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(54) **HIGH-CARBON COLD-ROLLED STEEL SHEET AND PRODUCTION METHOD THEREFOR, AND MECHANICAL PARTS MADE OF HIGH-CARBON STEEL**

(57) Provided is a high carbon cold rolled steel sheet which can have good impact characteristics and hardness characteristics and excellent wear resistance after rapid cooling (quenching) treatment after short-time solution treatment and low-temperature tempering treatment (quenching and tempering treatment), has little decrease in secondary workability before the quenching and tempering treatment, and has a sheet thickness of less than 1.0 mm.

The high carbon cold rolled steel sheet has a steel sheet chemical composition consisting of, by mass%, C: 0.85% to 1.10%, Mn: less than 0.60%, Si: 0.10% to 0.35%, P: 0.030% or less, S: 0.030% or less, Cr: less

than 0.60%, Mn + Cr satisfying less than 1.0%, Nb: 0.005% to 0.020%, and the balance being Fe and inevitable impurities. Thereby, compared with conventional steel materials, there is little decrease in the secondary workability before quenching and tempering. In addition, by adopting a steel sheet structure with an average particle diameter of carbide of 0.2 to 0.7 (μm) and a spheroidization rate of 90% or more, even with a quenching and tempering treatment in such a short time as 3 to 15 min, it is possible to provide a machine part having excellent impact characteristics with an impact value of 9 J/cm², sufficient hardness characteristics in a range of 600 to 750 HV, and excellent wear resistance.

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Description

Technical Field

5 **[0001]** The present invention relates to a high carbon cold rolled steel sheet serving as a material for various machine parts produced by quenching and tempering treatment and a method for manufacturing the high carbon cold rolled steel sheet, and relates particularly to a high carbon cold rolled steel sheet with a thickness of less than 1.0 mm applied to knitting needles and the like.

10 Background Art

[0002] Generally, carbon steels for machine structural use (SxxC) and carbon tool steels (SK) specified in JIS are used for various types of machine parts. When used as flat-rolled materials, these steels are formed into a part shape through punching and various plastic processing, and quenching and tempering treatment is then carried out to impart a predetermined hardness and toughness (impact characteristics). Among them, a knitting needle for knitting a knit fabric knits a knitting fabric by pulling yarn while repeating reciprocating motion at a high speed, so that a butt portion of a needle body coming into contact with a rotary driving part is required to have sufficient strength and wear resistance, and, in addition, a hook portion rubbing against the yarn is required to have excellent impact characteristics at its tip portion due to reciprocating motion in addition to sufficient wear resistance.

20 **[0003]** A high carbon cold rolled steel sheet used as a material for knitting needles is suitable for knitting needles for flat knitting machines when the thickness is 1.0 mm or more. When the thickness is less than 1.0 mm, the high carbon cold rolled steel sheet is used for knitting needles for circular knitting machines and warp knitting machines. Since the latter needles knit small diameter yarns at high speed, the thickness of a material used is often 0.4 to 0.7 mm. In addition to excellent cold workability (also referred to as secondary workability), the material is required to have sufficient hardness and sufficient toughness at the needle tip when quenched and tempered after secondary working into a needle shape.

25 **[0004]** In addition, so-called high carbon steel sheets such as carbon steels for machine structural use (SxxC) and carbon tool steels (SK) specified in JIS are classified in detail according to a C content. In a region where the C content is less than 0.8% by mass, that is, a steel sheet with a hypo-eutectoid composition, since the fraction of the ferrite phase is high, the cold workability is excellent. However, it is difficult to obtain sufficient quenching hardness, so that this steel sheet is not suitable for knitting needle applications that require wear resistance of a hook portion and durability of a needle body. On the other hand, out of the hypo-eutectoid composition of 0.8% by mass or more, a high carbon steel sheet having a C content greater than 1.1% by mass has excellent hardenability. However, the cold workability is extremely poor due to a large amount of carbide (cementite), and this high carbon steel sheet is not suitable for knitting needle applications where precise and fine working such as grooving is performed, and is limited to use for parts such as cutlery and cold forming dies that have a simple shape and require high hardness.

35 **[0005]** Conventionally, carbon tool steel and alloy tool steel with C: 0.8 to 1.1% by mass or materials having a steel composition to which a third element is added based on these steel compositions have been widely used for knitting needles. In the manufacturing process of this knitting needle, the material is subjected to a wide variety of plastic working such as punching (shearing), cutting, swaging, mechanical joining and bending. Therefore, the material for manufacturing knitting needles is required to have hardness characteristics and impact characteristics (toughness) after quenching and tempering treatment required when actually used as a needle, in addition to having sufficient workability (secondary workability) during material processing in the needle manufacturing process.

[0006] In the manufacture of knitting needles, the material is subjected to a quenching and tempering treatment in order to ensure a predetermined hardness characteristic. In general, the temperature of the tempering treatment is a low temperature of 200 to 350°C. However, emphasizing the hardness characteristics, when the contents of Mn and Cr effective for hardenability are increased, or when a large amount of other third elements is contained, in the above-mentioned low-temperature tempering treatment in the temperature range of 200 to 350°C, a martensite phase is not sufficiently tempered, so that in some cases, the impact characteristics (toughness) are not sufficiently improved, and a toughness value may vary.

50 **[0007]** On the other hand, for the purpose of improving the impact characteristics of knitting needles, reduction in P and S which are impurity elements in the chemical composition of the material, suppression of grain-boundary segregation of P and inclusion (MnS) formation, and reduction of adverse effects of the elements are also effective measures. However, from the viewpoint of steelmaking technology and economy, there is a limit to improve the impact characteristics of knitting needles by reducing P and S.

55 **[0008]** It has been conventionally known that refinement of metal structures is effective as means for improving the impact characteristics.

[0009] For example, Patent Literature 1 describes "HIGH CARBON STEEL SHEET EXCELLENT IN HARDENABILITY, FATIGUE CHARACTERISTICS, AND TOUGHNESS AND METHOD FOR MANUFACTURING THE SAME". The high

carbon steel sheet described in Patent Literature 1 includes a composition containing, by mass%, C: 0.5 to 0.7%, Si: 0.5% or less, Mn: 1.0 to 2.0%, P: 0.02% or less, S: 0.02% or less, and Al: 0.001 to 0.10% and one or two or more elements selected from V: 0.05 to 0.50%, Ti: 0.02 to 0.20%, and Nb: 0.01 to 0.50%, with the balance being Fe and inevitable impurities, has a spheroidization rate of carbides is 95% or more, and has a structure in which the carbide having a maximum particle size of 2.5 μm or less is dispersed. In the technique described in Patent Literature 1, for hypo-eutectoid steel, carbonitride forming elements V, Ti, and Nb are added to form fine carbonitrides. It is described that prior austenite grains are refined using the pinning effect of these fine carbonitrides to improve toughness.

[0010] Patent Literature 2 describes "HIGH CARBON STEEL MEMBER EXCELLENT IN IMPACT CHARACTERISTICS". The high carbon steel member described in Patent Literature 2 has a composition consisting of, by mass%, C: 0.60 to 1.30%, Si: 1.0% or less, Mn: 0.2 to 1.5%, P: 0.02% or less, S: 0.02% or less, and the balance being Fe except inevitable impurities. In a matrix after quenching and tempering, undissolved carbides remain at a volume fraction V_f (volume%) satisfying the following formula:

$$8.5 < 15.3 \times C\% - V_f < 10.0;$$

and the undissolved carbides having a particle size of 1.0 μm or more are regulated to 2 or less per observation area: 100 μm^2 . Patent Literature 2 describes that the high carbon steel member may, in addition to the above composition, contain, by mass%, one or two or more elements selected from Ni: 1.8% or less, Cr: 2.0% or less, V: 0.5% or less, Mo: 0.5% or less, Nb: 0.3% or less, Ti: 0.3% or less, B: 0.01% or less, and Ca: 0.01% or less. Although the technique described in Patent Literature 2 targets steels with a wide range of carbon content from hypo-eutectoid to hyper-eutectoid, it is described that it is possible to obtain a high carbon steel member exhibiting excellent impact characteristics with an impact value of 25 J/cm² or more while maintaining a target hardness of 600 to 900 HV.

[0011] Patent Literature 3 describes "HIGH CARBON COLD ROLLED STEEL SHEET AND METHOD FOR MANUFACTURING THE SAME". The high carbon cold rolled steel sheet described in Patent Literature 3 contains, by mass%, C: 0.85 to 1.10%, Mn: 0.50 to 1.0%, Si: 0.10 to 0.35%, P: 0.030% or less, S: 0.030 % or less, Cr: 0.35 to 0.45%, and Nb: 0.005 to 0.020%, the balance being Fe and inevitable impurities. An average particle diameter (d_{av}) of carbides dispersed in the steel sheet satisfies the following formula (1):

$$0.2 \leq d_{av} \leq 0.7 (\mu\text{m}) \quad \dots \quad (1),$$

and a spheroidization rate $(N_{SC}/N_{TC}) \times 100\%$ satisfies the following formula (2):

$$(N_{SC}/N_{TC}) \times 100 \geq 90\% \quad \dots \quad (2).$$

[0012] The high carbon cold rolled steel sheet has a thickness of less than 1.0 mm. In the technique described in Patent Literature 3, it is described that one or two elements selected from Mo and V are further contained in addition to the above-described composition, and each content is preferably 0.001% or more and less than 0.05%. Further, in the technique described in Patent Literature 3, it is described that the content of Nb: 0.005 to 0.020% is effective for improving the hardenability and impact characteristics (toughness) after a short-time solution treatment and a low-temperature tempering treatment.

