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

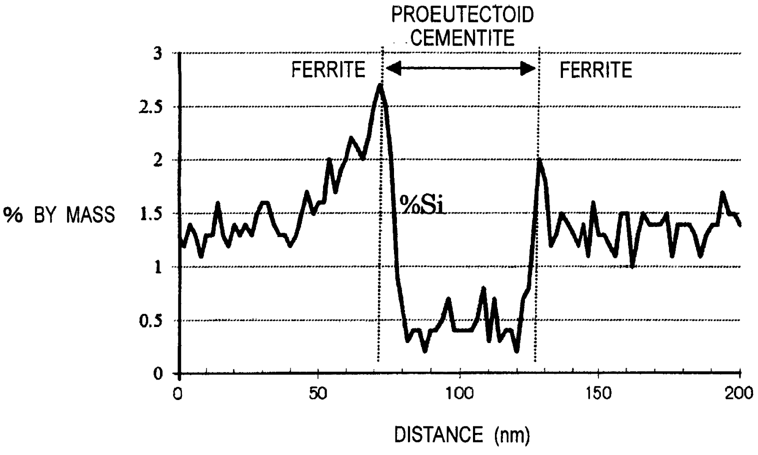
(72) Inventors:
- **ISHIDA, Tomonobu**
  **Hyogo 657-0863 (JP)**
- **MASUDA, Tomokazu**
  **Hyogo 657-0863 (JP)**

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

# (54) HIGH-CARBON STEEL WIRE MATERIAL WITH EXCELLENT WIRE DRAWABILITY, AND STEEL WIRE

(57) To provide a high-carbon steel wire rod with excellent wire drawability. The high-carbon steel wire rod of the present invention includes predetermined components and also includes pearlite and proeutectoid cementite, and an area ratio of pearlite is 90% or more relative to the entire structure, a maximum length of proeutectoid cementite is 15 μm or less, and a concentration difference between an average of the Si concentration inside proeutectoid cementite and a maximum value of the Si concentration inside ferrite that forms a lamellar structure of pearlite is 0.50 to 3%.

*Fig. 1*



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## Description

### Technical Field

**[0001]** The present invention relates to a high-carbon steel wire rod with excellent wire drawability, and a steel wire obtained by wire drawing of the high-carbon steel wire rod mentioned above. More particularly, the present invention relates to a high-carbon steel wire rod produced by hot rolling, which is a raw material of a high strength steel wire to be used mainly for steel cords, wire ropes, saw wires and the like.

### Background Art

**[0002]** There have been known as, a high strength steel wire used for steel cords, wire rope and the like, for example, piano wires mentioned in JIS G 3522(1991). The piano wires are roughly classified into three types such as classes A, B, and V, and examples of the high strength piano wire class B include SWP-class B having a wire diameter of 0.2 mm and a tensile strength of 2,840 to 3,090 MPa. Generally, pearlite steels such as SWRS82A mentioned in JIS G 3502 (2004) are used as the raw material of the piano wire.

**[0003]** A common method for producing a high strength steel wire is as follows. First, a steel wire rod produced by hot rolling (also referred to as the rolled wire rod) is placed in a ring shape on a cooling conveyor, thereby allowing to undergo pearlite transformation, and then coiled into a coil shape to obtain a wire rod coil. Then, wire drawing is performed and a steel wire having desired wire diameter and strength is obtained by making use of the work hardening function of pearlite. When it is impossible to be drawn to a desired wire diameter due to working limit of the steel wire rod, a heat treatment called patenting is applied between wire drawings. For example, to obtain an extra fine steel wire having a wire diameter of 0.2 mm, wire drawing and a patenting treatment are generally performed by repeating several times.

**[0004]** To increase the strength of the steel wire, there is a need to increase the C content of the steel wire rod which is the raw material. However, a high-carbon steel wire containing 0.90% or more of C had a problem that proeutectoid cementite is precipitated in the structure, thus degrading the wire drawability.

**[0005]** Thus, to produce a high-carbon steel wire with excellent wire drawability, various techniques have been proposed.

**[0006]** For example, Patent Document 1 relates to a wire rod for a high strength steel wire which is useful as the raw material of a galvanized steel wire to be used for ropes for a bridge, and particularly mentions a wire rod for a high strength steel wire, which is excellent in workability when wire drawing is performed by so-called cold drawing without subjecting to a heat treatment after rolling. In Patent Document 1, precipitation of proeutectoid cementite is suppressed by precipitating fine TiC near grain boundaries, so that the lower limit of the Ti content is set at 0.02% or more.

**[0007]** Patent Document 2 relates to a small diameter high-carbon hot-rolled wire rod which is capable of wire drawing at true strain of 2.2 or more even in an as-hot-rolled state. Specifically, Patent Document 2 mentions that a steel billet having the Si content suppressed to 0.50% or less is thinned to a wire rod diameter of 4.5 mm or less by increasing rolling reduction during hot rolling, thereby making austenite grains ($\gamma$ grains) finer leading to acceleration of pearlite transformation, thus making it possible to prevent precipitation of particles of proeutectoid ferrite and proeutectoid cementite.

**[0008]** Patent Document 3 relates to a deformed wire for a submarine optical fiber cable in which a wire rod for a high tensile steel wire is used. Specifically, Patent Document 3 mentions that, by using a wire rod in which Si is segregated so as to satisfy the following inequality expression: Si maximum segregation degree of cementite/ferrite interface in a range of 30 nm from an interface between cementite and ferrite to a ferrite phase side in a pearlite structure (maximum Si concentration in a range of 30 nm from an interface between cementite and ferrite to a ferrite phase side / Si content of bulk) $\geq 1.1$, it is possible to prevent wire breakage during deformation working.

### Prior Art Document

### Patent Document

**[0009]**

Patent Document 1: JP 2014-189855 A
Patent Document 2: JP 2001-181789 A
Patent Document 3: JP 2003-301240 A

## Disclosure of the Invention

### Problems to be Solved by the Invention

**[0010]** However, the above-mentioned techniques of Patent Documents 1 to 3 respectively have the following problems.

**[0011]** First, Patent Document 1 is intended for a wire rod to be used for a galvanized steel wire, and is not intended for a steel wire having an extra fine wire diameter of approximately 0.2 mm, such as a piano wire. Like Patent Document 1, when an extra fine steel wire is produced using a wire rod having a large Ti content, wire breakage during wire drawing becomes remarkable due to Ti based inclusions. Therefore, it is difficult to apply the technique of Patent Document 1 to the extra fine steel wire to be supplied for steel cords.

**[0012]** Like Patent Document 2, when using a wire rod having a diameter of 4.5 mm or less, the productivity is degraded to cause a problem that wire rods are easily entangled with each other during the production of a coil.

