydrogen embrittlement resistance of a high-strength steel wire having a tensile strength of 1,800 MPa or more, it is effective to allow the metallographic microstructure of the steel wire to be a pearlite structure in which a pearlite block extends along the direction of the axis of the steel wire (the longitudinal direction of the steel wire). The pearlite structure includes a layer structure of a cementite phase and a ferrite phase. The layer structure forms hydrogen intrusion resistance to the growth of a crack (hydrogen embrittlement resistance). In a case in which the pearlite block extends along the direction of the axis of the steel wire, the orientation of the layer structure of the pearlite structure becomes uniform, and therefore, the deterioration of the hydrogen embrittlement resistance is suppressed.

[0013] In other words, even when the strength of the steel wire is 1,800 MPa or more, the steel wire can have excellent hydrogen embrittlement resistance in a case in which the metallographic microstructure satisfies all of the following conditions.

- 1) The metallographic microstructure is a pearlite structure having an areal ratio of 95% or more.
- 2) The average aspect ratio R of the pearlite block, measured in a surface layer in a cross section in the direction of an axis including the axis of the steel wire, is 2.0 or more.
- 3) Assuming that the diameter of the steel wire is D, (average aspect ratio of pearlite block, measured in surface layer)/(average aspect ratio of pearlite block, measured at a position of 0.25D) in the cross section in the direction of the axis including the axis of the steel wire is 1.1 or more.

[0014] Accordingly, the high-strength steel wire of the present disclosure is a steel wire having high strength and excellent hydrogen embrittlement resistance, and is therefore useful in, for example, applications such as wires for ropes and wires for bridges, used in civil engineering and building structures.

[0015] Herein, "cross section in direction of axis including axis of steel wire" refers to a cross section that is cut along the direction of the axis (the longitudinal direction, i.e., the wire drawing direction) of a steel wire, including the central axis of the steel wire, and that is parallel to the direction of the central axis.

[0016] Herein, "central axis" refers to an imaginary line that passes through the center point of a cross section orthogonal to the direction of the axis (the longitudinal direction) of a steel wire, and that extends in the direction of the axis.

[0017] Referring now to Fig. 2, Fig. 2 is a schematic view illustrating a cross section in the direction of an axis including the axis of a steel wire. In Fig. 2, S represents a surface layer, Q represents a central axis, and D represents the diameter of the steel wire. As illustrated in Fig. 2, the cross section in the direction of the axis including the axis of the steel wire refers to a plane cut along a plane parallel to the central axis Q along the central axis Q of the steel wire in the direction of the central axis Q.

[0018] Herein, "surface layer" refers to a region from the surface of a steel wire to a depth of 100 μm toward a central axis (toward a radial direction).

[0019] Herein, "0.25D" refers to a position at a depth that is 0.25 times a diameter D from the surface of a steel wire toward a central axis (toward a radial direction) assuming that the diameter of the steel wire is D.

[0020] Referring now to Fig. 1, Fig. 1 is a schematic view illustrating a cross section orthogonal to the direction of the axis of a steel wire. In Fig. 1, S represents a surface layer, D represents the diameter of the steel wire, and 0.25D represents a position of 0.25D. As illustrated in Fig. 1, the surface layer S refers to a region from the surface of the steel wire to a depth of 100  $\mu$ m toward a central axis. 0.25D refers to a position at a depth that is 0.25 times the diameter D from the surface of the steel wire toward the central axis.

[0021] A numerical range expressed by "x to y" herein includes the values of x and y in the range as the minimum and

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maximum values, respectively. A numerical range in a case in which "more than" or "less than" is attached to the numerical value of x or y in the numerical range expressed by "x to y" means a range excluding the numerical value as the minimum or maximum value.

[0022] The content of a component (element) expressed by "%" herein means "% by mass".

[0023] The content of C (carbon) may be herein occasionally expressed as "C content". The content of another element may be expressed similarly.

**[0024]** The term "step" herein encompasses not only an independent step but also a step of which the desired object is achieved even in a case in which the step is incapable of being definitely distinguished from another step.

**[0025]** First, the reason why the ranges of elements contained in the high-strength steel wire in the present disclosure are limited will be described.

**[0026]** The chemical composition of the high-strength steel wire of the present disclosure includes a chemical composition including, in terms of % by mass: C : from 0.70 to 1.20%, Si : from 0.10 to 2.00%, Mn : from 0.20 to 1.00%, P : 0.030% or less, S : 0.030% or less, N : from 0.0010 to 0.0100%, Al from 0 to 0.100%, Cr : from 0 to 2.00%, V : from 0 to 0.30%, B : from 0 to 0.0050%, Ti : from 0 to 0.050%, Nb : from 0 to 0.050%, Zr : from 0 to 0.050%, Ni: from 0 to 2.00%, Cu : from 0 to 1.00%, Sn : from 0 to 0.50%, Mg : from 0 to 0.010%, and Ca : from 0 to 0.010%, the balance being Fe and impurities.

**[0027]** C is added to secure the tensile strength of the steel wire. A C content of less than 0.70% results in generation of pro-eutectoid ferrite, thereby precluding security of a predetermined tensile strength. In contrast, a C content of more than 1.20% results in an increase in the amount of pro-eutectoid cementite, thereby deteriorating wire drawability. Therefore, the C content was set at from 0.70 to 1.20%. In view of achieving both high strength and wire drawability, the preferred range of the C content is from 0.80 to 1.15%, and the more preferred range of the C content is from 0.90 to 1.10%.

**[0028]** Si has the effects of enhancing relaxation characteristics and of enhancing a tensile strength by solid solution strengthening. A Si content of less than 0.10% causes the effects to be insufficient. In contrast, a Si content of more than 2.00% results in the saturation of the effects and in the deterioration of hot ductility, thereby deteriorating productability. Therefore, the Si content was set at from 0.10 to 2.00%. The preferred range of the Si content is from 0.20 to 1.80%, and the more preferred range of the Si content is from 0.50 to 1.50%.