[0013] Patent Literature 4 describes "WEAR RESISTANT STEEL SHEET HAVING EXCELLENT TOUGHNESS". The wear resistant steel sheet described in Patent Literature 4 has a chemical composition consisting of, by mass%, C: 0.60 to 1.25%, Si: 0.50% or less, Mn: 0.30 to 1.20%, P: 0.030% or less, S: 0.030% or less, Cr: 0.30 to 1.50%, Nb: 0.10 to 0.50%, Ti: 0 to 0.50%, Mo: 0 to 0.50%, V: 0 to 0.50%, Ni: 0 to 2.00%, the balance being Fe and inevitable impurities, and has a metal structure in which cementite particles and carbide particles containing one or more of Nb and Ti are dispersed in a metal matrix of a ferrite phase. In a cross section (L cross section) parallel to a rolling direction and a sheet thickness direction, a number density of Nb/Ti carbide particles with an equivalent circle diameter of 0.5 μm or more is 3000 to 9000/mm², and the number density of voids with an equivalent circle diameter of 1.0 μm or more is 1250/mm² or less. Patent Literature 4 describes that wear resistant steel sheet is a steel sheet having both excellent wear resistance and toughness.

Citation List

Patent Literature

5 **[0014]**

Patent Literature 1: JP 2009-24233 A

Patent Literature 2: JP 2006-63384 A

Patent Literature 3: JP 2017-36492 A

10 Patent Literature 4: JP 2017-190494 A

Summary of Invention

Technical Problem

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[0015] A high carbon cold rolled steel sheet used as a material for knitting needles is required to have sufficient hardness and sufficient impact characteristics (toughness) after quenching and tempering treatment. In recent years, higher speeds of knitting machines have been demanded in order to improve productivity, so that load on the knitting needles has increased, and the knitting needles often break in a shorter time than conventional ones, or their service life is often shorter than conventional ones, which becomes problematic. Thus, there is a demand for a knitting needle having improved impact characteristics and wear resistance. Such a knitting needle is considered to be achieved by adding a third element or increasing the amount of alloy elements such as Cr, Mn, and Mo; however, there is a concern that the secondary workability in the needle manufacturing process is hindered. For these reasons, there is a demand for a material for knitting needles that can improve the wear resistance and impact characteristics (toughness) after quenching and tempering without lowering the secondary workability further than conventional one.

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[0016] However, the technique described in Patent Literature 1 is difficult to apply to machine parts that require high hardness. The technique described in Patent Literature 1 is limited to hypo-eutectoid steel composition. In this technique, by adding a carbonitride forming element such as V, Ti, and Nb as the third element, the prior austenite grains are refined with these fine carbonitrides, and the effect of improve toughness is expected. The technique described in Patent Literature 1 is also a technique that improves formability of a ferrite matrix because the carbon level is a hypo-eutectoid composition.

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[0017] Patent Literature 2 shows only an example for steel with a carbon content in the range of 0.67 to 0.81% by mass for the addition of Mo, V, Ti, Nb, and B as the third elements. In the technique described in Patent Literature 2, it is presumed that the third element such as Mo, V, Ti, Nb, and B is added to improve properties of hypo-eutectoid steel. Moreover, Patent Literature 2 does not describe anything about the action of the third element such as Mo, V, Ti, Nb, and B and the optimization for steel with a carbon content exceeding 0.81% by mass.

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[0018] Furthermore, Patent Literature 1 and Patent Literature 2 do not describe a technique in which a high carbon cold rolled steel sheet is quenched after solution treatment for a short time such as 3 to 15 min and tempered at a low temperature of 200 to 350°C to advantageously improve desired impact characteristics and predetermined hardness.

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[0019] In the technique described in Patent Literature 3, it is described that the content of Nb: 0.005 to 0.020% is effective for improving the hardenability/impact characteristics (toughness) after quenching after holding solutionizing for a short time and a low-temperature tempering treatment; however, Patent Literature 3 does not specifically describe secondary workability of a high carbon cold rolled steel sheet before quenching (rapid cooling) after holding solutionizing for a short time and low-temperature tempering treatment (hereinafter, also referred to as quenching and tempering treatment). Patent Literature 3 describes a high carbon cold rolled steel sheet that can have both excellent toughness and excellent wear resistance after quenching and tempering treatment. However, this high carbon cold rolled steel sheet has a problem that the secondary workability before the quenching and tempering treatment is insufficient and it is not possible to meet recent demands for improving productivity.

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[0020] In the technique described in Patent Literature 4, it is described that in the high carbon cold rolled steel sheet, both wear resistance and toughness after quenching and tempering can be increased. However, there is no description about the secondary workability before the quenching and tempering treatment, and Patent Literature 4 does not mention that the wear resistance and toughness after quenching and tempering can be improved without lowering the secondary workability before quenching and tempering treatment.

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[0021] The present invention solves the above-described problems of the prior art, and an object of the present invention is to provide a high carbon cold rolled steel sheet which suppresses lowering of secondary workability before quenching (rapid cooling) after a short-time solution treatment and a low-temperature tempering treatment (quenching and tempering treatment), and, when evaluated by an impact test near an actually used sheet thickness after the quenching (rapid cooling) after the short-time solution treatment and the low-temperature tempering treatment (quenching

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and tempering treatment), has an impact value of 9 J/cm² or more, a hardness satisfying a range of 600 to 750 HV, excellent wear resistance, and a sheet thickness of less than 1.0 mm.

Solution to Problem

[0022] In order to achieve the above-mentioned object, the present inventors have made intensive studies on a relationship of a composition of the high carbon cold rolled steel sheet with secondary workability before quenching and tempering treatment, hardness after the quenching and tempering treatment, impact characteristics, and wear resistance. As a result, it has been found that performing a predetermined manufacturing method with limitation of C to a range of 0.85 to 1.10% by mass, and Nb in a range of 0.005 to 0.020% by mass, which is suitable for knitting needle from the viewpoints of hardenability, hardness after quenching and low-temperature tempering, impact characteristics, etc., enables adjustment of an average particle diameter of carbide and a degree of spheroidization, and thus is effective to secure desired characteristics after quenching and tempering treatment. Further, it has been found that by adjusting Mn to less than 0.60% by mass and adjusting (Mn + Cr) to less than 1.0%, it is possible to suppress lowering of secondary workability before the quenching and tempering treatment, and the hardness after the quenching and tempering treatment, impact characteristics (toughness), and wear resistance satisfy the desired characteristics.

[0023] The present invention has been made on the basis of the above-described findings and further investigations. Embodiments of the present invention can be summarized as follows.

(1) A high carbon cold rolled steel sheet including a steel sheet composition consisting of, by mass%, C: 0.85% or more and 1.10% or less, Mn: less than 0.60%, Si: 0.10% or more and 0.35% or less, P: 0.030% or less, S: 0.030% or less, Cr: less than 0.60%, and Nb: 0.005% or more and 0.020% or less, a total of an Mn content and a Cr content (Mn + Cr) satisfying less than 1.0%, and the balance being Fe and inevitable impurities, in which a steel sheet thickness is less than 1.0 mm.

(2) The high carbon cold rolled steel sheet according to (1), including the steel sheet composition and further having a steel sheet structure in which an average particle diameter (d_{av}) and a spheroidization rate (N_{SC}/N_{TC}) $\times$ 100% of carbide dispersed in a steel sheet satisfy the following formulas (1) and (2), respectively:

$$0.2 \leq d_{av} \leq 0.7 \text{ } (\mu\text{m}) \quad \dots \quad (1),$$

$$(N_{SC}/N_{TC}) \times 100 \geq 90\% \quad \dots \quad (2)$$

(where d_{av} is an average value of an equivalent circle diameter of the carbide (average particle diameter μm), N_{TC} is a total number of the carbides per observed area of 100 μm^2 , and N_{SC} is a number of the carbides satisfying a condition where (major axis d_L)/(minor axis d_S) per observed area of 100 μm^2 is 1.4 or less).

(3) The high carbon cold rolled steel sheet according to (1) or (2), including, instead of the steel sheet composition, a steel sheet composition consisting of, by mass%, C: 0.85% or more and 1.10% or less, Mn: less than 0.60%, Si: 0.10% or more and 0.35% or less, P: 0.030% or less, S: 0.030% or less, Cr: less than 0.50%, and Nb: 0.005% or more and 0.020% or less, the total of the Mn content and the Cr content (Mn + Cr) satisfying less than 0.90%, and the balance being Fe and inevitable impurities.

(4) The high carbon cold rolled steel sheet according to any one of (1) to (3), in which the steel sheet composition is a steel sheet composition further containing, by mass, one or two selected from Mo: 0.001% or more and less than 0.05% and V: 0.001% or more and less than 0.05%.

(5) A method for manufacturing a high carbon cold rolled steel sheet, including repeatedly applying cold rolling and spheroidizing annealing to a hot rolled steel sheet having the steel sheet composition according to any one of (1) to (4), in which an average particle diameter (d_{av}) and a spheroidization rate (N_{SC}/N_{TC}) of carbide dispersed in the high carbon cold rolled steel sheet satisfy the following formulas (1) and (2), respectively:

$$0.2 \leq d_{av} \leq 0.7 \text{ } (\mu\text{m}) \quad \dots \quad (1),$$

$$(N_{SC}/N_{TC}) \times 100 \geq 90\% \quad \dots \quad (2)$$

(where d_{av} is an average value of an equivalent circle diameter of the carbide (average particle diameter μm), N_{TC} is a total number of the carbides per observed area of 100 μm^2 , and N_{SC} is a number of the carbides satisfying a

condition where (major axis d_L)/(minor axis d_S) per observed area of $100 \mu\text{m}^2$ is 1.4 or less), and a sheet thickness of the high carbon cold rolled steel sheet is less than 1.0 mm.

(6) The method for manufacturing a high carbon cold rolled steel sheet according to (5), in which the number of times of repeated cold rolling and spheroidizing annealing is 2 to 5 times.