**[0013]** Like Patent Document 3, when using a method in which an Si concentration difference is applied at an interface between cementite and ferrite in the pearlite structure, it is impossible to sufficiently reduce proeutectoid ferrite which is harmful for the wire drawability. The degree of working carried out in Patent Document 3 is 82.6% in terms of an area reduction rate even when summing up wire drawing and cold rolling. Since the area reduction rate of wire drawing required to an extra fine steel wire such as a steel cord is larger, it is insufficient to apply the extra fine steel wire to the above-mentioned applications.

**[0014]** The present invention has been made in light of the foregoing circumstance, and it is an object of the present invention to provide a high-carbon steel wire rod with excellent wire drawability which can also be applied to extra fine steel wires such as steel cord, and a steel wire.

### Means for Solving the Problems

**[0015]** The present invention that can solve the foregoing problems provides a high-carbon steel wire rod including, in % by mass, C: 0.90 to 1.3%, Si: 0.4 to 1.2%, Mn: 0.2 to 1.5%, P: more than 0% and 0.02% or less, S: more than 0% and 0.02% or less, Al: more than 0% and 0.008% or less, Ti: 0 to 0.005%, and N: 0.001 to 0.008%, with the balance being iron and inevitable impurities, wherein the structure includes pearlite and proeutectoid cementite, an area ratio of pearlite is 90% or more relative to the entire structure, a maximum length of proeutectoid cementite is 15 μm or less, and a concentration difference between an average of the Si concentration inside proeutectoid cementite and a maximum value of the Si concentration inside ferrite that forms a lamellar structure of pearlite is 0.50 to 3%.

**[0016]** Further, in a preferred embodiment, the above-mentioned high-carbon steel wire includes: in % by mass, at least one belonging to any one of the following (a) to (d):

(a) B: more than 0% and 0.01% or less,
(b) Co: more than 0% and 1.5% or less,
(c) at least one selected from the group consisting of V: more than 0% and 0.5% or less, and Cr: more than 0% and 0.5% or less, and
(d) at least one selected from the group consisting of Cu: more than 0% and 0.5% or less, Ni: more than 0% and 0.5% or less, and Nb: more than 0% and 0.5% or less.

**[0017]** A steel wire obtained by wire drawing of the above-mentioned high-carbon steel wire rod is also included in the scope of the present invention.

### Effects of the Invention

**[0018]** The present invention can provide a high-carbon steel wire rod with excellent wire drawability which can also be applied to extra fine steel wires such as steel cord.

### Brief Description of the Drawings

**[0019]** Fig. 1 is a diagram showing an Si concentration difference at an interface between a proeutectoid cementite phase and a ferrite phase in the sample of test No. 12 in Table 2 of Example.

### Mode for Carrying Out the Invention

**[0020]** To solve the above problems, the inventors of the present invention have intensively studied using a high-carbon steel wire rod having the C content of 0.90% or more. As a result, it has been found that, when applying an Si concentration difference of 0.50% or more at an interface between proeutectoid cementite and ferrite that forms a lamellar structure of pearlite (hereinafter may be simply referred to as ferrite) (specifically, a concentration difference between an average of the Si concentration inside proeutectoid cementite, and a maximum value of the Si concentration inside ferrite is 0.50% or more), it is possible to suppress the precipitation and growth of proeutectoid ferrite which is harmful for the wire drawability, thus completing the present invention.

**[0021]** There is also some mention of Si segregation in Patent Document 3. However, in Patent Document 3, the Si concentration difference at an interface between cementite (lamellar cementite that forms a lamellar structure of pearlite) and ferrite in a pearlite structure is controlled, and the cementite is not. Therefore, on this point, the invention of Patent Document 3, and the present invention in which the Si concentration at an interface between proeutectoid cementite that is not cementite in the pearlite structure and ferrite is controlled, differ in structure of interest. The cementite in the pearlite structure is essentially different from proeutectoid cementite, and the precipitation starting temperature of proeutectoid cementite is approximately 750°C and is higher than that of pearlite that precipitates at approximately 590 to 650°C. Therefore, it is considered that proeutectoid cementite which is harmful for the wire drawability cannot be sufficiently reduced by the technique of Patent Document 3. Patent Document 3 also mentions that it is effective to set a rate of blast cooling after rolling of the wire rod at 1 to 10°C/second so as to efficiently segregate Si to the above-mentioned interface, and blast cooling at approximately 7°C/second is performed in all Examples. However, in the below-mentioned sample No.6 in Table 2 in which rolling was performed under the cooling conditions mentioned above, the Si concentration difference defined by the present invention could not be achieved and a maximum length of proeutectoid cementite increased, leading to degradation of the wire drawability.

**[0022]** Next, a description will be made of the steel wire rod of the present invention.

**[0023]** First, components in the steel of the steel wire rod according to the present invention are as follows. Unit of each component is % by mass unless otherwise specified.

C: 0.90 to 1.3%

**[0024]** Carbon (C) is effective in increasing the strength, and the strength of the steel wire after cold working increases with the increase of the C content. To achieve desired strength of 4,000 MPa or more, the lower limit of the C content is set at 0.90% or more, preferably 0.93% or more, and more preferably 0.95% or more. Any excessive C content, however, cannot achieve sufficient reduction of proeutectoid cementite which is harmful for the wire drawability, thus degrading the wire drawability. Therefore, the upper limit of the C content is set at 1.3% or less, and preferably 1.25% or less.

Si: 0.4 to 1.2%

**[0025]** Silicon (Si) is an effective deoxidizing agent and has not only the effect of reducing oxide based inclusions in the steel, but also the effect of increasing the strength of the steel wire rod. As mentioned later, Si also has the effect of suppressing the growth of proeutectoid cementite. To effectively exhibit these effects, the lower limit of the Si content is set at 0.4% or more, preferably 0.45% or more, more preferably more than 0.50%, and still more preferably 0.55% or more. Addition of excessive Si accelerates the embrittlement during wire drawing, thus degrading twisting properties of the drawn wire rod. Therefore, the upper limit of the Si content is set at 1.2% or less, and preferably 1.15% or less.

Mn: 0.2 to 1.5%

**[0026]** Manganese (Mn) has the effect of extremely improving the hardenability of the steel, thus lowering the transformation temperature during blast cooling, leading to increased strength of the pearlite structure. To effectively exhibit these effects, the lower limit of the Mn content is set at 0.2% or more, and preferably 0.3% or more. However, Mn is an element which easily segregates into the center of the wire rod and addition of excessive Mn excessively enhances the hardenability of a Mn segregation portion, which may form a supercooled structure such as martensite. Therefore, the upper limit of the Mn content is set at 1.5% or less, preferably 1.0% or less, and more preferably 0.95% or less.

