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(54) **WIRE ROD FOR STEEL WIRE, AND STEEL WIRE**

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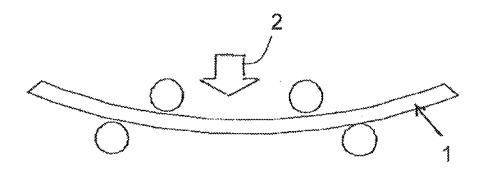|	
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(57) **ABSTRACT**

An object of the present invention is to provide a wire rod for a steel wire, which is excellent in low cycle fatigue characteristics and is useful as a material for a high-strength steel wire such as a wire rope or a PC steel wire, and to provide a steel wire that can exhibit such characteristics. A wire rod for a steel wire of the present invention comprises by mass: C: 0.70 to 1.3%; Si: 0.1 to 1.5%; Mn: 0.1 to 1.5%; N: 0.001 to 0.006%; Al: 0.001 to 0.10%; Ti: 0.02 to 0.20%; B: 0.0005 to 0.010%; P: 0% or more and 0.030% or less; and S: 0% or more and 0.030% or less, with the balance being iron and inevitable impurities, wherein, the wire rod having pearlite as a main phase and a hydrogen diffusion coefficient D in steel at 300° C. satisfies formula (1) below:

$$D \leq 2.5 \times 10^{-7} (\text{cm}^2/\text{sec}) \tag{1}$$

Fig. 1

WIRE ROD FOR STEEL WIRE, AND STEEL WIRE

TECHNICAL FIELD

[0001] The present invention relates to a wire rod for a steel wire, which is a material for a high-strength steel wire used for a wire rope, a PC steel wire, and the like, and to such a steel wire.

BACKGROUND ART

[0002] In steel stranded wires to which repetitive bending stress is applied, such as a rope for elevators and a winding rope of cranes, the bending fatigue characteristics of an element wire are important factors to determine the design strength and life of a rope. In recent years, needs for reduction in weight of a rope are increasing along with the acceleration of elevators and the reduction in size of cranes, and a high-strength wire rod for a steel wire is demanded, which satisfies the needs and is excellent in the bending fatigue characteristics. The high-strength wire rod for a steel wire, which is excellent in the bending fatigue characteristics, is also useful as a material for a PC (Prestressed Concrete) steel wire. Specifically, such a wire rod for a steel wire is required not to generate low cycle fatigue that occurs in 10^4 to 10^5 repeating cycles.

[0003] Various techniques for improving the characteristics of a wire rod have been heretofore proposed. For example, Patent Literature 1 discloses a technique of improving the fatigue strength by finely precipitating a BN-based inclusion in steel.

[0004] Patent Literature 2 discloses a technique of improving the fatigue characteristics which are evaluated by a 10 cycle rotary bending fatigue test, by reducing the amount of hydrogen in an extra fine steel wire having a wire drawing-processed pearlite structure.

PRIOR ART DOCUMENT

Patent Literatures

[0005] Patent Literature 1: JP 2011-225900 A
[0006] Patent Literature 2: JP 11-256274 A

SUMMARY OF THE INVENTION

Problems to be Solved by the Invention

[0007] The characteristic to be an issue in the technique of Patent Literature 1 is high cycle fatigue that occurs near the fatigue limit of 10^7 repeating cycles, and the mechanism of the high cycle fatigue is different from that of the above-mentioned low cycle fatigue. In products that are exposed to outside air over a long period of time, such as a wire rope, a fatigue crack easily occurs by oxidation on a surface layer part and friction between element wires, and hydrogen intruded into steel accelerates development of a crack. Thus, the material breaks much earlier than its fatigue limit, resulting in a short life. Therefore, it is necessary to take measures against hydrogen.

[0008] Further, the fatigue characteristic considered in Patent Literature 2 is also high cycle fatigue. However, in products that are subjected to intrusion of hydrogen from the outside, such as a wire rope and a PC steel wire, low cycle fatigue characteristics are deteriorated by hydrogen intruded

into the products from the outside. Therefore, it is insufficient only to reduce the amount of hydrogen in steel as in Patent Literature 2.

[0009] The present invention has been made under the circumstances as described above, and an object of the present invention is to provide a wire rod for a steel wire, which is excellent in low cycle fatigue characteristics and is useful as a material for a high-strength steel wire such as a wire rope or a PC steel wire, and to provide a steel wire that can exhibit such characteristics.

Means for Solving the Problems

[0010] A wire rod for a steel wire of the present invention, which can solve the above problems, comprises by mass: C: 0.70 to 1.3%; Si: 0.1 to 1.5%; Mn: 0.1 to 1.5%; N: 0.001 to 0.006%; Al: 0.001 to 0.10%; Ti: 0.02 to 0.20%; B: 0.0005 to 0.010%; P: 0% or more and 0.030% or less; and S: 0% or more and 0.030% or less, with the balance being iron and inevitable impurities, wherein, the wire rod having pearlite as a main phase and a hydrogen diffusion coefficient D in steel at 300° C. satisfies formula (1) below:

$$D \le 2.5 \times 10^{-7} (\text{cm}^2/\text{sec}) \tag{1}$$

[0011] The phrase "having pearlite as a main phase" means that 95 area % or more of the metallographic structure is a pearlite structure.

[0012] It is also preferred that the wire rod for a high-strength steel wire of the present invention further comprises by mass:

[0013] (a) at least one of Cr: more than 0% and 1.0% or less, and V: more than 0% and 0.5% or less;

[0014] (b) at least one of Ni: more than 0% and 0.5% or less, and Nb: more than 0% and 0.5% or less;

[0015] (c) Co: more than 0% and 1.0% or less;

[0016] (d) at least one of Mo: more than 0% and 0.5% or less, and Cu: more than 0% and 0.5% or less; and the like.

