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(54) **ROLLED STEEL MATERIAL FOR HIGH-STRENGTH SPRING AND WIRE FOR HIGH-STRENGTH SPRING USING SAME**

(57) An object of the present invention is to provide a rolled material for high strength spring, which has excellent wire drawability even when suppressing the addition amount of an alloying element, and which can exhibit corrosion fatigue properties after quenching and tempering.

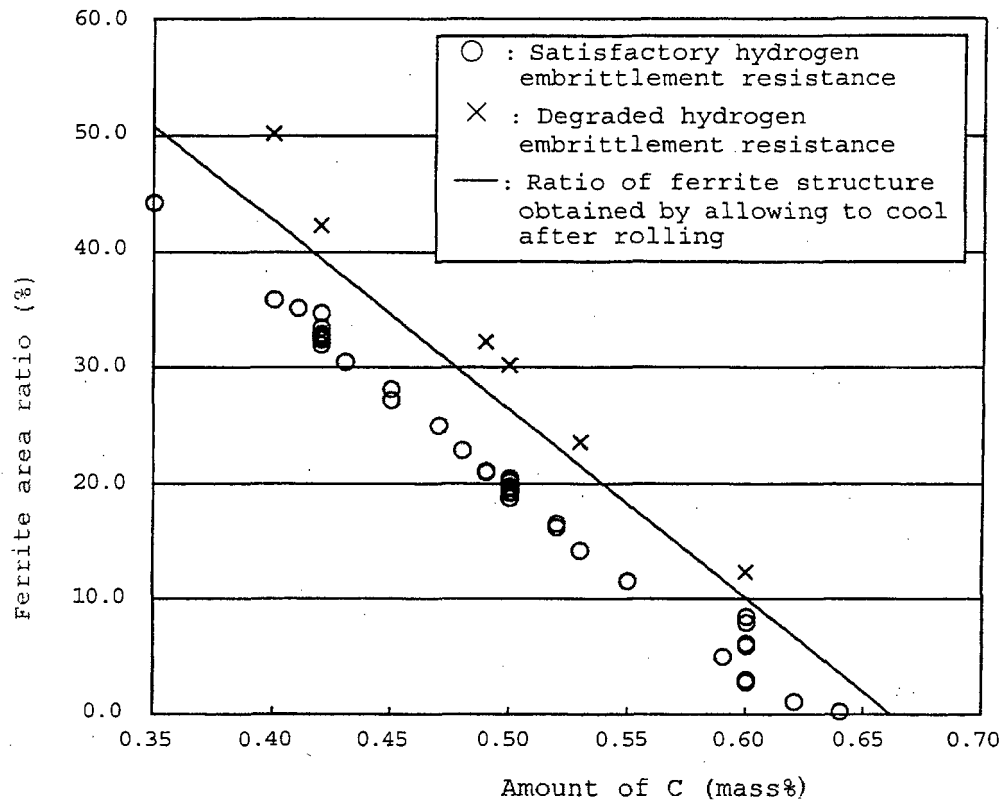
The present invention provides a rolled material for high strength spring, including C, Si, Mn, P, S, Al, Cu and Ni, wherein an amount of nondiffusible hydrogen is 0.40 ppm by mass or less, and an area ratio of ferrite expressed as a percentage satisfies an inequality expression (1) below, and a total area ratio of bainite and martensite is 2% or less:

$$\text{Ferrite area ratio} < \{ (0.77 - [C]) / 0.77 - [C] / 3 + 0.08 \} \times 100 \quad (1)$$

where [name of element] in the above inequality expression (1) means a content expressed in % by mass of each element.

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Fig. 1



Description

Technical Field

[0001] The present invention relates to a rolled material for high strength spring, and a wire for high strength spring using the same. More particularly, the present invention relates to a rolled material and a wire, which are useful as raw materials of high strength springs that are used in a state of being subjected to heat treatment, namely, quenching and tempering, particularly a rolled material having excellent wire drawability, and a wire for high strength spring, which are excellent in corrosion fatigue properties even though a tensile strength is a high strength in a range of 1,900 MPa or more after wire drawing.

Background Art

[0002] Coil springs used in automobiles, for example, a valve spring and a suspension spring used in the engine, suspension, and the like are required to reduce the weight and to increase the strength so as to achieve exhaust gas reduction and improvement in fuel efficiency. In the manufacture of a high strength wire, wire drawing is applied for the purpose of achieving improvement in dimensional accuracy of a wire diameter and uniformization of a structure due to plastic working before a heat treatment of quenching and tempering. Particularly, a wire drawing reduction rate is sometimes increased so as to further uniformize the structure in the high strength wire, and a rolled material is required to have satisfactory wire drawability. The spring imparted with high strength is likely to cause hydrogen brittleness because of its poor toughness and ductility, leading to degradation of corrosion fatigue properties. Therefore, the steel wire (wire) for high strength spring used in the manufacture of a spring is required to have excellent corrosion fatigue properties. Hydrogen generated by corrosion enters into a steel and may lead to embrittlement of a steel material, thus causing corrosion fatigue fracture, so that there is a need to improve corrosion resistance and hydrogen embrittlement resistance of the steel material so as to improve corrosion fatigue properties.

[0003] There has been known, as a method for enhancing wire drawability of a rolled material for high strength spring and corrosion fatigue properties of a wire for high strength spring, a method for controlling by the chemical composition. However, such a method is not necessarily desirable from a viewpoint of an increase in manufacturing costs and resource saving because of use of a large amount of an alloying element.

[0004] Meanwhile, there have been known, as a method for manufacturing a spring, a method in which a steel wire is heating to a quenching temperature and hot-formed into a spring shape, followed by oil cooling and further tempering, and a method in which a steel wire is subjected to quenching and tempering, and then cold-formed into a spring shape. In the cold forming method of the latter, it is also known that quenching and tempering before forming is performed by high frequency induction heating. For example, Patent Document 1 discloses technology in which a wire rod is cold-drawn and then the structure is adjusted by quenching and tempering through high frequency induction heating. According to this technology, a structural fraction of pearlite is set at 30% or less and a structural fraction composed of martensite and bainite is set at 70% or more and then cold drawing is performed at a predetermined area reduction rate, followed by quenching and tempering to thereby reduce the unsolved carbides, leading to an improvement in delayed fracture properties.

[0005] In Examples of Patent Document 2, a rolled wire rod is subjected to wire drawing, followed by a quenching and tempering treatment through high frequency induction heating. This technology focuses primarily on achievement of the reconciliation of high strength and formability (coiling properties), and gives no consideration to hydrogen embrittlement resistance..

[0006] While paying attention to the amount of hydrogen in a steel that is evaluated by the total amount of hydrogen released when the temperature is raised from room temperature to 350°C, Patent Document 3 proposes a hot rolled wire rod having excellent wire drawability under severe wire drawing conditions. However, Patent Document 3 focuses only on wire drawability during special processing such as severe wire drawing, and also gives no consideration to hydrogen embrittlement resistance after quenching and tempering, which becomes most important in a suspension spring.

Patent Document 1: JP 2004-143482 A

Patent Document 2: JP 2006-183137 A

Patent Document 3: JP 2007-231347 A

Summary of Invention

Problems to be Solved by the Invention

5 **[0007]** In light of aforementioned circumstances, the present invention has been made, and it is an object thereof is to provide a rolled material for high strength spring, which is a material for high strength spring including both materials for hot coiling and cold coiling, and which has excellent wire drawability even when suppressing the addition amount of an alloying element, and also can exhibit corrosion fatigue properties after quenching and tempering.

Means for Solving the Problems

[0008] The present invention that can solve the foregoing problems provides a rolled material for high strength spring, including, in % by mass:

15 C: 0.39 to 0.65%,
Si: 1.5 to 2.5%,
Mn: 0.15 to 1.2%,
P: exceeding 0% and 0.015% or less,
S: exceeding 0% and 0.015% or less,
20 Al: 0.001 to 0.1%,
Cu: 0.1 to 0.80%, and
Ni: 0.1 to 0.80%, with the balance being iron and inevitable impurities, wherein

an amount of nondiffusible hydrogen is 0.40 ppm by mass or less, and
25 an area ratio of ferrite expressed as a percentage satisfies an inequality expression (1) below, and a total area ratio of bainite and martensite is 2% or less:

$$30 \quad \text{Ferrite area ratio} < \left\{ (0.77 - [C]) / 0.77 - [C] / 3 + 0.08 \right\} \times 100 \quad (1)$$

where [name of element] in the above inequality expression (1) means a content expressed in % by mass of each element.

35 **[0009]** The rolled material for high strength spring of the present invention preferably includes, in % by mass, at least one belonging to any one of the following (a), (b), (c) and (d):

- (a) Cr: exceeding 0% and 1.2% or less,
- (b) Ti: exceeding 0% and 0.13% or less,
- (c) B: exceeding 0% and 0.01% or less, and
- 40 (d) at least one selected from the group consisting of Nb: exceeding 0% and 0.1% or less, Mo: exceeding 0% and 0.5% or less, and V: exceeding 0% and 0.4% or less.

[0010] In the rolled material for high strength spring of the present invention, an ideal critical diameter D_i is preferably in a range of 65 to 140 mm, and is calculated using an equation (2) below when B is not included or using an equation (3) below when B is included. If some elements are not included in the rolled material of the present invention among elements mentioned in the equations, calculation is made under the condition that the content of the elements is 0%.

$$50 \quad D_i = 25.4 \times (0.171 + 0.001 \times [C] + 0.265 \times [C]^2) \times (3.3333 \times [Mn] + 1) \times (1 + 0.7 \times [Si]) \times (1 + 0.363 \times [Ni]) \times (1 + 2.16 \times [Cr]) \times (1 + 0.365 \times [Cu]) \times (1 + 1.73 \times [V]) \times (1 + 3 \times [Mo]) \quad (2)$$

$$\begin{aligned}
 D_i = & 25.4 \times (0.171 + 0.001 \times [C] + 0.265 \times [C]^2) \times (3.3333 \\
 & \times [Mn] + 1) \times (1 + 0.7 \times [Si]) \times (1 + 0.363 \times [Ni]) \times (1 + 2.16 \\
 & \times [Cr]) \times (1 + 0.365 \times [Cu]) \times (1 + 1.73 \times [V]) \times (1 + 3 \times [Mo]) \\
 & \times (6.849017 - 46.78647 \times [C] + 196.6635 \times [C]^2 - 471.3978 \times [C]^3 \\
 & + 587.8504 \times [C]^4 - 295.0410 \times [C]^5) \quad (3)
 \end{aligned}$$

where [name of element] in the above equations (2) and (3) means a content expressed in % by mass of each element.