P: more than 0% and 0.02% or less

**[0027]** Phosphorus (P) is contained as impurities, and segregates in the prior austenite grain boundary to thereby cause embrittlement, leading to steel billet cracking and degradation of fatigue-resistant characteristics of the steel wire after wire drawing. Therefore, to prevent these harmful influences, the upper limit of the P content is set at 0. 02% or less, and preferably 0.018% or less. It is difficult to set the lower limit of the P content at 0% in view of industrial production.

S: more than 0% and 0.02% or less

**[0028]** Like P, sulfur (S) is contained as impurities, and segregates in the prior austenite grain boundary to thereby cause embrittlement, leading to steel billet cracking and degradation of fatigue-resistant characteristics of the steel wire after wire drawing. Therefore, to prevent these harmful influences, the upper limit of the S content is set at 0.02% or less, and preferably 0.018% or less. It is difficult to set the lower limit of the S content at 0% in view of industrial production.

Al: more than 0% and 0.008% or less

**[0029]** Aluminum (Al) is contained as impurities, and forms Al based inclusions such as $Al_2O_3$ to thereby increase a wire breakage ratio during wire drawing. Therefore, to ensure sufficient wire drawability, the upper limit of the Al content is set at 0.008% or less, and preferably 0.006% or less. It is difficult to set the lower limit of the Al content at 0% in view of industrial production.

Ti: 0 to 0.005%

**[0030]** Titanium (Ti) is contained as impurities, and forms Ti based inclusions such as TiN to thereby increase a wire breakage ratio during wire drawing. Therefore, to ensure sufficient wire drawability, the upper limit of the Ti content is set at 0.005% or less, and preferably 0.003% or less.

N: 0.001 to 0.008%

**[0031]** N is solid-soluted in the steel to thereby cause strain aging during wire drawing, thus degrading the toughness of the steel wire. Therefore, to prevent these harmful influences, the upper limit of the N content is set at 0.008% or less, and preferably 0.007% or less. The lower the N content is, the better, and the lower limit of the N content is set at 0.001% or more, and preferably 0.0015% or more, in view of industrial production.

**[0032]** The steel wire rod of the present invention contains components mentioned above, the balance being iron and inevitable impurities.

**[0033]** To improve properties such as strength, toughness, and ductility, the steel wire rod of the present invention can further include the following selective elements.

B: more than 0% and 0.01% or less

**[0034]** Boron (B) has the effect of concentrating on the austenite grain boundary to thereby prevent the formation of grain boundary ferrite, thus improving the wire drawability. B also has the effect of chemically combining with N to form nitrides such as BN, and suppressing the degradation of the toughness due to solid-soluted N, thus improving twisting properties. To effectively exhibit the wire drawability and twisting properties of the steel wire rod due to the addition of B, the lower limit of the B content is preferably set at 0.0005% or more. Addition of excessive B causes cracking during hot rolling as a result of the precipitation of a compound with Fe (B-constituent), so that the upper limit of the B content is preferably set at 0.01% or less, and more preferably 0.008% or less.

Co: more than 0% and 1.5% or less

**[0035]** Cobalt (Co) has the effect of accelerating pearlite transformation to thereby reduce proeutectoid cementite. Particularly, the wire drawability is accelerated by adding Co, in addition to Si. To effectively exhibit these functions, the lower limit of the Co content is preferably set at 0.05% or more, and more preferably 0.1%. However, Co is a very expensive element and the effect is saturated even if being added excessively, resulting in economic waste. Therefore, the upper limit of the Co content is preferably set at 1.5% or less, more preferably 1.3% or less, and still more preferably 1% or less.

At least one selected from the group consisting of V: more than 0% and 0.5% or less, and Cr: more than 0% and 0.5% or less

**[0036]** Vanadium (V) and chromium (Cr) are elements contributing to improve the strength of the steel wire rod. These elements may be added alone or used in combination.

**[0037]** Specifically, V has the effect of increasing the strength due to the formation of fine carbonitrides, and also can exhibit the effect of improving twisting properties due to the reduction of solid-soluted N. To effectively exhibit these effects, the lower limit of the V content is preferably set at 0.05% or more, and more preferably 0.1% or more. V is an expensive element and the effect is saturated even if being added excessively, resulting in economic waste. Therefore, the upper limit of the V content is preferably set at 0.5% or less, and more preferably 0.4% or less.

**[0038]** Cr has the effect of making lamellar spacing of pearlite finer to thereby enhance the strength of the steel wire rod. To effectively exhibit such effect, the lower limit of the Cr content is preferably set at 0.05% or more, and more preferably 0.1% or more. However, the effect is saturated even if being added excessively, resulting in economic waste. Therefore, the upper limit of the Cr content is preferably set at 0.5% or less, and more preferably 0.4% or less.

At least one selected from the group consisting of Cu: more than 0% and 0.5% or less, Ni: more than 0% and 0.5% or less, and Nb: more than 0% and 0.5% or less

**[0039]** All of these elements are elements contributing to improve the manufacturability and corrosion resistance of the steel wire. These elements may be added alone or used in combination.

**[0040]** Specifically, copper (Cu) has the effect of being concentrated on a surface of the steel wire rod to thereby enhance the peelability of scales, leading to the enhancement of mechanical descaling (MD) properties. To effectively exhibit these functions, the lower limit of the Cu content is preferably set at 0.05% or more. However, blisters occur on a surface of the steel wire rod when being added excessively, so that the upper limit of the Cu content is preferably set at 0.5% or less, and more preferably 0.4% or less.

**[0041]** Nickel (Ni) has the effect of enhancing the corrosion resistance of the steel wire rod. To effectively exhibit such function, the lower limit of the Ni content is preferably set at 0.05% or more. The effect is saturated even if being added excessively, resulting in economic waste. Therefore, the upper limit of the Ni content is preferably set at 0.5% or less, and more preferably 0.4% or less.

**[0042]** Niobium (Nb) has the effect of making crystal grains finer to thereby enhance the ductility of the wire rod. To effectively exhibit such function, the lower limit of the Nb content is preferably set at 0.05% or more. However, the effect is saturated even if being added excessively, resulting in economic waste. Therefore, the upper limit of the Nb content is preferably set

at 0.5% or less, and more preferably 0.4% or less.

**[0043]** Next, a description will be made of the structure of the steel wire rod according to the present invention. As mentioned above, the steel wire rod of the present invention includes pearlite and proeutectoid cementite, and an area ratio of pearlite is 90% or more relative to the entire structure, a maximum length of proeutectoid cementite is 15 μm or less, and a concentration difference between an average of the Si concentration inside proeutectoid cementite and a maximum value of the Si concentration inside ferrite (hereinafter may simply referred to as the Si concentration difference) is 0.50 to 3%.