**[0029]** Mn has the effect of enhancing the tensile strength of a steel after pearlite transformation. A Mn content of less than 0.20% causes the effect to be insufficient. In contrast, a Mn content of more than 1.00% results in the saturation of the effect. Therefore, the Mn content was set at from 0.20 to 1.00%. The preferred range of the Mn content is from 0.30 to 0.90%, and the more preferred range of the Mn content is from 0.40 to 0.80%.

**[0030]** P and S are contained as impurities. P and S segregate in crystal grain boundaries, thereby deteriorating hydrogen embrittlement resistance, and therefore, P and S contents should be reduced. Therefore, each of the upper limits of the P and S contents was set at 0.030%. Each of the preferred ranges of the P and S contents is 0.020% or less, and each of the more preferred ranges of the P and S contents is 0.015% or less. The lower limit values of the P and S contents are not particularly limited, and may be more than 0%. For example, each of the lower limit values may be 0.0001% or more in view of reducing a dephosphorization cost and a desulfurization cost.

**[0031]** An excessive N content results in the deterioration of hydrogen embrittlement resistance. Therefore, the N content was set at 0.0100% or less. In contrast, N has the effect of enhancing relaxation characteristics. N has the effects of forming a nitride with Al, Ti, Nb, and V and reducing a crystal particle diameter to improve ductility. A N content of less than 0.0010% precludes the obtainment of the effects. Therefore, the N content was set at from 0.0010 to 0.0100%. The N content is preferably from 0.0010 to 0.0080%, and more preferably from 0.0010 to 0.0050%.

**[0032]** The high-strength steel wire of the present disclosure may include one or more elements of Al, Cr, V, B, Ti, Nb, Zr, or Ni. In a case in which the high-strength steel wire of the present disclosure includes the elements, the steel wire may include, in terms of % by mass, one or more of: Al :from 0.005 to 0.100%, Cr : from 0.01 to 2.00%, V : from 0.01 to 0.30%, B : from 0.0001 to 0.0050%, Ti : from 0.001 to 0.050%, Nb : form 0.001 to 0.050%, Zr : 0.001 to 0.050%, or Ni from 0.01 to 2.00%.

[0033] Al is an optional element. Accordingly, an Al content may be 0%.

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[0034] Al functions as a deoxidization element. Al has the effect of forming AlN and reducing the diameters of crystal grains to improve ductility, and the effect of reducing solid solution N to improve hydrogen embrittlement resistance. In this respect, the Al content may also be more than 0%. An Al content of 0.005% or more is preferred for enabling the effects to be sufficiently obtained. The Al content is still more preferably more than 0.005%, still more preferably 0.008% or more, still more preferably 0.010% or more, and still more preferably 0.020% or more. In contrast, an Al content of more than 0.100% may result in the saturation of the effects and in the deterioration of productability. Therefore, the Al content is preferably set at 0.100% or less, and preferably set at 0.060 or less. Accordingly, the Al content in the case of the inclusion of Al is preferably set at from 0.005 to 0.100%, preferably from more than 0.005 to 0.100%, and may be from 0.008 to 0.060%.

[0035] Cr is an optional element. Accordingly, a Cr content may be 0%.

[0036] Cr has the effect of enhancing the tensile strength of a steel after pearlite transformation. In this respect, the Cr content may also be more than 0%. A Cr content of 0.01% or more is preferred for enabling the effect to be sufficiently obtained. In contrast, a Cr content of more than 2.00% results in an increase in alloy cost. In addition, the generation of a martensite structure may be facilitated, thereby deteriorating wire drawability and hydrogen embrittlement resistance.

Therefore, the Cr content in the case of the inclusion of Cr is preferably set at from 0.01 to 2.00%. The preferred range thereof is from 0.10 to 0.50%.

[0037] V is an optional element. Accordingly, a V content may be 0%.

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**[0038]** V has the effect of precipitating a carbide VC to enhance a tensile strength and to improve hydrogen embrittlement resistance. In this respect, the V content may also be more than 0%. A V content of 0.01% or more is preferred for enabling the effect to be sufficiently obtained. In contrast, a V content of more than 0.30% results in an increase in alloy cost. Therefore, the V content in the case of the inclusion of V is preferably set at from 0.01 to 0.30%. The preferred range thereof is from 0.02 to 0.10%.

[0039] B is an optional element. Accordingly, a B content may be 0%.

**[0040]** B has the effects of enhancing a tensile strength after pearlite transformation and of improving hydrogen embrittlement resistance. In this respect, the B content may also be more than 0%. A B content of 0.0001 % or more is preferred for enabling the effects to be sufficiently obtained. In contrast, a B content of more than 0.0050% results in the saturation of the effects. Therefore, the B content in the case of the inclusion of B is preferably set at from 0.0001 to 0.0050%. The preferred range thereof is from 0.0005 to 0.0020%.

**[0041]** Ti is an optional element. Accordingly, a Ti content may be 0%.

**[0042]** Ti functions as a deoxidization element, and has the effects of precipitating a carbide and a nitride to enhance a tensile strength and of reducing the diameters of crystal grains to improve ductility. In this respect, the Ti content may also be more than 0%. A Ti content of 0.001 % or more is preferred for enabling the effects to be sufficiently obtained. In contrast, a Ti content of more than 0.050% results in the saturation of the effects, and may result in the generation of a coarse oxide, thereby deteriorating wire drawability. Therefore, the Ti content in the case of the inclusion of Ti is preferably set at from 0.001 to 0.050%. The preferred range thereof is from 0.005 to 0.020%.

[0043] Nb is an optional element. Accordingly, a Nb content may be 0%.

**[0044]** Nb has the effects of precipitating a carbide and a nitride to enhance a tensile strength and of reducing the diameters of crystal grains to improve ductility. In this respect, the Nb content may be more than 0%. A Nb content of 0.001 % or more is preferred for enabling the effects to be sufficiently obtained. In contrast, a Nb content of more than 0.050% may result in the saturation of the effects and in the deterioration of twisting characteristics. Therefore, the Nb content in the case of the inclusion of Nb is preferably set at from 0.001 to 0.050%. The preferred range thereof is from 0.005 to 0.020%.

[0045] Zr is an optional element. Accordingly, a Zr content may be 0%.