[0011] The present invention also includes a wire for high strength spring, having a tensile strength of 1,900 MPa or more, obtained by wire-drawing any one of the rolled materials for high strength spring mentioned above, followed by a quenching and tempering treatment.

Effects of the Invention

[0012] According to the present invention, since the amount of nondiffusible hydrogen in a rolled material is suppressed and formation of supercooled structures such as bainite and martensite is suppressed, the rolled material exhibits excellent wire drawability without adding a large amount of an alloying element. In the rolled material of the present invention, an area ratio of ferrite is appropriately adjusted according to the concentration of C, specifically, the area ratio of ferrite decreases as the concentration of C increases, so that a wire obtained by wire-drawing this rolled material, followed by quenching and tempering is excellent in corrosion fatigue properties even though the strength is a high strength in a range of 1,900 MPa or more. In such a rolled material, it is possible to improve wire drawability of the rolled material and corrosion fatigue properties of the wire even when suppressing the cost of steel materials, thus making it possible to supply a high strength spring which is excellent in manufacturability and is very unlikely to cause corrosion fatigue fracture, for example, a coil spring such as a suspension spring that is one of automobile components, at a cheap price.

Brief Description of the Drawings

[0013] Fig. 1 is a graph showing an influence of an amount of C and a ferrite area ratio on hydrogen embrittlement resistance.

Mode for Carrying Out the Invention

[0014] Wire drawability of a rolled material is usually influenced by ductility of the rolled material. Poor ductility of a basis material or degradation of ductility due to the presence of a supercooled structure may lead to fracture during wire drawing, resulting in drastic degradation of manufacturability. Therefore, wire drawability can be improved by enhancing ductility of the rolled material.

[0015] Meanwhile, if corrosion occurs, pits are generated on a surface of a steel material, and wall thinning due to corrosion may lead to a decrease in wire diameter of the steel material. Hydrogen generated by corrosion enters into a steel and may lead to embrittlement of the steel material. Corrosion fatigue fracture occurs with these corrosion pits, wall thickness reduction sections, and embrittled sections of the steel material as starting points. Therefore, corrosion fatigue fracture can be improved by improving hydrogen embrittlement resistance and corrosion resistance of the steel material.

[0016] The inventors of the present invention have made a study of factors that exert an influence on ductility, hydrogen embrittlement resistance and corrosion resistance of a steel material from various viewpoints. As a result, they have found that proper control of both a ferrite area ratio of a rolled material and the amount of hydrogen in a steel expressed particularly by the amount of nondiffusible hydrogen enables an improvement in ductility of the rolled material and significant improvement in hydrogen embrittlement resistance when the rolled material is subjected to wire drawing, followed by quenching and tempering. They have also found that corrosion resistance can also be improved by appropriately adjusting the chemical composition, leading to significant improvement in corrosion fatigue properties, thus completing the present invention. The structure, the amount of hydrogen in steel, and the chemical composition of the rolled material of the present invention will be sequentially described below.

[0017] The ferrite structure is likely to form a carbide depleted region after quenching and tempering, and formation

of the carbide depleted region serves as a fracture starting point, as a strength lowering section. While carbides are capable of detoxicating hydrogen by trapping hydrogen, the carbide depleted region becomes an area lacking such a capability, so that hydrogen embrittlement is likely to occur, leading to fracture. In order to suppress formation of the carbide depleted region after a quenching and tempering treatment to thereby uniformly disperse carbides, there is a need to form a structure in which carbides are uniformly dispersed in a stage of a rolled material before quenching and tempering. Namely, there is a need that a ratio of a pearlite structure, which is a structure that ferrite and carbides form layers, is increased to thereby decrease a ratio of a ferrite structure. The inventors of the present invention have found that it is important to make an area ratio of the ferrite structure smaller than that of the ferrite structure obtained by allowing to cool after rolling, so as to improve hydrogen embrittlement resistance, and that the ferrite structure obtained by allowing to cool after rolling has a close relation with the amount of C.

[0018] As a result of examination of the ratio of the ferrite structure obtained by allowing to cool after rolling with respect to a steel material in which the amount of C is variously changed, it became clear that the ratio of the ferrite structure obtained by allowing to cool after rolling is represented by the right side of an inequality expression (1) below. The rolled material of the present invention is characterized by controlling the ratio of the ferrite structure so as to satisfy the inequality expression (1) below. The [name of element] in the inequality expression (1) below means a content expressed in % by mass of each element. As used herein, the ferrite area ratio means a ratio expressed as a percentage.

$$\text{Ferrite area ratio} < \left\{ (0.77 - [C]) / 0.77 - [C] / 3 + 0.08 \right\} \times 100 \quad (1)$$

[0019] Fig. 1 is a graph showing an influence of an amount of C and a ferrite area ratio on hydrogen embrittlement resistance on the basis of Example data mentioned later. As shown by a straight line in Fig. 1, the ratio of the ferrite structure obtained by allowing to cool after rolling tends to decrease as the amount of C increases. The rolled material of the present invention is significantly characterized by decreasing an area ratio of ferrite as the amount of C increases. The steel material including a large amount of C is required to reduce the ratio of the ferrite structure from a viewpoint that a martensite structure is likely to embrittle, particularly. The less an area ratio of ferrite, the better, and the area ratio of ferrite may be 0%.

[0020] Regarding the rolled material of the present invention, the ratio of the ferrite structure is preferably reduced by at least 10% lower than that of the ferrite structure obtained by allowing to cool after rolling, namely, the ratio of the ferrite structure preferably satisfies an inequality expression (1-2) below.

$$\text{Ferrite area ratio} \leq \left\{ (0.77 - [C]) / 0.77 - [C] / 3 + 0.08 \right\} \times 100 \times 0.9 \quad (1-2)$$

[0021] In the rolled material of the present invention, when the content of supercooled structures such as bainite and martensite increases, wire drawability is drastically degraded. Therefore, even if supercooled structures are included, the area percentage is 2 percentage or less, preferably 1 percentage or less, most preferably 0 percentage or less.

[0022] In the rolled material of the present invention, formation of ferrite, bainite and martensite is suppressed, and the structure except for them is pearlite.

[0023] The amount of hydrogen in the rolled material of the present invention will be described below. In the rolled material of the present invention, an amount of nondiffusible hydrogen is set at 0.40 ppm by mass or less. If a large amount of nondiffusible hydrogen exists, hydrogen is accumulated around inclusions and segregating zones in the rolled material to thereby generate microcracks, resulting in degraded wire drawability of the rolled material. If a large amount of nondiffusible hydrogen exists, a permissible amount of hydrogen, which further enters until the steel material embrittles, decreases. Therefore, even though a small amount of hydrogen entered during use as a spring, embrittlement of the steel material occurs and early fracture is likely to occur, resulting in degraded hydrogen embrittlement resistance. The amount of nondiffusible hydrogen is preferably 0.35 ppm by mass or less, and more preferably 0.30 ppm by mass or less. The less the amount of nondiffusible hydrogen, the better. However, it is difficult to set at 0 ppm by mass and the lower limit is about 0.01 ppm by mass.

[0024] The amount of nondiffusible hydrogen is an amount of hydrogen measured by the method mentioned in Examples below, and specifically means the total amount of hydrogen released at 300 to 600°C when the temperature of a steel material is raised at 100°C/hour.

[0025] The rolled material for high strength spring according to the present invention is a low alloy steel in which the content of an alloying element is suppressed, and the chemical composition is as follows. The present invention also

includes a wire obtained by wire-drawing the above-mentioned rolled material, followed by quenching and tempering, and the chemical composition is the same as that of the rolled material.

C: 0.39 to 0.65%

[0026] Carbon is an element that is required to ensure the strength of a wire for spring, and is also required to generate fine carbides that serve as hydrogen trapping sites. From such a viewpoint, the amount of C is determined in a range of 0.39% or more. The lower limit of the amount of C is preferably 0.45% or more, and more preferably 0.50% or more. Excessive C amount, however, might generate coarse residual austenite and unsolved carbides after quenching and tempering, which further degrades hydrogen embrittlement resistance. C is an element that degrades corrosion resistance, so that there is a need to suppress the amount of C so as to enhance corrosion fatigue properties of a spring product such as a suspension spring which is a final product. From such a viewpoint, the amount of C is determined in a range of 0.65% or less. The upper limit of the amount of C is preferably 0.62% or less, and more preferably 0.60% or less.

Si: 1.5 to 2.5%

[0027] Si is an element that is required to ensure the strength, and also exhibits the effect of refining carbides. To effectively exhibit these effects, the amount of Si is determined in a range of 1.5% or more. The lower limit of the amount of Si is preferably 1.7% or more, and more preferably 1.9% or more. Meanwhile, since Si is also an element that accelerates decarburization, excessive Si amount accelerates formation of a decarburized layer on a surface of a steel material, thus requiring the peeling step for removal of the decarburized layer, resulting in increased manufacturing costs. Unsolved carbides also increase, thus degrading hydrogen embrittlement resistance. From such a viewpoint, the amount of Si is determined in a range of 2.5% or less. The upper limit of the amount of Si is preferably 2.3% or less, more preferably 2.2% or less, and still more preferably 2.1% or less.

Mn: 0.15 to 1.2%

[0028] Mn is an element that is employed as a deoxidizing element and reacts with S, which is a harmful element in a steel, to form MnS, and is useful for detoxication of S. Mn is also an element that contributes to an improvement in strength. To effectively exhibit these effects, the amount of Mn is determined in a range of 0.15% or more. The lower limit of the amount of Mn is preferably 0.2% or more, and more preferably 0.3% or more. Excessive Mn amount, however, degrades toughness, thus causing embrittlement of a steel material. From such a viewpoint, the amount of Mn is determined in a range of 1.2% or less. The upper limit of the amount of Mn is preferably 1.0% or less, more preferably 0.85% or less, and still more preferably 0.70% or less.

