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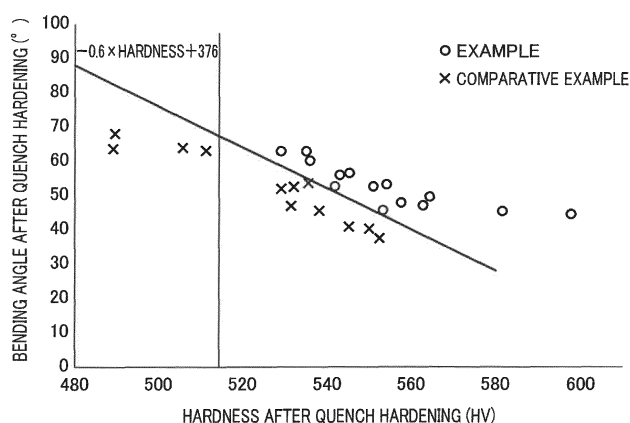
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(54) **STEEL SHEET FOR HARDENING, HARDENED MEMBER, AND METHOD FOR MANUFACTURING STEEL SHEET FOR HARDENING**

(57) An aspect of the present invention is a steel sheet for quench hardening, satisfying a prescribed composition and having a Mn concentration satisfying the formula (1): $S1 + S2 < -10 \times [Mn] + 44$ (1), where [Mn] is Mn concentration in a steel sheet analyzed by inductively coupled plasma emission spectrography (% by mass); S1 is an area % of the region where the Mn con-

centration analyzed by an electron beam microprobe analyzer in the structure at a position of 1/4 of the steel sheet thickness is two times or more the [Mn]; and S2 is an area % of the region where the Mn concentration analyzed by an electron beam microprobe analyzer in the structure at a position of 1/4 of the steel sheet thickness is 0.5 times or less the [Mn].

FIG. 1



Description**Technical Field**

[0001] The present invention relates to a steel sheet for quench hardening, a quench hardened member, and a method for manufacturing steel sheet for quench hardening, and more specifically to a steel sheet for quench hardening useful as a material for providing a quench hardened member which has hardness of 515 HV or more after quench hardening, and marked bending workability in T direction bending for making the bending ridgeline parallel to the rolling direction, and a method for making the steel sheet for quench hardening.

Background Art

[0002] In order to achieve low fuel consumption in automobiles and transportation machines, reduction of self-weight of automobiles and transportation machines has been desired. For weight reduction, for example, reduction of sheet thickness through the use of a high strength steel sheet is effective. However, if a high strength steel sheet having a tensile strength of more than 980 MPa is subjected to cold forming, problems such as the increase in the press molding load and deterioration of dimensional accuracy may occur.

[0003] As a method for solving the above-described problems, adopted is a hot press molding technique for heating steel to a temperature at which an austenite single phase is formed, to decrease its strength, and press-molding the steel with a die with the easier moldability. However, if the tensile strength of the hot press molded article increases, rupture tends to occur upon collision. In order to suppress the occurrence of rupture, the hot press molded article must have marked bendability.

[0004] Examples of the steel material for hot press forming to make a hot press molded article include the steel materials described in Patent Literature 1 and Patent Literature 2.

[0005] Patent Literature 1 describes a steel material for hot press forming, the steel material having a specific chemical composition, and steel structure in which the spherical rate of carbides in the steel is from 0.60 to 0.90.

[0006] Patent Literature 2 describes a hot press steel sheet member having mechanical properties including a specific chemical composition, steel structure having a prior austenite average particle size of 10 μm or less, and a tensile strength of 1.8 GPa or more and 2.0 GPa or less.

Citation List**Patent Literature**

[0007]

Patent Literature 1: JP 2011-195958 A

Patent Literature 2: JP 2014-15638 A

Summary of Invention

[0008] The present invention aims to provide a quench hardened member having marked T direction bendability even if the hardness after quench hardening is in a high strength region of 515 HV or more, a steel sheet for quench hardening for manufacturing the quench hardened member, and a method for manufacturing the steel sheet.