**[0046]** Zr functions as a deoxidization element. Zr has the effect of forming a sulfide to reduce solid solution S and to improve hydrogen embrittlement resistance. In this respect, the Zr content may also be more than 0%. A Zr content of 0.001 % or more is preferred for enabling the effect to be sufficiently obtained. In contrast, a Zr content of more than 0.050% may result in the saturation of the effect and in the generation of a coarse oxide, thereby deteriorating wire drawability. Therefore, the Zr content in the case of the inclusion of Zr is preferably set at from 0.001 to 0.050%. The preferred range thereof is from 0.002 to 0.020%.

[0047] Ni is an optional element. Accordingly, a Ni content may be 0%.

**[0048]** Ni has the effect of suppressing the intrusion of hydrogen. In this respect, the Ni content may also be more than 0%. A Ni content of 0.01% or more is preferred for enabling the effect to be sufficiently obtained. In contrast, a Ni content of more than 2.00% results in an increase in alloy cost. In addition, the generation of a martensite structure may be facilitated, thereby deteriorating wire drawability and hydrogen embrittlement resistance. Therefore, the Ni content in the case of the inclusion of Ni is preferably set at from 0.01 to 2.00%. The preferred range thereof is from 0.05 to 0.50%.

**[0049]** One or more elements of Cu, Sn, Mg, or Ca may further be included as optional constituents. Accordingly, the contents of the elements may be, in terms of % by mass, 0%. In a case in which the elements are included, in terms of % by mass, Cu: from more than 0 to 1.00%, Sn: from more than 0 to 0.50%, Mg: from more than 0 to 0.010%, and Ca: from more than 0 to 0.010%, are acceptable.

**[0050]** The balance is Fe and impurities. In the chemical composition of the high-strength steel wire of the present disclosure, the balance excluding each element described above is Fe and impurities.

[0051] The impurities refer to components which are contained in a raw material or mixed into in a production step, and which are not intentionally incorporated into a steel.

[0052] Examples of the impurities include O (oxygen).

**[0053]** In a steel, O is contained as an impurity and present as an oxide of Al, Ti, or the like. A large O content results in the formation of a coarse oxide, thereby causing disconnection in wire drawing. Therefore, an O content is preferably reduced to 0.01% or less. The lower limit of the O content is not particularly limited, and may be, for example, more than 0%, and 0.001% or more.

**[0054]** In the high-strength steel wire of the present disclosure, a steel wire having the constituents described above is allowed to have the specific metallographic microstructure described above. The reason for limiting the metallographic microstructure will now be described.

**[0055]** In a case in which the areal ratio of the pearlite structure is less than 95% in the metallographic microstructure of the steel wire, a strength is decreased, and twisting characteristics are deteriorated. Therefore, the lower limit of the areal ratio of the pearlite structure was set to 95%. The areal ratio of the pearlite structure may be 96% or more. The upper limit of the areal ratio of the pearlite structure may be 100% or less, and may be 99% or less.

[0056] In the high-strength steel wire of the present disclosure, a region in which the average aspect ratio R of the pearlite block is defined is from the surface of the steel wire to a position having a depth of 100  $\mu$ m (surface layer). In the high-strength steel wire of the present disclosure, the rate of the average aspect ratio of the pearlite block, measured in the surface layer, with respect to the average aspect ratio of the pearlite block, measured at a position of 0.25D, is defined.

**[0057]** The extension of the pearlite block in the surface layer of the steel wire in a wire drawing direction is effective for imparting excellent hydrogen embrittlement resistance to the high-strength steel wire having a tensile strength of 1,800 MPa or more.

**[0058]** The pearlite structure includes a layer structure of a cementite phase and a ferrite phase. The layer structure forms resistance to the intrusion of hydrogen from the surface layer (hydrogen embrittlement resistance). In a case in which the pearlite block in the surface layer of the steel wire extends along the wire drawing direction (the longitudinal direction of the steel wire), the orientation of the layer structure of the pearlite structure in the surface layer of the steel wire becomes uniform. Therefore, a large number of layers having the pearlite structure are layered, and therefore, the deterioration of hydrogen embrittlement resistance is suppressed.

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**[0059]** In a case in which the average aspect ratio R of the pearlite block, measured in the surface layer of the steel wire, in a cross section in the direction of an axis including the axis of the steel wire is less than 2.0, it is impossible to obtain the effects described above. Therefore, the resistance to the intrusion of hydrogen from the surface is not sufficiently improved, and therefore, the hydrogen embrittlement resistance is deteriorated. Accordingly, the average aspect ratio R is set at 2.0 or more. The average aspect ratio R is preferably 2.5 or more, and still more preferably 3.0 or more. The upper limit of the average aspect ratio R is not particularly limited, and may be for example, 15 or less, 12 or less, and 10 or less in view of productivity.

**[0060]** The concentration of a strain on the surface layer is effective for efficiently suppressing the deterioration of the hydrogen embrittlement resistance of the steel wire. An internal strain becomes higher, thereby deteriorating hydrogen embrittlement resistance, in a case in which the rate of an average aspect ratio, expressed by the following equation, is less than 1.1, assuming that the diameter of the steel wire is D in a cross section in the direction of an axis including the axis of the steel wire. The average aspect ratio of the pearlite block, measured in the surface layer, represents the same meaning as the above-described average aspect ratio R.

**[0061]** (Equation) Rate of average aspect ratio = (average aspect ratio of pearlite block, measured in surface layer)/(average aspect ratio of pearlite block, measured at position of 0.25D)

[0062] The strain of the surface layer is equivalent to the strain of the interior, or the strain received by the interior is higher than the strain received by the surface layer in a case in which the rate of the average aspect ratio of the above equation is low (less than 1.1) in the cross section in the direction of the axis including the axis of the steel wire (i.e., in a case in which the extension of the pearlite block in the surface layer is equal to or less than that of the pearlite block in the interior). Therefore, the strain applied to the surface layer is insufficient with respect to the strain applied to the interior. In the steel wire, ductility is deteriorated, and a crack is prone to be generated, whereby hydrogen embrittlement resistance is deteriorated, in a case in which the strain is not sufficiently applied to the surface layer, and the strain of the interior is high. Therefore, a strain is concentrated on the surface layer to set the rate of the average aspect ratio of the equation described above at 1.1 or more. For example, the total reduction of area in wire drawing is increased in order to apply high strains to both of the surface layer and interior of the steel wire. As a result, the rate of the average aspect ratio of the equation described above is less than 1.1, the ductility of the steel wire is deteriorated, and a crack is prone to be generated.