Area ratio of pearlite relative to the entire structure: 90% or more

**[0044]** As mentioned above, the steel wire rod of the present invention includes pearlite and proeutectoid cementite. Since the low temperature transformation structure, such as bainite or martensite (may also be referred to as the supercooled structure) inhibits the wire drawability, an area ratio of the pearlite structure is set at 90% or more, and preferably 95% or more, so as to ensure sufficient wire drawability. The upper limit may be appropriately controlled depending on a relation with proeutectoid cementite, and is preferably approximately 99 area % or less.

**[0045]** The steel wire rod of the present invention can include, in addition to pearlite and proeutectoid cementite, the residual structure that is inevitably included during production process. Examples of such residual structure include non-pearlite structures, such as bainite and proeutectoid ferrite. To effectively exhibit the functions of the present invention, the total content of the non-pearlite structure (including proeutectoid cementite) is preferably controlled to approximately 10 area % or less relative to the entire structure.

Maximum Length of Proeutectoid Cementite: 15 μm or less

**[0046]** Proeutectoid cementite precipitating in a plate shape is the structure which is harmful for the wire drawability, and disturbs orientation of pearlite colonies of the steel wire rod and increases wire breakage as a starting point of cracking. However, proeutectoid cementite having a short maximum length exert less harmful influences mentioned above. Mechanism due to such proeutectoid cementite is as mentioned in detail in Patent Document 1. To ensure sufficient wire drawability, the upper limit of the maximum length of proeutectoid cementite is set at 15 μm or less, preferably 13 μm or less, and more preferably 10 μm or less. The lower limit of the maximum length of proeutectoid cementite is not particularly limited and may be, for example, approximately 0.1 μm.

Concentration difference between average of Si concentration inside proeutectoid cementite and maximum value of Si concentration inside ferrite (Si concentration difference): 0.50 to 3%

**[0047]** Silicon (Si) is an element which is hardly solid-soluted in cementite and is discharged to an austenite phase from a cementite phase when proeutectoid cementite precipitates, and Si concentration difference is generated at the interface (interface between proeutectoid cementite and a ferrite phase). The test results of the inventors revealed that, the more this Si concentration difference is large, the more the growth of a proeutectoid cementite phase is suppressed, thus enabling the reduction of the maximum length of proeutectoid cementite. Si concentration distribution formed at this time is inherited even through subsequent pearlite transformation, so that observation of the structure of the thus produced steel wire rod leads to confirmation as an Si concentration difference at an interface between the proeutectoid cementite phase and the ferrite phase around the proeutectoid cementite phase.

**[0048]** For reference, a graph showing an Si concentration difference in the sample of test No. 12 in Table 2 of Example mentioned later is shown in Fig. 1. In Fig. 1, an average of the Si concentration of the proeutectoid cementite phase in the center, and a maximum value of the Si concentration of each ferrite phase existing around the proeutectoid cementite phase are measured, and a difference therebetween is defined as the Si concentration difference. The method for measuring the Si concentration will be mentioned in detail in the columns of Examples mentioned later.

**[0049]** In the present invention, the Si concentration difference calculated as mentioned above is set at 0.50% or more. Whereby, the maximum length of proeutectoid cementite can be set at 15 μm or less. The Si concentration difference is preferably 0.6% or more. The effect mentioned above is saturated even if the Si concentration difference is excessively formed, so that the upper limit is set at 3% or less, and preferably 2.8% or less.

**[0050]** In the present invention, the Si concentration difference is generated at an interface between the proeutectoid cementite phase and ferrite in the pearlite structure, and the Si concentration difference is not generated at an interface between the proeutectoid cementite phase and the cementite (lamellar cementite that forms a lamellar structure of pearlite) phase in the pearlite structure.

**[0051]** A description will be made of a preferred method for producing the above-mentioned the steel wire rod of the present invention.

**[0052]** The high-carbon steel wire rod as mentioned in the present invention is generally produced by the following procedure in which a steel billet with a predetermined chemical component adjusted in advance is austenitized by heating and then hot-rolled into a steel wire rod having a predetermined wire diameter.

**[0053]** After hot rolling, the steel wire rod is placed in a ring shape on a cooling conveyor and then cooled. At this time, the placing temperature is preferably set at 880 to 980°C. When the placing temperature is too high or low, scale characteristics may change, thus exerting an adverse influence on a mechanical descaling (MD) treatment before wire drawing. The placing temperature is preferably 900°C or higher and 960°C or lower. Although the other descaling treatment such as pickling may be used, it is recommended to control to the placing temperature within the above range taking the productivity into consideration.

**[0054]** Then, cooling is started at a temperature of 800°C or higher. The cooling conditions are extremely important so as to control the desired Si concentration difference within a predetermined range. There is a need that the entire coil placed in a ring shape falls within the above-mentioned range of the cooling stop temperature and holding temperature.

**[0055]** Specifically, cooling is performed to the cooling stop temperature of 480 to 620°C at an average cooling rate of 12 to 60°C/s. At this time, when the average cooling rate is low, the Si concentration difference generated at a proeutectoid cementite interface is lost by diffusion of Si atoms, thus failing to obtain the desired Si concentration difference. Meanwhile, when the average cooling rate is high, a supercooled structure is formed and a pearlite area ratio becomes less than 90%. The average cooling rate is more preferably 15°C/s or more and 55°C/s or less.

**[0056]** When the cooling starting temperature is low, precipitation of proeutectoid cementite starts during being allowed to cool, thus corresponding to the case where the average cooling rate is low, so that the Si concentration difference decreases. When the cooling stop temperature is low, a supercooled structure such as bainite is formed to thereby decrease the pearlite area ratio. Meanwhile, when the cooling stop temperature is high, Si atoms diffuse to thereby decrease the Si concentration difference. The cooling stop temperature is more preferably 500°C or higher and 600°C or lower.

**[0057]** After stopping of cooling, the temperature is raised to the holding temperature of 590 to 650°C and pearlite transformation is performed. When the holding temperature is too high, Si atoms diffuse to thereby decrease the Si concentration difference. Meanwhile, when the holding temperature is too low, a supercooled structure is generated to thereby decrease the pearlite area ratio. The holding temperature is more preferably 600°C or higher and 640°C or lower.

**[0058]** The steel wire rod of the present invention was obtained by the procedure mentioned above, and then coiled into a coil shape to obtain a wire rod coil. Then, wire drawing is performed to obtain a steel wire having desired wire diameter and strength.

**[0059]** A patenting treatment is preferably performed after wire drawing. An extra fine steel wire having a wire diameter of approximately 0.2 mm can be obtained by further subjecting to wire drawing after the patenting treatment. There is no particular limitation on conditions of the patenting treatment and, for example, it is possible to employ conditions such as heating temperature of 950°C and patenting temperature of 600°C. The patenting treatment may be performed not only once, but also plural times (for example, 2 to 3 times).