(7) The method for manufacturing a high carbon cold rolled steel sheet according to (5) or (6), in which a reduction rate in the cold rolling is 25 to 65%, and a temperature of the spheroidizing annealing is 640 to 720°C.

(8) A method for manufacturing a high-carbon steel machine part including: applying secondary working to the high carbon cold rolled steel sheet according to any one of (1) to (4) as a material to form the steel sheet into a machine part having a predetermined shape; and applying a rapid cooling treatment after a short-time solution treatment and a tempering treatment to the machine part, the rapid cooling treatment after the short-time solution treatment is a treatment in which the machine part is held at a temperature in a range of 760 to 820°C for a time in a range of 3 to 15 minutes and rapidly cooled, and the tempering treatment is a treatment in which tempering is performed at a temperature in a range of 200 to 350°C to make the machine part have both excellent wear resistance and excellent toughness is produced.

(9) A high-carbon steel machine part being produced by the method for producing a high-carbon steel machine part according to (8).

Advantageous Effects of Invention

[0024] The high carbon cold rolled steel sheet of the present invention suppresses lowering of secondary workability such as a machinability, and the life of tools used for punching, swaging, bending, secondary working, etc. is comparable to that of a conventional high carbon cold rolled steel sheet. In addition, after a rapid cooling treatment after a short-time solution treatment and a low-temperature tempering treatment (quenching and tempering treatment), compared to conventional high-carbon steel sheets, it is possible to produce machine parts having a high balance of high hardness characteristics, excellent impact characteristics, and excellent wear resistance, which has a marked effect on the industry. Furthermore, the high carbon cold rolled steel sheet of the present invention is excellent in impact characteristics (toughness), wear resistance, and fatigue resistance characteristics after quenching and tempering treatment, and particularly has an effect that the steel sheet is suitable for a material for machine parts that requires excellent durability in a severe use environment, such as a knitting needle.

Brief Description of Drawings

[0025]

Fig. 1 is a schematic explanatory view showing an outline of an endmill working test (secondary workability evaluation test).

Fig. 2 is a schematic explanatory view showing an outline of a wear testing machine.

Fig. 3 is a schematic explanatory view showing an outline of (a) a shape of a wear test piece and (b) a wear condition of the wear test piece.

Fig. 4 is a schematic explanatory view showing an outline of a shape of a Charpy impact test piece used in the present invention.

Fig. 5 is a schematic explanatory view showing a condition of installation of a test piece on a Charpy impact tester used in the present invention.

Description of Embodiments

[0026] A high carbon cold rolled steel sheet of the present invention is a high carbon cold rolled steel sheet including a steel sheet composition consisting of, by mass%, C: 0.85% or more and 1.10% or less, Mn: less than 0.60%, Si: 0.10% or more and 0.35% or less, P: 0.030% or less, S: 0.030% or less, Cr: less than 0.60%, and Nb: 0.005% or more and 0.020% or less, a total of an Mn content and a Cr content (Mn + Cr) satisfying less than 1.0%, and the balance being Fe and inevitable impurities. This steel sheet has a sheet thickness of less than 1.0 mm. First, the reasons for limiting the steel sheet composition will be described. Hereinafter, the mass% relating to the composition is simply expressed as %.

C: 0.85% or more and 1.10% or less

[0027] C is an essential element for obtaining sufficient hardness (600 to 750 HV) with precision parts such as knitting needles after heat treatment (quenching and tempering treatment). In order to stably secure a hardness of 600 HV or more after heat treatment (quenching and tempering treatment), the content of C needs to be 0.85% or more. On the

other hand, when the amount of C increases, the amount of carbide increases, cold workability is lowered, and it becomes impossible to withstand various plastic working (cold working) such as punching, swaging, bending, and secondary working. The cold workability is improved by repeating cold rolling and spheroidizing annealing, and spheroidizing the carbide; however, if more than 1.10% C is contained, problems in manufacturing process become apparent, for example, when rolling load increases in a hot rolling process and a cold rolling process, or when a frequency of cracks at coil ends remarkably increases. Therefore, the amount of C is limited to 0.85% or more and 1.10% or less. The amount of C is preferably 0.95 to 1.05%.

Mn: Less than 0.60%

[0028] Mn is an element that effectively acts on deoxidation of steel, and can improve hardenability of steel and stably ensure a predetermined hardness. However, if the content is 0.60% or more, MnS inclusions increase, which adversely affects secondary workability before quenching and tempering treatment. When cleanliness, particularly dA, is 0.10% or more, probability of inclusions hitting a cutting blade increases, the cutting resistance is increased, and the secondary workability is significantly deteriorated. Thus, in the present invention, Mn is limited to less than 0.60% as a range where dA is less than 0.10%. The amount of Mn is preferably 0.50% or less. The cleanliness is measured according to JIS G 0555. Here, an attention is paid to dA especially for A-type inclusions.

Si: 0.10% or more and 0.35% or less

[0029] Si acts as a deoxidizer for molten steel and is an effective element for producing clean steel. Si is an element that contributes to tempering softening resistance of martensite. In order to obtain such an effect, the content of 0.10% or more is required. On the other hand, a large amount of Si exceeding 0.35% results in insufficient tempering of martensite during low-temperature tempering treatment, and impact characteristics are deteriorated. For these reasons, Si is limited to the range of 0.10% or more and 0.35% or less.

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

[0030] Both P and S are elements that are unavoidably present in steel and adversely affect impact characteristics. Although it is desirable to reduce P and S as much as possible, it is practically acceptable so long as the content of P is up to 0.030% and the content of S is up to 0.030%. For these reasons, P is limited to 0.030% or less, and S is limited to 0.030% or less. From the viewpoint of maintaining excellent impact characteristics, it is preferable to adjust P to 0.020% or less and S to 0.020% or less.

Cr: Less than 0.60%

[0031] Cr is an element that improves hardenability of steel and is solid-dissolved in carbide (cementite) to harden the carbide, thereby contributing to improvement of wear resistance. In order to acquire such an effect, it is desirable to contain Cr in the amount of 0.10% or more. Since Cr is solid-dissolved in the carbide (cementite) to delay re-dissolution of the carbide in a heating stage, residual carbides after quenching and tempering increase with an increase in Cr content. Here, the residual carbide refers to, among carbides which were not able to be completely solved into a base matrix during heating and holding during quenching treatment, the carbide remaining in the base matrix after rapid cooling for martensitic transformation. As residual carbides increase, wear resistance improves. However, if a large amount, 0.60% or more, of Cr is contained, in addition to an increase in residual carbide, the effect of delaying dissolution of the carbide during quenching, heating, and holding increases, thereby inhibiting hardenability and lowering toughness. For these reasons, Cr is limited to less than 0.60%. Cr is preferably 0.10% or more and less than 0.50%.

Nb: 0.005% or more and 0.020% or less

[0032] Conventionally, it is known that Nb is an element that enlarges an unrecrystallization temperature range of steel during hot rolling, mainly in low-carbon steel, at the same time, is precipitated as NbC, and contributes to refinement of austenite grains. Also in high carbon steel, Nb may be added in anticipation of a structure refining effect after the cold rolling process. In the present invention, Nb is contained in an amount of 0.005% or more and 0.020% or less mainly for the purpose of recovering toughness by low-temperature tempering after quenching. If the Nb content is small, NbC contributing to structure refinement is not formed, and Nb is in a dilute solid solution state. It is considered that diffusion of C in a ferrite phase and a martensite phase, which have BCC structures, is promoted by the fact that Nb is in the dilute solid solution state. That is, it is considered that diffusion of C dissolved in the ferrite phase from carbide into the austenite phase during heating in the quenching treatment and diffusion and precipitation of a supersaturated solid

solution C in the martensite phase during heating in the tempering treatment are promoted, and as a result, it is possible to achieve both improvement in hardenability by short-time heating and recovery of toughness by low-temperature tempering treatment. Such an effect becomes prominent when the Nb content is 0.005% or more; however, when the Nb content exceeds 0.020%, precipitation of NbC becomes prominent, and the dilute solid solution state of Nb cannot be secured, so that the effect of promoting the C diffusion due to the dilute solid solution state of Nb cannot be recognized. Thus, Nb was limited to 0.005% or more and 0.020% or less. Nb is preferably 0.015% or less.

(Mn + Cr): Less than 1.0%

[0033] In the present invention, in order to improve the toughness and wear resistance after quenching and tempering treatment while suppressing lowering of secondary workability before the quenching and tempering treatment, the total of the Mn content and the Cr content (Mn + Cr) is adjusted to less than 1.0%. According to the study by the present inventors, since both Mn and Cr are easily solid-dissolved in carbides, as the total of the Mn content and the Cr content (Mn + Cr) increases, an effect of delaying re-dissolution of the carbide in the heating stage during quenching is greater than in a case that Mn alone is used and Cr alone is used, residual carbides increase, and the wear resistance also increases. However, when (Mn + Cr) increases to 1.0% or more, the residual carbide becomes 6% or more in terms of area ratio, the effect of hardenability deterioration increases, and an impact value (toughness) after quenching and tempering also decreases. If (Mn + Cr) is less than 1%, the residual carbide is less than 6% in terms of area ratio, and it is possible to provide both excellent wear resistance and toughness. On the other hand, if (Mn + Cr) is too small, the residual carbides decrease, and desired wear resistance cannot be ensured. Thus, the residual carbide is preferably 3% or more in terms of area ratio. (Mn + Cr) for achieving the amount of the residual carbides of 3% or more in terms of area ratio is preferably 0.15% or more. On the other hand, in the secondary workability before quenching and tempering treatment, due to the increase in (Mn + Cr), especially the increase in Mn, MnS inclusions adversely affecting the secondary workability increase. Therefore, in order to improve both the wear resistance and the toughness while suppressing lowering of the secondary workability, (Mn + Cr) is limited to less than 1.0% in the present invention. (Mn + Cr) is preferably less than 0.90%.