**[0063]** The rate of the average aspect ratio expressed by the equation described above is preferably 1.2 or more, and more preferably 1.3 or more, in view of further suppressing the deterioration of hydrogen embrittlement resistance. The upper limit of the rate of the average aspect ratio is not particularly limited, and may be, for example, 5 or less, 3 or less, and 2 or less in view of productivity.

[0064] A method of measuring a metallographic microstructure was as follows.

[0065] The areal ratio of the pearlite structure of the steel wire was determined by the following procedure. First, a cross section orthogonal to the axis of the steel wire (hereinafter also referred to as "C cross section") is etched using picral, to allow a metallographic microstructure to appear. Then, metallographic microstructures at the center position of the surface layer (a position having a depth of 50  $\mu$ m from the surface of the steel wire) and a position having a depth of 0.25D, assuming that the diameter of the steel wire is D, are observed. The observation of the metallographic micro-

structures is performed by photographing nine spots in total of four spots formed by rotating the steel wire every  $90^{\circ}$  about the axis of the steel wire and one spot in the center by using an SEM. The metallographic microstructures in a region of  $120~\mu m$  in a circumferential direction and  $90~\mu m$  in a central direction are photographed with the SEM at a magnification of 1,000 times.

[0066] Referring now to Fig. 1, spots at which the areal ratio of the pearlite structure of the steel wire is measured are nine spots in total of four spots at the center position of the surface layer S (a position having a depth of 50  $\mu$ m from the surface of the steel wire), four spots at a position of 0.25D, and one spot in the center C.

**[0067]** Non-pearlite structures (each structure of ferrite, bainite, martensite, or pro-eutectoid cementite) in the taken structure photographs are marked by visual observation, and the areal ratio of each structure is determined by image analysis. The areal ratio of the pearlite structure is determined by subtracting the areas of the non-pearlite structures from the whole of an observed visual field. Such areal ratios are measured for two samples, and the average value of the areal ratios is determined as the pearlite areal ratio of the whole steel wire.

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[0068] The average aspect ratio of the pearlite block in the surface layer was determined by the following procedure. [0069] First, a pearlite block grain boundary in a cross section in the direction of an axis including the axis of the steel wire (hereinafter also referred to as "L cross section") is detected using an EBSD (electron back scatter diffraction pattern) device. In this case, the crystal orientation of bcc-Fe at each measurement point is measured at a measurement step set at 0.3 µm, and boundaries having an orientation difference of 9 degrees or more are determined in a region from the surface of the steel wire to 100 µm in the central axis direction (radial direction) of the steel wire and 500 µm in the longitudinal direction of the steel wire, per L cross section. A region surrounded by the boundaries is regarded as a pearlite block grain. In an obtained crystal orientation map, 20 pearlite blocks is chosen in the order from the maximum equivalent circle diameter in the group of pearlite blocks in a measurement region. Then, each aspect ratio of the 20 chosen pearlite blocks (the ratio of the major diameter to the minor diameter of each pearlite block, i.e., major diameter/minor diameter) is determined, and the average value of the aspect ratios of the 20 pearlite blocks is determined. Four samples in total sampled from two spots in both sides per L cross section and further from other sites in the steel wire are investigated in the pearlite block, and the average value of the average aspect ratios of eight spots in total is regarded as the average aspect ratio of the pearlite block in the surface layer.

[0070] Then, the average aspect ratio of the pearlite blocks at eight spots in total is similarly determined in a region of 100  $\mu$ m in the direction of a central axis about a position having a depth of 0.25D from the surface of the steel wire, assuming that the diameter of the steel wire is D, and 500  $\mu$ m in a longitudinal direction steel wire in the samples in a similar manner. The rate thereof to the average aspect ratio of the pearlite block in the surface layer (average aspect ratio of pearlite block, measured in surface layer)/(average aspect ratio of pearlite block, measured at position of 0.25D) is determined.

[0071] Referring now to Fig. 2, in the surface layer S, the spot at which the aspect ratio is measured is a region of 100  $\mu$ m in the direction of the central axis of the steel wire and 500  $\mu$ m in the longitudinal direction of the steel wire from the surface. In 0.25D, the spot is a region of 100  $\mu$ m in the direction of a central axis about a position having a depth of 0.25D (range of 100  $\mu$ m of up to 50  $\mu$ m in a direction from 0.25D to a surface and up to 50  $\mu$ m in a direction from 0.25D to a central axis about a position having a depth of 0.25D) and 500  $\mu$ m in the longitudinal direction of the steel wire. As illustrated in Fig. 2, the measurement is performed in the surface layer in both sides and 0.25D in both sides with respect to the central axis Q in the L cross section.

**[0072]** The tensile strength of the steel wire according to the embodiment will now be described. In a case in which the tensile strength of the steel wire is less than 1,800 MPa, the effects of reducing a construction cost and a weight become small in the case of, for example, application to an application of a civil engineering or building structure. Therefore, the lower limit of the tensile strength was set at 1,800 MPa in the high-strength steel wire of the present disclosure.

**[0073]** The upper limit of the tensile strength is not particularly limited. In a case in which the tensile strength is too high, ductility may be deteriorated, and a crack may be generated in wire drawing. In this respect, the tensile strength may be 3,000 MPa or less, and may be 2,800 MPa or less.

**[0074]** From the viewpoint of producing the steel wire having the metallographic microstructure and tensile strength described above and the viewpoint of the applications described above, the diameter (wire diameter) of the high-strength steel wire of the present disclosure is preferably from 2.5 mm to 9.5 mm, may be from 3.0 mm to 9.0 mm, and may be from 3.5 mm to 8.5 mm.

[0075] The diameter of the steel wire represents the same meaning as the wire diameter of the steel wire.

**[0076]** An example of a preferred method of producing the high-strength steel wire of the present disclosure will now be described. The method of producing the high-strength steel wire of the present disclosure is not particularly limited, and examples of the preferred production method include the following aspects.

