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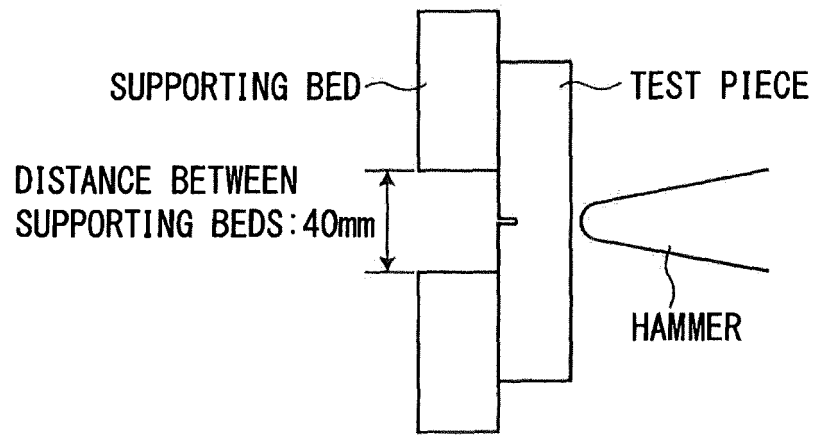
(54) **HIGH-CARBON COLD-ROLLED STEEL SHEET AND METHOD FOR MANUFACTURING SAME**

(57) Provided is a high-carbon cold-rolled steel sheet having a thickness of less than 1.0 mm and capable of having good impact and hardness characteristics after a short solution treatment, and thereafter quenching and low-temperature tempering. A high-carbon cold-rolled steel sheet having a steel sheet chemical composition containing, in terms of mass%, C: 0.85-1.10%, Mn: 0.50-1.0%, Si: 0.10-0.35%, P: 0.030% or less, S: 0.030% or less, and Cr: 0.35-0.45%, and furthermore containing Nb: 0.005-0.020 mass% with the remainder being Fe and unavoidable impurities, having a steel sheet structure in which the average particle diameter (d_{av}) of carbide dis-

persed in the steel sheet is 0.2-0.7 (μm) and the spheroidization ratio is 90% or higher, and having a thickness of less than 1.0 mm. Mechanical characteristics having an excellent impact characteristic in which the impact value is 5 J/cm² or higher and a sufficient hardness characteristic within the range of 600-750 HV can thereby be manifested by a short solution treatment of 3-15 minutes, and thereafter quenching and low-temperature tempering.

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Fig. 1



Description

Technical Field

[0001] The present invention relates to a high carbon cold-rolled steel sheet manufactured by quenching-tempering treatment for a material for various machine parts. In particular, the present invention relates to a high carbon cold-rolled steel sheet having a thickness of less than 1.0 mm, which has both of a sufficient hardness (600 to 750 HV) and an excellent impact property (toughness) after quenched by a short time solution treatment and then subjected to a low temperature tempering treatment, capable of being suitably applied to a knitting needle or the like which further has strict requirements in durability, wear resistance, etc. As used herein, the short time solution treatment refers to a treatment in a temperature range of from 760 to 820°C for a time of 3-15 minutes, and the low temperature tempering treatment refers to a treatment in a temperature range of from 200 to 350°C.

Background Art

[0002] Generally, carbon steels for machine structural use (SxxC) or carbon tool steels (SK) which is prescribed in JIS are used in various machine parts of various sizes. When used as a flat-rolled material, the quenching-tempering treatment is conducted after formed into a shape of component through punching or various plastic deformation. In this manner, a predetermined hardness and toughness (impact property) are imparted. Particularly, for example, a knitting needle for knitting a knit fabric knits a knit fabric with hauling a thread, in a repeated reciprocating motion in high speed. Therefore, a knitting needle requires a sufficient strength and a wear resistance in a butt portion of a main body of the needle which contacts with a rotary driving part, and requires an excellent impact property of the end portion, in addition to a sufficient wear resistance, in a hook portion which rubs against the thread.

[0003] A high carbon cold-rolled steel sheet to be used as a material for knitting needles is used in knitting needles for flat knitting machines when a thickness thereof is 1.0 mm or more, and for knitting needles for circular knitting machines or warp knitting machines when a thickness thereof is less than 1.0 mm. For a knitting needle for a circular knitting machine or a warp knitting machine, a material having a thickness of 0.4 to 0.7 mm is often used, since such knitting needle knits a thread of small diameter at high speed. A material for knitting needles is required to have, in addition to an excellent cold workability (hereinbelow also referred to as secondary workability), a sufficient hardness and a sufficient toughness in the needle end portion after formed into a shape of needle (the secondary working) and quenched and tempered.

[0004] Carbon steels for machine structural use (SxxC) or carbon tool steels (SK), so-called high-carbon steels, prescribed in JIS have minutely categorized usages according to amount of C. In a class where the C content is less than 0.8 mass%, namely, of steels having a hypo-eutectoid composition, fraction of ferrite phase is high, and therefore, cold workability is excellent, while it is difficult to obtain a sufficient quenched hardness. Therefore, a steel having a hypo-eutectoid composition is not suitable for a use in knitting needles or the like that requires a wear resistance in a hook portion or a durability in a main body of the needle. On the other hand, in a class of 0.8 mass% or more, namely, of high carbon steels having a C content of more than 1.1 mass% among steels having a hyper-eutectoid composition, hardenability is excellent, while cold workability is extremely inferior due to carbides (cementite) contained in large amount. Therefore, the class is not suitable for a use in knitting needles or the like, where a precise and minute process, such as a grooving process is conducted. Use of the high carbon steels having C content of more than 1.1 mass% is limited to components having a simple shape and requiring a high hardness, such as cutlery or cold forming dies.

[0005] Conventionally, broadly used in knitting needles are carbon tool steels or alloy tool steels containing C: 0.8 to 1.1 mass%, or materials having a steel composition containing a composition of these steels as a base, and a third element added thereto. In this process of manufacturing a knitting needle, the material is subjected to various and variety of plastic deformations, such as punching (shearing process), cutting, wiredrawing, mechanical joining, bending, or the like. Therefore, a material for manufacturing a knitting needle needs to have a hardness characteristic and an impact property (toughness) after a quenching-tempering treatment, which is required during a time of an actual use as a needle, in addition to have a sufficient workability (the secondary workability) during a material processing in a manufacturing process of a needle.

[0006] In a manufacture of knitting needles, a material is subjected to a quenching-tempering treatment, in order to secure a predetermined hardness characteristic. In this tempering treatment, generally, a low temperature tempering treatment in a temperature range of from 200 to 350°C is employed. However, when addition content of Mn or Cr which is effective for hardenability is increased, or another third element is added in a large amount, giving weight on hardness characteristic, tempering of a martensite phase is not sufficiently done, causing an insufficient enhancement of impact property (toughness), or scattered toughness values, in some cases.

[0007] On the other hand, for the purpose of enhancing an impact property of a knitting needle, it has been considered to be an effective measure to decrease P or S which is an impurity element in a chemical composition of a material, and

minimize grain-boundary segregation of P or formation of MnS inclusion, aiming for reduction of undesirable influence of those elements. However, there is a limit in aiming an enhancement of impact property of a knitting needle by decreasing P or S, from viewpoints of steel production technology and cost economy.

[0008] As a means for enhancing impact property, it has conventionally known that refinement of microstructure is effective. For example, Patent Literatures 1 and 2 disclose technologies of refining a microstructure by adding a carbo-nitride forming element such as Ti, Nb, V, and using a fine carbo-nitride of those elements. However, these elements have generally been added as measures for enhancing toughness of a steel of a hypo-eutectoid composition containing 0.8 mass% or less of carbon.

[0009] In particular, influence (especially, an interaction) of each of the third elements in an impact property of a martensite phase under a condition of a low temperature tempering of 200 to 350 °C has not sufficiently been clarified, and in many cases, compositions have been designed under a presumption that effects of each of the elements are equivalent.

[0010] For example, the technique described in Patent Literature 1 targets a hypoeutectoid steel containing C: 0.5 to 0.7 mass%, adds a carbo-nitride forming element such as V, Ti, Nb thereto, in order to refining prior austenite grains, to thereby enhance toughness (impact property).

[0011] The technique described in Patent Literature 2 targets steels having a wide range of carbon content, from a hypoeutectoid steel to a hypereutectoid steel containing C: 0.60 to 1.30 mass%; adds one or two or more kinds of Ni: 1.8 mass% or less, Cr: 2.0 mass% or less, V: 0.5 mass% or less, Mo: 0.5 mass% or less, Nb: 0.3 mass% or less, Ti: 0.3 mass% or less, B: 0.01 mass% or less, and Ca: 0.01 mass% or less thereto, as needed; and controls volume fraction (Vf) of undissolved carbides to be in a range where $(15.3 \times \text{C mass\%} - \text{Vf})$ makes more than 8.5 and less than 10.0, to thereby enhance impact property.

Citation List

Patent Literatures

[0012]

Patent Literature 1: JP 2009-24233 A

Patent Literature 2: JP 2006-63384 A

Summary of Invention

Technical Problem

[0013] However, the technique described in Patent Literature 1 is limited to hypoeutectoid steels, and is a technique of adding a carbo-nitride forming element such as V, Ti, Nb, etc. , expecting fine carbo-nitride thereof to refine prior austenite grains. The technique described in Patent Literature 1 also is a technique in which formability of ferrite matrix is improved, since carbon level is that of a hypo-eutectoid composition. Therefore, it is difficult to apply this technique to machine parts which require a high hardness, such as knitting needles.