P: exceeding 0% and 0.015% or less

[0029] P is a harmful element that degrades ductility such as coiling properties of a rolled material, namely, a wire rod, and the amount thereof is preferably as small as possible. P is likely to segregate in grain boundaries to cause grain boundary embrittlement, and hydrogen is likely to cause fracture of grain boundaries, thus exerting an adverse influence on hydrogen embrittlement resistance. From such a viewpoint, the amount of P is determined in a range of 0.015% or less. The upper limit of the amount of P is preferably 0.010% or less, and more preferably 0.008% or less. The amount of P is preferably as small as possible, and is usually about 0.001%.

S: exceeding 0% and 0.015% or less

[0030] Like P mentioned above, S is a harmful element that degrades ductility such as coiling properties of a rolled material, and the amount thereof is preferably as small as possible. S is likely to segregate in grain boundaries to cause grain boundary embrittlement, and hydrogen is likely to cause fracture of grain boundaries, thus exerting an adverse influence on hydrogen embrittlement resistance. From such a viewpoint, the amount of S is determined in a range of 0.015% or less. The upper limit of the amount of S is preferably 0.010% or less, and more preferably 0.008% or less. The amount of S is preferably as small as possible, and is usually about 0.001%.

Al: 0.001 to 0.1%

[0031] Al is mainly added as a deoxidizing element. This element reacts with N to form AlN to thereby detoxicate solid-soluted N, and also contributes to refining of the structure. To adequately exhibit these effects, the amount of Al is determined in a range of 0.001% or more. The lower limit of the amount of Al is preferably 0.002% or more, and more

preferably 0.005% or more. However, since Al is an element that accelerates decarburization, like Si, there is a need to suppress the amount of Al in a steel for spring, which includes a large amount of Si. Therefore, in the present invention, the amount of Al is determined in a range of 0.1% or less. The upper limit of the amount of Al is preferably 0.07% or less, more preferably 0.030% or less, and particularly preferably 0.020% or less.

Cu: 0.1 to 0.80%

[0032] Cu is an element that is effective in suppressing surface decarburization and improving corrosion resistance. Therefore, the amount of Cu is determined in a range of 0.1% or more. The lower limit of the amount of Cu is preferably 0.15% or more, more preferably 0.20% or more, and still more preferably 0.25% or more. Excessive Cu amount, however, causes cracks during hot working and increases costs. Therefore, the amount of Cu is determined in a range of 0.80% or less. The upper limit of the amount of Cu is preferably 0.70% or less, more preferably 0.60% or less, still more preferably 0.48% or less, particularly preferably 0.35% or less, and most preferably 0.30% or less.

Ni: 0.1 to 0.80%

[0033] Like Cu, Ni is an element that is effective in suppressing surface decarburization and improving corrosion resistance. Therefore, the amount of Ni is determined in a range of 0.1% or more. The lower limit of the amount of Ni is preferably 0.15% or more, more preferably 0.20% or more, and still more preferably 0.35% or more, and most preferably 0.45% or more. Excessive Ni amount, however, increases costs. Therefore, the amount of Ni is determined in a range of 0.80% or less. The upper limit of the amount of Ni is preferably 0.70% or less, more preferably 0.60% or less, still more preferably 0.55% or less, and yet preferably 0.48% or less, 0.35% or less, and 0.30% or less.

[0034] Basic components of the rolled material of the present invention are as mentioned above, the balance being substantially iron. As a matter of course, including of inevitable impurities introduced by the state of raw material, material, manufacturing facility, and the like is permitted. The rolled material for spring of the present invention has the chemical composition mentioned above even when suppressing an alloying element such as Cu, and can achieve excellent coiling properties and hydrogen embrittlement resistance while having high strength. Elements mentioned below may be further included for the purpose of improving corrosion resistance according to application.

Cr: exceeding 0% and 1.2% or less

[0035] Cr is an element that is effective in improving corrosion resistance. To effectively exhibit these effects, the amount of Cr is preferably 0.01% or more, more preferably 0.05% or more, and still more preferably 0.10% or more. However, Cr is an element that has a strong tendency to form carbides, and forms peculiar carbides in a steel material and is likely to be dissolved in cementite in a high concentration. It is effective to include a small amount of Cr, however, the heating time of the quenching step decreases in high frequency induction heating, leading to insufficient austenitizing of dissolving carbide, cementite, and the like into a base material. Therefore, when including a large amount of Cr, dissolving residue of cementite, in which Cr-based carbide and metallic Cr in high concentration are solid-soluted, is generated as a stress concentration source, so that fracture likely to occur, thus degrading hydrogen embrittlement resistance. Therefore, the amount of Cr is preferably 1.2% or less, more preferably 0.8% or less, and still more preferably 0.6% or less.

Ti: exceeding 0% and 0.13% or less

[0036] Ti is an element that is useful to react with S to form sulfide to thereby detoxicate S. Ti also has the effect of refining the structure by forming carbonitride. To effectively exhibit these effects, the amount of Ti is preferably 0.02% or more, more preferably 0.05% or more, and still more preferably 0.06% or more. Excessive Ti amount, however, may form coarse Ti sulfide, thus degrading ductility. Therefore, the amount of Ti is preferably 0.13% or less. From a viewpoint of cost reduction, the amount of Ti is preferably 0.10% or less, and more preferably 0.09% or less.

B: exceeding 0% and 0.01% or less

[0037] B is an element that improve hardenability and strengthens prior austenite crystal grain boundaries, and also contributes to suppression of fracture. To effectively exhibit these effects, the amount of B is preferably 0.0005% or more, and more preferably 0.0010% or more. Excessive B amount, however, causes saturation of the above effects, so that the amount of B is preferably 0.01% or less, more preferably 0.0050% or less, and still more preferably 0.0040% or less.

Nb: exceeding 0% and 0.1% or less

[0038] Nb is an element that forms carbonitride together with C and N, and mainly contributes to refining of the structure. To effectively exhibit these effects, the amount of Nb is preferably 0.003% or more, more preferably 0.005% or more, and still more preferably 0.01% or more. Excessive Nb amount, however, form coarse carbonitride, thus degrading ductility of a steel material. Therefore, the amount of Nb is preferably 0.1% or less. From a viewpoint of cost reduction, the amount is preferably set at 0.07% or less.

Mo: exceeding 0% and 0.5% or less

[0039] Like Nb, Mo is also an element that forms carbonitride together with C and N, and contributes to refining of the structure Mo is an element that is also effective in ensuring the strength after tempering. To effectively exhibit these effects, the amount of Mo is preferably 0.15% or more, more preferably 0.20% or more, and still more preferably 0.25% or more. Excessive Mo amount, however, form coarse carbonitride, thus degrading ductility such as coiling properties of a steel material. Therefore, the amount of Mo is preferably 0.5% or less, and more preferably 0.4% or less.

V: exceeding 0% and 0.4% or less

[0040] V is an element that contributes to an improvement in strength and refining of crystal grains. To effectively exhibit these effects, the amount of V is preferably 0.1% or more, more preferably 0.15% or more, and still more preferably 0.20% or more. Excessive V amount, however, increases costs. Therefore, the amount of V is preferably 0.4% or less, and more preferably 0.3% or less.

[0041] Nb, Mo and V may be included individually, or two or more kinds of them may be included in combination.

[0042] The rolled material of the present invention includes O and N as inevitable impurities, and the amount of them is preferably adjusted in a range mentioned below.

O: exceeding 0% and 0.002% or less

[0043] Excess amount of O forms oxide inclusions such as coarse Al_2O_3 and exerts an adverse influence on fatigue properties. Therefore, the upper limit of the amount of O is preferably 0.002% or less, more preferably 0.0015% or less, and still more preferably 0.0013% or less. Meanwhile, the lower limit of the amount of O is generally 0.0002% or more (preferably 0.0004% or more) from an industrial viewpoint.

N: exceeding 0% and 0.007% or less

[0044] As the amount of N increases, it forms coarse nitride together with Ti and Al, thus exerting an adverse influence on fatigue properties. Therefore, the amount of N is preferably as small as possible, for example, 0.007% or less, and more preferably 0.005% or less. Meanwhile, if the amount of N is too reduced, productivity is drastically degraded. N forms nitride together with Al to thereby contribute to refining of crystal grains. From such a viewpoint, the amount of N is preferably 0.001% or more, more preferably 0.002% or more, and still more preferably 0.003% or more.

[0045] In the rolled material and the wire of the present invention, an ideal critical diameter D_i represented by the equation (2) or (3) below is preferably in a range from 65 to 140 mm. To use the rolled material as a raw material for spring after wire drawing without being subjected to soft annealing, there is a need to reduce supercooled structures to a predetermined content or less so as not to cause wire breakage during wire drawing. If the ideal critical diameter D_i is large, hardenability is enhanced and supercooled structures are likely to be generated, so that the upper limit of the ideal critical diameter D_i is preferably 140 mm or less. The upper limit of the ideal critical diameter D_i is more preferably 135 mm or less, still more preferably 130 mm or less, and particularly preferably 120 mm or less. To perform quenching to the inside as a spring, it is important to ensure given hardenability. Therefore, the lower limit of the ideal critical diameter D_i is preferably 65 mm or more, more preferably 70 mm or more, and still more preferably 80 mm or more.