**[0077]** The first aspect includes a step of heating a billet having a specific chemical composition to from 1,000 to 1,150°C, a step of hot-rolling the billet at a finish rolling temperature of from 800 to 950°C, to thereby obtain a wire rod, a step of directly immersing the wire rod at from 800 to 950°C in a molten salt bath at from 500 to 600°C for 50 seconds

or more, to thereby perform pearlite transformation treatment of the wire rod, a step of further water-cooling the wire rod from 400°C or more to 300°C or less, a step of performing wire drawing, at a total reduction of area of from 70 to 95%, of the wire rod subjected to the pearlite transformation treatment, and a step of performing aging treatment, at 450°C or less, of the wire rod subjected to the wire drawing.

**[0078]** The second aspect includes a step of heating a billet having a specific chemical composition to from 1,000 to 1,150°C, a step of hot-rolling the billet at a finish rolling temperature of from 800 to 950°C, to thereby obtain a wire rod, a step of air-blast-cooling the wire rod at from 800 to 950°C, to thereby perform pearlite transformation treatment of the wire rod, a step of performing wire drawing, at a total reduction of area of from 70 to 95%, of the wire rod subjected to the pearlite transformation treatment, and a step of performing aging treatment, at 450°C or less, of the wire rod subjected to the wire drawing.

**[0079]** The third aspect includes a step of heating a billet having a specific chemical composition to from 1,000 to 1,150°C, a step of hot-rolling the billet at a finish rolling temperature of from 800 to 950°C, to thereby obtain a wire rod, a step of cooling the wire rod at from 800 to 950°C and reheating the cooled wire rod in a temperature range of 950°C or more, a step of immersing the reheated wire rod in a Pb bath or a molten salt bath and maintaining the wire rod at from 500 to 600°C, to thereby perform pearlite transformation treatment of the wire rod, a step of performing wire drawing, at a total reduction of area of from 70 to 95%, of the wire rod subjected to the pearlite transformation treatment, and a step of performing aging treatment, at 450°C or less, of the wire rod subjected to the wire drawing.

**[0080]** In each of the aspects described above, the wire drawing is performed in the following manner. A strength is applied at a reduction of area of 12% or less (preferably from 3% to 9%) by using a die having an approach half angle of 10 degrees or more (preferably 20 degrees or less) in the case of wire drawing in at least a final pass at a total reduction of area ranging from 70 to 95%. In other words, such conditions may be adopted not only in the final pass but also in the final pass and plural passes including the final pass.

**[0081]** In each of the aspects described above, the chemical composition of the billet is similar to the chemical composition of the high-strength steel wire described above. The chemical composition of the billet is described below.

 $\begin{tabular}{ll} \textbf{[0082]} & The chemical composition of the billet includes: C: from 0.70 to 1.20\%, Si: from 0.10 to 2.00\%, Mn: from 0.20 to 1.00\%, P: 0.030\% or less, S: 0.030\% or less, N: from 0.0010 to 0.0100\%, Al: from 0 to 0.100\%, Cr: from 0 to 2.00\%, V: from 0 to 0.30\%, B: from 0 to 0.0050\%, Ti: from 0 to 0.050\%, Nb: from 0 to 0.050\%, Zr: from 0 to 0.050\%, Ni: from 0 to 2.00\%, Cu: from 0 to 1.00\%, Sn: from 0 to 0.50\%, Mg: from 0 to 0.010\%, and Ca: from 0 to 0.010\%, the balance being Fe and impurities. } \end{tabular}$ 

**[0083]** The aspects have been described above as the examples of the preferred method of producing the high-strength steel wire of the present disclosure. According to the aspects described above, a steel wire having high strength and excellent hydrogen embrittlement resistance can be easily produced.

#### **EXAMPLES**

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[0084] Steel types A to L having chemical compositions set forth in Table 1 were heated under conditions set forth in Table 2, hot-rolled, coiled in a ring shape, and immersed in a molten salt tank in rear of a hot-rolling line at a temperature set forth in Table 2, to be subjected to patenting treatment and to produce wire rods. Instead of immersing the steel types in the molten salt tank to be subjected to the patenting treatment, some thereof were air-blast-cooled to thereby produce wire rods. Then, the wire drawing of the obtained wire rods was performed to achieve wire diameters after the wire drawing, set forth in Table 3, and the wire rods were heated after the wire drawing and subjected to aging treatment, to thereby produce steel wires set forth in test numbers 1 to 22.

[0085] The wire rods that had been hot-rolled and then cooled were reheated under conditions set forth in Table 4 and immersed in a Pb bath at a temperature set forth in Table 4, to be subjected to patenting treatment and to produce wire rods. Then, the wire drawing of the obtained wire rods was performed to achieve wire diameters after the wire drawing, set forth in Table 5, and the wire rods were heated after the wire drawing and subjected to aging treatment, to thereby produce steel wires set forth in test numbers 23 to 25.

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v	

	Zr				0.004			0.012			0.011		
	īZ		0.25			0.18							
	qN	0.007				0.013							
	Ι				0.008		0.011					0.008	
	В				0.0011		0.0009	0.0008				0.0012	
	۸		0.03							90'0			
	Cr	0.38							0.22	0.24		0.25	
[lable l]	A	0.032	0.012	0.032	0.033	0.029	0.034	0.057	0.034	0.035	0.009		
	Z	0.0032	0.0037	0.0039	0.0039	0.0040	0.0039	0.0035	0.0037	0.0029	0.0041	0.0040	0.0040
	S	0.012	0.011	0.007	0.009	0.011	0.013	0.014	0.007	0.007	0.005	600.0	0.008
	Ь	0.013	0.014	0.012	0.017	900.0	0.012	0.011	600.0	0.007	0.012	0.010	0.011
	Mn	0.79	0.82	0.75	0.52	0.38	0.47	0.51	0.31	0.40	0.31	0.44	0.41
	Si	0.24	0.25	0.21	0.20	1.10	1.21	1.46	1.18	0.92	1.04	0.91	1.05
	Э	0.72	0.77	0.82	0.88	0.92	96.0	66'0	66'0	66'0	1.10	26'0	1.00
	Steel type	A	В	O	Q	Э	ш	9	Н	-	٢	У	٦