[0014] In the technique described in Patent Literature 2, Mo, V, Ti, Nb, B, or the like are added to a hypoeutectoid steel having a carbon content in a range of from 0.67 to 0.81 mass%. The addition of Mo, V, Ti, Nb, B, or the like clearly is an addition with the intention of improving a characteristic of a hypoeutectoid steel. Patent Literature 2 does not include any disclosure regarding action of each of the third elements in steels having a carbon content exceeding 0.81 mass%, and optimization thereof.

[0015] Moreover, the technique described in Patent Literature 2 only defines an upper limit value of addition amount of the third elements where an impact value is not influenced adversely by the third elements, and does not define lower limit value thereof. From these facts, it can be said that Patent Literature 2 does not include disclosure of a technique of adding a third element in an intended range, with positively expecting an effect of the added element to enhance impact property.

[0016] Moreover, with respect to a high carbon cold-rolled steel sheet, Patent Literature 1 and Patent Literature 2 do not include disclosure of a technique which advantageously improves a desired impact property and a predetermined hardness by a quenching after a short solution treatment soaking time such as 3 to 15 minutes, and a low temperature tempering of 200 to 350°C; and do not include disclosure of a technique which evaluated an impact property of a steel plate having a thickness of less than 1.0 mm.

[0017] Therefore, the purpose of the present invention is to provide a high carbon cold-rolled steel sheet (hereinafter also simply referred to as "cold-rolled steel sheet"), having a thickness of less than 1.0 mm, capable of exhibiting a mechanical characteristic with an impact value of 5 J/cm² or more, and a hardness in a range of from 600 to 750 HV,

after subjected to a short time solution treatment and subsequent quenching and low temperature tempering treatment.

Solution to Problem

[0018] The present inventors have extensively researched a proper addition ranges of chemical components of a high carbon cold-rolled steel sheet, and particle diameter or presence form of a carbide in a steel, in order to solve the problem described above.

[0019] The present invention limits a carbon content to C: 0.85 mass% or more and 1.10 mass% or less which is preferred to a knitting needle, from viewpoints of workability, hardenability, and, hardness and toughness after a low temperature tempering, etc.; and a core of the present technique is an obtained knowledge that, in order for the objective characteristic to be exhibited, it is effective to add Nb as the third element in a predetermined range within the range of carbon content, and to control an average particle diameter and a degree of spheroidizing of a carbide.

[0020] In particular, the present inventors have developed a new test method (new impact test method) for toughness evaluation, targeting steel sheets having a thickness of less than 1.0 mm which has conventionally been difficult to be evaluated for toughness. The new test method (new impact test method) is shown in Fig. 1 and Fig. 2.

[0021] By using this new impact test method, a high carbon cold-rolled steel sheets having thicknesses of less than 1.0 mm which were added with various third elements were checked for impact values after the quenching and low temperature tempering. As a result, obtained was a novel knowledge that only an addition of Nb in a predetermined amount satisfied the objective characteristics described above. The present invention has been achieved on the basis of such knowledge.

[0022] That is, the present inventors have earnestly researched to solve the above problem, and have found that it is possible to obtain a high carbon cold-rolled steel sheet having both of an excellent hardenability and an excellent toughness, by essentially adding 0.005 to 0.020 mass% Nb to a high-carbon steel containing fundamental components prescribed to be in a range of C: 0.85 to 1.10 mass%, Mn: 0.50 to 1.0 mass%, Si: 0.10 to 0.35 mass%, P: 0.030 mass% or less, S: 0.030 mass% or less, and Cr: 0.35 to 0.45 mass%; and controlling a spheroidizing and an average particle diameter of a carbide to be in predetermined ranges; and have also found that it is possible to shorten a time for quenching treatment, or to lower a tempering temperature. Furthermore, it has become possible to prescribe proper chemical components, a spheroidization rate and an average particle diameter of a carbide, by employing the test method for properly evaluating an impact property of a thin plate.

[0023] In the first place, results of experiments conducted by the inventors will be described.

[0024] A cold-rolled steel sheet (less than 1 mm thickness) was produced in such a manner that a hot-rolled steel plate (4 mm thickness) having a composition containing 1.01% of C-0.26% of Si-0.73% of Mn-0.42% of Cr-0.02% of Mo, by mass%, which is further added with Nb, with changing the amount thereof to 0%, 0.010%, 0.020%, 0.055%, and containing Fe and inevitable impurities as the remainder is repeatedly subjected to a cold rolling (rolling reduction rate: 25 to 65%, last: 3 to 50%), a softening annealing, and a spheroidizing annealing (640 to 700°C) each 5 times. The obtained cold-rolled steel sheet was subjected to a solution treatment in which soaking time was changed within a range of from 0 to 16 minutes, at two levels of heating temperature of 780°C and 800°C, and after that, the sheet was oil-quenched, and then measured for Vickers hardness (HV). The obtained results are shown in Fig. 3 (heating temperature: 800°C) and Fig. 4 (heating temperature: 780°C), in terms of a relationship between a soaking time (minute) of the solution treatment and a quenched hardness (HV).

[0025] It is understood from Fig. 3 and Fig. 4 that a cold-rolled steel sheet having Nb content of 0.010 mass% can secure a quenched hardness exceeding 700 HV, with the shortest soaking time. When Nb content increases exceeding 0.010 mass%, the increase of hardness in a short soaking time slows down. A soaking time in which a quenched hardness reached 700 HV, when the heating temperature of the solution treatment was 780°C was obtained from the results shown in Fig. 4, and is shown in Fig. 5 in terms of a relationship with Nb content.

[0026] Fig. 5 shows that when Nb content is 0.020 mass% or more, the soaking time of the solution treatment in which a quenched hardness reaches 700 HV is substantially constant. When Nb content is in a range of from 0.005 to 0.015 mass%, a soaking time of the solution treatment for securing a desired quenched hardness (700 HV) becomes the shortest, and at the same time, it is possible to secure a stable hardenability. It is further possible, with the Nb content in this range, to shorten a soaking time of a solution treatment. From the above facts, it has been found that making Nb content to be in the range of from 0.005 to 0.015 mass% is effective as a measure capable of preventing an uneven expansion by quenching and a warp by quenching which have been problems in needle processing makers.

[0027] Meanwhile, the cold-rolled steel sheets having various Nb content were subjected to a solution treatment with a heating temperature: 800°C and soaking time: 10 minutes, and were oil-quenched, and further subjected to a tempering treatment. In the tempering treatment, tempering temperatures were varied temperatures of 150°C, 200°C, 250°C, 300°C and 350°C, and holding time was set to one hour. After the tempering treatment, impact property was checked. Incidentally, the impact property was conducted by using the new test method as shown in Fig. 1 and Fig. 2. The obtained results are shown in Fig. 6. The impact value was the highest in the case where Nb content was 0.010 mass%, when the

tempering temperature was 200°C or more.

[0028] Tempering temperature at which an impact value: 5 J/cm² can be obtained was obtained from Fig. 6, and shown in Fig. 7 in terms of a relationship with Nb content. Fig. 7 shows that the tempering temperature at which the impact value: 5 J/cm² can be obtained is the lowest in a case of a steel plate having an Nb content: 0.010 mass%. When the Nb content increases exceeding 0.020 mass%, the tempering temperature at which the impact value : 5 J/cm² can be obtained comes to the high temperature side. When the tempering temperature becomes high temperature, hardness lowers and durability as a needle lowers. It was also found that when Nb content was less than 0.005 mass%, it was necessary to make a tempering temperature to be a high temperature, in order to secure a desired impact value.

[0029] Fig. 5 and Fig. 7 show that a lower limit of the Nb content is 0.005 mass% and a higher limit of the Nb content is 0.020 mass%, in order to obtain both of a high hardness and an excellent impact property after a tempering. In addition, it is preferred that the upper limit of Nb content be set to 0.015 mass %, in order to make the soaking time of the solution treatment to be a short time.

[0030] The present invention has been accomplished on the basis of such knowledge, and by adding further investigations. That is, the gist of the present invention is as follows.

[1] A high carbon cold-rolled steel sheet, wherein

a chemical composition of the steel sheet contains C: 0.85 to 1.10 mass%, Mn: 0.50 to 1.0 mass%, Si: 0.10 to 0.35 mass%, P: 0.030 mass% or less, S: 0.030 mass% or less, Cr: 0.35 to 0.45 mass%, and Nb: 0.005 to 0.020 mass%, with Fe and an inevitable impurity as the remainder, with an average particle diameter (d_{av}) and a spheroidization rate (N_{SC}/N_{TC}) $\times 100\%$ of a carbide dispersed in the steel sheet respectively satisfying an equation (1) and an equation (2) below, and a thickness of the steel sheet being less than 1.0 mm;

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

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

wherein the average particle diameter (d_{av}) of the equation (1) is an average value of diameters of each circle, when a circle having an area equivalent to that of each carbide observed on a cross section of the steel sheet is supposed (circle equivalent diameter), and

N_{TC} and N_{SC} in the equation (2) respectively represent N_{TC} : total number of carbide per an observed area of 100 μm^2 , and N_{SC} : number of carbide which satisfies a condition that d_L/d_S is 1.4 or less, with d_L being a major axis and d_S being a minor axis of a carbide.