[0017] The present invention also encompasses a steel wire comprising the above-mentioned chemical composition, wherein a hydrogen diffusion coefficient D in steel at 300° C. satisfies formula (1) below:

$$D \le 2.5 \times 10^{-7} (\text{cm}^2/\text{sec}) \tag{1}$$

Effects of the Invention

[0018] According to the present invention, an effect of trapping hydrogen Ti-based inclusions such as TiC diffused finely can inhibit diffusion of hydrogen in steel to reduce the diffusion coefficient of hydrogen, so that a steel wire rod excellent in fatigue characteristics can be obtained. Particularly, the steel wire exhibits excellent characteristics against low cycle fatigue caused by repetitive stress load of about 10^4 to 10^5 cycles.

BRIEF DESCRIPTION OF THE DRAWING

[0019] FIG. 1 is a schematic diagram illustratively showing an execution state of a four point bending fatigue test.

MODE FOR CARRYING OUT THE INVENTION

[0020] The present inventors have earnestly searched for a factor that affects the low cycle fatigue characteristics in a steel wire rod of a metallographic structure having pearlite as a main phase. The deterioration in fatigue characteristics

caused by hydrogen occurs when hydrogen in steel diffuses into minute cracks generated in a steel material by repetitive load of stress to embrittle a structure around the cracks. In addition to hydrogen that has been occluded in steel during a manufacturing process, hydrogen intruded from the outside also deteriorates the fatigue characteristics in the same manner. Therefore, by inhibiting diffusion of hydrogen in steel and reducing the amount of hydrogen accumulated around cracks, the fatigue characteristics can be improved. Specifically, the fatigue characteristics are improved by setting the hydrogen diffusion coefficient in steel at 300° C. to 2.5×10^{-7}(cm²/sec) or less.

[0021] The hydrogen diffusion coefficient D is a physical property value depending on the temperature. In the present invention, the hydrogen diffusion coefficient D in steel at 300° C. is set as an index. The reason therefor derives from a measuring method of the hydrogen diffusion coefficient. For measurement of the hydrogen diffusion coefficient D, a method of analyzing a release curve of hydrogen gas obtained by raising the temperature of a specimen in a measuring instrument is employed, while a low temperature part of the release curve is susceptible to the influence of disturbance, and therefore is not suitable for accurate evaluation. This is because hydrogen to be released at a low temperature is so-called diffusible hydrogen, diffusion of the hydrogen at room temperature cannot be ignored, and therefore the method is affected by the storage state of a specimen subjected to the measurement. The hydrogen diffusion coefficient D is preferably 2.3×10^{-7}(cm²/sec) or less, more preferably 2.0×10^{-7}(cm²/sec) or less.

[0022] As means of inhibiting diffusion of hydrogen, it is effective to finely disperse in steel Ti-based, inclusions such as TiC, which have an effect of adsorbing hydrogen.

[0023] In the wire rod for a steel wire according to the present invention, it is necessary to also appropriately adjust the chemical composition of the wire rod so as to exhibit the basic characteristics of the ire rod when the wire rod is applied. The chemical composition is as follows. It is to be noted that "%" in the chemical composition is "% by mass" in any case.

(C: 0.70 to 1.3%)

[0024] C is an element effective for enhancing the strength, and a wire rod (steel wire rod) before cold working and a steel wire after cold working are improved in the strength with the increasing amount of C. Therefore, the amount of C is determined to be 0.70% or more. The amount of C is preferably 0.74% or more, more preferably 0.78% or more. An excessive amount of C, however, causes precipitation proeutectoid cementite (hereinafter, may be abbreviated as "proeutectoid θ") to lead to breaking of a wire during a wire drawing process. Therefore, the amount of C is determined to be 1.3% or less. The amount of C is preferably 1.2% or less, more preferably 1.1% or less.

(Si: 0.1 to 1.5%)

[0025] Si has an action as a deoxidizing agent, and also has an action of improving the strength of a wire rod. For effective exhibition of these actions, the amount of Si is determined to be 0.1% or more. The amount of Si is preferably 0.15% or more, more preferably 0.18% or more. On the other hand, an excessive amount of Si deteriorates cold wire drawability to cause the increase in the ratio of

breaking of a wire. Therefore, the amount of Si is determined to be 1.5% or less. The amount of Si is preferably 1.4% or less, more preferably 1.3% or less.

(Mn: 0.1 to 1.5%)

[0026] Mn particularly has, in addition to a deoxidizing action as with Si, an action of fixing S in steel as MnS to enhance toughness and ductility of steel. For effective exhibition of these actions, the amount of Mn is set to 0.1% or more. The amount of Mn is preferably 0.15% or more, more preferably 0.20% or more. Mn is, however, an element that is easily segregated, and excessive addition thereof may possibly cause excessive increase of hardenability at a Mn segregated portion to produce a supercooled structure such martensite. Therefore, the amount of Mn is determined to be 1.5% or less. The amount of Mn is preferably 1.4% or less, more preferably 1.3% or less.

(N: 0.001 to 0.006%)

[0027] N chemically combines with B in steel to form BN, so that the effect of B is lost. Further, N in a solid solution state causes deterioration of torsion characteristics due to strain aging during wire drawing, and causes a longitudinal crack in significant cases. For prevention of these adverse effects, the amount of N is set to 0.006% or less. The amount of N is preferably 0.005% or less, more preferably 0.004% or less. On the other hand, a small amount of N gives an effect of refining crystal grains by a nitride such as TiN or AlN to enhance ductility of a wire rod. For exhibition of such an effect, the amount of N is set to 0.001% or more. The amount of N is preferably 0.0015% or more, more preferably 0.0020% or more.