[0046] When including no B, the following equation (2) defined in ASTM A255 is used as the ideal critical diameter D_i . When including B, there is a need to add a boron factor B.F. defined in ASTM A255-02 by multiplying right side of the equation (2) by the boron factor, and the ideal critical diameter D_i is calculated by the following equation (3).

$$D_i = 25.4 \times (0.171 + 0.001 \times [C] + 0.265 \times [C]^2) \times (3.3333 \times [Mn] + 1) \times (1 + 0.7 \times [Si]) \times (1 + 0.363 \times [Ni]) \times (1 + 2.16 \times [Cr]) \times (1 + 0.365 \times [Cu]) \times (1 + 1.73 \times [V]) \times (1 + 3 \times [Mo]) \quad (2)$$

$$D_i = 25.4 \times (0.171 + 0.001 \times [C] + 0.265 \times [C]^2) \times (3.3333 \times [Mn] + 1) \times (1 + 0.7 \times [Si]) \times (1 + 0.363 \times [Ni]) \times (1 + 2.16 \times [Cr]) \times (1 + 0.365 \times [Cu]) \times (1 + 1.73 \times [V]) \times (1 + 3 \times [Mo]) \times (6.849017 - 46.78647 \times [C] + 196.6635 \times [C]^2 - 471.3978 \times [C]^3 + 587.8504 \times [C]^4 - 295.0410 \times [C]^5) \quad (3)$$

where [name of element] in the above equations (2) and (3) means a content expressed in % by mass of each element.

[0047] A method for producing a rolled material of the present invention will be described below. In a series of steps of melting a steel having the above chemical composition, followed by continuous casting, blooming, and hot rolling, it is possible to control the amount of nondiffusible hydrogen of the rolled material by adjusting at least one of (A) the amount of hydrogen in a molten steel stage, (B) the homogenizing treatment temperature and time before blooming, and (C) the average cooling rate in a range of 400 to 100°C after hot rolling. It is also possible to adjust the structure of the rolled material, namely, ferrite, martensite and bainite in the range mentioned above by adjusting all of (i) the coiling temperature (TL) after rolling, (ii) the average cooling rate in a range of TL to 650°C, and (iii) the average cooling rate in a range of 650 to 400°C.

[0048] There is a need to remove hydrogen in a steel by diffusion so as to reduce hydrogen in the steel after solidification, and heating at a high temperature for a long time is effective to increase a diffusion rate of hydrogen so as to release hydrogen from a surface of a steel material. Specific examples of the method of reducing the amount of hydrogen in the steel include a method of adjusting in a molten steel stage, a method of adjusting in a stage of a continuously cast material at 1,000°C or higher after solidification, a method of adjusting in a heating stage before hot rolling, a method of adjusting in a heating stage during rolling, and a method of adjusting in a cooling stage after rolling. It is particularly preferred to perform at least one of treatments for reducing nondiffusible hydrogen (A) to (C) mentioned below.

[0049]

(A) A degassing treatment is performed by a molten steel treatment to thereby adjust the amount of hydrogen in a molten steel at 2.5 ppm by mass or less.

For example, it is effective that a vacuum tank equipped with two immersion tubes is mounted in a ladle in a secondary refining step and then an Ar gas is blown from the side of one immersion tube, followed by vacuum degassing that enables circulation of a molten steel to the vacuum tank utilizing the buoyancy. This method is excellent in hydrogen removing capability and reduction in inclusion. The amount of hydrogen in the molten steel is preferably 2.0 ppm by mass or less, more preferably 1.8 ppm by mass or less, still more preferably 1.5 ppm by mass or less, and particularly preferably 1.0 ppm by mass or less.

(B) A homogenizing treatment before blooming is performed at 1,100°C or higher, and preferably 1,200°C or higher for 10 hours or more.

(C) An average cooling rate in a range of 400 to 100°C after rolling is set at 0.5°C/second or less, and preferably 0.3°C/second or less.

[0050] When a steel material has a large cross-sectional area, particularly, it becomes necessary to perform heating for a long time. If the steel material is heated for a long time, decarburization is accelerated, so that the amount of hydrogen in the steel is preferably reduced by performing the treatment (A) mentioned above.

[0051] To adjust an area ratio of the structure in the rolled material, namely, ferrite, bainite and martensite in the range mentioned above, it is preferred to adjust rolling conditions as follows, and to adjust to rolling conditions that satisfy all conditions (i) to (iii).

(i) Coiling temperature TL before initiation of cooling: 900°C or higher

[0052] To reduce the ratio of ferrite, there is a need that the coiling temperature TL before initiation of cooling is adjusted at a temperature in an austenitic single phase. Therefore, TL is more preferably 910°C or higher, and still more preferably 930°C or higher. The upper limit of TL is not particularly limited and is about 1,000°C, although it depends on a finish rolling temperature.

(ii) Average cooling rate in a range of TL to 650°C: 2 to 5°C/second

[0053] To allow pearlite transformation to take place, there is a need to suppress formation of ferrite by increasing a cooling rate in a temperature range of TL to 650°C. Therefore, an average cooling rate in a range of TL to 650°C is preferably 2°C/second or more, more preferably 2.3°C/second or more, and still more preferably 2.5°C/second or more. If the cooling rate in a range of TL to 650°C is excessively increased, supercooled structures such as martensite and bainite are likely to be formed. Therefore, the cooling rate at TL to 650°C is preferably 5°C/second or less, more preferably 4.5°C/second or less, and still more preferably 4°C/second or less.

(iii) Average cooling rate in a range of 650 to 400°C: 2°C/second or less

[0054] Further, a cooling rate in a range of 650 to 400°C, at which formation of supercooled structures is initiated, is preferably decreased. An average cooling rate in a range of 650 to 400°C is preferably 2°C/second or less, more preferably 1.5°C/second or less, and still more preferably 1°C/second or less. The lower limit of the average cooling rate is not particularly limited and is, for example, about 0.3°C/second.

[0055] To manufacture a coil spring used in automobiles, there is a need that a wire is manufactured by wire processing of the rolled material mentioned above, namely, wire drawing. For example, in a cold coiled spring, quenching and tempering such as high frequency induction heating are performed after wire drawing, and such a wire is also included in the present invention. For example, the rolled material is subjected to wire drawing at an area reduction rate of about 5 to 35%, followed by quenching at about 900 to 1,000°C and further tempering at about 300 to 520°C. The quenching temperature is preferably 900°C or higher so as to sufficiently perform austenitizing, and preferably 1,000°C or lower so as to prevent grain coarsening. The heating temperature for tempering may be set at an appropriate temperature in a range of 300 to 520°C according to a target value of a wire strength. When quenching and tempering are performed by high frequency induction heating, quenching and tempering times are respectively in a range of about 10 to 60 seconds.

[0056] The thus obtained wire of the present invention can realize a high tensile strength in a range of 1,900 MPa or more. The tensile strength is preferably 1,950 MPa or more, and more preferably 2,000 MPa or more. The upper limit of the tensile strength is not particularly limited and is about 2,500 MPa. The wire of the present invention can exhibit corrosion fatigue properties even at a high strength in a range of 1,900 MPa or more because of use of the rolled material of the present invention.

[0057] This application claims priority based on Japanese Patent Application No. 2013-272569 filed on December 27, 2013 in Japan, the disclosure of which is incorporated by reference herein.

Examples

[0058] The present invention will be described in more detail below by way of Examples. It should be noted that, however, these examples are never construed to limit the scope of the invention; various modifications and changes may be made without departing from the scope and spirit of the invention and should be considered to be within the scope of the invention.

[0059] Each of steel materials having chemical compositions shown in Tables 1 to 3 was melted by melting in converter and then subjected to continuous casting and a homogenizing treatment at 1,100°C or higher. After the homogenizing treatment, blooming was performed, followed by heating at 1,100 to 1,280°C and further hot rolling to obtain a wire rod having a diameter of 14.3 mm, namely, a rolled material. Whether or not a degassing treatment of a molten steel is implemented, coiling temperature TL after hot rolling, and cooling conditions after cooling are as shown in Tables 4 to 6. In test examples in which "Implementation" is written in the column of the homogenizing treatment, the homogenizing treatment is performed at 1,100°C for 10 hours or more. In test examples in which the mark "-" is written, the time of the homogenizing treatment at 1,100°C is less than 10 hours.

[0060] With respect to the thus obtained wire rods, namely, rolled materials, the structure was identified by the procedure below, and the amount of nondiffusible hydrogen was measured and also wire drawability was measured.

(1) Identification of Structure

[0061] A cross section of each rolled material was subjected to buffing and etched with an etching solution, and then a microstructure was observed by an optical microscope and each area ratio of a ferrite structure, and bainite and martensite structures (hereinafter, bainite and martensite structures are collectively referred to as supercooled structures) was measured. The measurement was performed at the position of 1 mm deep from a surface. The observation field has a size of $400\ \mu\text{m} \times 300\ \mu\text{m}$ and the measurement was performed with respect to five visual fields, and the average was regarded as a ratio of each structure. The ratio of the pearlite structure was determined by subtracting the ratios of ferrite and supercooled structures from 100%.

(2) Amount of Nondiffusible Hydrogen

[0062] A specimen measuring 20 mm in width $\times$ 40 mm in length was cut out from the rolled material. After raising the temperature of the specimen at a temperature rise rate of $100^\circ\text{C}/\text{hour}$, a hydrogen release amount at 300 to 600°C was measured using a gas chromatogram, and the hydrogen release amount was regarded as the amount of nondiffusible hydrogen.

(3) Wire Drawability

[0063] Wire drawability was evaluated by reduction of area of a tensile test. A JIS No. 14 specimen was cut out from the rolled material and a tensile test was performed under the conditions of a crosshead speed of 10 mm/minute in accordance with JIS Z2241 (2011) using a universal tester, and then reduction of area RA was measured

[0064] Next, the rolled material was subjected to wire drawing, namely, cold drawing to obtain a wire having a diameter of 12.5 mm, followed by quenching and tempering. An area reduction rate of the drawn wire mentioned above is about 23.6% and the conditions of quenching and tempering are as follows.

Quenching and Tempering Conditions

[0065]

- High frequency induction heating
- Heating rate: $200^\circ\text{C}/\text{second}$
- Quenching: 950°C , 20 seconds, water cooling
- Tempering: each temperature in a range of 300 to 520°C , 20 seconds, water cooling

[0066] With respect to the wire after wire drawing, and quenching and tempering, the tensile strength, hydrogen embrittlement resistance and corrosion resistance were evaluated.