[2] The high carbon cold-rolled steel sheet according to [1], wherein the chemical composition further contains one or two kinds selected from Mo and V, the content of each being 0.001 mass% or more and less than 0.05 mass%.

[3] A method of manufacturing a high carbon cold-rolled steel sheet by repeatedly subjecting a hot-rolled steel plate containing the chemical composition as described in [1] or [2] to a cold rolling and a spheroidizing annealing, wherein an average particle diameter (d_{av}) and a spheroidization rate (N_{SC}/N_{TC}) of a carbide dispersed in the high carbon cold-rolled steel sheet respectively satisfying the equation (1) and equation (2) below; and a thickness of the high carbon cold-rolled steel sheet is less than 1.0 mm;

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

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

wherein the average particle diameter (d_{av}) of the equation (1) is an average value of diameters of each circle, when a circle having an area equivalent to that of each carbide observed on a cross section of the steel sheet is supposed (circle equivalent diameter), and

N_{TC} and N_{SC} in the equation (2) respectively represent N_{TC} : total number of carbide per an observed area of 100 μm^2 , and N_{SC} : number of carbide which satisfies a condition that d_L/d_S is 1.4 or less, with d_L representing a major axis and d_S representing a minor axis of the carbide.

[4] The method of manufacturing a high carbon cold-rolled steel sheet according to [3], wherein number of repeatedly subjecting the hot-rolled steel plate to a cold rolling and a spheroidizing annealing is two to five.

[5] The method of manufacturing a high carbon cold-rolled steel sheet according to [3] or [4], wherein a rolling reduction rate of the cold rolling is 25 to 65%, and a temperature of the spheroidizing annealing is 640 to 720°C.

Effects of Invention

[0031] The high carbon cold-rolled steel sheet of the present invention is a thin high carbon cold-rolled steel sheet having a thickness of less than 1.0 mm, particularly thickness of from 0.4 to 0.7 mm, and is a steel sheet in which an average particle diameter of a carbide is controlled to be a size of from 0.2 to 0.7 μm , and at the same time, a spheroidization rate is controlled to be 90% or more. By subjecting this steel sheet to a heat treatments of quenching and tempering, it is possible to obtain a good impact property (impact value: 5 J/cm² or more) and good hardness characteristic (600 to 750 HV) by a heat treatments of quenching and low temperature tempering, even by a solution treatment having a short soaking time such as 3 to 15 minutes.

[0032] Moreover, the high carbon cold-rolled steel sheet of the present invention exhibits a definite advantage to conventional high carbon cold-rolled steel sheets, in the point of a balance of hardness and impact property (toughness), under a condition that the steel sheet is subjected to a short time solution treatment, and subsequent quenching so as to be converted into a martensite phase containing an inevitable retained γ phase, and then subjected to a so-called low temperature tempering of from 200 to 350°C. In other words, by use of the high carbon cold-rolled steel sheet according to the present invention, it is possible to obtain machine-parts made by high carbon steel which are excellent in toughness after a quenching-tempering, with securing the excellent hardenability. In particular, the cold-rolled steel sheet disclosed in the present invention is preferred in a use which requires not only a balance of hardness and toughness, but also a wear resistance or a fatigue resistance, such as a use in knitting needles which requires an excellent durability under a severe use condition.

Brief Description of Drawings

[0033]

Fig. 1 is an explanatory view showing an example of a testing machine for an impact test used in the evaluation of the present invention.

Fig. 2 is an explanatory view showing a shape of a test piece for an impact test used in the evaluation of the present invention.

Fig. 3 is a graph showing a relationship between a quenched hardness and a soaking time of the solution treatment (heating temperature: 800°C).

Fig. 4 is a graph showing a relationship between a quenched hardness and a soaking time of the solution treatment (heating temperature: 780°C).

Fig. 5 is a graph showing a relationship between a soaking time of the solution treatment capable of obtaining a quenched hardness of 700 HV and an Nb content.

Fig. 6 is a graph showing a relationship between an impact value and a tempering temperature.

Fig. 7 is a graph showing a relationship between a tempering temperature capable of obtaining an impact value: 5 J/cm² and an Nb content.

Description of Embodiments

[0034] Hereinbelow, an embodiment of the present invention will be described.

[0035] First of all, the steel sheet according to the present invention is obtained as a high carbon cold-rolled steel sheet having a thickness of less than 1.0 mm, in such a manner that a hot-rolled steel plate is subjected to a softening annealing as needed, and repeatedly subjected to a cold rolling and a spheroidizing annealing alternately. After that, this high carbon cold-rolled steel sheet is subjected to a predetermined secondary working and solution treatment, and then subjected to a quenching and a tempering treatment, so as to be used in a member (machine part), such as a knitting needle.

[0036] In the first place, described hereinbelow is a reason why the chemical components of the steel sheet of the present invention were specified to be C: 0.85 to 1.10 mass%, Mn: 0.50 to 1.0 mass%, Si: 0.10 to 0.35 mass%, P: 0.030 mass% or less, S: 0.030 mass% or less, Cr: 0.35 to 0.45 mass%, Nb: 0.005 to 0.020 mass%.

C: 0.85 to 1.10 mass%

[0037] C is an essential element to obtain a sufficient hardness after a heat treatment of the high carbon cold-rolled steel sheet. The lower limit value thereof was determined so as to secure a hardness of 600 to 750 HV in a precision part such as a knitting needle, and the upper limit value was determined so as to be capable of controlling amount of carbides to be in a level where various and variety of cold works were not inhibited. In other words, the lower limit value was specified to be 0.85 mass%, in order to stably secure a hardness of 600 HV in a short time quenching-tempering treatment. The upper limit value was specified to be 1.10 mass% as an upper limit for being capable of resisting to wide variety of plastic deformation, such as punching property, swaging property, bending property, cutting property, or the like. A cold workability is improved when a spheroidizing treatment of carbides is conducted by repeating a cold rolling and a spheroidizing annealing. However, when C exceeds 1.10 mass%, problems in the manufacturing process become revealed, such that a rolling load becomes high in a hot rolling process or a cold rolling process, or frequency of occurrence of crack in a coil end portion becomes significantly high. Therefore, C was defined to be in a range of from 0.85 to 1.10 mass%. Preferably, the range is from 0.95 to 1.05 mass%.

Mn: 0.50 to 1.0 mass%

[0038] Mn is an element which is effective in deoxidization of a steel, and at the same time, an element capable of stably obtaining a predetermined hardness by enhancing hardenability of a steel. When a high carbon steel sheet to be applied to a severe use is targeted, the effect of the present invention becomes notable by 0.50 mass% or more of Mn. Thus, the lower limit value was specified to be 0.50 mass%. On the other hand, when Mn exceeds 1.0 mass%, MnS precipitates in a large amount and becomes coarse during the hot rolling, causing a frequent occurrence of a crack during parts processing. Therefore, the upper limit value was specified to be 1.0 mass%. In view of the above, Mn was defined to be in a range of from 0.50 to 1.0 mass%. Preferably, the range is from 0.50 to 0.80 mass%.

Si: 0.10 to 0.35 mass%

[0039] Si is a deoxidizing element for steels, and therefore is an element effective in smelting a clean steel. Si also is an element providing a temper-softening resistance of a martensite. In view of the above, the lower limit value was specified to be 0.10 mass%. The upper limit value thereof was specified to be 0.35 mass%, since when added in a large amount, tempering of a martensite becomes insufficient in a low temperature tempering, causing a deteriorated impact property. Therefore, Si was defined to be in a range of from 0.10 to 0.35 mass%.

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

[0040] P and S inevitably present in a steel as impurity elements, both adversely affecting an impact property (toughness), and therefore, preferably are lowered as much as possible. Containing of P up to 0.030 mass% or S up to 0.030 mass% makes no problem in an actual use. From such fact, content of P was specified to be 0.030 mass% or less, and content of S was specified to be 0.030 mass% or less. Incidentally, in order to maintain an excellent impact property, it is preferred that the content of P is set to 0.020 mass% or less, and the content of S is set to 0.010 mass% or less.

Cr: 0.35 to 0.45 mass%

[0041] Cr is an element which enhances a hardenability of a steel. However, Cr solid-solutes into a carbide (cementite) to cause a delay in redissolution of a carbide in the heating step, and thus, Cr inhibits a hardenability on the contrary, when added in a large amount. Thus, the upper limit value of Cr was specified to be 0.45 mass%. A lower limit value of Cr was specified to be 0.35 mass%, considering a balance of hardness and impact property after a quenching-tempering. In view of the above, Cr was defined to be in a range of from 0.35 to 0.45 mass%.