(Al: 0.001 to 0.10%)

[0028] Al is an effective deoxidizing element. Al also has an effect of forming a nitride such as AlN to refine crystal grains. For effective exhibition of such an effect, the amount of Al is set to 0.001% or more. The amount of Al is preferably 0.002% or more, more preferably 0.003% or more. On the other hand, excessive addition of Al forms an oxide such as Al_2O_3 to increase breaking of a wire during wire drawing. From the viewpoint described above, the amount of Al is set to 0.10% or less. The amount of Al is preferably 0.09% or less, more preferably 0.08% or less.

(Ti: 0.02 to 0.20%)

[0029] Ti has an action of forming a carbide such as TiC to reduce the hydrogen diffusion coefficient, so that Ti improves the fatigue characteristics of a steel wire. Further, Ti also has an action of chemically combining with N in steel to form a nitride such as TiN, so that Ti prevents the deterioration of torsion characteristics caused by N. For effective exhibition of those effects, the amount of Ti is set to 0.02% or more. The amount of Ti is preferably 0.03% or more, more preferably 0.04% or more. On the other hand, an excessive amount of Ti causes precipitation of large amounts of Ti inclusions such as TiC and TiN to increase breaking of a wire during wire drawing. Therefore, the amount of Ti is set to 0.20% or less. The amount of Ti is preferably 0.15% or less, further preferably 0.10% or less.

(B: 0.0005 to 0.010%)

[0030] B has an action of suppressing proeutectoid ferrite (hereinafter, may be abbreviated as "proeutectoid α") to be precipitated in a grain boundary, and is effective to improve the fatigue characteristics. B can also be expected to give an effect of improving the torsion characteristics by forming BN to fix a solid solution N in steel. For effective exhibition of the effects B, the amount of B is necessary to be 0.0005% or more. The lower limit of the amount of B is preferably 0.0007% or more, more preferably 0.001% or more. On the other hand, an excessive amount of B causes precipitation of a Fe—B compound as a compound of B and Fe, e.g., FeB_2 to cause a crack during hot rolling. Therefore, it is necessary to set the amount of B to 0.010% or less. The amount of B is preferably 0.008% or less, more preferably 0.006% or less.

(P: 0% or More and 0.030% or Less)

[0031] P is segregated in a prior austenite grain boundary to embrittle the grain boundary, so that the fatigue strength is deteriorated. Therefore, the less the content of P, the more preferable it is. Therefore, the amount of P is set to 0.030% or less. The amount of P is preferably 0.025% or less, more preferably 0.020% or less. The amount of P may be 0%, but P is generally contained in an amount of 0.001% or more.

(S: 0% or More and 0.030% or Less)

[0032] S is segregated in a prior austenite grain boundary as with P to embrittle the grain boundary, so that the fatigue strength is deteriorated. Therefore, the less the content of S, the more preferable it is. Thus, the amount of S is set to 0.030% or less. The amount of S is preferably 0.025% or less, more preferably 0.020% or less. The amount of S may be 0%, but S is generally contained in an amount of 0.001% or more.

[0033] The basic components of the wire rod of the present invention are as described above, and the balance is substantially iron. However, inclusion of inevitable impurities in steel, which are brought depending on the state of a raw material, a material, manufacturing equipment or the like, is naturally accepted.

[0034] It is also preferred that the wire rod of the present invention further contain, as necessary, for further improvement of characteristics such as strength, toughness and ductility:

   [0035]   (a) at least one of Cr: more than 0% and 1.0% or less, and V: more than 0% and 0.5% or less;
   [0036]   (b) at least one of Ni: more than 0% and 0.5% or less, and Nb: more than 0% and 0.5% or less;
   [0037]   (c) Co: more than 0% and 1.0% or less;
   [0038]   (d) at least one of Mo: more than 0% and 0.5% or less, and Cu: more than 0% and 0.5% or less; and the like.

(At Least One of Cr: More than 0% and 1.0% or Less, and V: More than 0% and 0.5% or Less)

[0039] Cr and V are elements useful for enhancing the strength (tensile strength) of a wire rod, and one or two in combination of these elements may be contained.

[0040] Particularly, Cr has an action of reducing the lamellar spacing of pearlite to enhance the strength and toughness of a wire rod. For effective exhibition of such an action, the amount of Cr is preferably 0.05% or more. The amount of Cr is more preferably 0.10% or more, further preferably

0.15% or more. On the other hand, an excessive amount of Cr increases hardenability to increase a risk of generating a supercooled structure during hot rolling. Therefore, the amount of Cr is preferably set to 1.0% or less. The amount of Cr is more preferably 0.8% or less, further preferably 0.6% or less.

[0041] V has an effect of forming a carbonitride to improve the strength of a wire rod. In addition, V not only forms a nitride with an excessive solid solution N after precipitation of AlN as with Nb to contribute to refining of crystal grains, but also has an effect of suppressing aging embrittlement by fixation of the solid solution N. For effective exhibition of such actions, the amount of V is preferably 0.01% or more, more preferably 0.02% or more, further preferably 0.03% or more. V is, however, an expensive element, and even excessive addition of V only causes saturation of the effect of V, leading to economical waste. Therefore, the amount of V is preferably 0.5% or less, more preferably 0.4% or less, further preferably 0.2% or less.

(At Least One of Ni: More than 0% and 0.5% or Less, and Nb: More than 0% and 0.5% or Less)

[0042] Ni and Nb are elements useful for enhancing the toughness of a steel wire, and one or two in combination of these elements may be contained.