[0009] One aspect of the present invention is a steel sheet for quench hardening, having a composition satisfying C: more than 0.2% and 0.4% or less, Si: 0.8% or more and 1.4% or less, Mn: 1% or more and 3% or less, P: more than 0% and 0.02% or less, S: more than 0% and 0.002% or less, sol.Al: 0.02% or more and 0.06% or less, N: more than 0% and 0.01% or less, O: more than 0% and 0.01% or less, B: 0.0005% or more and 0.005% or less, and Ti: 0.005% or more and 0.1% or less in terms of % by mass, the balance being iron and unavoidable impurities, and having a Mn concentration satisfying the following formula (1):

$$S1 + S2 < -10 \times [Mn] + 44 \quad (1)$$

where

[Mn] is Mn concentration in a steel sheet analyzed by inductively coupled plasma emission spectrography (% by mass),

S1 is an area % of the region where the Mn concentration analyzed by an electron beam microprobe analyzer in the structure at a position of 1/4 of the steel sheet thickness is two times or more the [Mn],

S2 is an area % of the region where the Mn concentration analyzed by an electron beam microprobe analyzer in the structure at a position of 1/4 of the steel sheet thickness is 0.5 times or less the [Mn].

[0010] The above-described and other objects, features, and advantages of the present invention will be clarified by the following detailed description and attached drawings.

Brief Description of Drawings

[0011] Fig. 1 depicts a relationship between hardness of a quench hardened member and T direction bend angle.

Description of Embodiments

[0012] Generally, strength and bendability tend to be contrary to each other. More specifically, as the strength increases, the bendability decreases. In particular, as the strength increases, bending workability in T direction bending for making the bending ridgeline parallel to the rolling direction tends to decrease.

[0013] According to the studies by the inventors, the steel sheets described in Patent Literature 1 and Patent Literature 2 have marked bending workability in L direction bending for making the bending ridgeline vertical to the rolling direction, but have insufficient bending workability in T direction bending for making the bending ridgeline parallel to the rolling direction (hereinafter referred to as T direction bendability).

[0014] A hot press molding technique has been described above as an example, but not only hot press molded articles but also general quench hardened members have the above-described problem of difficulty in achieving both of high strength and bendability (in particular, high strength and T direction bendability).

[0015] The inventors carried out dedicated research for providing a steel sheet for quench hardening for making a quench hardened member having marked T direction bendability, even if the tensile strength after quench hardening is about 1600 MPa or more, more specifically the hardness after quench hardening is 515 HV or more.

[0016] As a result of this, they found that a quench hardened member having improved T direction bendability is obtained by using a steel sheet for quench hardening in which the concentration distribution of Mn is adequately controlled based on the premise that the composition is adequately controlled, even if the hardness after quench hardening is in a high strength region of 515 HV or more, and thus accomplished the present invention.

[0017] In the present specification, "quench hardening" means not only the mode in which a steel sheet is pressed in a softened state under heating to about 900°C such as hot pressing, and concurrently quench hardened by cooling effect caused by contact with a die, and also includes the mode in which a steel sheet is quench hardened after warm pressing other than hot pressing and cold pressing.

[0018] Embodiments according to the present invention are described below, but the present invention will not be limited to them.

[0019] Firstly, the composition of the steel sheet for quench hardening according to one embodiment of the present invention are described.

[C: more than 0.2% and 0.4% or less]

[0020] Since hardness of the quench hardened member largely depends on the C content, C is an essential element. In order to increase hardness of the quench hardened member, the C content is more than 0.2%, preferably 0.22% or more, and more preferably 0.24% or more. However, if the C content is excessive, the strength after hot rolling increases and cracks may occur during cold rolling, or weldability of the steel sheet decreases. Accordingly the C content is 0.4% or less, preferably 0.38% or less, and more preferably 0.36% or less.

[Si: 0.8% or more and 1.4% or less]

[0021] Si is one of the important elements in the present invention. Si improves adhesion of scales after quench hardening and prevents exfoliation of scales. Additionally, the inclusion of Si improves hardenability, which improves hardness of the quench hardened member. In order to effectively achieve such effects, the Si content is 0.8% or more, preferably 0.9% or more, and more preferably 1% or more. However, if the Si content is excessive, residual austenite tends to occur, which promotes diffusion of Mn into the residual austenite and tends to result in the nonuniform Mn concentration in the steel sheet. Accordingly, the Si content is 1.4% or less, preferably 1.35% or less, and more preferably

1.3% or less.