5		Die approach half angle in final pass	(6)	12	13	12	12	12	12	12	12	12	12	12	12	5	2	12	2	12	5	5	12	12	12
10		Reduction of area in final pass	(%)	2.7	12	7.5	5.7	5.7	7.5	2.7	5.7	5.7	5.7	5.7	15	15	5.7	20	20	20	20	20	5.7	5.7	7.5
15		Total reduction of area	(%)	0.78	0.78	88.9	87.0	87.2	84.0	84.0	9.62	81.2	82.7	8.67	0.78	87.0	88.9	84.0	84.0	9.62	82.7	88.9	84.0	89.7	81.2
20		Wire	(mm)	12.5	12.5	13.5	12.5	14.0	12.5	12.5	11.5	12.0	13.0	12.0	12.5	12.5	13.5	12.5	12.5	11.5	13.0	13.5	12.5	14.0	12.0
25		Temperature after water cooling	(0.)	210	210	210	210	210	210	210	210	210	210	210	ı	210	-	210	220	200	210	200	210	-	210
30 = 1	[Table 2]	Time for immersion in molten salt tank	(s)	63	63	63	63	63	63	63	63	63	63	63		63	-	63	63	63	63	63	63	-	63
35 40		Temperature of molten salt tank	(၁့)	550	550	550	550	550	550	550	550	550	550	550	1	550	-	550	450	550	550	550	550	-	550
45	•	Finish rolling temperature	(°C)	910	930	920	880	920	940	068	850	006	920	006	910	910	006	930	880	870	910	850	068	880	850
50		Heating temperature	(°C)	1130	1120	1130	1090	1100	1150	1090	1150	1120	1130	1140	1130	1070	1070	1110	1090	1120	1090	1080	1120	1110	1140
	=	Steel	;	⋖	4	В	C	Q	ш	ட	9	I	_	ſ	∢	В	C	Ш	ь	Э			¥	В	_
55	•	Test		-	2	က	4	2	9	2	8	6	10	11	12	13	14	15	16	17	18	19	20	21	22

									1		1										
5			Kemarks		Example	Comparative Example	Comparative Example	Comparative Example	Comparative Example	Comparative Example	Comparative Example										
10		Hydrogen embrittlement resistance	Evaluation		9	9	9	9	ŋ	ŋ	9	9	9	9	ŋ	9	9N	9N	9N	9N	9N
15		Hyd embri resi	Fracture	(h)	20	20	17	17	18	15	13	13	15	12	13	36	4.1	7.4	3.8	6.2	2.6
20		Tensile strength of	steel wire	(MPa)	2096	2108	2174	2156	2153	2291	2349	2391	2305	2374	2382	1722	2182	1890	2283	2205	2384
25		Rate between aspect ratios in	surface layer and 0.25D		1.5	1.4	1.6	1.4	1.5	1.4	1.5	1.3	1.4	1.5	1.3	1.0	1.3	1.2	1.3	1.2	1.0
30	[Table 3]	Average aspect ratio of pearlite	block in surface layer		6.9	6.1	8.2	7.0	7.5	4.8	5.1	3.3	4.2	4.5	3.6	1.7	1.8	2.0	8.	1.6	1.9
35		Areal ratio of	pearlite	(%)	96	26	26	26	26	86	86	66	86	86	66	81	96	85	86	84	86
40		Heat treatment temperature after	wire drawing	(°C)	380	380	380	400	400	400	400	400	400	410	410	380	380	380	400	400	400
45 50		Wire diameter after wire	drawing	(mm)	4.5	4.5	4.5	4.5	5.0	5.0	5.0	5.2	5.2	5.4	5.4	4.5	4.5	4.5	5.0	5.0	5.2
		Steel	type		٧	Α	В	ပ	۵	ш	ш	ტ	ェ	_	7	٧	В	O	Ш	Ь	g
55		Test	number		_	2	3	4	5	9	7	8	6	10	<del>-</del>	12	13	41	15	16	17
						1			ı	1	ı	1	Ц	ı	<b>.</b>						

5	C	Yellars		Comparative Example	Comparative Example	Example	Example	Example
10	Hydrogen embrittlement resistance	tlement stance Evaluation			9N	ŋ	9	9
15	Hyc embri resi	Fracture time	(h)	31	2.2	11	12	11
	Tensile strength of	steel wire	(MPa)	1742	2382	2308	1982	2312
25	Rate between aspect ratios in	surface layer and 0.25D		1.0	1.0	1.4	1.2	1.3
30 (continued)	Average aspect ratio of pearlite	block in surface layer		2.2	2.2	5.2	5.0	5.0
35	Areal ratio of	pearlite	(%)	91	86	86	96	86
40	Heat treatment temperature after	wire drawing	(°C)	200	410	400	400	390
50	Wire diameter after wire	drawing	(mm)	5.4	4.5	5.0	4.5	5.2
	Steel	type		-	-	ᅩ	Ш	٦
55	Test	number		18	19	20	21	22

### [Table 4]

5	Test number	Steel type	Wire diameter (mm)	Reheating temperature	Patenting temperature	Total reduction of area (%)	Reduction of area in final pass (%)	Die approach half angle in final pass (°)
	23	Е	13.0	950	580	82.1	7.5	12
10	24	F	13.5	950	580	83.4	7.5	12
10	25	I	13.0	950	580	82.1	7.5	12

5	-	Kemarks		Example	Example	Example	
	Hydrogen embrittlement resistance	Evaluation		9	ŋ	9	
10	Hydr embrit resis	Fracture time	( <del>l</del> )	16	41	13	
15	Tensile strength of	steel wire	(MPa)	2218	2297	2388	
20	Rate between aspect ratios in	surface layer and 0.25D		1.5	4.1	1.5	
30 G	Average aspectratio	Average aspectratio of pearlite block in surface layer					
35	Areal ratio of	pearlite	(%)	66	86	66	
40	Heat treatment temperature after	wire drawing	(°C)	400	400	400	
50	Wire diameter after wire	drawing	(mm)	5.5	5.5	5.5	
	Steel	type		Э	Щ	_	
55	Test	number		23	24	25	

[0086] The following tests were conducted on the steel wires.