[0034] Although the above-described components are basic components, in addition to the basic components, one or two selected from Mo: 0.001% or more and less than 0.05% and V: 0.001% or more and less than 0.05% may be contained as selected elements.

[0035] Mo and V as one or two selected from Mo: 0.001% or more and less than 0.05% and V: 0.001% or more and less than 0.05% are both elements contributing to improvement in the hardenability of steel and improvement in impact characteristics (toughness) after quenching and tempering treatment, and one or two selected as necessary can be contained in an amount greater than an unavoidably contained level (0.001%).

[0036] Although Mo is an element effective for improving the hardenability of steel, if the Mo content is 0.05% or more, the effect of delaying dissolution of carbides increases, so that the hardenability is further lowered and sufficient hardness is not obtained. In addition, the effect of Nb is lost, and the impact characteristics after low-temperature tempering are reduced. Thus, when Mo is contained, Mo is preferably limited to 0.001% or more which is the inevitably contained level or more, and less than 0.05%, Mo is preferably 0.01% or more and 0.03% or less.

[0037] Although V is an element that contributes to improvement in impact characteristics through refinement of a steel structure, if a large amount, 0.05% or more, of V is contained, the effect of delaying dissolution of carbides increases, so that the hardenability is further lowered and sufficient hardness is not obtained. In addition, the effect of Nb is lost, and the impact characteristics after low-temperature tempering treatment are reduced. For this reason, when V is contained, V is preferably limited to 0.001% or more which is the inevitably contained level or more, and less than 0.05%, Mo is preferably 0.01% or more and 0.03% or less.

[0038] The balance other than the above components contains Fe and inevitable impurities.

[0039] The high carbon cold rolled steel sheet of the present invention has the above-described composition and a structure in which a carbide having an average particle diameter (d_{av}) (μm) satisfying the following formula (1) :

$$0.2 \leq d_{av} \leq 0.7 (\mu\text{m}) \quad \dots \quad (1),$$

and

a spheroidization rate (N_{SC}/N_{TC}) satisfying the following formula (2):

$$(N_{SC}/N_{TC}) \times 100 \geq 90\% \quad \dots \quad (2),$$

is dispersed.

[0040] Here, the average particle diameter (d_{av}) in the formula (1) is an average value of diameters of individual circles (equivalent circle diameters) when assuming a circle having the same area as each carbide observed in a cross section of the steel sheet. When the average particle diameter (d_{av}) of the dispersed carbide is in a range satisfying the formula (1), the impact characteristics are excellent, and, in addition, there is an effect that desired quenching hardness can be easily secured even in a rapid cooling (quenching) treatment after a short-time solution treatment. If the average particle diameter (d_{av}) of the dispersed carbide is less than $0.2\ \mu\text{m}$, the carbide becomes finer, and the number of dispersed carbides increases, so that load of secondary working on a needle shape increases. On the other hand, when the average particle diameter (d_{av}) exceeds $0.7\ \mu\text{m}$, it is difficult to secure desired quenching hardness in the rapid cooling treatment after the short-time solution treatment.

[0041] In the present invention, the spheroidization rate is defined by (N_{SC}/N_{TC}) in the formula (2). Here, N_{TC} is a total number of carbides per observed area of $100\ \mu\text{m}^2$, and N_{SC} is a number of carbides regarded as spheroidized in the same observation field and is the number of carbides satisfying a condition of $d_L/d_S \leq 1.4$. Here, the major axis of the carbide is d_L and the minor axis is d_S .

[0042] It cannot be said that the carbide is completely formed into a spherical shape, and the carbide is often observed as an elliptical shape depending on the observed surface, so that a degree of spheroidization is specified by a ratio (d_L/d_S) of the major axis to the minor axis. In the present invention, carbides satisfying a condition of (d_L/d_S): 1.4 or less are defined as spheroidized carbides, and the number thereof is N_{SC} . From empirical knowledge, it is necessary that the spheroidization rate ($N_{SC}/N_{TC} \times 100$) is 90% or more in order to keep good secondary workability of the steel sheet.

[0043] The average particle diameter and spheroidization rate of the carbides described above were calculated by observing a secondary electron microscope image (magnification: 2000 times) using a scanning electron microscope and performing image analysis.

[0044] A test piece for carbide observation was sampled from a cold rolled steel sheet (sheet-thickness central portion), embedded in resin, polished, and etched with an etching solution, and the carbide was observed using a scanning electron microscope. The equivalent circle diameter, the ratio of the major axis d_L to the minor axis d_S , N_{TC} , and N_{SC} of the carbide were measured in the range of the observed area of $100\ \mu\text{m}^2$ near the sheet-thickness central portion. Such measurement was carried out for five fields of view, and each average value was calculated. For these measurements and calculations, commercially available image analysis software winroof was used.

[0045] The high carbon cold rolled steel sheet of the present invention has the above-described steel sheet composition and structure, and while secondary workability such as a machinability is held, the life of tools used for punching, swaging, bending, secondary working, etc. is comparable to that of a conventional high carbon cold rolled steel sheet. In addition, after a rapid cooling treatment after a short-time solution treatment and a low-temperature tempering treatment (quenching and tempering treatment), compared to conventional high-carbon steel sheets, it is possible to produce machine parts having a high balance of high hardness characteristics, excellent impact characteristics, and excellent wear resistance.

[0046] The expression "excellent in secondary workability" used herein refers to that, as shown in Fig. 1, when a cutting (end milling) test is performed, a force applied to a tool (end mill) is less than 40 N (tool rotational speed is low (1300 rpm)) or less than 35 N (tool rotational speed is high (2300 rpm)).

[0047] In the present invention, focusing on general end milling, as shown in Fig. 1, a steel sheet (work material) was subjected to cutting work (end milling) using an end mill. At that time, an X-direction component force, a Y-direction component force, and a Z-direction component force as cutting resistance forces applied to the tool (end mill: $\phi 6\text{mm}$ diameter) were measured by a cutting dynamometer (not shown) attached to the tool, and the resultant force was calculated and used as a secondary workability evaluation index. The conditions of the endmill working test were: cutting speed 25 m/min (low speed), 45 m/min (high speed); feed amount per blade 0.016 mm/tooth; cut amount 0.2mm; tool protrusion length 25mm; cutting distance 30 mm, and no cutting oil was used.

[0048] By adopting such an endmill working test, the secondary workability can be evaluated in a state closer to an actual use environment. If the cutting resistance force applied to the tool is less than 40 N (or less than 35 N), it means to provide excellent secondary workability equal to or better than the secondary workability of conventional high carbon cold rolled steel sheets.

[0049] The term "excellent wear resistance" used herein refers to a case where a wear test using a wear testing machine shown in Fig. 2 is performed and the obtained wear depth is less than $485\ \mu\text{m}$.

[0050] A wear testing machine 10 shown in Fig. 2 includes a yarn unwinding device 11 for unwinding yarn, a tension adjusting means 12 for applying a desired tension to unwound yarn 2, a wear test piece 1 having holes 1a to 1d for passing the tensioned yarn, and a yarn winding device 13 for winding the yarn and can reproduce wear of a knitting needle due to knitting yarn in a situation close to an actual machine. The wear testing machine 10 has a structure in which the tension is zero when the yarn breaks, and the machine automatically stops at that point.

[0051] The wear test piece 1 to be used is a wear test piece having the shape shown in Fig. 3(a), and the yarn 2 continuously unwound from a bobbin (yarn unwinding device) 11 is subjected to a proper tension by the tension adjusting means 12. Then, the yarn 2 passes through, for example, the hole 1a formed in the wear test piece 1 and is wound by the yarn winding device 13 while being in contact with the hole 1a to wear the hole 1a. Four holes (1a to 1d) were formed

per one test piece. The conditions for the wear test were: polyester full dull knitting yarn (standard 110T48); yarn feed speed 160 m/s; tension 10 ± 2 N/cm. The wear test was performed until the yarn with a length of 100,000 m was fed out from one hole, and the wear depth in the hole was measured. Such a wear test was performed on each of the four holes 1a to 1d formed in one wear test piece, the wear depth of each hole was measured, and the average value thereof

was taken as the wear depth (average) of the wear test piece.
[0052] As a result of the wear test under the above-described conditions, if the wear depth is less than 485 μm , it means to provide excellent wear resistance equal to or better than the wear resistance of conventional high carbon cold rolled steel sheets. By adopting such a wear test, the wear resistance can be evaluated in a state close to wear due to yarn of a hook portion of a knitting needle. It was found that the wear resistance was evaluated in the state close to the wear due to the yarn of the hook portion of the knitting needle, so that presence of residual carbides greatly affected the wear resistance. The wear resistance is proportional to the area ratio of the residual carbide. If the residual carbide is less than 3% in terms of area ratio, desired wear resistance cannot be ensured. The residual carbide is preferably 3% or more in terms of area ratio.

[0053] The term "excellent impact characteristics" used herein refers to a case where an impact test piece (a U-notch test piece with a notch width of 0.2 mm (notch depth 2.5 mm, notch radius 0.1 mm)) shown in Fig. 4 was used, and when a test was performed at room temperature and at a supporting bed distance of 40 mm as shown in Fig. 5 by a Charpy impact tester (Toyo Seiki Seisaku-sho, Ltd. model DG-GB) with a rated capacity of 1 J based on JIS K 7077, an impact value was 9 J/cm² or more.