Nb: 0.005 to 0.020 mass%

[0042] Nb has conventionally been known as an element that enlarges an unrecrystallization temperature region of a steel during a hot-rolling, and at the same time, known as an element that precipitates as NbC and contribute to a refinement of austenite grains. Therefore, Nb is sometimes also added to a high carbon steel, expecting the refining effect to a microstructure after a cold rolling process. In the present invention, Nb is added in an amount of 0.005 to 0.020 mass%, for the main purpose of recovering toughness by a low temperature tempering after a quenching. When Nb is added in an extremely small amount, Nb is in a dilute solid solution state, without forming enough NbC to contribute to the refinement of a microstructure. Due to the dilute solid solution state of Nb, diffusion of C in a ferrite phase and

martensite phase having BCC structure is considered to be encouraged. That is, C which has been dissolved from a spherical carbide to a ferrite phase at the time of heating in a quenching treatment is encouraged to be diffused into an austenite phase; and a supersaturated solid solution C in a martensite phase is encouraged to be diffused and to be precipitated at the time of heating in a tempering treatment. It is considered at this moment that, as a result, it is possible to achieve both of an enhancement of hardenability by a short time heating, and a recovery of toughness by a low temperature tempering treatment. When Nb is added exceeding 0.020 mass%, precipitation of NbC become noticeable, which makes it impossible to secure the dilute solid solution state of Nb, and accordingly, the effect of encouraging diffusion of C, due to the dilute solid solution state of Nb, become not observed. Therefore, the upper limit of the Nb addition amount was specified to be 0.020 mass%. Preferably, the upper limit is 0.015 mass% or less. On the other hand, when the Nb addition amount is less than 0.005 mass%, it becomes impossible to expect the effect described above. Therefore, the lower limit of the Nb addition amount was specified to be 0.005 mass%. In view of the above, Nb was specified to be in a range of from 0.005 to 0.020 mass%.

[0043] In the present invention, although the components described above are the basic components, it is possible to further contain one kind or two kinds selected from Mo and V as needed, as optional selectable elements.

[0044] Mo and V can inevitably be contained in an amount of Mo: less than 0.001 mass%, and V: less than 0.001 mass%. In the present invention, Mo and V may be added in an amount more than the level contained inevitably, in order to enhance the hardenability or the impact property after a tempering. However, when Mo or V is added more than a predetermined amount, the effect of addition of Nb is lost. Therefore, it is preferred that when Mo or V is added, content thereof be controlled to be in the following range, so that the effect of addition of Nb is exerted at maximum.

Mo: 0.001 mass% or more and less than 0.05 mass%

[0045] Mo is an element which is effective in enhancing a hardenability. However, when an addition amount is excessive, an impact property can be deteriorated in some cases of low temperature tempering of 200 to 350°C. Therefore, when Mo is added, the amount thereof was specified to be 0.001 mass% or more which is larger than the level contained inevitably, and less than 0.05 mass% which is a range in which an impact property is not inhibited. Preferably, addition of Mo is 0.01 to 0.03 mass%.

V: 0.001 mass % or more and less than 0.05 mass%

[0046] V is an element which is effective in enhancing an impact property by refining steel microstructure, but is an element which can sometimes deteriorates a hardenability. Therefore, when V is added, the amount thereof was specified to be 0.001 mass% or more which is larger than the level contained inevitably, and less than 0.05 mass% which is a range in which a hardenability is not inhibited. Preferably, addition of V is 0.01 to 0.03 mass%. The remainder other than the components described above contains Fe and inevitable impurities.

[0047] In the next place, carbide of the steel sheet according to the present invention will be described.

[0048] In the high carbon cold-rolled steel sheet of the present invention, it is necessary that an average particle diameter (d_{av}) and a spheroidization rate (N_{SC}/N_{TC}) of a carbide dispersed in the steel sheet satisfying the following equation (1) and equation (2), respectively.

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

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

[0049] Here, the average particle diameter (d_{av}) (μm) of the equation (1) is an average value of diameters of each circle, when a circle having an area equivalent to that of each carbide observed on a cross section of the steel sheet is supposed (circle equivalent diameter). An average particle diameter (d_{av}) in this range causes an excellent impact property and an effect of easily achieving a desired quenched hardness even by a short time solution treatment. From experience, an average particle diameter (d_{av}) less than 0.2 μm causes an increased load at the time of a secondary working which is a process of making a shape of needle. An average particle diameter (d_{av}) exceeding 0.7 μm is not preferred, because it makes it difficult to achieve a desired enhancement of hardenability by a short time solution treatment.

[0050] The present invention further defined a spheroidization rate which is a spheroidization rate of carbides, by N_{TC} and N_{SC} of the equation (2). As used herein, N_{TC} refers to a total number of carbides per an observed area of 100 μm^2 . N_{SC} refers to a number of carbides which can be deemed as spheroidized in the same observation view and which satisfying the condition of d_L/d_S : 1.4 or less. Here, d_L represented a major axis and d_S represented a minor axis.

[0051] A carbide cannot be said to be formed into a perfect spherical shape, but observed as an oval shape in many cases, depending on a face observed. Therefore, a spheroidization degree was defined by a ratio of a major axis and a minor axis (d_L/d_S). According such circumstances, the present invention deemed a carbide which satisfied the condition of d_L/d_S : 1.4 or less as spheroidized, and defined N_{SC} as a number thereof. The spheroidization rate (N_{SC}/N_{TC}) $\times 100$ was specified to be 90% or more, because it has been found, from experience, that the spheroidization rate in this range enhances a secondary workability of a steel plate.

[0052] The measurement of the average particle diameter and the spheroidization rate of a carbide as described above was conducted by observing secondary electron microscope images at a magnification of 2,000 times by using a scanning electron microscope.

[0053] By using a steel sheet after subjected to the cold rolling, test pieces in a shape of plate were cut out from a sample before subjected to the heat treatment, in the direction vertical to the rolled direction. A treatment such as a resin embedding was conducted, and the carbides were measured for the circle equivalent diameter, the d_L/d_S ratio, and the N_{TC} and N_{SC} within the observed area of 100 μm^2 around the center portion of the thickness, and an average value of five views was calculated. For these measurements and the calculation, an image analysis software "winroof" (trade name) which is commercially available was used.

[0054] In the next place, a method of manufacturing the steel sheet according to the present invention will be described.

[0055] A hot-rolled steel plate used in the present invention may be those obtainable in an ordinary manufacturing condition. For example, a hot-rolled steel plate to be used in the present invention may be manufactured by heating steel pieces (slabs) having the chemical composition described above to 1,050 to 1,250°C, hot-rolling the heated slabs at a finishing temperature of 800 to 950°C, and coiling the resultant at a coiling temperature of from 600 to 750°C. In this connection, a thickness of the hot-rolled steel plate may appropriately be set, so as to obtain a preferred cold-rolling reduction rate, on the basis of a thickness of a desired cold-rolled steel sheet.

[0056] A high carbon cold-rolled steel sheet having a thickness of less than 1.0 mm is manufactured by repeating a cold rolling (25 to 65%) and a spheroidizing annealing (640 to 720°C) two or more times. It is preferred that the cold rolling (25 to 65%) and the spheroidizing annealing (640 to 720°C) be each conducted 2 to 5 times.

[0057] In the present invention, the cold rolling (25 to 65%) and the spheroidizing annealing (640 to 720°C) are repeated for two or more times. The reason is to control an average particle diameter (d_{av}) and a spheroidization rate (N_{SC}/N_{TC}) $\times 100$ of a carbide to satisfy the above described equation (1) and equation (2), respectively, as set forth below.

[0058] In the beginning, a crack is introduced into carbides by the cold rolling, and carbides which have started to be crushed are spheroidized by the spheroidizing annealing. However, by only a single time spheroidizing annealing, it is difficult to increase the spheroidization rate of the carbides up to 90% or more, and a carbide in a stick-like shape or a plate-like shape is left. In such a case, a hardenability is also affected adversely, which will deteriorate a cold workability to form a precision part. Thus, it is ideal to repeat the cold rolling and the spheroidizing annealing alternately, in order to obtain 90% or more of spheroidization rate (N_{SC}/N_{TC}) $\times 100$ of a carbide. This results in a distribution of fine carbides in a high spheroidization rate in a steel sheet.

[0059] Particularly preferred is 2 to 5 times of cold rolling and 2 to 5 times of spheroidizing annealing.

[0060] When a steel sheet (a cold-rolled steel sheet) prepared by a cold rolling of a rolling reduction rate of less than 25% is subjected to a spheroidizing annealing, carbides become coarse. On the other hand, a cold rolling of a rolling reduction rate exceeding 65% can sometimes impose too much load to a cold rolling operation. Therefore, it is preferred that a rolling reduction rate of cold rolling be in a range of from 25 to 65%.

[0061] Incidentally, in the last cold rolling, a lower limit of rolling reduction rate is not particularly limited, since the cold rolling is not followed by the spheroidizing annealing.

[0062] When a temperature for spheroidizing annealing is lower than 640°C, the spheroidizing tends to be insufficient. When the spheroidizing annealing is repeated at a temperature higher than 720°C, a carbide tends to become coarse. Therefore, it is preferred that a temperature for a spheroidizing annealing be in a range of from 640 to 720°C. A holding time for the spheroidizing annealing may appropriately be selected within a range of from 9 to 30 hours, at a temperature in this range.

[0063] In this connection, the same temperature range is also preferred for a softening annealing for the purpose of softening a hot-rolled steel plate before the cold rolling.

[0064] The above is a method of manufacturing the high carbon cold-rolled steel sheet according to the present invention. In order to make machine parts such as a knitting needle, which is the final purpose of this steel sheet, it is preferred that the following heat treatment be conducted after the steel sheet is processed into a predetermined shape.

[0065] A high carbon cold-rolled steel sheet, in which carbides are distributed, with 90% thereof spheroidized, is processed (presswork, grooving process, swaging process, etc.) into various machine parts, which are then subjected to a solution treatment and rapid cooling (quenched), and a subsequent tempering treatment. In the solution treatment, the heating temperature is set to 760 to 820°C, and the soaking time is set to a short time such as 3 to 15 minutes. An oil is preferably used in the quenching (rapid cooling). In the tempering treatment, it is preferred that the tempering temperature be set to 200 to 350°C. More preferably, the tempering temperature is 250 to 300°C. In this manner, it is

possible to manufacture various machine parts having a hardness of 600 to 750 HV.