[0043] Particularly, Ni is an element that enhances the toughness of a steel wire after wire drawing. For effective exhibition of such an action, the amount of Ni is preferably 0.05% or more, more preferably 0.1% or more, further preferably 0.2% or more. However, even excessive addition of Ni only causes saturation of the effect of Ni, leading to economical waste. Therefore, the amount of Ni is preferably 0.5% or less, more preferably 0.4% or less, further preferably 0.3% or less.

[0044] Nb not only forms a nitride as with Ti and Al to contribute to refining of crystal grains for improvement of the toughness of a steel wire, but also has an effect of suppressing aging embrittlement by fixation of a solid solution N. For effective exhibition of such actions, the amount of Nb is preferably 0.01% or more, more preferably 0.03% or more, further preferably 0.05% or more. Nb is, however, an expensive element, and even excessive addition of Nb only causes saturation of the effect of Nb, leading to economical waste. Therefore, the amount of Nb is preferably 0.5% or less, more preferably 0.4% or less, further preferably 0.3% or less.

(Co: More than 0% and 1.0% or Less)

[0045] Co has an action of reducing production of proeutectoid cementite to make the structure a uniform pearlite structure, particularly when the amount of C is high. For effective exhibition of such an action, the amount of Co is preferably 0.05% or more, more preferably 0.1% or more, further preferably 0.2% or more. However, even excessive addition of Co only causes saturation of the effect of Co, leading to economical waste. Therefore, the amount of Co is preferably 1.0% or teas, more preferably 0.8% or less, further preferably 0.6% or less.

(At Least One of Mo: More than 0% and 0.5% or Less, and Cu: More than 0% and 0.5% or Less)

[0046] Mo is an element that improves corrosion resistance of a steel wire. For effective exhibition of such an action, the amount of Mo is preferably 0.05% or more, more preferably 0.1% or more, further preferably 0.2% or more. An excessive amount of Mo, however, easily causes generation of a supercooled structure during hot rolling and also

deteriorates the ductility. Therefore, the amount of Mo is preferably 0.5% or less, more preferably 0.4% or less, further preferably 0.3% or less.

[0047] Cu is an element that improves corrosion resistance of a steel wire as with Mo. For effective exhibition of such an action, the amount of Cu is preferably 0.05% or more, more preferably 0.08% or more, further preferably 0.10% or more. An excessive amount of Cu, however, causes reaction of Cu with S to segregate CuS in a grain boundary portion, so that a flaw is generated during a manufacturing process of a wire rod. For avoidance of such an adverse effect, the amount of Cu is preferably 0.5% or less, more preferably 0.4% or less, further preferably 0.3% or less.

[0048] One or two in combination of Mo and Cu may be contained.

[0049] Next described is a method that enables manufacturing of the wire rod for a steel wire according to the present invention.

[0050] A wire rod before cold wire drawing is generally manufactured by melting, bloom rolling and hot rolling of steel obtained by appropriately controlling the chemical components thereof, further followed by a patenting treatment as necessary. It is important to appropriately control the precipitation behavior of Ti-based inclusions such as TiC in addition to appropriate control of the content of Ti to the above-mentioned range, for manufacturing the wire rod of the present invention while satisfying the requirements (metallographic structure and hydrogen diffusion coefficient) defined in the present invention.

[0051] First, it is preferred that a slab cast is heated to 1200° C. or higher in bloom rolling to decompose coarse TiC precipitated during casting. A heating temperature lower than 1200° C. causes coarse TiC to remain in a wire rod so that the hydrogen diffusion coefficient cannot be sufficiently reduced, resulting in deterioration of the fatigue strength. The heating temperature is more preferably 1250° C. or higher, further preferably 1300° C. or higher. An excessively high heating temperature, however, causes melting of a wire rod, and therefore the heating temperature is generally set to up to about 1400° C.

[0052] For subsequent hot rolling, it is preferred that in addition to heating to 1000° C. or higher, the strain rate at final 4 passes of the rolling is set to 0.5 sec^{-1} or more, and crystal grains are refined by dynamic recrystallization, so that fine TiC is precipitated. The strain rate of less than 0.5 sec^{-1} does not allow sufficient refining of TiC so that the hydrogen diffusion coefficient D cannot be sufficiently reduced. The strain rate at this time is more preferably 0.8 sec^{-1} or more, further preferably 1.0 sec^{-1} or more. However, in terms of equipment load, generally, the strain rate is preferably set to 5 sec^{-1} or less. A strain rate Vϵ can be represented by the following formula (2), with a sectional area $S_0(m^2)$ of a wire rod before entry into the first roll that is a roll 4 passes before the final pass, a sectional area $S_4(m^2)$ after passing the final pass, and the total passing time (rolling time) t (sec) of the 4 passes:

$$V\epsilon = \{\ln(S_0/S_4)\}/t \qquad (2).$$

[0053] It is preferred that after the hot rolling, the rolled material (wire rod) is sufficiently cooled with water, and placing temperature of the rolled material is controlled to 800 to 1000° C. A placing temperature exceeding 1000° C. may possibly cause coarsening of TiC during cooling on a conveyor after the placing. The placing temperature is more preferably 980° C. or lower, further preferably 950° C. or lower. A placing temperature lower than 800° C. causes increase in deformation resistance of a wire rod so that a placing defect in a laying head, e.g., unavailable coiling and the like, may occur. Therefore, the placing temperature is preferably 800° C. or higher. The placing temperature is more preferably 820° C. or higher, further preferably 850° C. or higher.