[Mn: 1% or more and 3% or less]

5 **[0022]** Mn is an element contributing to high hardness of the quench hardened member. In order to effectively achieve this effect, the Mn content is 1% or more, preferably 1.1% or more, and more preferably 1.2% or more. However, if the Mn content is excessive, the strength after hot rolling may increase, cracks may occur during cold rolling, and weldability of the steel sheet may deteriorate. Additionally, the addition of an excessive amount of Mn can cause segregation of Mn and deterioration of formability. Accordingly, the Mn content is 3% or less, preferably 2.8% or less, and more preferably 2.6% or less.

[P: more than 0% and 0.02% or less]

15 **[0023]** P is an element which is inevitably included and deteriorates weldability of the steel sheet. Accordingly, the P content is 0.02% or less, preferably 0.018% or less, and more preferably 0.017% or less. The P content is preferably as low as possible, so that its content is more than 0%, and industrially 0.0005% or more.

[S: more than 0% and 0.002% or less]

20 **[0024]** Similarly to P, S is an element which is inevitably included and deteriorates weldability of the steel sheet. Additionally, the inclusion of S forms MnS in the steel sheet, which results in the decrease in homogeneity of the concentration distribution of Mn, and causes segregation of Mn. Accordingly, the S content is 0.002% or less, preferably 0.0018% or less, and more preferably 0.0015% or less. The S content is preferably as low as possible, so that its content is more than 0%, and industrially 0.0001% or more.

25 [sol.Al: 0.02% or more and 0.06% or less]

30 **[0025]** sol.Al is an element which works as a deoxidizer. In order to effectively achieve this effect, the sol.Al content is 0.02% or more, and more preferably 0.025% or more. However, if the sol.Al content is excessive, hardness of the quench hardened member decreases, so that the sol.Al content is 0.06% or less, preferably 0.055% or less, and more preferably 0.05% or less.

[N: more than 0% and 0.01% or less]

35 **[0026]** N is an element which is inevitably included. If the N content is excessive, borides are formed and the B content decreases, so that hardenability of the steel sheet may decrease. Accordingly, the N content is 0.01% or less, preferably 0.008% or less, and more preferably 0.005% or less. The N content is preferably as low as possible, so that its content is more than 0%, and industrially 0.0001% or more.

40 [O: more than 0% and 0.01% or less]

45 **[0027]** O is an element which is inevitably included, and its excessive inclusion may decrease T direction bendability of the quench hardened member. Accordingly, the O content is 0.01% or less, preferably 0.005% or less, and more preferably 0.003% or less. The O content is preferably as low as possible, so that its content is more than 0%, and industrially 0.0001% or more.

[B: 0.0005% or more and 0.005% or less]

50 **[0028]** B is an element which improves hardenability of the steel sheet. In order to effectively achieve this effect, the B content is 0.0005% or more, preferably 0.001% or more, more preferably 0.0012% or more, and even more preferably 0.0015% or more. However, if the B content is excessive, coarse iron nitrides are formed to deteriorate toughness. Accordingly, the B content is 0.005% or less, preferably 0.004% or less, and more preferably 0.0035% or less.

[Ti: 0.005% or more and 0.1% or less]

55 **[0029]** Ti forms TiN to suppress the decrease of the B content, and improves hardenability of the steel sheet owing to B. Therefore the Ti content is 0.005% or more, preferably 0.01% or more, and more preferably 0.015% or more. However, if the Ti content is excessive, carbides deposit at grain boundaries, which deteriorates hardenability of the

steel sheet. Accordingly, the Ti content is 0.1% or less, preferably 0.08% or less, and more preferably 0.06% or less.

[Other component]

[0030] The above-described steel sheet for quench hardening satisfies the above-described composition, and the balance is composed of iron and unavoidable impurities. Examples of the unavoidable impurities included in the steel sheet for quench hardening include the above-described P, S, N, and O, and tramp elements such as Pb, Bi, Sb, and Sn, which may be carried in depending on the conditions of the feeds, materials, and production facilities. The unavoidable impurities herein means the impurities other than P, S, N, and O, and examples include tramp elements such as Pb, Bi, Sb, and Sn.

[0031] Additionally, the steel sheet for quench hardening may further contain at least one other element (A) selected from the group consisting of Cr: more than 0% and 3% or less and Mo: more than 0% and 3% or less, and (B) Nb: more than 0% and 0.1% or less, and V: more than 0% and 0.1% or less, without impairing the above-described advantages of the present invention. These elements (A) and (B) may be used alone or in combination of the elements listed in (A) and the elements listed in (B). The reason for defining these ranges is as follows.