(4) Measurement of Tensile Strength

[0067] After quenching and tempering, a wire was cut into a predetermined length and a tensile test was performed at a distance between chucks of 200 mm and a tensile speed 5 mm/minute in accordance with JIS Z2241 (2011).

(5) Evaluation of Hydrogen Embrittlement Resistance

[0068] A specimen measuring 10 mm in width $\times$ 1.5 mm in thickness $\times$ 65 mm in length was cut out from the wire after quenching and tempering. In a state where stress of 1,400 MPa is applied to the specimen by four-point bending, the specimen was immersed in a mixed solution of 0.5 mol/L of sulfuric acid and 0.01 mol/L of potassium thiocyanate. Using a potentiostat, a voltage of -700 mV, which is less nobler than that of a saturated calomel electrode (SCE), was applied and the fracture time required for the occurrence of cracking was measured.

(6) Evaluation of Corrosion Resistance

[0069] A specimen measuring 10 mm in diameter $\times$ 100 mm in length was cut out from the wire after quenching and tempering by cutting. The specimen was subjected to a salt spray test with an aqueous 5%NaCl solution for 8 hours and then held in a wet atmosphere at 35°C and a relative humidity of 60% for 16 hours. After repeating this cycle seven times in total, a difference in weight before and after the test was measured and the thus obtained difference was regarded as a corrosion weight loss.

[0070] The results (1) to (6) mentioned above are shown in Tables 4 to 6.

[Table 1]

		Chemical composition (% by mass) The balance being iron and inevitable impurities															D _i value	
Steel	C	Si	Mn	P	S	Al	Cu	Ni	Cr	Ti	B	Nb	Mo	V	O	N	B is not added	B is added
A1	0.42	2.1	0.86	0.008	0.006	0.027	0.22	0.23	0.35	0.09					0.0012	0.0042	109	
A2	0.41	1.8	0.86	0.006	0.007	0.028	0.21	0.21	0.35	0.08					0.0013	0.0054	97	
A3	0.42	2.1	0.91	0.007	0.007	0.025	0.26	0.26	0.36	0.10					0.0009	0.0043	117	
A4	0.43	2.2	0.89	0.010	0.006	0.029	0.23	0.24	0.35	0.10					0.0010	0.0038	117	
A5	0.42	2.1	0.85	0.005	0.003	0.027	0.26	0.24	0.33	0.09					0.0014	0.0044	107	
A6	0.41	2.1	0.89	0.006	0.002	0.029	0.20	0.23	0.34	0.10					0.0013	0.0042	108	
A7	0.42	2.1	0.89	0.010	0.011	0.025	0.26	0.23	0.35	0.06					0.0012	0.0052	113	
A8	0.60	2.0	0.80	0.004	0.006	0.030	0.35	0.30	0.08	0.09					0.0009	0.0055	87	
A9	0.59	2.0	0.71	0.008	0.003	0.025	0.36	0.37	0.06	0.10	0.0032				0.0012	0.0039		80
A10	0.62	2.1	0.80	0.004	0.004	0.031	0.34	0.33	0.08						0.0014	0.0039	93	
A11	0.60	2.0	0.71	0.008	0.005	0.027	0.34	0.30			0.0030				0.0014	0.0040		68
A12	0.61	1.9	0.80	0.005	0.005	0.030	0.30	0.37	0.06						0.0013	0.0045	83	
A13	0.61	2.0	0.69	0.008	0.009	0.031	0.35	0.35	0.08						0.0012	0.0049	81	
A14	0.60	2.0	0.68	0.005	0.006	0.028	0.33	0.30	0.09	0.09					0.0011	0.0039	79	
A15	0.59	2.0	0.72	0.008	0.009	0.031	0.37	0.36	0.60						0.0010	0.0040	161	
A16	0.62	2.0	0.65	0.006	0.005	0.025	0.37	0.36	0.80						0.0012	0.0039	185	
A17	0.60	2.0	0.66	0.003	0.003	0.031	0.31	0.32	0.55		0.003%				0.0008	0.0054		141
A18	0.35	2.1	0.79	0.010	0.012	0.032	0.28	0.30	0.50						0.0015	0.0056	118	
A19	0.40	2.0	0.77	0.010	0.005	0.025	0.25	0.27	0.40						0.0013	0.0055	104	
A20	0.64	1.9	0.80	0.009	0.004	0.032	0.25	0.28							0.0013	0.0054	73	
A21	0.68	2.0	0.79	0.008	0.004	0.026	0.30	0.26			0.0030				0.0015	0.0047		43
A22	0.50	1.3	0.80	0.005	0.001	0.030	0.29	0.27	0.21						0.0014	0.0043	75	
A23	0.52	1.6	0.80	0.005	0.006	0.030	0.31	0.27	0.42						0.0012	0.0046	112	
A24	0.49	2.0	0.20	0.008	0.009	0.025	0.30	0.30	0.90						0.0014	0.0053	86	

(continued)

	Chemical composition (% by mass) The balance being iron and inevitable impurities																D _i value	
Steel	C	Si	Mn	P	S	Al	Cu	Ni	Cr	Ti	B	Nb	Mo	V	O	N	B is not added	B is added
A25	0.50	2.0	0.80	0.005	0.004	0.032	0.28	0.28	0.50	0.09	0.0035				0.0008	0.0053		163
A26	0.53	2.0	0.80	0.003	0.006	0.027	0.27	0.27	0.20						0.0014	0.0045	95	

[Table 2]

	Chemical composition (% by mass) The balance being iron and inevitable impurities																D _i value	
	C	Si	Mn	P	S	Al	Cu	Ni	Cr	Ti	B	Nb	Mo	V	O	N	B is not added	B is added
Steel	0.50	2.1	1.50	0.005	0.005	0.032	0.31	0.32							0.0015	0.0047	111	
A27	0.50	2.1	1.50	0.005	0.005	0.032	0.31	0.32							0.0015	0.0047	111	
A28	0.55	2.1	0.76	0.032	0.027	0.029	0.28	0.26							0.0010	0.0051	67	
A29	0.50	2.0	0.77	0.005	0.030	0.025	0.29	0.31	0.20		0.0030				0.0014	0.0041		111
A30	0.55	1.9	0.75	0.006	0.004	0.029	0.00	0.00	0.32						0.0011	0.0054	88	
A31	0.50	2.0	0.82	0.009	0.008	0.032	0.13	0.27	0.15						0.0011	0.0049	82	
A32	0.50	2.1	0.78	0.010	0.011	0.027	0.32	0.25							0.0012	0.0045	65	
A33	0.45	2.0	0.77	0.004	0.002	0.030	0.45	0.30	0.30	0.08	0.0035				0.0010	0.0049		138
A34	0.5%	1.9	0.81	0.007	0.008	0.025	0.29	0.00	0.30						0.0011	0.0051	95	
A35	0.52	2.0	0.82	0.004	0.005	0.028	0.30	0.12	0.15						0.0009	0.0041	85	
A36	0.50	2.0	0.76	0.008	0.003	0.029	0.31	0.029	0.22	0.08	0.0030				0.0014	0.0040		113
A37	0.49	2.0	0.82	0.009	0.008	0.030	0.29	0.45	0.31						0.0011	0.0043	115	
A38	0.50	2.1	0.76	0.008	0.005	0.026	0.30	0.25	0.50						0.0015	0.0054	133	
A39	0.45	1.8	0.40	0.005	0.004	0.031	0.28	0.28	1.10						0.0013	0.0051	124	
A40	0.55	1.9	0.75	0.008	0.009	0.029	0.29	0.26	1.50						0.0010	0.0040	268	
A41	0.50	2.1	0.95	0.010	0.008	0.028	0.31	0.32		0.05					0.0009	0.0045	77	
A42	0.50	2.0	0.95	0.008	0.007	0.029	0.31	0.27		0.08					0.0010	0.0052	74	
A43	0.47	1.9	0.95	0.005	0.004	0.031	0.26	0.27			0.0030				0.0012	0.0050	68	
A44	0.48	2.0	0.98	0.008	0.002	0.030	0.32	0.30				0.08			0.0012	0.0038	75	
A45	0.50	2.0	0.76	0.007	0.004	0.032	0.25	0.26					0.40		0.0014	0.0056	134	
A46	0.50	2.0	0.78	0.007	0.004	0.025	0.30	0.26						0.30	0.0014	0.0045	96	
A47	0.40	2.0	0.77	0.010	0.005	0.025	0.25	0.27	0.40						0.0013	0.0055	104	
A48	0.49	2.0	0.20	0.008	0.009	0.025	0.30	0.30	0.90						0.0014	0.0053	86	
A49	0.50	2.0	0.80	0.005	0.004	0.032	0.28	0.28	0.50	0.09	0.0035				0.0008	0.0053		163
A50	0.53	2.0	0.80	0.003	0.006	0.027	0.27	0.27	0.20						0.0014	0.0045	95	

[Table 3]