[0054] After the placing, the wire rod is cooled on a cooling conveyor to cause pearlite transformation during the cooling. It is preferred that the wire rod is rapidly cooled by setting the average cooling rate before the start of the pearlite transformation to 5° C./sec or more. A low average cooling rate at this time easily causes coarsening of TiC so that the hydrogen diffusion coefficient may possibly increase. Further, in some cases, an average cooling rate of less than 5° C./sec causes local precipitation of a structure in which the lamellar spacing is extremely coarse, which is so-called coarse pearlite, so that the wire drawability deteriorated. The start of the pearlite transformation may be obtained by measuring the temperature of the wire rod and determining a changing point (inflection point) caused by transformation heating in a cooling curve. The average cooling rate is more preferably 10° C./sec or more, further preferably 15° C./sec or more. The upper limit of the average cooling rate is preferably 100° C./sec or less, more preferably 50° C./sec or less.

[0055] The wire rod obtained as described above can be used as a steel wire after directly performing a wire drawing process (cold working) on the wire rod, while a patenting treatment may be performed on the wire rod before the wire drawing process. Such a patenting treatment before the wire drawing process can enhance the strength of the wire rod and reduce the variation in strength.

[0056] When the degree of the wire drawing process is predicted to be large as in the case of manufacturing a steel wire having a small diameter, it is also useful to perform a patenting treatment after drawing a wire from a rolled material to some extent, to return the structure of the wire rod to an unprocessed pearlite structure, followed by a further wire drawing process. At this time, when finely precipitated TiC is retained even after the reheating treatment, it is possible to keep the hydrogen diffusion coefficient D low even by a common patenting treatment.

[0057] The heating temperature during the patenting treatment (hereinafter, this temperature may be referred to as a "reheating temperature") is preferably about 900 to 1000° C., more preferably 920° C. or higher and 980° C. or lower. The reheating temperature is preferably 900° C. or higher from the viewpoints of preventing a carbide from remaining in a non-solid solution state and completely austenitizing the structure, while an excessively high reheating temperature causes coarsening of TiC so that the hydrogen diffusion coefficient D increases. The holding temperature at the patenting treatment is preferably about 530 to 600° C., more preferably 550° C. or higher and 580° C. or lower.

[0058] In the wire rod of the present invention, the hydrogen diffusion coefficient D in steel is sufficiently reduced, and therefore a steel wire obtained by performing cold working on the wire rod, and products such as a wire rope and a PC steel wire, which partially or wholly include the steel wire, are excellent in fatigue characteristics compared to a general product.

[0059] The present application claims the benefit of the right of priority based on the Japanese Patent Application No. 2014-136223 filed on Jul. 1, 2014. The entire contents of the specification of the Japanese Patent Application No. 2014-136223 are incorporated herein by reference.

EXAMPLES

[0060] Hereinafter, the present invention will be described more specifically with reference to examples. The present invention is not limited by the following examples, but can be naturally carried out by adding appropriate modifications thereto within a range that is suitable for the gist described

above and below, and the modifications are included in the technical range of the present invention.

[0061] Steel ingots each having the chemical composition shown in Table 1 below were subjected to bloom rolling and hot rolling under the conditions shown in Table 2 below to process the ingots into wire rod coils, and a part of the coils was further subjected to a patenting treatment under the conditions shown in Table 3 below. It means that one having a rolling wire diameter shown in Table 2 below different from a patenting wire diameter shown in Table 3 below was subjected to a heat treatment after intermediate wire drawing.

TABLE 1

| Steel type | Chemical composition [mass %], balance being iron and inevitable impurities | | | | | | | | | | | | | | | |
	C	Si	Mn	Al	P	S	N	Ti	B	Cr	V	Ni	Nb	Co	Mo	Cu
A	0.97	0.40	0.30	0.035	0.010	0.010	0.0042	0.06	0.0018	0.20	—	—	—	—	—	—
B	0.92	0.90	0.50	0.040	0.011	0.006	0.0037	0.02	0.0010	—	—	—	—	—	—	—
C	0.82	0.20	0.70	0.030	0.008	0.008	0.0053	0.08	0.0020	—	—	—	—	—	—	—
D	0.88	0.40	0.75	0.033	0.010	0.010	0.0044	0.07	0.0015	—	0.09	—	—	—	—	—
E	0.80	0.25	0.50	0.002	0.010	0.011	0.0032	0.09	0.0030	—	—	—	—	—	—	—
F	0.97	0.62	0.51	0.060	0.007	0.010	0.0046	0.05	0.0020	—	—	—	0.10	—	—	—
G	0.84	0.43	1.20	0.040	0.010	0.020	0.0051	0.10	0.0025	—	—	—	—	—	—	—
H	1.10	0.60	0.70	0.080	0.020	0.008	0.0048	0.09	0.0022	—	—	0.05	—	—	—	—
I	0.90	0.50	0.81	0.090	0.007	0.010	0.0052	0.09	0.0017	—	—	—	—	—	—	0.07
J	0.75	0.40	0.60	0.050	0.008	0.012	0.0031	0.05	0.0035	—	—	—	—	—	0.10	—
K	0.85	0.24	0.61	0.020	0.006	0.008	0.0042	0.16	0.0055	—	—	—	—	0.20	—	—
L	1.30	0.69	0.51	0.003	0.010	0.007	0.0058	0.20	0.0005	—	—	—	—	—	—	—
M	0.80	0.25	0.50	0.020	0.015	0.011	0.0036	0.08	0.0007	—	—	—	—	—	—	—
N	0.93	1.43	1.50	0.030	0.010	0.010	0.0052	0.02	0.0090	—	—	—	—	—	—	—
O	0.70	0.20	0.80	0.050	0.008	0.013	0.0047	0.07	0.0080	—	—	—	—	—	—	—
P	0.65	0.39	0.68	0.070	0.010	0.010	0.0018	0.05	0.0012	—	—	—	—	—	—	—
Q	1.40	0.40	0.58	0.060	0.008	0.011	0.0037	0.03	0.0024	—	—	—	—	—	—	—
R	0.96	0.61	0.59	0.050	0.008	0.011	0.0044	0.01	0.0055	—	—	—	—	—	—	—
S	0.89	0.69	0.70	0.080	0.008	0.010	0.0053	0.25	0.0023	—	—	—	—	—	—	—
T	0.84	0.50	0.50	0.040	0.010	0.007	0.0055	0.04	0.0150	—	—	—	—	—	—	—
U	0.92	0.40	0.80	0.080	0.015	0.010	0.0041	0.05	0.0003	—	—	—	—	—	—	—