**[0060]** The thus obtained steel wire of the present invention has a high tensile strength such as approximately 4,000 MPa or more. According to the present invention, a steel wire having a wire diameter of approximately 0.1 to 0.4 mm is obtained, so that the thus obtained steel wire is suitably used for steel cords, wire ropes, saw wires and the like.

**[0061]** This application claims priority based on Japanese Patent Application 2015-070095 filed on March 30, 2015, and Japanese Patent Application 2015-188843 filed on September 25, 2015, the disclosure of which is incorporated by reference herein.

## Examples

**[0062]** While the present invention will be more specifically described below by way of Examples, it is to be understood that the present invention is not limited to the Examples, and various design variations made in accordance with the purports described hereinbefore and hereinafter are also included in the scope of the present invention.

**[0063]** Each of steels A to Z (cross-sectional shape: 155 mm ×155 mm) shown in Table 1 was heated to a temperature of 1,000°C and hot-rolled into a predetermined wire diameter of 5.5 mm. Then, the hot-rolled steel was placed in a ring shape on a cooling conveyor and allowed to undergo pearlite transformation while control cooling by blast cooling, and then coiled into a coil shape to obtain a coil of rolled material. The cooling conditions after rolling and the wire rod diameter after rolling are shown in Table 2.

**[0064]** Using the thus obtained coil of rolled material, the following items were measured.

### Measurement of Pearlite (P) Area Ratio

**[0065]** After cutting off the unsteady part of the end of the coil of rolled material, the end of the non-defective product was collected to obtain a specimen having a length of 5 cm. A micrograph of a transverse section perpendicular to a wire rod longitudinal direction of the thus obtained specimen was taken by a scanning electron microscope (SEM). Using the thus obtained micrograph, an area ratio of a pearlite structure and a non-pearlite structure was determined by a point counting method. The point counting method is a method in which the micrograph is sectioned into meshes and the number of structures existing in lattice points is counted to thereby easily determine an area ratio of the structure. Specifically, a micrograph of the center of the transverse section was taken at a magnification of 4,000 times to fabricate three SEM micrographs. The each micrograph was sectioned into 100 lattice points and a pearlite area ratio was determined, and then an average was calculated. An evaluation area of one SEM micrograph is 868 $\mu m^2$. The pearlite area ratio and details of the structure in each specimen are shown in Table 2. The non-pearlite structure detected by the above point counting method (proeutectoid cementite structure, bainite structure) are also shown in Table 2. In the table, P denotes a pearlite structure, B denotes a bainite structure, and $\theta$ denotes proeutectoid cementite.

### Evaluation of Maximum Length of Proeutectoid Cementite ($\theta$)

**[0066]** Using the thus obtained SEM micrograph, a length of each observed proeutectoid cementite was measured and a maximum length was determined. The proeutectoid cementite is precipitated in a plate shape and, when lamellar cementite is divided into multiple branches, the total value of lengths of each branch was employed.

### Measurement of Si Concentration Difference

**[0067]** Using the thus obtained SEM micrograph, regarding the thus observed proeutectoid cementite, line analysis of the Si concentration was performed by energy dispersive X-ray spectrometry (EDX) using a spherical aberration corrected scanning transmission electron microscope (Cs-STEM), and then an Si concentration difference between inside the proeutectoid cementite phase and a ferrite phase existing around the proeutectoid cementite phase was determined. Specifically, an average of the Si concentration of the proeutectoid cementite phase, and a maximum value of the Si concentration of the ferrite phase were respectively measured, and then the difference was defined as the Si concentration difference. A step width of line analysis was set at 2 nm, and an evaluation length was set at 200 nm.

### Evaluation of Mechanical Properties of Coil of Rolled Material

**[0068]** After cutting off the unsteady part of the end of the coil of rolled material, one ring was collected from the coil end of the non-defective product and then divided into eight samples in a longitudinal direction. In accordance with JIS Z2201, a tensile test was performed and a tensile strength TS was measured. An average of the tensile strength of eight samples in total was determined, and then TS of the coil of rolled material was calculated.

Evaluation of Wire Drawability

**[0069]** Using the above coil of rolled material, cold wire-drawing was performed to a predetermined wire diameter at wire drawing strain in Table 2, and then a tensile strength TS after wire drawing was determined. Each amount of wire drawing is 200 kg. When wire breakage occurred during wire drawing, "wire breakage" was filled in the table.

**[0070]** These results are collectively shown in Table 2.

[Table 1A]

| Steel | Chemical composition (% by mass) *Balance being iron and inevitable impurities | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | Si | Mn | Al | P | S | Ti | N | B | Co | Cr | V | Cu | Ni | Nb |
| A | 1.10 | 0.55 | 0.50 | 0.003 | 0.010 | 0.010 | | 0.0027 | | | | | | | |
| B | 0.97 | 0.80 | 0.40 | 0.002 | 0.011 | 0.006 | 0.001 | 0.0040 | | | | | | | |
| C | 1.05 | 0.60 | 0.45 | 0.002 | 0.008 | 0.008 | 0.001 | 0.0035 | 0.0020 | | | | | | |
| D | 1.25 | 0.90 | 0.48 | 0.003 | 0.010 | 0.010 | | 0.0044 | 0.0030 | 0.50 | | | | | |
| E | 1.30 | 1.20 | 0.30 | 0.002 | 0.010 | 0.011 | 0.003 | 0.0032 | 0.0015 | 0.30 | 0.30 | | | | |
| F | 0.95 | 0.70 | 0.50 | 0.001 | 0.007 | 0.010 | | 0.0044 | 0.0020 | | 0.15 | | | | |
| G | 0.98 | 0.90 | 0.40 | 0.001 | 0.010 | 0.020 | 0.002 | 0.0028 | 0.0025 | | 0.10 | 0.05 | | | |
| H | 1.05 | 0.60 | 0.30 | 0.002 | 0.020 | 0.008 | | 0.0048 | | | 0.20 | | | | |
| I | 1.00 | 0.70 | 0.50 | 0.003 | 0.007 | 0.010 | | 0.0052 | 0.0028 | | | | 0.11 | | |
| J | 1.12 | 0.66 | 0.70 | 0.002 | 0.008 | 0.012 | 0.002 | 0.0031 | 0.0080 | | | | | 0.20 | |
| K | 0.98 | 0.80 | 0.70 | 0.001 | 0.006 | 0.008 | | 0.0042 | 0.0075 | | | | | | 0.15 |
| L | 1.10 | 1.15 | 1.10 | 0.003 | 0.010 | 0.007 | 0.001 | 0.0055 | | | | | | | |
| M | 1.06 | 0.51 | 0.60 | 0.002 | 0.015 | 0.011 | 0.003 | 0.0036 | 0.0012 | | | | | | |
| N | 0.97 | 0.90 | 0.40 | 0.002 | 0.008 | 0.011 | | 0.0031 | 0.0012 | | | | | | |
| O | 1.35 | 1.10 | 0.50 | 0.005 | 0.010 | 0.010 | 0.003 | 0.0052 | 0.0034 | | | | | | |
| P | 1.00 | 0.20 | 0.60 | 0.003 | 0.010 | 0.010 | | 0.0018 | 0.0070 | | | | | | |