Chemical composition (% by mass) The balance being iron and inevitable impurities																		D _i value	
	C	Si	Mn	P	S	Al	Cu	Ni	Cr	Ti	B	Nb	Mo	V	O	N	B is not added	B is added	
Steel																			
A51	0.59	2.1	0.35	0.006	0.008	0.027	0.29	0.47	0.31	0.10					0.0012	0.0040	77		
A52	0.61	2.2	0.55	0.007	0.008	0.027	0.31	0.52	0.29	0.09					0.0009	0.0040	106		
A53	0.58	2.2	0.41	0.006	0.008	0.025	0.32	0.60	0.35	0.08					0.0014	0.0051	95		
A54	0.61	2.1	0.55	0.010	0.010	0.032	0.28	0.80	0.25	0.07					0.0009	0.0041	105		
A55	0.58	2.2	0.40	0.008	0.009	0.029	0.12	0.53	0.28	0.11					0.0012	0.0043	78		
A56	0.60	2.2	0.70	0.007	0.006	0.030	0.20	0.58	0.28	0.08					0.0010	0.0043	120		
A57	0.61	2.1	0.62	0.008	0.010	0.027	0.58	0.62	0.27	0.09					0.0011	0.0054	122		
A58	0.62	2.2	0.48	0.008	0.008	0.025	0.29	0.56	0.31						0.0012	0.0041	102		
A59	0.59	2.2	0.59	0.010	0.007	0.030	0.32	0.47	0.22						0.0009	0.0040	97		
A60	0.49	2.2	0.58	0.007	0.009	0.032	0.32	0.56	0.21	0.08					0.0012	0.0043	87		
A61	0.55	2.1	0.52	0.009	0.006	0.025	0.29	0.51	0.19	0.10					0.0012	0.0041	80		
A62	0.60	2.2	0.65	0.010	0.007	0.029	0.31	0.56		0.10					0.0009	0.0053	73		
A63	0.61	2.2	0.75	0.008	0.008	0.030	0.28	0.49		0.08					0.0011	0.0053	79		
A64	0.61	2.3	0.60	0.007	0.007	0.032	0.35	0.56	0.35	0.07					0.0012	0.0051	128		
A65	0.58	2.4	0.54	0.008	0.009	0.029	0.28	0.62	0.32	0.08					0.0012	0.0041	113		
A66	0.61	2.1	0.50	0.009	0.008	0.025	0.28	0.58	0.19	0.07				0.13	0.0009	0.0054	104		
A67	0.63	2.1	0.42	0.008	0.006	0.029	0.45	0.55	0.27	0.07				0.18	0.0009	0.0043	121		

[Table 4]

Test No.	Steel No.	Whether or not treatment for reduction of hydrogen in steel is implemented			Rolling/cooling conditions			Amount of nondiffusible hydrogen (ppm by mass)	Ferrite area ratio (%)	Value of right side of inequality expression (1)	(Value of right side of inequality expression (1)) - (Ferrite area ratio)	Reduction rate (%)	Area ratio of supercooled structure (%)	Area ratio of pearlite structure (%)	Wire tensile strength (MPa)	Reduction of area of rolled material (%)	Hydrogen embrittlement resistance (sec)	Corrosion weight loss (g)
		Molten steel treatment	Homogenizing treatment	Cooling (iii) in a range of 400 to 100°C after rolling	TL temperature (°C)	Average cooling rate in a range of TL to 650°C (°C/sec)	Average cooling rate in a range of 650 to 400°C (°C/sec)											
1	A1	Implementation	-	-	950	4	1	0.20	32.9	39.5	6.6	17	≤ 1%	67.1	1943	44.8	1081	3.2
2	A2	-	Implementation	-	950	4	1	0.35	35.2	41.1	5.9	14	≤ 1%	64.8	1918	43.0	1070	4.5
3	A3	-	-	Implementation	950	4	1	0.34	32.6	39.5	6.9	17	≤ 1%	67.4	1936	39.5	1056	4.1
4	A4	Implementation	Implementation	Implementation	950	4	1	0.05	30.5	37.8	7.3	19	≤ 1%	69.5	1945	47.7	1093	4.3
5	A5	-	-	-	950	4	1	0.60	32.9	39.5	6.6	17	≤ 1%	67.1		25.3		
6	A6	-	-	-	950	4	1	0.43	34.3	41.1	6.8	17	≤ 1%	65.7		24.3		
7	A7	Implementation	-	-	950	2.3	1	0.13	34.8	39.5	4.7	12	≤ 1%	65.2	1936	46.0	1025	4.4
8	A7	Implementation	-	-	950	3	1	0.16	33.5	39.5	6.0	15	≤ 1%	66.5	1926	46.0	1042	4.2
9	A7	Implementation	-	-	950	4.8	1	0.20	32.0	39.5	7.5	19	≤ 1%	68.0	1944	43.9	1125	4.1
10	A7	Implementation	-	-	950	4	0.5	0.09	32.4	39.5	7.1	18	≤ 1%	67.6	1926	48.1	1065	4
11	A7	Implementation	-	-	950	4	1.8	0.22	33.0	39.5	6.5	16	≤ 1%	67.0	1928	43.6	1055	4
12	A7	Implementation	-	-	950	1	1	0.18	42.3	39.5	-2.8	-7	≤ 1%	57.7	1945	45.1	853	4
13	A7	Implementation	-	-	950	6	1	0.14	29.0	39.5	10.5	26	3.2	67.8		28.0		
14	A7	Implementation	-	-	950	4	3	0.33	32.6	39.5	6.9	17	15.4	52.0		14.0		
15	A8	Implementation	-	-	910	4	1	0.21	2.8	10.1	7.3	72	≤ 1%	97.2	2151	40.7	1063	3.9
16	A9	-	Implementation	-	910	4	1	0.35	5.0	11.7	6.7	57	≤ 1%	95.0	2140	37.4	1044	3.7
17	A10	-	-	Implementation	910	4	1	0.35	1.1	6.8	5.7	84	≤ 1%	98.9	2183	34.6	1027	4.1
18	A11	Implementation	Implementation	Implementation	910	4	1	0.04	3.0	10.1	7.1	70	≤ 1%	97.0	2158	46.7	1086	4
19	A12	-	-	-	910	4	1	0.52	1.5	8.4	6.9	82	≤ 1%	98.5		27.6		
20	A13	-	-	-	910	4	1	0.65	1.4	8.4	7.0	83	≤ 1%	98.6		21.5		
21	A14	Implementation	-	-	910	2	1	0.13	8.5	10.1	1.6	16	≤ 1%	91.5	2148	43.7	1008	4.2
22	A14	Implementation	-	-	910	3	1	0.11	8.0	10.1	2.1	21	≤ 1%	92.0	2150	44.3	1045	3.9
23	A14	Implementation	-	-	910	5	1	0.12	3.0	10.1	7.1	70	≤ 1%	97.0	2159	44.6	1156	4
24	A14	Implementation	-	-	910	4	0.5	0.08	6.0	10.1	4.1	40	≤ 1%	94.0	2149	46.1	1054	3.9
25	A14	Implementation	-	-	910	4	1.8	0.21	6.2	10.1	3.9	38	≤ 1%	93.8	2161	41.9	1088	3.9
26	A14	Implementation	-	-	910	1	1	0.08	12.3	10.1	-2.2	-22	≤ 1%	87.7	2155	46.1	932	3.9
27	A14	Implementation	-	-	910	6	1	0.09	1.1	10.1	9.0	89	2.9	96.0		15.3		
28	A14	Implementation	-	-	910	4	3	0.30	2.8	10.1	7.3	72	28	69.2		5.0		
29	A15	Implementation	-	-	910	4	1	0.08	3.5	11.7	8.2	70	30.5	66.0		4.5		
30	A16	Implementation	-	-	910	4	1	0.09	0.5	6.8	6.3	93	25.9	73.6		8.5		
31	A17	Implementation	-	-	910	4	1	0.09	2.2	10.1	7.9	78	40.5	57.3		2.0		
32	A18	Implementation	-	-	950	4	1	0.11	44.3	50.9	6.6	13	≤ 1%	55.7	1853	50.3	1105	4

[Table 5]

Test Steel No.	Whether or not treatment for reduction of hydrogen in steel is implemented			Rolling/cooling conditions			Amount of nondiffusible hydrogen (ppm by mass)	Ferrite area ratio (%)	Value of right side of inequality expression (1)	(Value of right side of inequality expression (1)) - (Ferrite area ratio)	Reduction rate (%)	Area ratio of surface-cooled structure (%)	Area ratio of structure (%)	Wire tensile strength (MPa)	Reduction of rolled material (%)	Hydrogen Corrosion embrittlement weight resistance loss (sec) (g)
	Molten steel treatment	Homogenizing treatment	Cooling (iii) in a range of 400 to 100°C after rolling	TL temperature (°C)	Average cooling rate in a range of TL to 650°C (°C/sec) Cooling (i)	average cooling rate in a range of 650 to 400°C (°C/sec) Cooling (ii)										
33	A19	-	-	950	4	1	0.12	35.9	42.7	6.8	16	≤1%	64.1	1913	50.0	1,100 4.2
34	A20	-	-	900	4	1	0.08	0.3	3.5	3.2	92	≤1%	99.7	2188	44.1	1068 4.4
35	A21	-	-	900	4	1	0.18	-	-	-	-	≤1%	-	2254	39.6	756 4.2
36	A22	-	-	930	4	1	0.12	20.9	26.4	5.5	21	≤1%	79.1	1855	53.1	
37	A23	-	-	930	4	1	0.10	16.3	23.1	6.8	30	≤1%	83.7	2043	50.1	1090 4.2
38	A24	-	-	930	4	1	0.12	21.0	28.0	7.0	25	<1%	79.0	2006	52.4	1116 3.8
39	A25	-	-	930	4	1	0.22	18.8	26.4	7.6	29	≤1%	81.2	2026	42.8	1073 4.1
40	A26	-	-	930	4	1	0.09	14.2	21.5	7.3	34	≤1%	85.8	2068	46.4	1092 4.1
41	A27	-	-	930	4	1	0.25	18.3	26.4	8.1	31	≤1%	81.7	2022	33.9	756 3.8

(continued)

Test Steel No.	Whether or not treatment for reduction of hydrogen in steel is implemented			Rolling/cooling conditions			Amount of nondiffusible hydrogen (ppm by mass)	Ferrite area ratio (%)	Value of right side of inequality expression (1)	(Value of right side of inequality expression (1)) -(Ferrite area ratio)	Reduction rate (%)	Area ratio of supercooled structure (%)	Area ratio of structure (%)	Wire tensile strength (MPa)	Reduction of rolled material (%)	Hydrogen Corrosion embrittlement weight resistance loss (sec) (g)	
	Molten steel treatment	Homogenizing treatment	Cooling range of 400 to 100°C after rolling	TL temperature (°C)	Average cooling rate in a range of TL to 650°C (°C/sec) Cooling (i)	average cooling rate in a range of 650 to 400°C (°C/sec) Cooling (ii)											
42 A28	Implementation	-	-	930	4	1	0.10	11.6	18.2	6.6	36	≤1%	88.4	2089	44.9	369	4.2
43 A29	Implementation	-	-	930	4	1	0.11	19.5	26.4	6.9	26	≤1%	80.5	2019	47.3	258	3.9
44 A30	Implementation	-	-	930	4	1	0.14	11.6	18.2	6.6	36	≤1%	88.4	2089	45.5	1080	5.3
45 A31	Implementation	-	-	930	4	1	0.30	19.3	26.4	7.1	27	≤1%	80.7	2033	40.2	1058	4.4
46 A32	Implementation	-	-	930	4	1	0.13	20.2	26.4	6.2	23	≤1%	79.8	2029	45.0	1081	4
47 A33	Implementation	-	-	930	4	1	0.20	28.2	34.6	6.4	18	≤1%	71.8	1965	45.5	1084	3.7
48 A34	Implementation	-	-	930	4	1	0.25	19.2	26.4	7.2	27	≤1%	80.8	2031	43.4	1075	5.4
49 A35	Implementation	-	-	930	4	1	0.16	16.6	23.1	6.5	28	≤1%	83.4	2056	44.7	1074	4.7
50 A36	Implementation	-	-	930	4	1	0.19	20.3	26.4	6.1	23	≤1%	79.7	2041	44.1	1073	4