TABLE 2

		Bloom rolling Heating temperature (° C.)	Hot rolling				
Test No.	Steel type		Heating temperature (° C.)	Strain rate (sec⁻¹)	Placing temperature (° C.)	Average cooling rate (° C./sec)	Rolling wire diameter (mm)
1	A	1250	1100	0.7	900	15	5.5
2	B	1300	1100	0.7	900	13	6.0
3	C	1200	1100	0.8	900	13	6.0
4	C	1100	1100	0.8	900	13	6.0
5	C	1200	1100	0.3	870	13	6.0
6	C	1200	1100	0.8	700	Placing defect	
7	C	1200	1100	0.8	1100	13	6.0
8	C	1200	1100	0.8	950	4	6.0
9	D	1250	1000	0.6	850	10	8.0
10	E	1250	1000	1.1	900	8	10.0
11	F	1250	1150	1.3	820	15	5.5
12	G	1250	1150	0.7	850	7	11.0
13	H	1250	1000	0.8	880	6	13.0
14	I	1250	1000	1.1	850	7	12.0
15	J	1250	1150	0.5	900	7	12.0
16	K	1300	1100	1.0	900	6	14.0
17	L	1250	1100	0.7	900	6	14.0
18	M	1300	1100	0.9	870	10	8.0
19	N	1300	1150	1.2	880	13	6.0
20	O	1300	1150	1.2	940	13	6.0
21	P	1250	1100	0.7	820	10	8.0
22	Q	1250	1100	0.6	820	10	8.0
23	R	1250	1100	0.5	850	10	8.0

TABLE 2-continued

		Hot rolling				
Test No.	Steel type	Bloom rolling Heating temperature (° C.)	Heating temperature (° C.)	Strain rate (sec⁻¹)	Placing temperature (° C.)	Average cooling rate (° C./sec)	Rolling wire diameter (mm)
24	S	1250	1100	0.8	880	10	8.0
25	T	1250		Wire breaking during rolling			
26	U	1250	1100	0.8	880	11	7.0

TABLE 3

		Patenting conditions		
Test No.	Steel type	Reheating temperature (° C.)	Holding temperature (° C.)	Wire diameter (mm)
1	A	—	—	—
2	B	—	—	—
3	C	950	580	6.0
4	C	950	580	6.0
5	C	950	580	6.0
6	C	—	—	—
7	C	950	580	6.0
8	C	1000	580	6.0
9	D	950	570	8.0
10	E	950	570	10.0
11	F	950	590	3.0
12	G	950	580	11.0
13	H	1000	550	13.0
14	I	950	560	12.0
15	J	950	560	12.0
16	K	1000	540	14.0
17	L	1000	540	14.0
18	M	950	570	8.0
19	N	950	580	4.0
20	O	950	580	4.0
21	P	950	580	8.0
22	Q	950	580	8.0
23	R	950	580	8.0
24	S	950	580	8.0
25	T	—	—	—
26	U	950	580	7.0

[0062] A sample obtained from each of the wire rods before finish wire drawing was used for a tensile test, evaluation of the metallographic structure, and measurement of the hydrogen diffusion coefficient D which were conducted by the following methods.

(Tensile Test)

[0063] The tensile strength TS of the obtained sample was measured in accordance with JIS Z 2241 (2011). Eight steel wires were prepared and the average value thereof was obtained. The results are shown in Table 4 below.

(Evaluation of Metallographic Structure)

[0064] As to the metallographic structure, a transverse section of the obtained sample was observed by an optical microscope. It means that one indicated by "P" in the item of the metallographic structure of Table 4 below has a pearlite structure of 95 area % or more, i.e., pearlite as a main phase. While, it means that one indicated by "P+α" or "P+θ" in the item of the metallographic structure has a pearlite structure of less than 95 area %, and has a mixed structure of pearlite with ferrite (α) or cementite (θ) having an area % of more than 5.

(Measurement of Hydrogen Diffusion Coefficient D)

[0065] Hydrogen was charged into the obtained sample to the saturation state, and a hydrogen release curve was obtained by temperature rise analysis. The temperature rise rate was set to 12° C./sec, and the hydrogen release amount was measured by an atmospheric pressure ionization mass spectrometer. The hydrogen charging conditions were use of H_2SO_4 aqueous solution (pH3)+KSCN (0.01 mol/L) as an electrolytic solution and charge of 48 hours at a current density of 5 mA/cm². The charged sample was stored in liquid nitrogen until the measurement so as to minimize scattering of hydrogen as much as possible.

[0066] The hydrogen diffusion coefficient D was obtained by fitting the obtained hydrogen release curve with a hydrogen release curve obtained by a numerical calculation with the diffusion coefficient as a parameter, supposing that hydrogen was approximately uniformly distributed in the sample and the shape of the sample was an infinite cylinder. The results are shown in Table 4 below. In order to make the approximation of the infinite cylinder effective, the length of the sample was set to not less than 5 times the diameter of the sample. At this time, a peak having a peak temperature of 200° C. or higher was used as a release peak of hydrogen used for the fitting. A peak that appeared at a low temperature of 200° C. or lower was not used for evaluation of the diffusion coefficient because such a peak is referred to as diffusible hydrogen and is considered to be affected by disturbance such as release of hydrogen even in diffusion at room temperature. From a correlation curve of the temperature and the diffusion coefficient, which was obtained in the manner described above, the diffusion coefficient at 300° C. was obtained as the hydrogen diffusion coefficient D.