[0054] By using such a Charpy impact tester, it is possible to perform a test under conditions close to JIS Z 2242, which is a Charpy impact test method for metal materials, even when a test piece having a sheet thickness of less than 1.0 mm is used. By using such an impact test piece, a stress concentration factor increases, a deflection during the impact test is minimized, and a stable impact value can be obtained. By adopting such an impact test method and an impact test piece, the impact characteristics can be evaluated in a state close to an actual use environment. Although the impact value tends to be higher when the amount of residual carbide is smaller, when the amount of residual carbide exceeds 6% in terms of area ratio, the impact value decreases significantly. Therefore, the present inventors have found that in order to ensure a desired impact value, the residual carbide is less than 6% in terms of area ratio.

[0055] As described above, by introducing a new wear test method for evaluating wear resistance and introducing an endmill working test method for evaluating secondary workability, it became possible to define a proper chemical component range based on evaluation in an environment close to the actual machine.

[0056] Next, a method for manufacturing the high carbon cold rolled steel sheet of the present invention will be described.

[0057] The high carbon cold rolled steel sheet of the present invention is manufactured by applying softening annealing to a hot rolled steel sheet as necessary, and repeatedly performing cold rolling and spheroidizing annealing.

[0058] The hot rolled steel sheet used in the present invention may be one obtained under normal manufactured conditions. For example, a steel piece (slab) having the above-described composition is heated to 1050 to 1250°C, hot rolled at a finishing temperature of 800 to 950°C, and formed into a coil at a coiling temperature of 600 to 750°C, whereby the hot rolled steel sheet can be produced. The sheet thickness of the hot rolled steel sheet may be appropriately set from the sheet thickness of a desired cold rolled steel sheet such that a suitable reduction rate in cold rolling is obtained.

[0059] The hot rolled steel sheet is repeatedly subjected to cold rolling and spheroidizing annealing multiple times to obtain a high carbon cold rolled steel sheet having a sheet thickness of less than 1.0 mm. The cold rolling and spheroidizing annealing are preferably repeated 2 to 5 times.

[0060] The reduction rate in cold rolling is preferably in a range of 25 to 65%. If a steel sheet (cold rolled steel sheet) with a cold rolling reduction rate of less than 25% is subjected to spheroidizing annealing, carbides become coarse. On the other hand, if the reduction rate in cold rolling exceeds 65%, load of cold rolling operation may be too large. Thus, the reduction rate in cold rolling is limited to the range of 25 to 65%. For a final cold rolling which does not give spheroidizing annealing after cold rolling, the lower limit of the reduction rate is not particularly limited.

[0061] The spheroidizing annealing is preferably performed at a temperature in a range of 640 to 720°C. If the spheroidizing annealing temperature is less than 640°C, spheroidization tends to be insufficient, whereas if the temperature is higher than 720°C, carbides tend to become coarse. Thus, the spheroidizing annealing is performed at a temperature in the range of 640 to 720°C. A holding time of the spheroidizing annealing is preferably selected as appropriate in a range of 9 to 30 hr.

[0062] The reason why cold rolling (25 to 65%) and spheroidizing annealing (640 to 720°C) are repeated multiple times is that control is performed such that the average particle diameter (d_{av}) of carbide and the spheroidization rate ($N_{SC}/N_{TC} \times 100$) satisfy the above formulae (1) and (2), respectively.

[0063] First, cracks are introduced into carbide by cold rolling, and the carbide having begun to break by spheroidizing annealing becomes spheroidized. However, with only one spheroidizing annealing, it is difficult to increase the spheroidization rate of the carbide to 90% or more, and a rod-like or plate-like carbide remains. In such a case, the hardenability is also adversely affected, and the cold workability of precision parts is deteriorated. Thus, in order to increase the carbide

spheroidization rate (N_{SC}/N_{TC}) $\times 100$ to 90% or more, it is optimal to alternately repeat cold rolling and spheroidizing annealing, and as a result, a distribution of fine carbide having a high spheroidization rate is obtained in the steel sheet. Particularly preferred are cold rolling from twice to five times and spheroidizing annealing from twice to five times. The same temperature range is preferable for softening annealing aiming at softening of a hot rolled steel sheet before cold rolling.

[0064] The above method is the method for manufacturing the high carbon cold rolled steel sheet of the present invention. In order to form this steel sheet into a machine part such as a knitting needle as a final object, it is preferable to form the steel sheet into a predetermined shape and then perform the following heat treatment.

[0065] A high carbon cold rolled steel sheet in which carbide spheroidized by 90% or more is distributed is processed into various machine parts, then subjected to a rapid cooling (quenching) treatment after solution treatment, and subsequently subjected to tempering treatment. In the solution treatment, the heating temperature is 760 to 820°C, and the holding time is a short time such as 3 to 15 min. It is preferable to use oil for quenching (rapid cooling). In the tempering treatment, the tempering temperature is preferably a low temperature, for example, 200 to 350°C. The tempering temperature is more preferably 250 to 300°C. As a result, various machine parts having a hardness of 600 to 750 HV can be obtained.

[0066] If the holding time of the solution treatment is longer than 15 min, the carbide is excessively dissolved, and austenite grains become coarse, so that the martensite phase after quenching becomes coarse and impact characteristics are deteriorated. On the other hand, if the holding time is shorter than 3 min, the carbide is not sufficiently dissolved, and it is difficult to obtain a desired high hardness after rapid cooling. Thus, the holding time of the solution treatment is preferably 3 min or more and 15 min or less. The holding time is more preferably 5 to 10 min.

[0067] On the other hand, if the tempering temperature is less than 200°C, toughness recovery of the martensite phase is insufficient. On the other hand, when the tempering temperature exceeds 350°C, the hardness is lower than 600 HV, and the impact value becomes high; however, durability and wear resistance are lowered, which becomes a problem. Thus, the tempering temperature is preferably in a range of 200 to 350°C. The tempering temperature is more preferably 250 to 300°C. A holding time of tempering treatment is preferably selected as appropriate in a range of 30 min to 3 hr.

[0068] The present invention is further described below with reference to Examples.

Examples

[0069] Molten steel having the chemical components shown in Table 1 was melted in a vacuum melting furnace and then cast into a mold to obtain small-size steel ingots (50 kgf). These small-size steel ingots were slabbed, formed into steel pieces, and then hot-rolled under conditions of a heating temperature of 1150°C and a rolling finishing temperature of 870°C to form a hot rolled steel sheet (sheet thickness: 4 mm). Subsequently, the obtained hot rolled steel sheet was subjected to cold rolling and spheroidizing annealing under the conditions shown in Table 2 to obtain a cold rolled steel sheet having a sheet thickness of 0.4 mm or more and less than 1.0 mm.

[0070] First, a test piece for structure observation was collected from the obtained cold rolled steel sheet, embedded in resin, polished and etched, and a structure was observed from a secondary electron microscope image (magnification: 2000 times) using a scanning electron microscope and imaged. The average particle diameter (d_{av}) and the spheroidization rate (N_{SC}/N_{TC}) of the carbide were calculated by image analysis. In a range of the observed area of 100 μm^2 near the sheet-thickness central portion, the equivalent circle diameter of each carbide and the ratio of the major axis d_L to the minor axis d_S of each carbide were determined, and the total number N_{TC} of carbides per observed area of 100 μm^2 and the total number N_{SC} of carbides satisfying the condition of d_L/d_S : 1.4 or less were measured. Such measurement was carried out for five fields of view, and their average values were calculated. For these measurements and calculations, commercially available image analysis software winroof was used. For the test piece for structure observation, cleanliness dA was measured for A-type inclusions in accordance with JIS G 0555. The measurement visual field was 60 visual fields.

[0071] In addition, a test piece was collected from the obtained cold rolled steel sheet, and under the conditions shown in Table 3, as shown in Fig. 1, a machinability test (endmill working test) was performed. After forces in the X direction, the Y direction, and the Z direction applied to a tool (end mill: 6 mm diameter) were measured, the resultant force was calculated and used as the cutting resistance force. Two types of rotational speeds of the tool were a low speed (1300 rpm) and a high speed (2300 rpm).

[0072] Next, the obtained cold rolled steel sheet was charged into a heating furnace and subjected to a short-time solution treatment under the conditions shown in Table 4, and then subjected to a rapid cooling (oil quenching) treatment. In addition, heat treatment that applies a low-temperature tempering treatment was performed. A test piece was collected from the heat-treated steel sheet and subjected to residual carbide investigation, hardness test, impact test, and wear test. The test method was as follows.

(1) Residual carbide investigation

[0073] A test piece for structure observation was collected from the heat-treated steel sheet, embedded in resin, polished and etched, and a structure was observed from a secondary electron microscope image (magnification: 2000 times) using a scanning electron microscope and imaged, and by image analysis, the area ratio (%) of residual carbide was calculated for residual carbide having an equivalent circle diameter of 0.1 μm or more. The measurement area was 100 μm^2 .

(2) Hardness test

[0074] A hardness test piece was cut out from the heat-treated steel sheet in a direction perpendicular to a rolling direction and embedded in resin, the cross section was polished, and the hardness was measured at the sheet-thickness central portion. The hardness was measured at five points for each piece in accordance with JIS Z 2244 using a Vickers hardness tester (test force: 49.0 N), and the average value thereof was taken as the hardness of the steel sheet.

(3) Impact test

[0075] The impact test piece (a U-notch test piece with a notch width of 0.2 mm (notch depth 2.5 mm, notch radius 0.1 mm)) shown in Fig. 4 was collected from the heat-treated steel sheet in parallel with the rolling direction, and a Charpy impact test was performed at room temperature and at a supporting bed distance of 40 mm as shown in Fig. 5 by a Charpy impact tester (Toyo Seiki Seisaku-sho, Ltd. model DG-GB) with a rated capacity of 1 J based on JIS K 7077, thus obtaining an impact value (J). Five test pieces were used, and an average of the obtained impact values was taken as the impact value of the steel sheet.