[Table 1B]

| Steel | Chemical composition (% by mass) *Balance being iron and inevitable impurities | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | Si | Mn | Al | P | S | Ti | N | B | Co | Cr | V | Cu | Ni | Nb |
| Q | 1.00 | 0.40 | 0.50 | 0.002 | 0.008 | 0.007 | | 0.0045 | | | | | | | |
| R | 1.05 | 0.45 | 0.48 | 0.001 | 0.006 | 0.008 | 0.001 | 0.0039 | | | | | | | |
| S | 1.15 | 0.90 | 0.65 | 0.003 | 0.010 | 0.008 | | 0.0031 | | 0.20 | | | | | |
| T | 1.23 | 1.05 | 0.35 | 0.002 | 0.006 | 0.011 | 0.003 | 0.0028 | | | 0.20 | | | | |
| U | 0.98 | 0.59 | 0.50 | 0.001 | 0.007 | 0.010 | | 0.0046 | | | | 0.10 | | | |
| V | 1.02 | 0.46 | 0.55 | 0.001 | 0.010 | 0.020 | 0.002 | 0.0026 | | | | | 0.08 | | |
| W | 0.98 | 0.78 | 0.25 | 0.002 | 0.020 | 0.008 | | 0.0046 | | | | | | 0.15 | |
| X | 0.99 | 0.55 | 0.66 | 0.003 | 0.007 | 0.010 | | 0.0051 | | | | | | | 0.20 |
| S | 1.15 | 0.90 | 0.65 | 0.003 | 0.010 | 0.008 | | 0.0031 | | 0.20 | | | | | |
| T | 1.23 | 1.05 | 0.35 | 0.002 | 0.006 | 0.011 | 0.003 | 0.0028 | | | 0.20 | | | | |
| U | 0.98 | 0.59 | 0.50 | 0.001 | 0.007 | 0.010 | | 0.0046 | | | | 0.10 | | | |
| V | 1.02 | 0.46 | 0.55 | 0.001 | 0.010 | 0.020 | 0.002 | 0.0026 | | | | | 0.08 | | |
| W | 0.98 | 0.78 | 0.25 | 0.002 | 0.020 | 0.008 | | 0.0046 | | | | | | 0.15 | |
| X | 0.99 | 0.55 | 0.66 | 0.003 | 0.007 | 0.010 | | 0.0051 | | | | | | | 0.20 |
| Y | 0.90 | 0.60 | 0.30 | 0.002 | 0.008 | 0.005 | | 0.0034 | | | | | | | |
| Z | 0.93 | 0.45 | 0.40 | 0.003 | 0.007 | 0.008 | | 0.0041 | | | | | | | |

[Table 2A]

| Test No. | Steel | Cooling conditions after rolling | | | | | Properties of rolled material | | | | | | Wire drawability | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Placing temperature | Cooling starting temperature | Average cooling rate | Cooling stop temperature | Holding temperature | Rolled wire diameter | TS | Maximum length of θ | Structure | P area ratio | Si concentration difference | Wire diameter | Wire drawing strain | TS |
| | | (°C) | (°C) | (°C/s) | (°C) | (°C) | (mm) | (MPa) | (μm) | | | (% by mass) | (mm) | | (MPa) |
| 1 | A | 930 | 900 | 15 | 550 | 610 | 5.5 | 1,402 | 10 | P+B | 97% | 0.88 | 2.2 | 1.83 | 2,217 |
| 2 | B | 910 | 880 | 20 | 570 | 620 | 5.5 | 1,307 | 12 | P+θ | 98% | 0.96 | 2.2 | 1.83 | 2.067 |
| 3 | C | 940 | 910 | 15 | 550 | 600 | 5.5 | 1,357 | 8 | P+B | 95% | 1.37 | 2.0 | 2.02 | 2,250 |
| 4 | C | 930 | 750 | 16 | 510 | 600 | 5.5 | 1,265 | 21 | P+θ | 98% | 0.38 | 2.0 | 2.02 | Wire breakage |
| 5 | C | 940 | 900 | 80 | 530 | 620 | 5.5 | 1,602 | 13 | P+B | 31% | 1.55 | 2.0 | 2.02 | Wire breakage |
| 6 | C | 920 | 880 | 7 | 540 | 610 | 5.5 | 1,304 | 17 | P+θ | 97% | 0.46 | 2.0 | 2.02 | Wire breakage |
| 7 | C | 920 | 880 | 55 | 430 | 610 | 5.5 | 1,579 | 12 | P+B | 48% | 1.30 | 2.0 | 2.02 | Wire breakage |
| 8 | C | 910 | 860 | 13 | 650 | 650 | 5.5 | 1,279 | 19 | P+θ | 95% | 0.41 | 2.0 | 2.02 | Wire breakage |
| 9 | C | 970 | 850 | 30 | 500 | 560 | 5.5 | 1,521 | 11 | P+B | 74% | 1.62 | 2.0 | 2.02 | Wire breakage |
| 10 | C | 930 | 850 | 15 | 620 | 680 | 5.5 | 1,255 | 22 | P+θ | 96% | 0.41 | 2.0 | 2.02 | Wire breakage |
| 11 | D | 900 | 830 | 35 | 510 | 630 | 5.5 | 1,467 | 3 | P+B | 95% | 1.88 | 1.8 | 2.23 | 2,564 |
| 12 | E | 890 | 800 | 40 | 500 | 630 | 5.5 | 1,481 | 4 | P+B | 96% | 2.10 | 1.9 | 2.13 | 2,570 |
| 13 | F | 910 | 840 | 60 | 480 | 590 | 5.5 | 1,341 | 9 | P+B+θ | 90% | 1.85 | 2.1 | 1.93 | 2,220 |
| 14 | G | 920 | 880 | 20 | 560 | 610 | 5.5 | 1,342 | 11 | P+θ | 99% | 1.79 | 2.1 | 1.93 | 2,222 |
| 15 | H | 900 | 820 | 12 | 620 | 650 | 5.0 | 1,381 | 15 | P+θ | 97% | 1.29 | 2.0 | 1.83 | 2,234 |