[0087] A tensile strength test was conducted using a specimen No. 9A according to JIS Z 2241: 2011. The results are set forth in Table 3 and Table 5.

**[0088]** The areal ratio of a metallographic microstructure, the average aspect ratio R of a pearlite block, measured in a surface layer, and a rate between the average aspect ratio of the pearlite block, measured in the surface layer, and an average aspect ratio at a position of 0.25D from the surface layer (average aspect ratio of pearlite block, measured in surface layer/average aspect ratio of pearlite block, measured at position of 0.25D) were determined as described above. The results are set forth in Table 3 and Table 5.

[0089] Hydrogen embrittlement resistance was evaluated by an FIP test. Specifically, the steel wires of the test numbers 1 to 25 were immersed in a NH<sub>4</sub>SCN solution having a concentration of 20% at 50°C, a load that was 0.8 times a breaking load was loaded on the steel wires, and fracture times were evaluated. A ratio of a solution volume to a specimen surface area (solution volume/specimen surface area) was set at 12 cc/cm2. In the FIP test, 12 wires were evaluated for each steel wire, and the average value thereof was regarded as a hydrogen embrittlement time. In a case in which the hydrogen embrittlement time was 10 hours or more, it was determined that hydrogen embrittlement resistance was favorable (expressed by G in each table). In the case that did not meet the condition described above, it was determined that hydrogen embrittlement resistance was poor (expressed by NG in each table). The results are set forth in Table 3 and Table 5.

**[0090]** Each of the steel wires of the test numbers 1 to 11, and 20 to 25, satisfying all the requirements of the high-strength steel wire of the present disclosure, has a tensile strength of 1,800 MPa or more and favorable hydrogen embrittlement resistance.

**[0091]** In contrast, the steel wire of the test number 12 has a low tensile strength although having favorable hydrogen embrittlement resistance. In addition, the areal ratio of the pearlite structure, the average aspect ratio R of the pearlite block, measured in the surface layer, and (average aspect ratio of pearlite block, measured in surface layer)/(average aspect ratio of pearlite block, measured at position of 0.25D) fall outside the scope of the present disclosure.

**[0092]** In each of the steel wires of the test numbers 13 and 15, the average aspect ratio R of the pearlite block, measured in the surface layer, is less than the lower limit of the present disclosure, and hydrogen embrittlement resistance is poor.

**[0093]** In the steel wire of the test number 14, the areal ratio of the pearlite structure is less than the lower limit of the present disclosure, and hydrogen embrittlement resistance is poor.

**[0094]** In the steel wire of the test number 16, the areal ratio of the pearlite structure, and the average aspect ratio R of the pearlite block, measured in the surface layer, are less than the lower limits of the present disclosure, and hydrogen embrittlement resistance is poor.

**[0095]** In the steel wire of the test number 17, the average aspect ratio R of the pearlite block, measured in the surface layer, and (average aspect ratio of pearlite block, measured in surface layer)/(average aspect ratio of pearlite block, measured at position of 0.25D) are less than the lower limits of the present disclosure, and hydrogen embrittlement resistance is poor.

**[0096]** In the steel wire of the test number 18, the tensile strength is less than the lower limit of the present disclosure although hydrogen embrittlement resistance is favorable. In addition, the areal ratio of the pearlite structure, and (average aspect ratio of pearlite block, measured in surface layer)/(average aspect ratio of pearlite block, measured at position of 0.25D) are less than the lower limits of the present disclosure.

**[0097]** In the steel wire of the test number 19, (average aspect ratio of pearlite block, measured in surface layer)/(average aspect ratio of pearlite block, measured at position of 0.25D) is less than the lower limit of the present disclosure, and hydrogen embrittlement resistance is poor.

[0098] The entire disclosure of Japanese Patent Application No. 2016-150584 is incorporated herein by reference.

**[0099]** All documents, patent applications, and technical standards described in this specification are herein incorporated by reference to the same extent as if each individual document, patent application, or technical standard was specifically and individually indicated to be incorporated by reference.

#### 50 Claims

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1. A high-strength steel wire comprising a chemical composition comprising, in terms of % by mass:

C: from 0.70 to 1.20%, Si: from 0.10 to 2.00%, Mn: from 0.20 to 1.00%,

P: 0.030% or less, S: 0.030% or less,

N: from 0.0010 to 0.0100%,
Al: from 0 to 0.100%,
Cr: from 0 to 2.00%,
V: from 0 to 0.30%,
B: from 0 to 0.050%,
Ti: from 0 to 0.050%,
Nb: from 0 to 0.050%,
Zr: from 0 to 0.050%,
Ni: from 0 to 0.050%,

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Cu: from 0 to 1.00%, Sn: from 0 to 0.50%, Mg: from 0 to 0.010%, and Ca: from 0 to 0.010%,

the balance being Fe and impurities, wherein:

a metallographic microstructure comprises a pearlite structure having an area ratio of 95% or more, an average aspect ratio R of a pearlite block, measured in a surface layer in a cross section in an axial direction including an axis of the steel wire, is 2.0 or more,

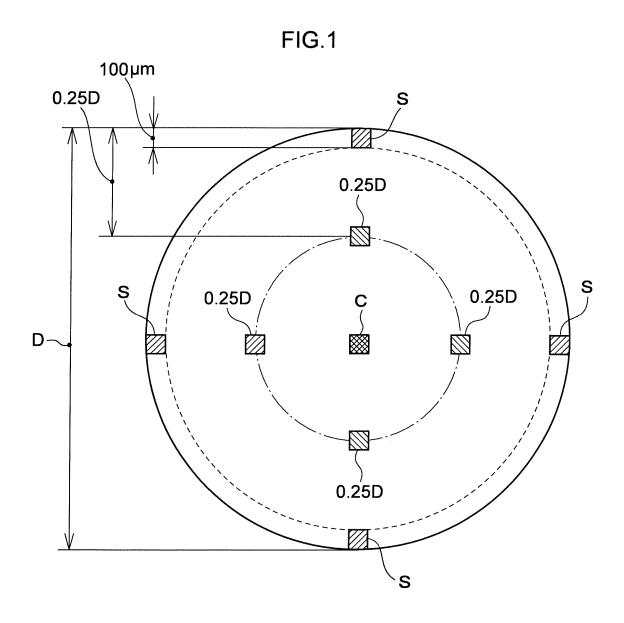
assuming that a diameter of the steel wire is D, a ratio of an average aspect ratio of pearlite block, measured in the surface layer, to an average aspect ratio of pearlite block, measured at a position of 0.25D, is 1.1 or more in the cross section in the axial direction including the axis of the steel wire, and a tensile strength of the steel wire is 1,800 MPa or more.