[0067] Next, the obtained wired rod coils were subjected to a wire drawing process to produce a steel wire (wire), and a tensile test, evaluation of the torsion characteristics, evaluation of the fatigue characteristics, and measurement of the hydrogen diffusion coefficient D were conducted. Table 5 below shows an area reduction ratio during the wire drawing process and a wire diameter of a steel wire obtained by the wire drawing process.

(Tensile Test)

[0068] The tensile strength TS and yield point YP of the steel wires were measured in accordance with JIS Z 2241 (2011). Eight steel wires were prepared and the average value thereof was obtained. The results are shown in Table 5 below. A value obtained by multiplying the tensile strength TS by 0.45 is also shown in Table 5 below.

(Evaluation of Torsion Characteristics)

[0069] The torsion characteristics were evaluated on the basis of a torsion value required before breaking (number of

times of torsion before breaking) by conducting a torsion test. The torsion value in Table 5 below is the average value of N=5 wires. At this time, the torsion rate was set to 52 times/min, and the tensile force was set to 500 gf (4.9N). The torsion value was normalized by converting the distance between chucks (length of the sample wire) to 100 times of the wire diameter d (100 d). In addition, a longitudinal crack was discriminated from a normal fracture surface by fracture surface observation, and one having even one longitudinal crack in 5 wires was described as "yes" in the item of the longitudinal crack in the following Table 5.

(Evaluation of Fatigue Characteristics)

[0070] The fatigue characteristics were evaluated by conducting a repetitive four point bending fatigue test with a jig having 4 supporting points. In FIG. 1, a numeral 1 is a test piece (wire rod), a numeral 2 is a direction to which a repetitive stress is applied, and a circle represents a supporting point. The test was conducted by one side bending, and the difference between the maximum stress and the minimum stress was defined as stress amplitude. Bending was repeated 100000 cycles with various types of stress amplitude, and in a test of N=3 wires, one that had no broken wire (breaking of a wire) was determined to be acceptable, while one that had even one broken wire was determined to be unacceptable. The maximum stress amplitude of the specimen determined to be acceptable was defined as 100000 cycle fatigue strength. The 100000 cycle fatigue strength is shown in Table 5 below. The stress wave form was a sine wave, and the frequency was set to 10 Hz.

(Measurement of Hydrogen Diffusion Coefficient D)

[0071] Also for the steel wire, the hydrogen diffusion coefficient D was obtained as a reference value under the same conditions as in the above. The results are shown in Table 5 below.

TABLE 4

		Steel wire rod		
Test No.	Steel type	Hydrogen diffusion coefficient D (cm²/sec)	Metallographic structure	TS (MPa)
1	A	1.2×10^{-7}	P	1205
2	B	1.6×10^{-7}	P	1212
3	C	2.1×10^{-7}	P	1252
4	C	4.3×10^{-7}	P	1252
5	C	5.4×10^{-7}	P	1241
6	C		—	
7	C	3.8×10^{-7}	P	1260
8	C	2.8×10^{-7}	P	1240
9	D	0.9×10^{-7}	P	1271
10	E	1.1×10^{-7}	P	1241
11	F	1.3×10^{-7}	P	1383
12	G	0.8×10^{-7}	P	1277
13	H	2.2×10^{-7}	P	1321
14	I	1.8×10^{-7}	P	1259
15	J	1.7×10^{-7}	P	1225
16	K	1.4×10^{-7}	P	1279
17	L	1.9×10^{-7}	P	1301
18	M	1.5×10^{-7}	P	1261
19	N	1.1×10^{-7}	P	1257
20	O	1.7×10^{-7}	P	1357
21	P	1.6×10^{-7}	P + α	1067
22	Q	1.9×10^{-7}	P + θ	1403
23	R	5.1×10^{-7}	P	1256
24	S	2.3×10^{-7}	P	1240
25	T		—	
26	U	3.4×10^{-7}	P	1301

TABLE 5

		Wire (steel wire)								
Test No.	Steel type	Wire diameter (mm)	Area reduction ratio (%)	TS (MPa)	YP (MPa)	Torsion value (times/100 d)	Longitudinal crack	Fatigue strength (MPa)	0.45TS (MPa)	Hydrogen diffusion coefficient D (cm²/sec)
1	A	1.5	92.6	2607	1846	34	—	1050	1038	1.3×10^{-7}
2	B	1.7	92.0	2277	1822	34	—	1100	1025	1.5×10^{-7}
3	C	1.7	92.0	2352	1882	32	—	1100	1058	2.3×10^{-7}
4	C	1.7	92.0	2311	1842	27	—	800	1040	4.5×10^{-7}
5	C	1 7	92.0	2331	1865	32	—	800	1049	5.2×10^{-7}
6	C						—			
7	C	1.7	92.0	2367	1894	32	—	700	1065	4.1×10^{-7}
8	C	1.7	92.0	2299	1811	21	—	700	1035	3.2×10^{-7}
9	D	2.3	91.7	2370	1896	42	—	1100	1067	1.1×10^{-7}
10	E	2.7	92.7	2388	1911	31	—	1100	1075	1.0×10^{-7}
11	F	1.1	86.6	2283	1827	46	—	1050	1028	1.2×10^{-7}
12	G	3.3	91.0	2332	1866	36	—	1100	1049	0.9×10^{-7}
13	H	5.1	84.6	2054	1643	44	—	1000	924	2.4×10^{-7}
14	I	3.3	92.4	2370	1896	32	—	1100	1067	1.8×10^{-7}
15	J	3.2	92.9	2372	1898	31	—	1200	1067	1.5×10^{-7}
16	K	5.2	86.2	1907	1526	33	—	1000	858	1.6×10^{-7}
17	L	7.0	75.0	1820	1456	32	—	900	819	1.9×10^{-7}
18	M	3.0	85.9	2069	1647	43	—	1100	927	1.5×10^{-7}
19	N	1.3	89.4	2205	1764	37	—	1100	992	1.3×10^{-7}
20	O	1.3	89.4	2381	1905	21	—	1200	1071	1.7×10^{-7}
21	P	2.7	88.6	1697	1358	5	Yes	400	764	1.7×10^{-7}