(4) Wear test

[0076] A wear test piece having the shape shown in Fig. 3 was collected from the heat-treated steel sheet and subjected to the wear test using the wear testing machine shown in Fig. 2. The conditions for the wear test were: polyester full dull knitting yarn (standard 110T48); yarn feed speed 160 m/s; tension 10 ± 2 N/cm. After the yarn was run through 100,000 m in one hole, the testing machine was stopped, and the wear depth formed in the hole (1a in this case) of the wear test piece 1 as shown in Fig. 3(b) was measured with an optical microscope. Such a wear test was performed on each hole (1a to 1d), the wear depth of each hole (four holes) was measured, and the average value thereof was obtained and taken as the wear depth of the wear test piece.

[0077] The obtained results are illustrated in Table 5.

[Table 1]

Steel No.	Chemical component (mass%)									Note
	C	Si	Mn	P	S	Cr	Mn + Cr	Nb	Other	
A	0.80	0.24	0.40	0.010	0.003	0.35	0.75	0.009	Mo: 0.010	Comparative Example
B	0.92	0.25	0.42	0.012	0.003	0.25	0.67	0.009	Mo: 0.012	Acceptable Example
C	0.97	0.24	0.43	0.010	0.001	0.25	0.68	<0.001	Mo: 0.012	Comparative Example
D	0.95	0.25	0.49	0.010	0.003	0.34	0.83	0.009	Mo: 0.013	Acceptable Example
E	0.98	0.25	0.68	0.015	0.003	0.39	1.07	0.001	Mo: 0.011	Comparative Example
F	1.01	0.24	0.71	0.010	0.002	0.41	1.12	0.010	Mo: 0.009	Comparative Example
G	1.00	0.24	0.40	0.010	0.003	0.49	0.89	0.010	Mo: 0.013, V: 0.010	Acceptable Example

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(continued)

Steel No.	Chemical component (mass%)									Note
	C	Si	Mn	P	S	Cr	Mn + Cr	Nb	Other	
H	1.01	0.23	0.35	0.013	0.003	0.54	0.89	0.010	Mo: 0.008, V: 0.005	Acceptable Example
I	0.98	0.25	<u>0.80</u>	0.010	0.001	0.45	<u>1.25</u>	0.010	Mo: 0.009, V: 0.008	Comparative Example
J	0.97	0.24	<u>0.85</u>	0.012	0.003	0.30	1.15	0.010	Mo: 0.015	Comparative Example
K	0.95	0.23	<u>0.90</u>	0.010	0.003	<u>0.60</u>	<u>1.50</u>	0.010	Mo: 0.007, V: 0.009	Comparative Example
L	<u>1.20</u>	0.23	<u>0.92</u>	0.012	0.002	0.40	<u>1.32</u>	0.010	Mo: 0.006, V: 0.009	Comparative Example
M	1.00	0.23	0.39	0.013	0.003	0.48	0.87	0.010	Mo: 0.013, V: 0.060	Comparative Example
N	0.99	0.23	0.43	0.011	0.001	0.38	0.81	0.009	<u>Mo: 0.100, V: 0.005</u>	Comparative Example
O	0.98	0.24	0.40	0.014	0.003	0.48	0.88	0.003	Mo: 0.007, V: 0.008	Comparative Example
P	0.95	0.23	0.39	0.010	0.004	0.46	0.85	<u>0.025</u>	MO: 0.009, V: 0.009	Comparative Example
Q	0.96	0.23	0.38	0.012	0.003	0.45	0.83	0.010	-	Acceptable Example
R	0.96	0.23	0.37	0.010	0.001	0.47	0.84	0.010	-	Acceptable Example
S	0.95	0.22	0.04	0.010	0.001	0.10	0.14	0.011	-	Acceptable Example
T	0.96	0.23	0.45	0.011	0.001	0.45	0.90	0.015	-	Acceptable Example
U	0.96	0.23	0.48	0.011	0.001	<u>0.58</u>	<u>1.06</u>	0.016	-	Comparative Example
V	0.95	0.24	0.11	0.011	0.002	<u>0.70</u>	0.81	0.015	-	Comparative Example

[Table 2]

Manufactural condition of cold rolled steel sheet (cold rolling (reduction rate), spheroidizing annealing (annealing temperature))	
Hot rolling (4 mm) → softening annealing (700°C) → cold rolling (25 to 65%) → spheroidizing annealing (690°C) → cold rolling (25 to 65%) → spheroidizing annealing (680°C) → cold rolling (25 to 65%) → spheroidizing annealing (660°C) → cold rolling (25 to 65%) → spheroidizing annealing (640°C) → cold rolling (3 to 50%)	

[Table 3]

Cutting speed (m/min)	25 (low speed), 45 (high speed)
Feed amount per blade (mm/tooth)	0.016

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(continued)

Cutting speed (m/min)	25 (low speed), 45 (high speed)
Cut amount (mm)	0.2
Cutting oil	Non-use
Tool protrusion length (mm)	25
Cutting distance (mm)	30

[Table 4]

Solution treatment		Quenching condition		Tempering treatment condition	
Heating temperature (°C)	Holding time (min)	Refrigerant	Temperature (°C)	Tempering temperature (°C)	Holding time (hr)
800	10	Quenching oil	80	250	1

[Table 5]

Steel sheet No.	Steel sheet No.	Steel sheet thickness (mm)	Characteristics before quenching and tempering treatment					Characteristics after quenching and tempering treatment					Note
			Cleanliness dA (%)	Average particle diameter (μm)	Spheroidization rate (%)	Secondary workability (force applied to tool) (N)		Residual carbide area ratio (%)	Hardness HV	Impact value (J/cm^2)	Wear depth (μm)	Evaluation	
1	A	0.40	0.020	0.6	93	Low speed	High speed	2.2	680	16	502	×	Comparative Example
2	B	0.41	0.025	0.6	95	33	30	3.5	696	14	481	○	Example
3	C	0.40	0.022	0.4	94	34	29	3.4	689	4	480	×	Comparative Example
4	D	0.39	0.032	0.5	95	37	29	4.1	687	12	480	○	Example
5	E	0.40	0.101	0.5	96	41	36	6.5	688	6	472	×	Comparative Example
6	F	0.39	0.102	0.6	97	42	37	6.8	691	6	470	×	Comparative Example
7	G	0.41	0.030	0.6	98	38	31	5.2	691	11	480	○	Example
8	H	0.40	0.023	0.6	95	35	30	5.5	691	11	475	○	Example
9	I	0.40	0.103	0.6	96	42	39	6.4	691	5	472	×	Comparative Example
10	J	0.39	0.111	0.5	97	45	37	6.5	691	6	470	×	Comparative Example
11	K	0.40	0.112	0.6	95	50	40	8.0	691	3	460	×	Comparative Example
12	L	0.42	0.120	0.5	96	60	50	6.9	691	3	468	×	Comparative Example
13	M	0.40	0.020	0.5	95	39	33	7.0	692	4	465	×	Comparative Example
14	N	0.41	0.023	0.5	94	38	32	6.8	680	3	470	×	Comparative Example

(continued)

Steel sheet No.	Steel No.	Steel sheet thickness (mm)	Characteristics before quenching and tempering treatment				Characteristics after quenching and tempering treatment						Note
			Cleanliness dA (%)	Average particle diameter (μm)	Spheroidization rate (%)	Secondary workability (force applied to tool) (N)		Residual carbide area ratio (%)	Hardness HV	Impact value (J/cm ²)	Wear depth (μm)	Evaluation	
						Low speed	High speed						
15	<u>Q</u>	0.40	0.025	0.6	95	35	28	5.0	690	4	480	×	Comparative Example
16	<u>P</u>	0.39	0.023	0.5	93	36	30	4.9	685	3	480	×	Comparative Example
17	Q	0.40	0.025	0.6	94	35	32	4.8	685	13	479	○	Example
18	R	0.39	0.026	0.5	92	36	29	5.2	685	11	477	○	Example
19	S	0.40	0.006	0.5	90	30	28	3.1	682	17	484	○	Example
20	T	0.41	0.030	0.6	92	38	33	4.8	689	10	477	○	Example
21	<u>U</u>	0.41	0.031	0.5	93	37	33	6.5	630	6	470	×	Comparative Example
22	<u>V</u>	0.41	0.015	0.6	92	31	28	7.5	691	5	465	×	Comparative Example

[0078] All of the examples of the present invention provide high carbon cold rolled steel sheets in which the force (cutting resistance) applied to the tool was less than 40 N at low speed working and less than 35 N at high speed working, and the secondary workability was equivalent to that of a conventional high carbon cold rolled steel sheet. After rapid cooling (oil quenching) treatment after short-time solution treatment and low-temperature tempering treatment, the high carbon cold rolled steel sheet had high hardness characteristics satisfying a hardness range of 600 to 750 HV, the impact value satisfied 9 J/cm² or more, and the impact characteristics were excellent. In addition, the high carbon cold rolled steel sheet had a wear depth of less than 485 μm, thus was excellent in wear resistance, and was evaluated as "○". On the other hand, in Comparative Examples out of the scope of the present invention, the force (cutting resistance) applied to the tool is 40 N or more at low speed working and 35 N or more at high speed working, and the secondary workability is poor. Alternatively, after the high carbon cold rolled steel sheets of Comparative Examples are subjected to rapid cooling (oil quenching) treatment after short-time solution treatment and further subjected to heat treatment that applies low-temperature tempering treatment, the impact value is less than 9 J/cm², and thus impact characteristics are deteriorated. Alternatively, the high carbon cold rolled steel sheet has a wear depth of 485 μm or more, thus has lowered wear resistance, and is evaluated as "×".