[0066] When a soaking time of the solution treatment is longer than 15 minutes, carbides dissolve in excessively, and austenite grains become coarse, resulting in a coarse martensite phase after the quenching, which deteriorates an impact property. Therefore, it is preferred that an upper limit of the soaking time of solution treatment be 15 minutes. On the other hand, when the soaking time is shorter than 3 minutes, carbides dissolve in insufficiently, which makes a quenching hard. Therefore, it is preferred that a lower limit of the soaking time of solution treatment be 3 minutes. A range of from 5 to 10 minutes is more preferred.

[0067] When a tempering temperature is less than 200°C, recovery of toughness of a martensite phase is insufficient. On the other hand, when the tempering temperature exceeds 350°C, although the impact value is recovered, a hardness lowers 600 HV, causing a problem in durability and wear resistance. Thus, it is preferred that a proper range of the tempering temperature be set to 200 to 350°C. More preferred is from 250 to 300°C. A holding time for a tempering may be selected from a range of from 30 minutes to 3 hours.

Examples

[0068] Steels having various chemical compositions were vacuum-melted and casted into 30 kg of steel ingot. This steel ingot was subjected to a slabbing, and then subjected to a hot rolling under a condition of heating temperature of 1,150°C and finishing temperature of 870°C, to produce hot-rolled steel plates of 4 mm and 2 mm. Thereafter, a cold rolling and a spheroidizing annealing were conducted under the manufacturing conditions as shown in Table 1, to produce cold-rolled steel sheets having thicknesses of 0.4 mm or more and less than 1.0 mm. Subsequently, these cold-rolled steel sheets were subjected to a solution treatment (soaked in a furnace of 800°C for 10 minutes) under the conditions as shown in Table 2, and subsequently, oil-quenched, and tempered (tempering temperature: 250°C).

[0069] Predetermined test pieces were sampled from the steel sheets after the tempering treatment, which were then subjected to an impact test and a hardness measurement test. The hardness test is conducted under a condition of 5 kg load (testing force: 49.0 N) as measured by a Vickers hardness testing machine, in conformity with the regulation of JIS Z 2244.

[0070] The impact property was evaluated by Charpy impact test. As a test piece for the impact test, a U-notch test piece having a notch width of 0.2 mm (notch depth: 2.5 mm; notch radius: 0.1 mm) was used. Fig. 1 shows the state of a testing machine on which the test piece is set, and Fig. 2 shows a shape of the test piece. Such test piece and test method were employed for the following reason.

[0071] There has been a problem that, in a Charpy impact testing machine for metal materials which has conventionally been used, the rated capacity of the testing machine was 50 J or more that is too large for a steel sheet with a thickness of less than 1.0 mm targeted in the present invention, and as a result, it has been impossible to conduct an accurate evaluation. As an impact testing machine in which the rated capacity of the testing machine is smaller than 50 J, an impact testing machine of 1 J (manufactured by Toyo Seiki Seisaku-sho, Ltd.; Model: DG-GB) was used. This testing-machine is a Charpy impact testing machine based on the test method for Charpy impact strength of carbon fiber reinforced plastics (JIS K 7077). This testing machine was used, with the distance between the supporting beds adjusted from 60 mm to 40 mm. The distance between the supporting beds was adjusted from 60 mm to 40 mm in the present testing machine, in order to obtain a condition close to that of the JIS Standard (JIS Z 2242) which is a Charpy impact test method for metal materials.

[0072] Used as the test piece was a test piece on which a U notch is formed by an electric discharge machining, so as to obtain a notch depth of 2.5 mm, a notch radius of 0.1 mm (a notch width of 0.2 mm), as shown in Fig. 2. In a case of a thin plate of less than 1.0 mm, a deflection of the plate will be a problem during the Charpy impact test. Therefore, the notch radius was made small in order to minimize the deflection of the plate during the Charpy impact test, by increasing a stress concentration factor, so that a stable impact value was obtained. It has been confirmed that, by employing this test method and this shape of test piece, it is possible to obtain an impact property in a condition close to an actual use environment. In the present invention, it has been judged that an impact property is excellent when a numerical value of an impact value is 5 J/cm² or more.

Table 1

Condition No.	Conditions for manufacturing cold-rolled steel sheet (Rolling reduction rate, Annealing temperature)
1	Hot rolling (2 mm) → Cold rolling (20-65%) → Spheroidizing annealing (700°C) → Cold rolling (3-50%)
2A	Hot rolling (2 mm) → Cold rolling (10-20%) → Spheroidizing annealing (600-635°C) → Cold rolling (10-20%) → Spheroidizing annealing (600-635°C) → Cold rolling (3-50%)

(continued)

Condition No.	Conditions for manufacturing cold-rolled steel sheet (Rolling reduction rate, Annealing temperature)
2B	Hot rolling (2 mm) → Cold rolling (25-65%) → Spheroidizing annealing (640-720°C) → Cold rolling (25-65%) → Spheroidizing annealing (640-720°C) → Cold rolling (3-50%)
2C	Hot rolling (2 mm) → Cold rolling (70-85%) → Spheroidizing annealing (600-635°C) → Cold rolling (70-85%) → Spheroidizing annealing (600-635°C) → Cold rolling (3-50%)
2D	Hot rolling (2 mm) → Cold rolling (10-20%) → Spheroidizing annealing (640-720°C) → Cold rolling (10-20%) → Spheroidizing annealing (640-720°C) → Cold rolling (3-50%)
5A	Hot rolling (4 mm) → Softening annealing (700°C) → Cold rolling (25-65%) → Spheroidizing annealing (690°C) → Cold rolling (25-65%) → Spheroidizing annealing (680°C) → Cold rolling (25-65%) → Spheroidizing annealing (660°C) → Cold rolling (25-65%) → Spheroidizing annealing (640°C) → Cold rolling (3-50%)
5B	Hot rolling (4 mm) → Softening annealing (700°C) → Cold rolling (10-20%) → Spheroidizing annealing (690°C) → Cold rolling (10-20%) → Spheroidizing annealing (680°C) → Cold rolling (10-20%) → Spheroidizing annealing (660°C) → Cold rolling (10-20%) → Spheroidizing annealing (640°C) → Cold rolling (3-50%)

Table 2

Solution treatment	Quenching condition	Tempering condition
800°C, Soaking time: 10 minutes	Oil for quenching, 80°C	Tempering temperature: 250°C holding time: 1 hour

(Example 1)

[0073] After a solution treatment, an oil quenching was conducted, and influences of every kind of added elements to a hardness of cross section and to an impact value were checked. Results of the test are shown in Table 3 and Table 4, together with the chemical compositions. As conditions for manufacturing the cold-rolled steel sheets, the condition of 5A (Table 1) was used in both cases. A rolling reduction rate was controlled within a range described in Table 1.

[0074] As for the hardness of cross section, a test piece cut out in the direction vertical to the rolled direction was embedded in a resin, and after the cross section was polished, the hardness of cross section was measured at the center portion of the thickness. An impact value was measured by using test pieces sampled in a direction parallel to the rolled direction. The obtained results (hardnesses and impact values) were shown in Table 3 and Table 4.

[0075] Those having an impact value larger than 5 J/cm² and at the same time, a hardness fulfilling 600 to 750 HV were evaluated as ◎, and those having any of impact value and hardness not fulfilling the target value were evaluated as x.

Table 3

Steel type No.	Cold-rolled steel sheet (Manufacturing method 5A)										Characteristics after quenching-tempering (Note 2)		Evaluation (Note 3)	Section
	thickness (mm)	Chemical components (mass%) (Note 1)							Spheroidization rate (%)	Average grain diameter (μm)	Quenched-tempered hardness (HV5)	Impact value (J/cm ²)		
		C	Si	Mn	Cr	Mo	V	Nb						
1	0.51	0.65	0.25	0.68	0.36	-	-	0.010	95	0.3	550	3	×	Comparative Example
2	0.40	0.85	0.27	0.68	0.40	-	-	-	96	0.4	650	4	×	Comparative Example
3	0.41	0.85	0.25	0.70	0.37	-	-	0.014	91	0.5	660	8	⊙	Examples of the invention
4	0.71	1.10	0.23	0.74	0.40	-	-	-	96	0.4	730	4	×	Comparative Example
5	0.70	1.10	0.25	0.70	0.42	-	-	0.015	97	0.5	735	12	⊙	Examples of the invention
6	0.71	1.30	0.26	0.72	0.41	-	-	0.017	95	0.6	760	4	×	Comparative Example
7	0.50	0.95	0.20	0.80	0.35	-	-	0.010	90	0.4	650	9	⊙	Examples of the invention
8	0.51	0.95	0.30	0.50	0.45	-	-	0.015	92	0.2	655	7	⊙	Examples of the invention
9	0.60	1.05	0.35	0.60	0.45	-	-	0.010	93	0.6	745	10	⊙	Examples of the invention
10	0.61	1.05	0.10	1.00	0.35	-	-	0.005	95	0.7	715	11	⊙	Examples of the invention
Note 1) The other elements; P: 0.010-0.020 mass%, S: 0.001-0.010 mass%														
Note 2) Temperature for solution treatment: 800°C, Soaking time: 10 minutes, Tempering temperature: 250°C														
Note 3) ⊙: Excellent, ×: Inferior														