TABLE 5-continued

			Area					Wire (steel wire)			
Test No.	Steel type	Wire diameter (mm)	reduction ratio (%)	TS (MPa)	YP (MPa)	Torsion value (times/100 d)	Longitudinal crack	Fatigue strength (MPa)	0.45TS (MPa)	Hydrogen diffusion coefficient D (cm²/sec)	
22	Q					Breaking of wire					
23	R	3.0	85.9	2051	1641	18	—	600	923	5.3×10^{-7}	
24	S					Breaking of wire					
25	T					—					
26	U	2.7	85.1	2031	1625	7	Yes	500	914	3.2×10^{-7}	

[0072] These results lead to the following considerations.

[0073] As to Test Nos. 1 to 3 and 9 to 20, any of the chemical composition, the metallographic structure (area ratio of pearlite), and the hydrogen diffusion coefficient D were within the ranges defined in the present invention, and therefore a steel wire (wire) was obtained, which had a tensile strength exceeding the tensile strength of the "piano wire B" described in JIS G 3522 (1991) (in the specification, 1620 to 1770 MPa in a wire having a wire diameter of 7.0 mm, for example), while achieving a fatigue strength exceeding 0.45 times the tensile strength TS.

[0074] On the other hand, Test Nos. 4 to 8 and 21 to 26 are examples that did not satisfy any of the requirements of the present invention. Among them, Test No. 4 was low in the heating temperature during bloom rolling, causing precipitation of coarse TiC to increase the hydrogen diffusion coefficient D so that the fatigue strength was deteriorated.

[0075] Test No. 5 was low in the strain rate at the final 4 passes during hot rolling, causing precipitation of coarse TiC to increase the hydrogen diffusion coefficient D so that the fatigue strength was deteriorated.

[0076] Test No. 6 was low in the placing temperature after hot rolling, causing a placing defect so that a specimen could not be obtained.

[0077] Test No. 7 was high in the placing temperature after hot rolling and Test No. 8 was low in the cooling rate after rolling, causing coarsening of TiC to increase the hydrogen diffusion coefficient D so that the fatigue strength was deteriorated.

[0078] Test No. 21 is an example of use of a steel type P containing a small amount of C, in which a mixed phase structure of ferrite and pearlite was formed so that the tensile strength and the torsion characteristics were low, and the fatigue strength was also deteriorated.

[0079] Test No. 22 is an example of use of a steel type Q containing a large amount of C, in which a large amount of proeutectoid cementite was precipitated to cause breaking of a wire during wire drawing.

[0080] Test No. 23 is an example of use of a steel type R containing a small amount of Ti, in which, due to the small amount of TiC, the hydrogen diffusion coefficient D increased so that the fatigue strength was deteriorated.

[0081] Test No. 24 is an example of use of a steel type S containing a large amount of Ti, in which large amounts of Ti-based inclusions were precipitated to cause breaking of a wire during wire drawing.

[0082] Test No. 25 is an example of use of a steel type T containing a large amount of B, in which breaking of a wire occurred during hot rolling so that a specimen could not be obtained.

[0083] Test No. 26 is an example of use of a steel type U containing a small amount of B, in which the torsion characteristics and the fatigue strength were deteriorated. In addition, the hydrogen diffusion coefficient D also increased.

1. A wire rod for a steel wire, comprising by mass:
C: 0.70 to 1.3%;
Si: 0.1 to 1.5%;
Mn: 0.1 to 1.5%;
N: 0.001 to 0.006%;
Al: 0.001 to 0.10%;
Ti: 0.02 to 0.20%;
B: 0.0005 to 0.010%;
P: 0% or more and 0.030% or less; and
S: 0% or more and 0.030% or less, with the balance being iron and inevitable impurities, wherein,
the wire rod has pearlite as a main phase, and
a hydrogen diffusion coefficient D in steel at 300° C. satisfies formula (1) below:

$$D \leq 2.5 \times 10^{-7} (cm^2/sec) \tag{1}$$

2. The wire rod for a steel wire according to claim 1, further comprising at least one selected from the group consisting of (a) to (d) below by mass:
(a) at least one of Cr: more than 0% and 1.0% or less, and V: more than 0% and 0.5% or less;
(b) at least one of Ni: more than 0% and 0.5% or less, and Nb: more than 0% and 0.5% or less;
(c) Co: more than 0% and 1.0% or less; and
(d) at least one of Mo: more than 0% and 0.5% or less, and Cu: more than 0% and 0.5% or less.

3. A steel wire comprising the chemical composition according to claim 1, wherein a hydrogen diffusion coefficient D in steel at 300° C. satisfies formula (1) below:

$$D \leq 2.5 \times 10^{-7} (cm^2/sec) \tag{1}$$

4. A steel wire comprising the chemical composition according to claim 2, wherein a hydrogen diffusion coefficient D in steel at 300° C. satisfies formula (1) below:

$$D \leq 2.5 \times 10^{-7} (cm^2/sec) \tag{1}$$

* * * * *