[0079] Specifically, in Comparative Example (steel sheet No. 1) in which the C content is lower than the range of the present invention, the cutting resistance is low, and the secondary workability is excellent. The impact value is 9 J/cm² or more, and thus the impact characteristics are excellent. However, the amount of residual carbide is small, the wear depth is 485 μm or more, and thus the wear resistance is lowered. In Comparative Example (steel No. 12) in which the C content is higher than the range of the present invention, the amount of residual carbide is large. The wear depth is less than 485 μm, and thus the wear resistance is excellent. However, the impact value is less than 9 J/cm², and thus the impact characteristics are deteriorated. (Mn + Cr) exceeds 1.0%, the cleanliness is poor, the force (cutting resistance) applied to the tool is high, and the secondary workability is lowered. In all Comparative Examples (steel sheets Nos. 9, 10, and 11) in which (Mn + Cr) is 1.0% or more and is higher than the range of the present invention, the amount of residual carbide is relatively large. The wear depth is less than 485 μm, and thus the wear resistance is excellent. However, the impact value is less than 9 J/cm², and thus the impact characteristics are deteriorated. In addition, the cleanliness is poor, the force (cutting resistance) applied to the tool is high, and the secondary workability is lowered. In Comparative example (steel sheet No. 13) in which the V content is higher than the range of the present invention and Comparative Example (steel sheet No. 14) in which the Mo content is higher than the range of the present invention, the amount of residual carbide is relatively large, and the wear resistance is excellent. However, the toughness is reduced. In both Comparative Examples (steel sheets Nos. 3 and 15) in which the Nb content is lower than the range of the present invention and Comparative Example (steel sheet No. 16) in which the Nb content is higher than the range of the present invention, the impact value is less than 9 J/cm², and thus the impact characteristics are deteriorated. The example of the present invention (steel sheet No. 19) in which (Mn + Cr) is as low as 0.14% shows a tendency for wear resistance to be somewhat lowered, and the example of the present invention (steel sheet No. 20) in which (Mn + Cr) is as high as 0.90% shows a tendency for secondary workability to be somewhat lowered. In Comparative Example (steel sheet No. 21) in which (Mn + Cr) exceeds 1.0% and Comparative Example (steel sheet No. 22) in which Cr is higher than the range of the present invention, the amount of residual carbide exceeds 6% in terms of area ratio, and thus the wear resistance is excellent. However, the impact value is less than 9 J/cm², and thus the impact characteristics are deteriorated.

Reference Signs List

[0080]

1	Wear test piece
1a, 1b, 1c, 1d	Hole
2	Yarn
10	Wear testing machine
11	Yarn unwinding device (bobbin)
12	Tension adjusting means
13	Yarn winding device

Claims

1. A high carbon cold rolled steel sheet comprising a steel sheet composition consisting of, by mass%,
C: 0.85% or more and 1.10% or less, Mn: less than 0.60%,

Si: 0.10% or more and 0.35% or less, P: 0.030% or less,
S: 0.030% or less, Cr: less than 0.60%, and
Nb: 0.005% or more and 0.020% or less,
a total of an Mn content and a Cr content (Mn + Cr) satisfying less than 1.0%, and a balance being Fe and inevitable
impurities, wherein a steel sheet thickness is less than 1.0 mm.

2. The high carbon cold rolled steel sheet according to claim 1, comprising the steel sheet composition and further having a steel sheet structure in which an average particle diameter (d_{av}) and a spheroidization rate (N_{SC}/N_{TC}) $\times$ 100% of carbide dispersed in a steel sheet satisfy the following formulas (1) and (2), respectively:

$$0.2 \leq d_{av} \leq 0.7 (\mu m) \quad \dots \quad (1),$$

$$(N_{SC}/N_{TC}) \times 100 \geq 90\% \quad \dots \quad (2)$$

wherein d_{av} is an average value of an equivalent circle diameter of the carbide (average particle diameter μm),
 N_{TC} is a total number of the carbides per observed area of 100 μm^2 , and
 N_{SC} is a number of the carbides satisfying a condition where (major axis d_L)/(minor axis d_S) per observed area of 100 μm^2 is 1.4 or less.

3. The high carbon cold rolled steel sheet according to claim 1 or 2, comprising,
instead of the steel sheet composition, a steel sheet composition consisting of, by mass%,
C: 0.85% or more and 1.10% or less, Mn: less than 0.60%,
Si: 0.10% or more and 0.35% or less, P: 0.030% or less,
S: 0.030% or less, Cr: less than 0.50%, and
Nb: 0.005% or more and 0.020% or less,
the total of the Mn content and the Cr content (Mn + Cr) satisfying less than 0.90%, and a balance being Fe and inevitable impurities.
4. The high carbon cold rolled steel sheet according to any one of claims 1 to 3, wherein the steel sheet composition is a steel sheet composition further containing, by mass%, one or two selected from Mo: 0.001% or more and less than 0.05% and V: 0.001% or more and less than 0.05%.
5. A method for manufacturing a high carbon cold rolled steel sheet, comprising repeatedly applying cold rolling and spheroidizing annealing to a hot rolled steel sheet having the steel sheet composition according to any one of claims 1 to 4, wherein an average particle diameter (d_{av}) and a spheroidization rate (N_{SC}/N_{TC}) of carbide dispersed in the high carbon cold rolled steel sheet satisfy the following formulas (1) and (2), respectively:

$$0.2 \leq d_{av} \leq 0.7 (\mu m) \quad \dots \quad (1),$$

$$(N_{SC}/N_{TC}) \times 100 \geq 90\% \quad \dots \quad (2)$$

wherein d_{av} is an average value of an equivalent circle diameter of the carbide (average particle diameter μm),
 N_{TC} is a total number of the carbides per observed area of 100 μm^2 , and
 N_{SC} is a number of the carbides satisfying a condition where (major axis d_L)/(minor axis d_S) per observed area of 100 μm^2 is 1.4 or less, and
a sheet thickness of the high carbon cold rolled steel sheet is less than 1.0 mm.

6. The method for manufacturing a high carbon cold rolled steel sheet according to claim 5, wherein a number of times of repeated cold rolling and spheroidizing annealing is 2 to 5 times.
7. The method for manufacturing a high carbon cold rolled steel sheet according to claim 5 or 6, wherein a reduction rate in the cold rolling is 25 to 65%, and a temperature of the spheroidizing annealing is 640 to 720°C.
8. A method for producing a high-carbon steel machine part comprising: applying secondary working to the high carbon

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cold rolled steel sheet according to any one of claims 1 to 4 as a material to form the steel sheet into a machine part having a predetermined shape; and applying a rapid cooling treatment after a short-time solution treatment and a tempering treatment to the machine part, wherein

the rapid cooling treatment after the short-time solution treatment is a treatment in which the machine part is held at a temperature in a range of 760 to 820°C for a time in a range of 3 to 15 minutes and rapidly cooled, and the tempering treatment is a treatment in which tempering is performed at a temperature in a range of 200 to 350°C to make the machine part have both excellent wear resistance and excellent toughness is produced.

9. A high-carbon steel machine part produced by the method for producing a high-carbon steel machine part according to claim 8.