Table 4

Steel type No.	Cold-rolled steel sheet (Manufacturing method 5A)										Characteristics after quenching-tempering Note 2)		Evaluati on Note 3)	Section
	thickness (mm)	Chemical components (mass%) Note 1)							Spheroidization rate (%)	Average particle diameter (μm)	Quenched- tempered hardness (HV5)	Impact value (J/cm ²)		
		C	Si	Mn	Cr	Mo	V	Nb						
11	0.41	1.01	0.26	0.73	0.42	0.02	-	-	95	0.6	717	4	×	Comparative Example
12	0.41	1.03	0.26	0.73	0.42	0.02	0.10	-	94	0.4	590	6	×	Comparative Example
13	0.42	1.03	0.25	0.71	0.44	0.10	-	-	95	0.5	712	3	×	Comparative Example
14	0.41	1.01	0.20	0.70	0.42	0.02	-	0.003	96	0.5	700	3	×	Comparative Example
15	0.42	1.01	0.25	0.71	0.38	0.01	-	0.005	97	0.6	702	6	⊙	Examples of the invention
16	0.41	1.01	0.24	0.71	0.41	0.02	-	0.010	98	0.6	708	7	⊙	Examples of the invention
17	0.40	1.02	0.25	0.71	0.39	0.02	-	0.020	95	0.6	703	6	⊙	Examples of the invention
18	0.42	1.01	0.25	0.72	0.39	0.02	-	0.055	96	0.6	709	4	×	Comparative Example
19	0.41	1.02	0.30	0.68	0.40	0.04	-	0.005	97	0.5	690	6	⊙	Examples of the invention
20	0.40	1.01	0.25	0.73	0.41	0.10	-	0.010	95	0.6	680	3	×	Comparative Example
21	0.41	1.02	0.25	0.73	0.39	0.02	0.04	0.005	96	0.5	705	7	⊙	Examples of the invention

(continued)

Cold-rolled steel sheet (Manufacturing method 5A)														Evaluation on Note 3)	Section
Steel type No.	Chemical components (mass%) Note 1)							Spheroidization rate (%)	Average particle diameter (μm)	Characteristics after quenching-tempering Note 2)		Comparative Example			
	thickness (mm)	C	Si	Mn	Cr	Mo	V			Nb	Quenched- tempered hardness (HV5)		Impact value (J/cm ²)		
22	0.41	1.00	0.25	0.70	0.43	0.03	0.10	0.015	97	0.6	550		4	×	
Note 1) The other elements; P: 0.010-0.020 mass%, S: 0.001-0.010 mass%															
Note 2) Temperature for solution treatment: 800°C, Soaking time: 10 minutes, Tempering temperature: 250°C															
Note 3) ◎: Excellent, ×: Inferior															

[0076] In the examples shown in Table 3, the case having an amount of C out of the lower limit value (steel type No. 1) exhibited an impact value and a quenched-tempered hardness out of the target values. The case having an amount of C out of the upper limit value (steel type No. 6) exhibited a quenched-tempered hardness exceeding the target value 600 to 750 HV, and an impact value lowering the target value 5 J/cm². As for the case not containing Nb, both of the case having an amount of C of 0.85 mass% (steel type No. 2, Comparative Example) and the case having an amount of C of 1.10 mass% (steel type No. 4, Comparative Example) exhibited an impact value lowering the target value 5 J/cm², and evaluated as $\times$. In contrast, the steel sheets having chemical components corresponding to those of the example of the invention (steel type Nos. 3, 5, 7, 8, 9 and 10) exhibited quenched-tempered hardnesses within the target range, and excellent impact properties.

[0077] In the examples shown in Table 4, the steel sheets having chemical components corresponding to those of the example of the invention (steel type Nos. 15, 16, 17, 19, and 21) all exhibited a quenched-tempered hardness fulfilling the target value 600 to 750 HV, and an excellent impact property. The case without added with Nb (steel type No. 11), the case without added with Nb and with a V addition amount of 0.05 mass% (steel type No. 12), the case without added with Nb and with an Mo addition amount exceeding 0.05 mass% (steel type No. 13), the case with a combined addition of Nb + Mo, the Nb addition amount being less than 0.005 mass% (steel type No. 14), the case with a combined addition of Nb + Mo, the Nb addition amount exceeding 0.020 mass% (steel type No. 18), the case with a combined addition of Nb + Mo, the Mo addition amount being more than 0.05 mass% (steel type No. 20), the case with a combined addition of Nb + Mo + V, the V addition amount being more than 0.05 mass% (steel type No. 22) exhibited a quenched-tempered hardness fulfilling the target value 600 to 750 HV, but exhibited an inferior impact property; or exhibited an impact properties fulfilling the target value 5 J/cm², but exhibited a lowered quenched-tempered hardness; or exhibited a quenched-tempered hardness and an impact property both lowering the lower limit of the target values.

(Example 2)

[0078] Cold-rolled steel sheets having thicknesses as shown in Table 5 were obtained by using a hot-rolled steel plate having the chemical components of the steel type No. 3 (Table 3), under the manufacturing conditions of cold rolling and spheroidizing treatment described in Table 1 altered. Table 5 shows spheroidization rates and average particle diameters of carbides of the obtained cold-rolled steel sheets. After a solution treatment, the obtained cold-rolled steel sheets were further subjected to an oil-quenching and a low temperature tempering, under the condition shown in Table 2, in the same manner as in Example 1. Hardnesses of cross section and impact values of the obtained cold-rolled steel sheets after subjected to the solution treatment and the subsequent quenching-tempering were measured in the same manner as in Example 1, and shown in Table 5.

Table 5

Cold-rolled steel sheet (Steel type No. 3) Note 1)							Characteristics after quenching-tempering Note 2)		Evaluation Note 3)
Manufacturing condition No.	thickness (mm)	Total number of carbide (piece/100 μm^2)	Number of spheroidized carbide (piece/100 μm^2)	Spheroidization rate (%)	Average particle diameter (μm)	Quenched-tempered hardness (HV5)	Impact value (J/cm ²)		
1	0.41	43	31	72	1.3	680	2	×	
2A	0.41	40	26	65	0.4	670	2	×	
2B	0.40	45	42	93	0.6	685	6	⊙	
2C	0.41	60	58	97	0.1	760	6	×	
2D	0.42	36	34	94	0.9	675	2	×	
5A	0.60	45	42	93	0.5	660	8	⊙	
5B	0.61	35	34	97	0.9	711	3	×	
Note 1) Steel type No. 3 described in TABLE 3									
Note 2) Temperature for solution treatment: 800°C, Soaking time: 10 minutes, Tempering temperature: 250°C									
Note 3) ⊙: Excellent, ×: Inferior									

[0079] In the case where number of the spheroidizing annealing was a single time (manufacturing condition No. 1), the spheroidization rate was insufficient, and the impact property was inferior. In the case where number of the spheroidizing annealing was two times, the spheroidizing was insufficient and the impact property was inferior, when the spheroidizing annealing and the cold rolling were each conducted two times, with combining a spheroidizing annealing temperature of 600 to 635°C and a rolling reduction rate of a cold rolling of 10 to 20% (manufacturing condition No. 2A). When a spheroidizing annealing and a cold rolling were each repeated two times, with combining a spheroidizing annealing temperature of 600 to 635°C and a rolling reduction rate of a cold rolling of 70 to 85%, although a sufficient impact property was obtained, average particle diameter of carbides was out of the lower limit, and a hardness after the quenching-tempering treatment exceeded the target value (manufacturing condition No. 2C).

[0080] When a spheroidizing annealing and a cold rolling were each repeated two times, with combining a temperature of the spheroidizing annealing of 640 to 720°C and a rolling reduction rate of the cold rolling of 10 to 20%, although the spheroidizing was sufficient, average particle diameter of carbides exceeded the upper limit of the target value, and impact property was inferior (manufacturing condition No. 2D). This is considered to be because when a carbide is too large, an undissolved carbide in a martensite substrate becomes comparatively large at the time of quenching, and due to a large area of an interface between the undissolved carbide and the martensite substrate which tends to be a starting point of destruction, an impact property was made inferior. In contrast, when a spheroidizing annealing and a cold rolling were each repeated two times, with a combination of a temperature of the spheroidizing annealing of 640 to 720°C and a rolling reduction rate of the cold rolling of 25 to 65%, the spheroidization rate, the carbide particle diameter, and the hardness after the quenching-tempering each came within the ranges of the target values, and a superior impact property was obtained (manufacturing condition No. 2B).

[0081] In the case where number of the spheroidizing annealing was four times, spheroidization rate and carbide particle diameter came within the ranges of the target values, and a superior impact property was obtained when the rolling reduction rate of the cold rolling was set to 25 to 65% in all of the first to fourth cycles (manufacturing condition No. 5A). When a temperature of the spheroidizing annealing was set to the same as that of the manufacturing condition No. 5A, and rolling reduction rates of the cold rolling in the first to fourth cycle were all set to 10 to 20%, the carbide particle diameter became too large, exceeding the target value, and an inferior impact property was obtained (manufacturing condition No. 5B).