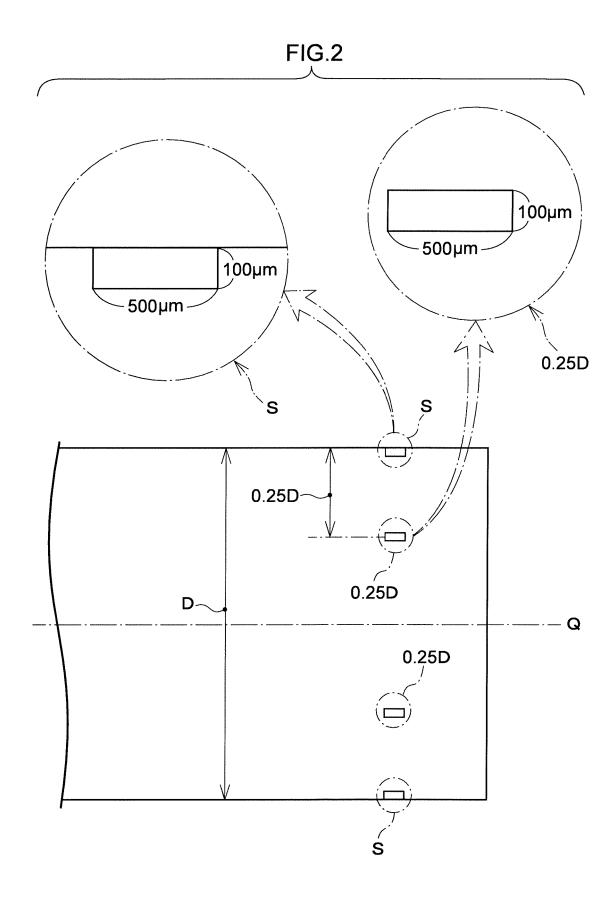
25 **2.** The high-strength steel wire according to claim 1, wherein the chemical composition comprises, in terms of % by mass, one or more of:

Al: from 0.005 to 0.100%, Cr: from 0.01 to 2.00%, V: from 0.01 to 0.30%, B: from 0.0001 to 0.0050%, Ti: from 0.001 to 0.050%,

Nb: from 0.001 to 0.050%, Zr: from 0.001 to 0.050%, or Ni: from 0.01 to 2.00%.

- 3. The high-strength steel wire according to claim 1 or 2, wherein a content of Al in the chemical composition is, in terms of % by mass, from more than 0.005 to 0.100%.
- **4.** The high-strength steel wire according to any one of claims 1 to 3, wherein the steel wire has a diameter of from 2.5 mm to 9.5 mm.





#### International application No. INTERNATIONAL SEARCH REPORT PCT/JP2017/027578 A. CLASSIFICATION OF SUBJECT MATTER C22C38/00(2006.01)i, C22C38/04(2006.01)i, C22C38/54(2006.01)i, C21D8/06 5 (2006.01)n, *C21D9/52*(2006.01)n According to International Patent Classification (IPC) or to both national classification and IPC FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) 10 C22C38/00-38/60, C21D8/06, C21D9/52 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched 1922-1996 Jitsuyo Shinan Koho Jitsuyo Shinan Toroku Koho 1996-2017 15 Kokai Jitsuyo Shinan Koho 1971-2017 Toroku Jitsuyo Shinan Koho 1994-2017 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) 20 DOCUMENTS CONSIDERED TO BE RELEVANT Relevant to claim No. Category\* Citation of document, with indication, where appropriate, of the relevant passages Α WO 2015/186801 A1 (Nippon Steel & Sumitomo Metal Corp.), 10 December 2015 (10.12.2015), 25 paragraphs [0010] to [0044] & KR 10-2017-0002541 A & CN 106414786 A WO 2013/031640 A1 (Nippon Steel & Sumitomo Α 1 - 4Metal Corp.), 07 March 2013 (07.03.2013), 30 & US 2014/0290806 A1 WO 2016/021556 A1 (Nippon Steel & Sumitomo Α 1 - 4Metal Corp.), 11 February 2016 (11.02.2016), & EP 3165626 A1 35 × Further documents are listed in the continuation of Box C. See patent family annex. 40 Special categories of cited documents: 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 "E" earlier application or patent but published on or after the international filing 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 "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) 45 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 "O" document referring to an oral disclosure, use, exhibition or other means being obvious to a person skilled in the art document published prior to the international filing date but later than the "P document member of the same patent family priority date claimed Date of the actual completion of the international search Date of mailing of the international search report 50 03 October 2017 (03.10.17) 15 September 2017 (15.09.17) Name and mailing address of the ISA/ Authorized officer Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan Telephone No. 55

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# INTERNATIONAL SEARCH REPORT International application No. PCT/JP2017/027578 C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT 5 Category\* Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. WO 2014/208492 A1 (Nippon Steel & Sumitomo 1-4 Α Metal Corp.), 31 December 2014 (31.12.2014), & US 2016/0145712 A1 & EP 3015563 A1 10 WO 2012/124679 A1 (Nippon Steel Corp.), 20 September 2012 (20.09.2012), 1 - 4Α & US 2014/0000767 A1 & EP 2687619 A1 15 Α JP 2012-041587 A (Nippon Steel Corp.), 1 - 401 March 2012 (01.03.2012), & US 2013/0133789 A1 20 25 30 35 40 45 50

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#### REFERENCES CITED IN THE DESCRIPTION

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#### Patent documents cited in the description

- JP 2004360005 A **[0005]**
- JP 2009280836 A **[0005]**

• JP 2016150584 A [0098]