(continued)

Test Steel No.	Whether or not treatment for reduction of hydrogen in steel is implemented			Rolling/cooling conditions			Amount of nondiffusible hydrogen (ppm by mass)	Ferrite area ratio (%)	Value of right side of inequality expression (1)	(Value of right side of inequality expression (1)) -(Ferrite area ratio)	Reduction rate (%)	Area ratio of supercooled structure (%)	Area ratio of structure (%)	Wire tensile strength (MPa)	Reduction of rolled material (%)	Hydrogen Corrosion embrittlement weight resistance loss (sec) (g)	
	Molten steel treatment	Homogenizing treatment	Cooling range of 400 to 100°C after rolling	TL temperature (°C)	Average cooling rate in a range of TL to 650°C (°C/sec) Cooling (i)	average cooling rate in a range of 650 to 400°C (°C/sec) Cooling (ii)											
51 A37	Implementation	-	-	930	4	1	0.08	21.1	28.0	6.9	25	≤1%	78.9	2020	48.0	1090	3.5
52 A38	Implementation	-	-	930	4	1	0.15	19.7	26.4	6.7	25	≤1%	80.3	2030	44.9	1081	4.2
53 A39	Implementation	-	-	930	4	1	0.08	27.3	34.6	7.3	21	≤1%	72.7	1977	55.1	1127	4.1
54 A40	Implementation	-	-	930	4	1	0.18	9.0	18.2	9.2	51	≤1%	91.0	2087	44.0	885	4
55 A41	Implementation	-	-	930	4	1	0.22	19.7	26.4	6.7	25	≤1%	80.3	2024	40.9	1057	3.9
56 A42	Implementation	-	-	930	4	1	0.25	19.6	26.4	6.8	26	< 1%	80.4	2031	40.7	1057	4
57 A43	Implementation	-	-	930	4	1	0.25	25.0	31.3	6.3	20	≤1%	75.0	1989	42.6	1064	4.2
58 A44	Implementation	-	-	930	4	1	0.22	22.9	29.7	6.8	23	≤1%	77.1	1998	41.9	1071	4
59 A45	Implementation	-	-	930	4	1	0.09	20.5	26.4	5.9	22	≤1%	79.5	2023	47.7	1088	4

(continued)

Test Steel No.	Whether or not treatment for reduction of hydrogen in steel is implemented			Rolling/cooling conditions			Amount of nondiffusible hydrogen (ppm by mass)	Ferrite area ratio (%)	Value of right side of inequality expression (1)	(Value of right side of inequality expression (1)) -(Ferrite area ratio)	Reduction rate (%)	Area ratio of supercooled structure (%)	Area ratio of structure (%)	Wire tensile strength (MPa)	Reduction of rolled material (%)	Hydrogen Corrosion embrittlement weight resistance loss (sec) (g)	
	Molten steel treatment	Homogenizing treatment	Cooling (iii) in a range of 400 to 100°C after rolling	TL temperature (°C)	Average cooling rate in a range of TL to 650°C (°C/sec) Cooling (i)	average cooling rate in a range of 650 to 400°C (°C/sec) Cooling (ii)											
60 A46	Implementation	-	-	930	4	1	0.15	19.6	26.4	6.8	26	≤1%	80.4	2022	46.0	1082	4.1
61 A47	Implementation	-	-	950	1	1	0.12	50.2	42.7	-7.5	-18	≤1%	49.8	1905	51.2	905	4.3
62 A48	Implementation	-	-	930	1	1	0.12	32.2	28.0	-4.2	-15	≤1%	67.8	2000	53.0	920	3.8
63 A49	Implementation	-	-	930	1	1	0.22	30.2	26.4	3.8	-14	≤1%	69.8	2025	42.5	775	4
64 A50	Implementation	-	-	930	1	1	0.09	23.5	21.5	-2.0	-9	≤1%	76.5	2060	46.0	799	4

[Table 6]

Test No.	Whether or not treatment for reduction of hydrogen in steel is implemented			Rolling/cooling conditions			Amount of nondiffusible hydrogen (ppm by mass)	Ferrite area ratio (%)	Value of in-quality expression (1)	(Value of right side of in-quality expression (1)) (Ferrite area ratio)	Reduction rate (%)	Area ratio of super-cooled structure (%)	Area ratio of pearlite structure (%)	Wire tensile strength (MPa)	Reduction rolled material (%)	Hydrogen embrittlement resistance (sec)	Corrosion weight loss (g)
	Molten steel treatment	Homogenizing treatment	Cooling range of 400 to 100°C after rolling	TL temperature (°C)	Average cooling rate in a range of TL to 650°C (°C/sec) Cooling (i)	Average cooling rate in a range of 650 to 400°C (°C/sec) Cooling (ii)											
65	A51	-	-	930	4	1	0.18	5.0	11.7	6.7	57	≤1%	95.0	1992	46.8	1079	2.5
66	A52	-	-	930	4	1	0.25	1.0	8.4	7.5	89	≤1%	99.0	2030	37.2	1069	2.2
67	A53	-	-	930	4	1	0.22	6.2	13.3	7.1	53	<1%	93.8	2010	40.3	1068	1.7
68	A54	-	-	930	4	1	0.16	1.2	8.4	7.2	86	≤1%	98.8	2004	47.7	1094	1.0
69	A55	-	-	930	4	1	0.22	6.2	13.3	7.2	54	≤1%	93.8	2018	32.6	1030	2.1
70	A56	-	-	930	4	1	0.16	2.5	10.1	7.6	75	≤1%	97.5	2018	35.1	1015	1.7
71	A57	-	-	930	4	1	0.20	1.0	8.4	7.4	88	≤1%	99.0	1994	43.6	1094	1.4
72	A58	-	-	930	4	1	0.24	0.5	6.8	6.3	93	≤1%	99.5	1995	44.9	1080	2.2

(continued)

Test No.	Steel No.	Whether or not treatment for reduction of hydrogen in steel is implemented			Rolling/cooling conditions			Amount of nondiffusible hydrogen (ppm by mass)	Ferrite area ratio (%)	Value of inquality expression (1)	(Value of right side of inquality expression (1)) - (Ferrite area ratio)	Reduction rate (%)	Area ratio of supercooled structure (%)	Area ratio of pearlite structure (%)	Wire tensile strength (MPa)	Reduction rolled material (%)	Hydrogen embrittlement resistance (sec)	Corrosion weight loss (g)
		Molten steel treatment	Homogenizing treatment	Cooling range of 400 to 100°C after rolling	TL temperature (°C)	Average cooling rate in a range of TL to 650°C (°C/sec) Cooling (i)	Average cooling rate in a range of 650 to 400°C (°C/sec) Cooling (ii)											
73	A59	Implementation	-	-	930	4	1	0.23	4.6	11.7	7.1	61	≤1%	95.4	2010	44.4	1064	2.4
74	A60	Implementation	-	-	930	4	1	0.24	21.4	28.0	6.6	24	≤1%	78.6	1981	50.8	1122	2.1
75	A61	Implementation	-	-	930	4	1	0.17	11.6	18.2	6.6	36	≤1%	88.4	2004	45.7	1085	2.3
76	A62	Implementation	-	-	930	4	1	0.19	3.2	10.1	6.8	68	<1%	96.8	2021	42.1	1060	1.8
77	A63	Implementation	-	-	930	4	1	0.22	1.1	8.4	7.3	87	≤1%	98.9	2011	42.0	1158	2.0
78	A64	Implementation	-	-	930	4	1	0.24	0.6	8.4	7.9	93	≤1%	99.4	2028	45.2	1178	1.7
79	A65	Implementation	-	-	930	4	1	0.24	5.6	13.3	7.8	58	≤1%	94.4	1988	42.4	1076	1.5
80	A66	Implementation	-	-	930	4	1	0.18	1.3	8.4	7.2	85	≤1%	98.7	1981	40.2	1024	1.8

(continued)

Test Steel No.	Whether or not treatment for reduction of hydrogen in steel is implemented	Rolling/cooling conditions			Amount of nondiffusible hydrogen (ppm by mass)	Ferrite area ratio (%)	Value of right side of inequality expression (1)	(Value of right side of inequality expression (1)) - (Ferrite area ratio)	Reduction rate (%)	Area ratio of supercooled structure (%)	Area ratio of pearlite structure (%)	Wire tensile strength (MPa)	Reduction rolled material (%)	Hydrogen embrittlement resistance (sec)	Corrosion weight loss (g)			
		TL temperature (°C)	Average cooling rate in a range of TL to 650°C (°C/sec) Cooling (i)	Average cooling rate in a range of 650 to 400°C (°C/sec) Cooling (ii)														
81	A67	Implementation	-	-	930	4	1	0.19	0.5	5.2	4.7	90	≤1%	99.5	2014	39.4	1069	1.9

[0071] Samples of test Nos. 1 to 4, 7 to 11, 15 to 18, 21 to 25, 33, 34, 37 to 40, 45 to 47, 49 to 53, 55 to 60, and 65 to 81 are manufactured from a steel having appropriately adjusted chemical composition under preferred manufacturing conditions mentioned above, so that the amount of nondiffusible hydrogen, and the area ratio of ferrite and supercooled structures satisfy the requirements of the present invention. Therefore, the rolled material exhibits a reduction of area RA of 30% or more in the tensile test and is excellent in wire drawability, and the wire obtained by wire drawing of the rolled material, followed by quenching and tempering has an excellent tensile strength in a range of 1,900 MPa or more. Further, the wire obtained after quenching and tempering exhibits a fracture time of 1,000 seconds or more in an evaluation test of hydrogen embrittlement resistance and a corrosion weight loss of 5.0 g or less in an evaluation test of corrosion resistance, so that the wire is excellent in both hydrogen embrittlement resistance and corrosion resistance. Further, "reduction rate" in Tables 4 to 6 is a value in which a ratio of a difference between a value of right side of the inequality expression (1) and an actual value of a ferrite area ratio to a value of right side of the inequality expression (1) is expressed as percentage.