(Example 3)

[0082] Cold-rolled steel sheets having thicknesses as shown in Table 6 were obtained by using a hot-rolled steel plate having the chemical components of the steel type No. 16 (Table 4), and the manufacturing conditions described in Table 1 altered. The spheroidization rates, average particle diameters of carbides of the obtained cold-rolled steel sheets are shown in Table 6. After a solution treatment, the obtained cold-rolled steel sheets were further subjected to an oil-quenching and a low temperature tempering, under the condition shown in Table 2, in the same manner as in Example 1. Hardnesses of cross section and impact values of the obtained cold-rolled steel sheets after subjected to the solution treatment and the subsequent quenching-tempering were measured in the same manner as in Example 1, and shown in Table 6.

[0083] The steel sheets which were subjected to the cold rolling and the spheroidizing annealing by using the manufacturing conditions No. 2B and No. 5A which correspond to the manufacturing method of the present invention fulfilled the target spheroidization rate and the target impact value.

Table 6

Cold-rolled steel sheet (Steel type No. 16) Note 1)							Characteristics after quenching-tempering Note 2)		Evaluation Note 3)
Manufacturing condition No.	thickness (mm)	Total number of carbide (piece/100 μm^2)	Number of spheroidized carbide (piece/100 μm^2)	Spheroidization rate (%)	Average particle diameter (μm)	Quenched-tempered hardness (HV5)	Impact value (J/cm ²)		
1	0.40	51	31	61	1.2	700	3	×	
2A	0.41	49	29	59	0.5	690	3	×	
2B	0.40	47	44	94	0.5	700	7	◎	
2C	0.41	65	62	95	0.1	760	6	×	
2D	0.41	38	36	95	0.8	695	3	×	
5A	0.60	46	45	98	0.6	695	8	◎	
5B	0.61	37	36	97	0.9	720	4	×	
Note 1) Steel type No. 16 described in TABLE 4									
Note 2) Temperature for solution treatment: 800°C, Soaking time: 10 minutes, Tempering temperature: 250°C									
Note 3) ◎: Excellent, ×: Inferior									

Industrial Applicability

[0084] A steel sheet having chemical components in the range of the present invention has an enhanced hardenability by an addition of Nb, and an improved impact property after a heat treatment, and therefore, suitable to be used as a hypereutectoid steel in a machine parts which are used in a severe environment.

[0085] A hypereutectoid steel containing C of 0.85 to 1.10 mass% is suitable for a use where a balance of hardness and toughness is required under a severe use environment, such as a use in knitting needles.

Claims

1. A high carbon cold-rolled steel sheet, wherein a chemical composition of the steel sheet comprises C: 0.85 to 1.10 mass%, Mn: 0.50 to 1.0 mass%, Si: 0.10 to 0.35 mass%, P: 0.030 mass% or less, S: 0.030 mass% or less, Cr: 0.35 to 0.45 mass%, and Nb: 0.005 to 0.020 mass%, with Fe and an inevitable impurity as the remainder, with an average particle diameter (d_{av}) and a spheroidization rate (N_{SC}/N_{TC}) $\times 100\%$ of a carbide dispersed in the steel sheet respectively satisfying an equation (1) and an equation (2) below, and a thickness of the steel sheet being less than 1.0 mm;

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

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

wherein the average particle diameter (d_{av}) of the equation (1) is an average value of diameters of each circle, when a circle having an area equivalent to that of each carbide observed on a cross section of the steel sheet is supposed (circle equivalent diameter), and

N_{TC} and N_{SC} in the equation (2) respectively represent N_{TC} : total number of carbide per an observed area of $100 \mu\text{m}^2$, and N_{SC} : number of carbide which satisfying a condition that d_L/d_S is 1.4 or less, with d_L being a major axis and d_S being a minor axis of a carbide.

2. The high carbon cold-rolled steel sheet according to claim 1, wherein the chemical composition further comprises one or two kinds selected from Mo and V, the content of each being 0.001 mass% or more and less than 0.05 mass%.

3. A method of manufacturing a high carbon cold-rolled steel sheet by repeatedly subjecting a hot-rolled steel plate comprising the chemical composition as described in claim 1 or claim 2 to a cold rolling and a spheroidizing annealing, wherein an average particle diameter (d_{av}) and a spheroidization rate (N_{SC}/N_{TC}) of a carbide dispersed in the high carbon cold-rolled steel sheet respectively satisfy the equation (1) and equation (2) below; and a thickness of the high carbon cold-rolled steel sheet is less than 1.0 mm;

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

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

wherein the average grain diameter (d_{av}) of the equation (1) is an average value of diameters of each circle, when a circle having an area equivalent to that of each carbide observed on a cross section of the steel plate is supposed (circle equivalent diameter), and

N_{TC} and N_{SC} in the equation (2) respectively represent N_{TC} : total number of carbide per an observed area of $100 \mu\text{m}^2$, and N_{SC} : number of carbide which satisfies a condition that d_L/d_S is 1.4 or less, with d_L representing a major axis and d_S representing a minor axis of the carbide.

4. The method of manufacturing a high carbon cold-rolled steel sheet according to claim 3, wherein number of repeatedly subjecting the hot-rolled steel plate to a cold rolling and a spheroidizing annealing is two to five.

5. The method of manufacturing a high carbon cold-rolled steel sheet according to claim 3 or 4, wherein a rolling reduction rate of the cold rolling is 25 to 65%, and a temperature of the spheroidizing annealing is 640 to 720°C.