[Table 2B]

| Test No. | Steel | Cooling conditions after rolling | | | | | Properties of rolled material | | | | | | Wire drawability | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Placing temperature | Cooling starting temperature | Average cooling rate | Cooling stop temperature | Holding temperature | Rolled wire diameter | TS | Maximum length of θ | Structure | P area ratio | Si concentration difference | Wire diameter | Wire drawing strain | TS |
| | | (°C) | (°C) | (°C/s) | (°C) | (°C) | (mm) | (MPa) | (µm) | | | (% by mass) | (mm) | | (MPa) |
| 16 | I | 910 | 810 | 25 | 530 | 620 | 5.5 | 1,326 | 12 | P | 100% | 1.66 | 2.1 | 1.93 | 2,146 |
| 17 | J | 920 | 850 | 13 | 610 | 630 | 5.5 | 1,389 | 13 | P+θ | 95% | 1.34 | 2.0 | 2.02 | 2,303 |
| 18 | K | 930 | 890 | 30 | 600 | 650 | 5.0 | 1,334 | 11 | P | 100% | 1.76 | 2.0 | 1.83 | 2,109 |
| 19 | L | 930 | 900 | 22 | 590 | 630 | 5.0 | 1,376 | 12 | P | 100% | 2.70 | 2.0 | 1.83 | 2,176 |
| 20 | M | 950 | 900 | 40 | 520 | 600 | 5.5 | 1,346 | 9 | P+B | 94% | 0.67 | 2.0 | 2.02 | 2,232 |
| 21 | N | 930 | 910 | 42 | 520 | 590 | 5.5 | 1,378 | 0 | P+B | 97% | 1.54 | 2.0 | 2.02 | 2,285 |
| 22 | O | 900 | 880 | 22 | 550 | 600 | 5.5 | 1,416 | 31 | P+θ | 97% | 2.10 | 2.2 | 1.83 | Wire breakage |
| 23 | P | 900 | 860 | 16 | 560 | 600 | 5.5 | 1,267 | 26 | P+θ | 96% | 0.35 | 2.2 | 1.83 | Wire breakage |
| 24 | Q | 910 | 880 | 18 | 570 | 590 | 5.0 | 1,311 | 8 | P+θ | 98% | 0.55 | 2.0 | 1.83 | 2,073 |
| 25 | R | 900 | 880 | 20 | 560 | 600 | 4.5 | 1,342 | 9 | P+θ | 97% | 0.60 | 1.8 | 1.83 | 2,122 |
| 26 | S | 920 | 880 | 12 | 580 | 600 | 5.5 | 1,451 | 9 | P | 98% | 1.22 | 2.2 | 1.83 | 2,294 |
| 27 | T | 910 | 890 | 14 | 560 | 600 | 5.5 | 1,423 | 11 | P+θ | 97% | 1.32 | 2.4 | 1.66 | 2,154 |
| 28 | U | 920 | 880 | 19 | 580 | 590 | 5.5 | 1,411 | 10 | P | 99% | 0.89 | 2.3 | 1.74 | 2,181 |
| 29 | V | 930 | 870 | 15 | 560 | 600 | 5.5 | 1,398 | 7 | P | 97% | 0.98 | 2.2 | 1.83 | 2,210 |
| 30 | X | 910 | 890 | 16 | 550 | 610 | 5.5 | 1,422 | 5 | P | 98% | 0.68 | 2.0 | 2.02 | 2,358 |
| 31 | Y | 920 | 900 | 15 | 570 | 610 | 5.5 | 1,397 | 5 | P | 99% | 0.96 | 2.0 | 2.02 | 2,331 |
| 32 | Z | 910 | 890 | 17 | 550 | 600 | 5.5 | 1,452 | 7 | P | 98% | 0.57 | 2.0 | 2.02 | 2,409 |

**[0071]** These results can be explained by the following consideration.

**[0072]** The samples of tests Nos. 1 to 3, 11 to 21, and 24 to 32 are examples that satisfy the requirements of the present invention, and satisfactory wire drawability was confirmed without causing wire breakage. Particularly, regarding all samples of tests Nos. 3, 11 to 14, 16 to 18, 20, and 21 in which steels C to G, I to K, M, and N, each containing B, in Table 1 are used, wire drawing could be performed to high wire drawing strain without causing wire breakage. Of these, regarding samples of tests Nos. 11 and 12 in which steels D and E, each containing Co in addition to B, in Table 1 are used, wire drawing could be performed to higher wire drawing strain range (2.13 or more).

**[0073]** To the contrary, examples mentioned below have the following defects.

**[0074]** Regarding all samples of tests Nos. 4 to 10, steel C that satisfies the requirements of the present invention in Table 1 was used. However, since the production was performed without satisfying any one of conditions recommended by the present invention, wire breakage occurred during wire drawing.

**[0075]** Specifically, regarding the sample of test No. 4, because of low cooling starting temperature, the Si concentration difference decreased and a maximum length of proeutectoid cementite increased, and thus wire breakage occurred during wire drawing.

**[0076]** Regarding the sample of test No. 5, because of large average cooling rate from the cooling starting temperature to the cooling stop temperature, the pearlite area ratio decreased and thus wire breakage occurred during wire drawing.

**[0077]** Regarding the sample of test No. 6, because of small average cooling rate from the cooling starting temperature to the cooling stop temperature, the Si concentration difference decreased and a maximum length of proeutectoid cementite increased, and thus wire breakage occurred during wire drawing.

**[0078]** Regarding the sample of test No. 7, because of low cooling stop temperature, the pearlite area ratio decreased and thus wire breakage occurred during wire drawing.

**[0079]** Regarding the sample of test No. 8, because of high cooling stop temperature, the Si concentration difference decreased and a maximum length of proeutectoid cementite increased, and thus wire breakage occurred during wire drawing.

**[0080]** Regarding the sample of test No. 9, because of low holding temperature, the pearlite area ratio decreased and thus wire breakage occurred during wire drawing.

**[0081]** Regarding the sample of test No. 10, because of high holding temperature, the Si concentration difference decreased and a maximum length of proeutectoid cementite increased, and thus wire breakage occurred during wire drawing.

**[0082]** Regarding the sample of test No. 22, since steel O having large C content in Table 1 was used, a maximum length of proeutectoid cementite increased and thus wire breakage occurred during wire drawing.

**[0083]** Regarding the sample of test No. 23, since steel P having small Si content in Table 1 was used, the Si concentration difference decreased and a maximum length of proeutectoid cementite increased, and thus wire breakage occurred during wire drawing.