[0072] In contrast, in examples other than the above-mentioned ones, at least any one of the requirements, including the chemical composition of a steel, the amount of nondiffusible hydrogen, the ferrite area ratio, and the supercooled structure area ratio does not satisfy the requirements of the present invention, leading to the result that at least any one property of wire drawability of a rolled material, tensile strength, hydrogen embrittlement resistance, and corrosion resistance of a wire is inferior.

[0073] All of samples of test Nos. 5, 6, 19 and 20 are not subjected to the above-mentioned treatment for reduction of nondiffusible hydrogen, so that the amount of nondiffusible hydrogen in the rolled material increased, thus degrading wire drawability.

[0074] In samples of tests Nos. 12 and 26, because of low average cooling rate in a range of a coiling temperature TL to 650°C, the ferrite area ratio increased, thus degrading hydrogen embrittlement resistance. In samples of tests Nos. 13 and 27, because of high average cooling rate in a range of a coiling temperature TL to 650°C, the supercooled structures increased, thus degrading wire drawability. In samples of tests Nos. 14 and 28, because of high average cooling rate in a range of 650 to 400°C, the supercooled structure increased, thus degrading wire drawability.

[0075] In samples of tests Nos. 29 to 31, the supercooled structure increased, thus degrading wire drawability. In sample of test No. 32, because of a small amount of C, the wire exhibited poor tensile strength. In sample of test No. 35, because of a large amount of C, residual austenite was generated, thus degrading hydrogen embrittlement resistance. In sample of test No. 36, because of a small amount of Si, the wire exhibited poor tensile strength.

[0076] In sample of test No. 41, because of a large amount of Mn, toughness was degraded, thus degrading hydrogen embrittlement resistance. In sample of test No. 42, because of a large amount of P and a large amount of S, grain boundary embrittlement occurred, thus degrading hydrogen embrittlement resistance. In sample of test No. 43, because of a large amount of S, grain boundary embrittlement occurred, thus degrading hydrogen embrittlement resistance. In sample of test No. 44, neither Cu nor Ni is not added, thus degrading corrosion resistance.

[0077] In sample of test No. 48, Ni is not added, occurred, thus degrading corrosion resistance. In sample of test No. 54, because of a large amount of Cr, dissolving residue of cementite, in which chromium-based carbide and metallic Cr in high concentration are solid-soluted, was generated as a stress concentration source, thus degrading hydrogen embrittlement resistance.

[0078] In samples of tests Nos. 61 to 64, because of low average cooling rate in a range of a coiling temperature TL to 650°C, the ferrite area ratio increased, thus degrading hydrogen embrittlement resistance.

Industrial Applicability

[0079] The rolled material and the wire of the present invention are industrially useful since they can be suitably used for coil springs that are used in automobiles, for example, a valve spring, a suspension spring and the like that are used in the engine, suspension, and the like.

Claims

1. A rolled material for high strength spring, comprising, in % by mass:

C: 0.39 to 0.65%,
Si: 1.5 to 2.5%,
Mn: 0.15 to 1.2%,
P: exceeding or and 0.015% or less,
S: exceeding 0% and 0.015% or less,
Al: 0.001 to 0.1%,

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Cu: 0.1 to 0.80%, and

Ni: 0.1 to 0.80%, with the balance being iron and inevitable impurities, wherein

an amount of nondiffusible hydrogen is 0.40 ppm by mass or less, and

an area ratio of ferrite expressed as a percentage satisfies an inequality expression (1) below, and a total area ratio of bainite and martensite is 2% or less:

$$\text{Ferrite area ratio} < \left\{ (0.77 - [C]) / 0.77 - [C] / 3 + 0.08 \right\} \times 100 \quad (1)$$

where [name of element] in the above inequality expression (1) means a content expressed in % by mass of each element.

2. The rolled material for high strength spring according to claim 1, further comprising, in % by mass, at least one belonging to any one of the following (a), (b), (c) and (d):

(a) Cr: exceeding 0% and 1.2% or less,

(b) Ti: exceeding 0% and 0.13% or less,

(c) B: exceeding 0% and 0.01% or less, and

(d) at least one selected from the group consisting of Nb: exceeding 0% and 0.1% or less, Mo: exceeding 0% and 0.5% or less, and V: exceeding 0% and 0.4% or less.

3. The rolled material for high strength spring according to claim 1 or 2, wherein an ideal critical diameter D_i , which is calculated using an equation (2) below when B is not included or using an equation (3) below when B is included, is in a range of 65 to 140 mm:

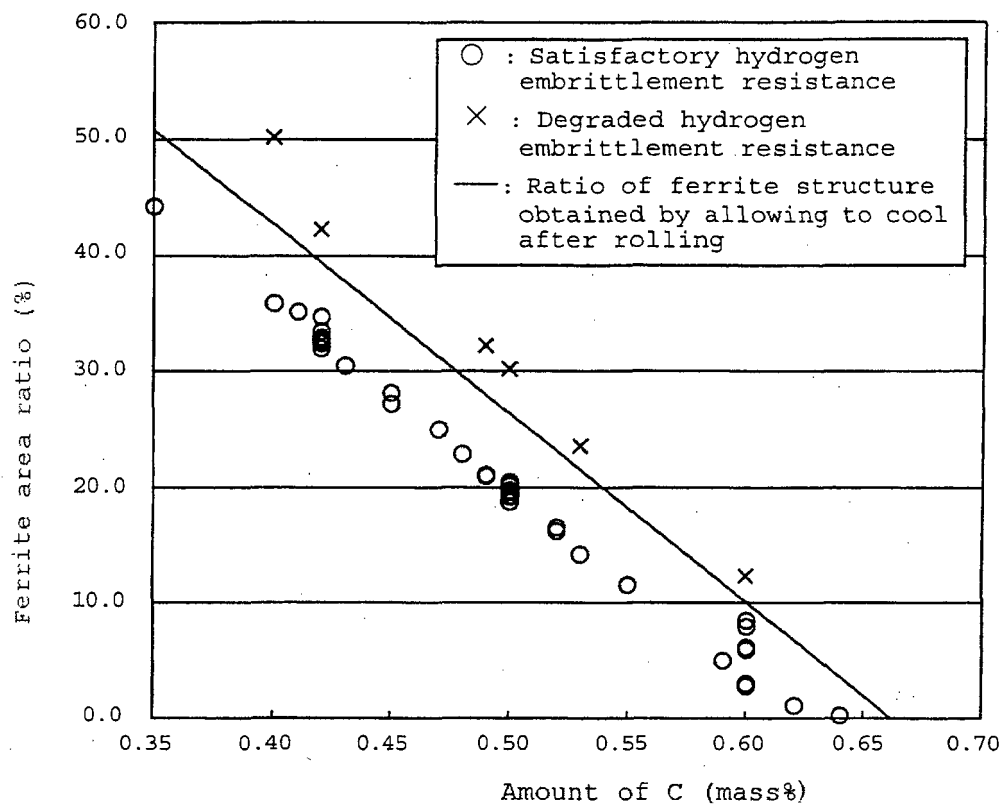
$$D_i = 25.4 \times (0.171 + 0.001 \times [C] + 0.265 \times [C]^2) \times (3.3333 \times [Mn] + 1) \times (1 + 0.7 \times [Si]) \times (1 + 0.363 \times [Ni]) \times (1 + 2.16 \times [Cr]) \times (1 + 0.365 \times [Cu]) \times (1 + 1.73 \times [V]) \times (1 + 3 \times [Mo]) \quad (2)$$

$$D_i = 25.4 \times (0.171 + 0.001 \times [C] + 0.265 \times [C]^2) \times (3.3333 \times [Mn] + 1) \times (1 + 0.7 \times [Si]) \times (1 + 0.363 \times [Ni]) \times (1 + 2.16 \times [Cr]) \times (1 + 0.365 \times [Cu]) \times (1 + 1.73 \times [V]) \times (1 + 3 \times [Mo]) \times (6.849017 - 46.78647 \times [C] + 196.6635 \times [C]^2 - 471.3978 \times [C]^3 + 587.8504 \times [C]^4 - 295.0410 \times [C]^5) \quad (3)$$

where [name of element] in the above equations (2) and (3) means a content expressed in % by mass of each element.

4. A wire for high strength spring, having a tensile strength of 1,900 MPa or more, obtained by wire-drawing the rolled material for high strength spring according to claim 1 or 2, followed by a quenching and tempering treatment.
5. A wire for high strength spring, having a tensile strength of 1,900 MPa or more, obtained by wire-drawing the rolled material for high strength spring according to claim 3, followed by a quenching and tempering treatment.

Fig. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/082728

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/00(2006.01)i, B21C1/00(2006.01)i, C21D3/06(2006.01)i, C21D8/06
(2006.01)i, C21D9/52(2006.01)i, C22C38/16(2006.01)i, C22C38/54(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C1/00-49/14, B21C1/00, C21D3/06, 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 1996-2015
Kokai Jitsuyo Shinan Koho 1971-2015 Toroku Jitsuyo Shinan Koho 1994-2015

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2011-184705 A (Kobe Steel, Ltd.), 22 September 2011 (22.09.2011), (Family: none)	1-5
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Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/082728

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