Fig. 1

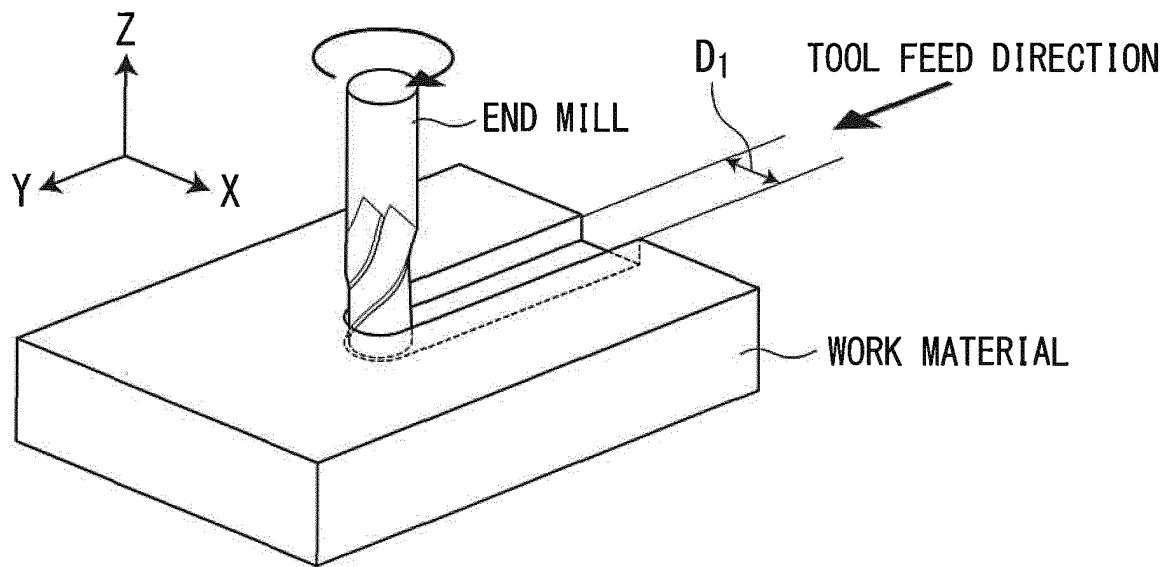


Fig. 2

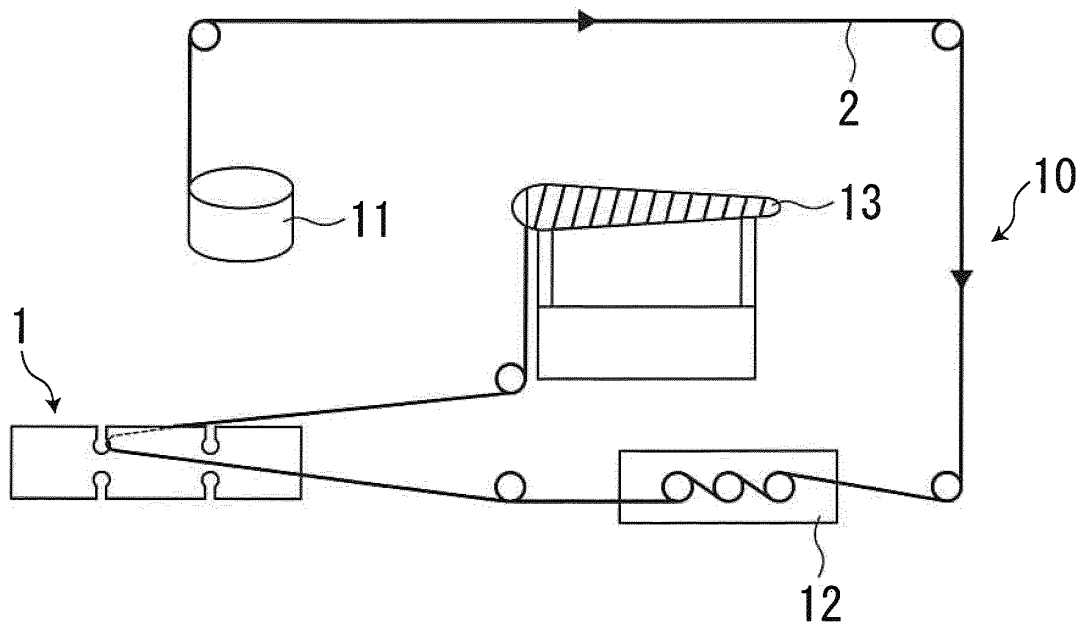
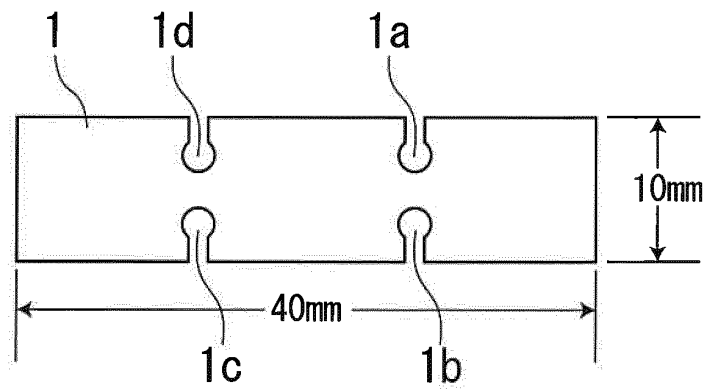


Fig. 3

(a)



(b)

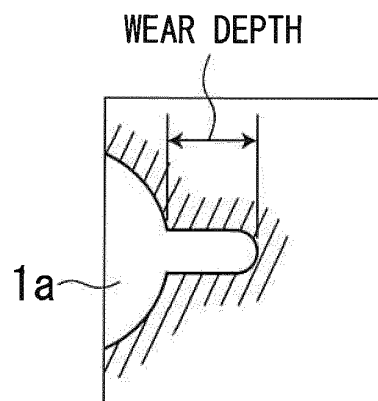


Fig. 4

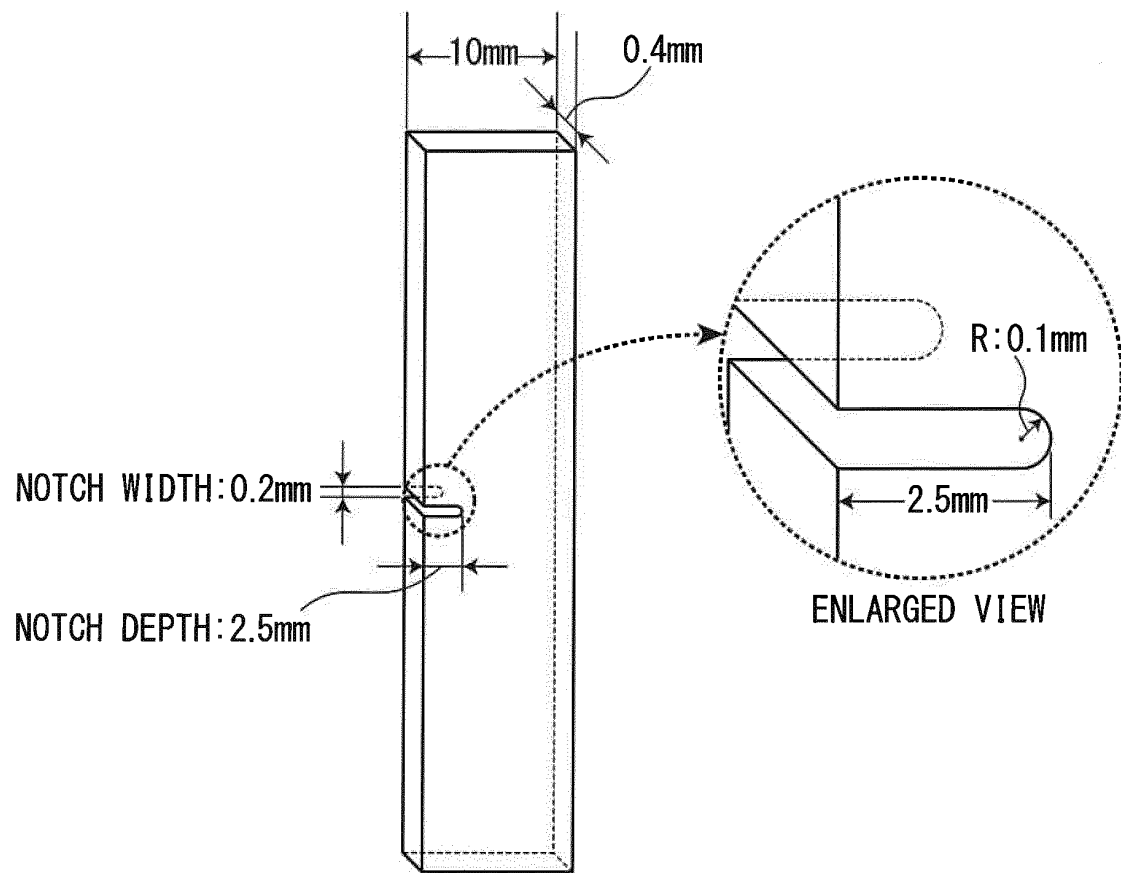
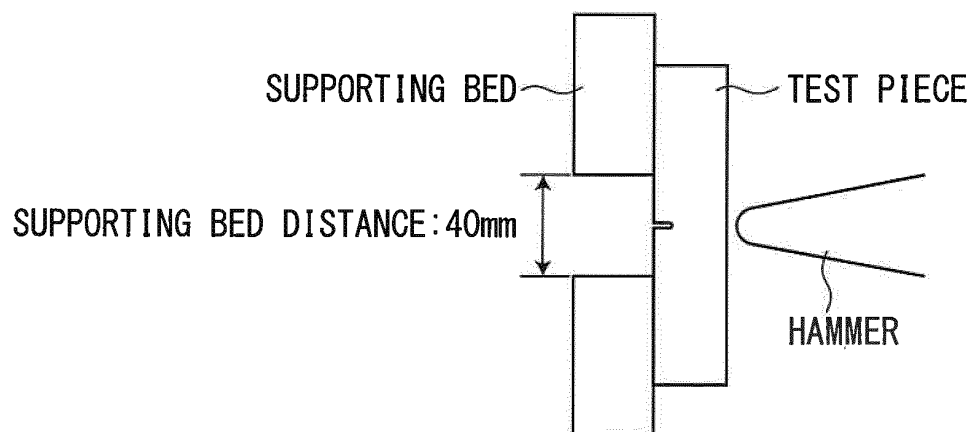


Fig. 5



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2019/043828

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C22C38/00(2006.01)i, C21D9/46(2006.01)i, C22C38/26(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)

Int.Cl. C22C38/00-38/60, C21D9/46-9/48

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996

Published unexamined utility model applications of Japan 1971-2019

Registered utility model specifications of Japan 1996-2019

Published registered utility model applications of Japan 1994-2019

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

JSTPlus/JMEDPlus/JST7580(JDreamIII)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 2017-36492 A (TOKUSHU KINZOKU EXCEL CO., LTD.) 16 February 2017, claims 1-5, examples, table 3, steel type no. 8 & EP 3216889 A1, claims 1-5, examples, table 3, steel type no. 8 & WO 2017/029922 A1 & KR 10-2017- 0075783 A & CN 107208224 A	1, 2, 4-9 1, 3, 4
Y A	CN 1772939 A (SHANGHAI LONGXING SPECIAL STEEL CO., LTD.) 17 May 2006, claims 1-3, 9, page 4, technical field (Family: none)	1, 3, 4 2, 5-9

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

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Date of the actual completion of the international search
17.12.2019Date of mailing of the international search report
07.01.2020Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2019/043828

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2013-540896 A (POSCO) 07 November 2013, table 1, paragraphs [0090]-[0100] & US 2013/018063 A1, table 1, paragraphs [0103], [0104] & WO 2012/036483 A2 & EP 2617840 A2 & KR 10-2012-0029347 A & CN 103210098 A	1-9
A	WO 2015/076384 A1 (NIPPON STEEL & SUMITOMO METAL CORPORATION) 28 May 2015, tables 1, 2 & US 2016/0289787 A1, tables 1, 2 & EP 3072987 A1 & CN 105745348 A & KR 10-2016-0072233 A	1-9
A	US 2011/0259483 A1 (POSCO) 27 October 2011, tables 1, 2 & WO 2010/074463 A2 & KR 10-2010-0074828 A & CN 102264933 A	1-9
A	CN 110306027 A (ZHEJIANG HAOHUAN NEW MAT CO., LTD.) 08 October 2019, table 1, paragraph [0003] (Family: none)	1-9

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2009024233 A [0014]
- JP 2006063384 A [0014]
- JP 2017036492 A [0014]
- JP 2017190494 A [0014]