## Claims

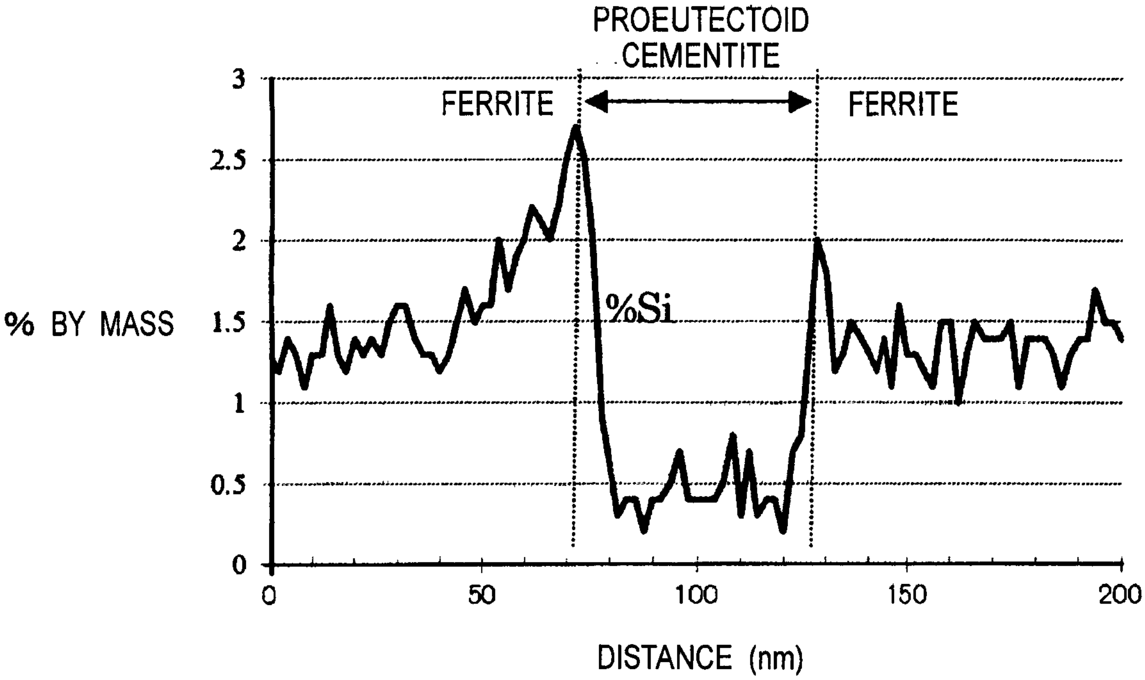
1. A steel wire rod comprising, in % by mass, C: 0.90 to 1.3%, Si: 0.4 to 1.2%, Mn: 0.2 to 1.5%, P: more than 0% and 0.02% or less, S: more than 0% and 0.02% or less, Al: more than 0% and 0.008% or less, Ti: 0 to 0.005%, and N: 0.001 to 0.008%, with the balance being iron and inevitable impurities, wherein
   the structure includes pearlite and proeutectoid cementite,
   an area ratio of pearlite is 90% or more relative to the entire structure,
   a maximum length of proeutectoid cementite is 15 μm or less, and
   a concentration difference between an average of the Si concentration inside proeutectoid cementite and a maximum value of the Si concentration inside ferrite that forms a lamellar structure of pearlite is 0.50 to 3%.

2. The steel wire rod according to claim 1, further comprising, in % by mass, at least one belonging to any one of the following (a) to (d):

   (a) B: more than 0% and 0.01% or less,
   (b) Co: more than 0% and 1.5% or less,
   (c) at least one selected from the group consisting of V: more than 0% and 0.5% or less, and Cr: more than 0% and 0.5% or less, and
   (d) at least one selected from the group consisting of Cu: more than 0% and 0.5% or less, Ni: more than 0% and 0.5% or less, and Nb: more than 0% and 0.5% or less.

3. A steel wire obtained by wire drawing of the steel wire rod according to claim 1 or 2.

Fig.1


PROEUTECTOID
CEMENTITE
FERRITE
FERRITE
%Si
% BY MASS
3
2.5
2
1.5
1
0.5
0
0
50
100
150
200
DISTANCE (nm)

## INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/060019

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 | 1996-2016 |
| Kokai Jitsuyo Shinan Koho | 1971-2016 | Toroku Jitsuyo Shinan Koho | 1994-2016 |

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<br>Y | JP 2001-181789 A (Nippon Steel Corp.),<br>03 July 2001 (03.07.2001),<br>claims; paragraphs [0022], [0039], [0057] to [0066]<br>(Family: none) | 1-3<br>1-3 |
| Y | JP 2003-183778 A (Sumitomo Metal Industries, Ltd.),<br>03 July 2003 (03.07.2003),<br>claims; paragraphs [0015], [0057] to [0062], [0069] to [0088]<br>(Family: none) | 1-3 |

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

* Special categories of cited documents:

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| | |
|---|---|
| Date of the actual completion of the international search<br>13 May 2016 (13.05.16) | Date of mailing of the international search report<br>24 May 2016 (24.05.16) |
| Name and mailing address of the ISA/<br>Japan Patent Office<br>3-4-3,Kasumigaseki,Chiyoda-ku,<br>Tokyo 100-8915,Japan | Authorized officer<br><br>Telephone No. |

Form PCT/ISA/210 (second sheet) (January 2015)

**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/JP2016/060019

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | JP 2010-270391 A (Nippon Steel Corp.),<br>02 December 2010 (02.12.2010),<br>claims; paragraphs [0032] to [0069]<br>& US 2012/0014831 A1<br>claims; paragraphs [0129] to [0189]<br>& US 2013/0263975 A1 & WO 2011/092905 A1<br>& EP 2532764 A1 & KR 10-2011-0101231 A<br>& CN 102301024 A | 1-3 |
| A | JP 2006-200039 A (Kobe Steel, Ltd.),<br>03 August 2006 (03.08.2006),<br>claims<br>& US 2006/0130946 A1<br>claims<br>& US 2009/0223610 A1 & EP 1674588 A1<br>& KR 10-2006-0072074 A & CN 1793399 A | 1-3 |
| A | JP 2005-2413 A (Sumitomo Metal Industries, Ltd.),<br>06 January 2005 (06.01.2005),<br>claims; paragraphs [0109] to [0129]<br>(Family: none) | 1-3 |
| A | JP 2007-39800 A (Nippon Steel Corp.),<br>15 February 2007 (15.02.2007),<br>claims; paragraphs [0043] to [0060]<br>& US 2009/0229711 A1<br>claims; paragraphs [0061] to [0092]<br>& WO 2007/001057 A1 & EP 1897964 A1<br>& KR 10-2008-0017465 A & CN 101208446 A | 1-3 |

## REFERENCES CITED IN THE DESCRIPTION

### Patent documents cited in the description

- JP 2014189855 A **[0009]**
- JP 2001181789 A **[0009]**
- JP 2003301240 A **[0009]**
- JP 2015070095 A **[0061]**
- JP 2015188843 A **[0061]**