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Fig. 1

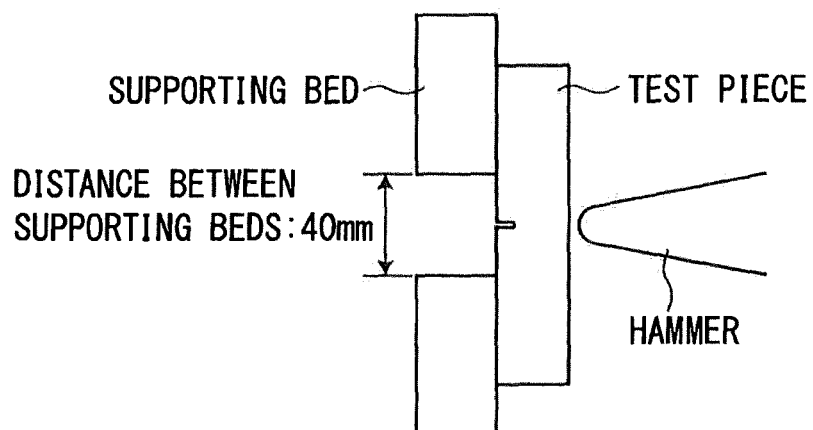


Fig. 2

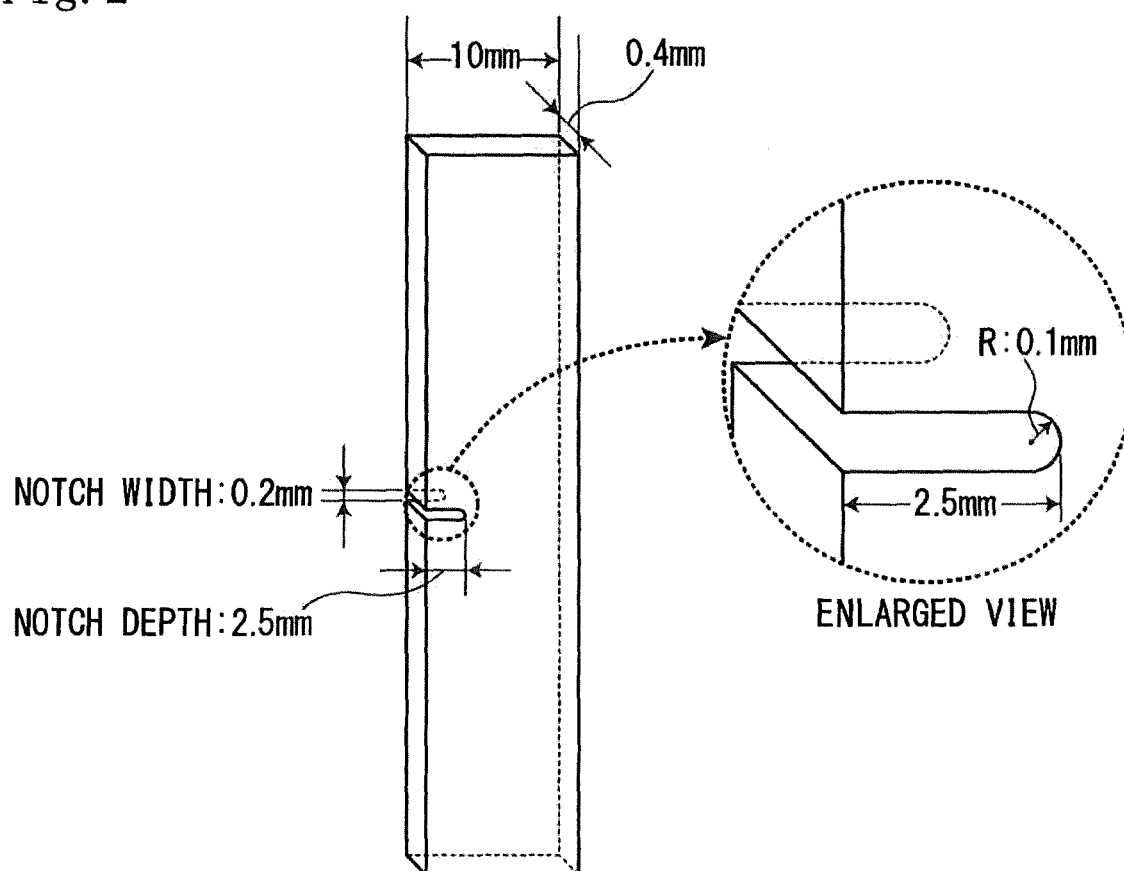


Fig. 3

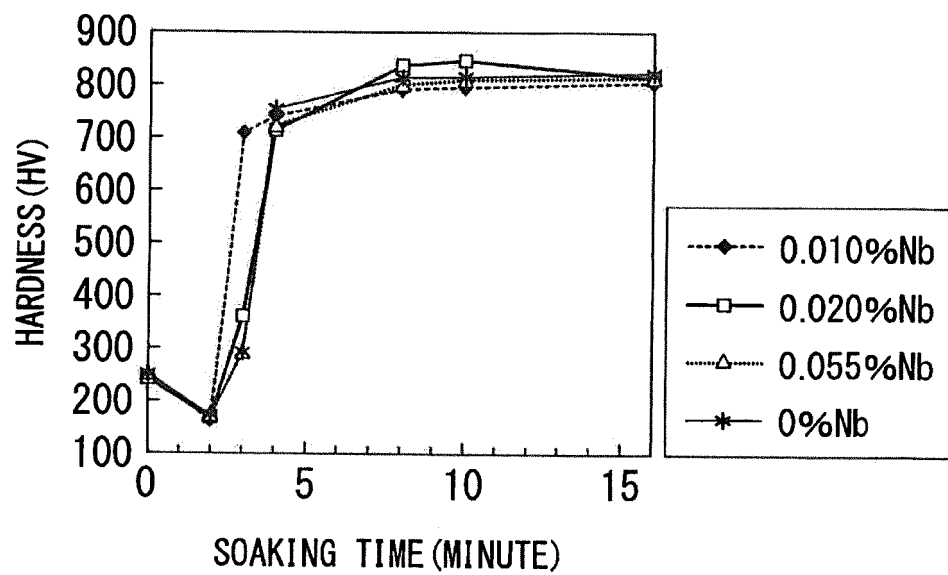


Fig. 4

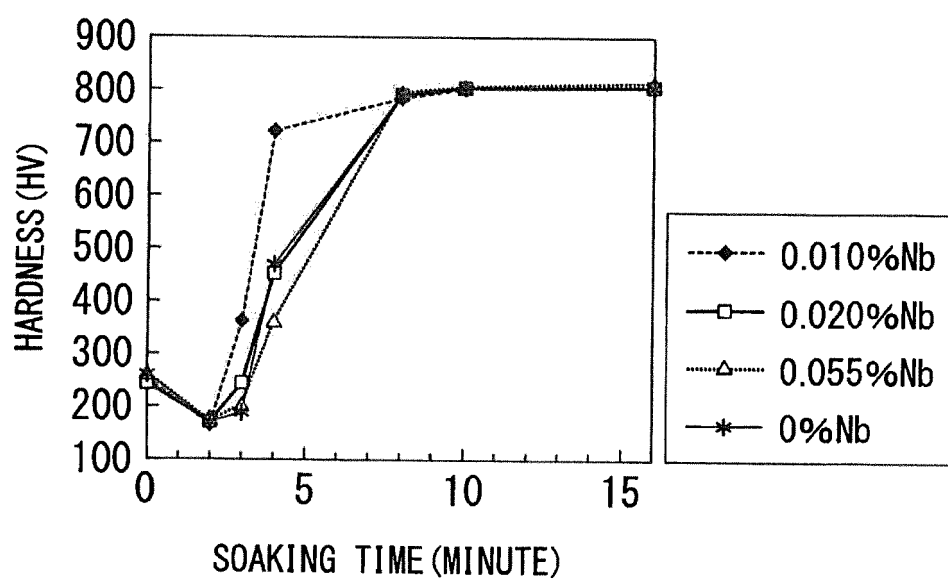


Fig. 5

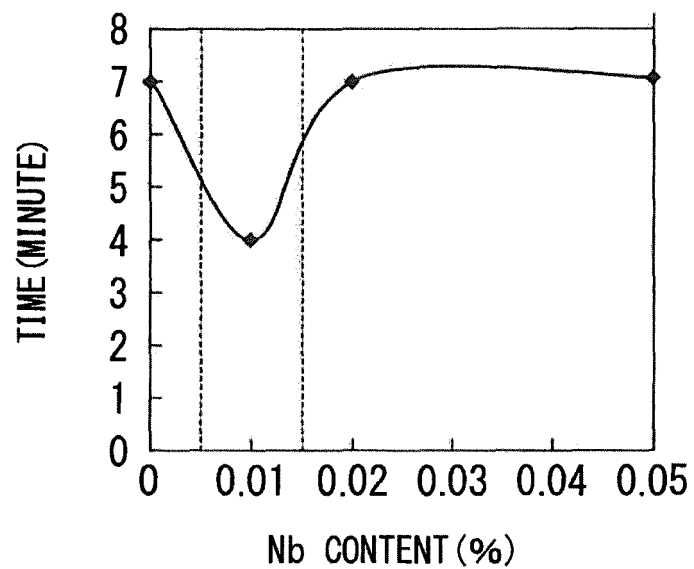


Fig. 6

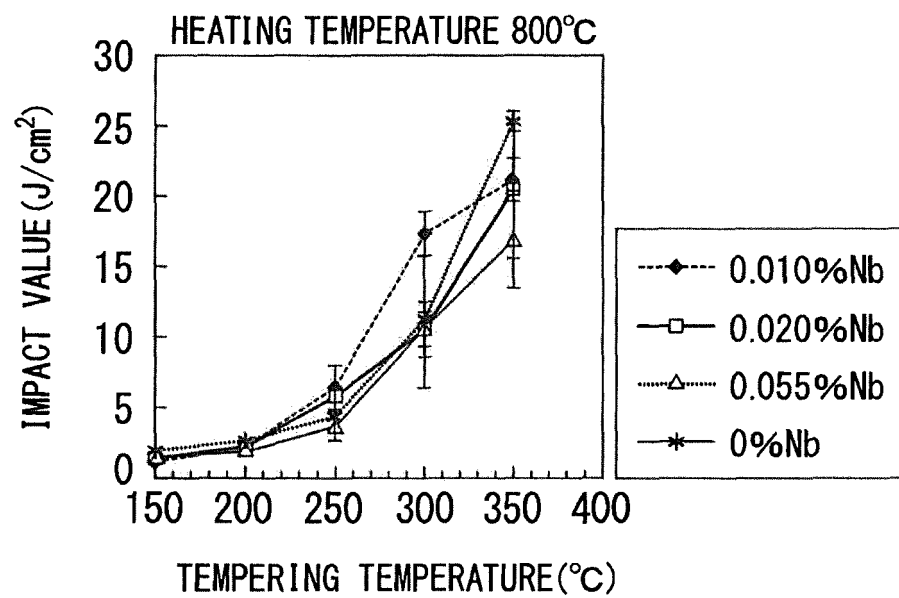
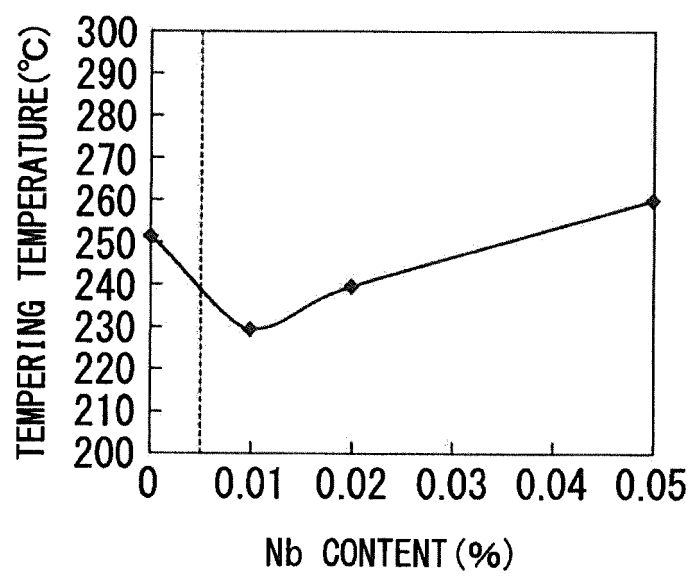


Fig. 7



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/071133

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/00(2006.01)i, C21D1/32(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)
C22C38/00-38/60, C21D1/32, C21D9/46

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

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2016
Kokai Jitsuyo Shinan Koho 1971-2016 Toroku Jitsuyo Shinan Koho 1994-2016

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2006-63384 A (Nisshin Steel Co., Ltd.), 09 March 2006 (09.03.2006), (Family: none)	1-5
A	JP 2003-147485 A (Nisshin Steel Co., Ltd.), 21 May 2003 (21.05.2003), (Family: none)	1-5
A	JP 2009-215612 A (Nisshin Steel Co., Ltd.), 24 September 2009 (24.09.2009), (Family: none)	1-5
A	JP 2005-139534 A (Kobe Steel, Ltd.), 02 June 2005 (02.06.2005), (Family: none)	1-5

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search
11 October 2016 (11.10.16)

Date of mailing of the international search report
25 October 2016 (25.10.16)

Name and mailing address of the ISA/
Japan Patent Office
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Tokyo 100-8915, Japan

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