[(A) at least one selected from the group consisting of Cr: more than 0% and 3% or less, and Mo: more than 0% and 3% or less]

[0032] Both of Cr and Mo are effective elements for improving the strength of the quench hardened member by increasing hardenability, and may be used alone or in combination. In order to effectively achieve this effect, each of the contents of Cr and Mo is more than 0%, preferably 0.1% or more, and more preferably 0.3% or more. However, if their contents are excessive, the strength after hot rolling increases, which can deteriorate cold rolling properties and increases the production cost, so that the contents of Cr and Mo are, when included individually, preferably 3% or less, and more preferably 2.5% or less, and more preferably 2% or less.

[(B) at least one selected from the group consisting of Nb: more than 0% and 0.1% or less, and V: more than 0% and 0.1% or less]

[0033] Both of Nb and V are effective elements for forming carbides in a steel sheet and improving the strength of the quench hardened member, and may be used alone or in combination. In order to effectively achieve these effects, each of the contents of Nb and V is more than 0%, preferably 0.005% or more, and more preferably 0.008% or more. However, if their contents are excessive, carbides deposits at grain boundaries, which deteriorates hardenability of the steel sheet. Accordingly, each of the contents of Nb and V is preferably 0.1% or less, and more preferably 0.08% or less, and more preferably 0.06% or less.

[Concentration distribution of Mn]

[0034] The inventors have found that a quench hardened member having marked T direction bendability is obtained by appropriately controlling the concentration distribution of Mn in the steel sheet for quench hardening which satisfies the above-described composition so as to fall within the range of the formula (1), that is, suppressing segregation of Mn, even if hardness after quench hardening is in a high strength region of 515 HV or more. More specifically, they have found that good T direction bendability is achieved when the steel sheet for quench hardening satisfies the formula (1) at the position of 1/4 of the steel sheet thickness (at the position of $1/4 \times t$ of the steel sheet for quench hardening having a thickness of t , hereinafter the same), even though the hardness of the quench hardened member is high. The method for evaluating T direction bendability is described below.

$$S1 + S2 < -10 \times [Mn] + 44(1)$$

[Mn]: Mn concentration in a steel sheet analyzed by inductively coupled plasma emission spectrography (% by mass)
 S1: area % of the region where the Mn concentration analyzed by an electron beam microprobe analyzer in the structure at a position of 1/4 of the steel sheet thickness is two times or more the [Mn]
 S2: area % of the region where the Mn concentration analyzed by an electron beam microprobe analyzer in the structure at a position of 1/4 of the steel sheet thickness is 0.5 times or less the [Mn]

[0035] In the present specification, "segregation of Mn" means that the total of the area % of the region whose Mn concentration is twice or more that in the base material (steel sheet for quench hardening) (S1) and the area % of the region whose Mn concentration is 0.5 times or less that in the base material (S2) (S1 + S2 (area %)) is high. The method for determining S1 + S2 (area %) is described below.

[0036] The Mn concentration in the base material [Mn] is calculated by chemically analyzing the steel sheet for quench hardening by inductively coupled plasma emission spectrography. Specifically, [Mn] is the average of the Mn concentrations in the whole steel sheet.

[0037] As indicated in the formula (1), the inventors have also found that segregation of Mn must be further suppressed when the Mn concentration in the base material is high, in comparison with the case where the Mn concentration in the base material is low. For example, when [Mn] is 1.3% by mass, S1 + S2 is less than 31 area %, but when [Mn] is 2.3% by mass, S1 + S2 must be less than 21 area %.

[0038] The value of S1 + S2 is smaller than the value of $-10 \times [\text{Mn}] + 44$, preferably less than 34 area %, more preferably 31 area % or less, even more preferably 25 area % or less, and particularly preferably, 21 area % or less, because the lower limit of the Mn content is 1%. The lower limit is also not particularly limited, and may be 0 area %, but industrially 5 area % or more, and practically 10 area % or more.

[0039] The value of S1 + S2 is smaller than the value of $-10 \times [\text{Mn}] + 44$. More specifically, $-10 \times [\text{Mn}] + 44 - (\text{S1} + \text{S2})$ is more than 0. Preferably, $-10 \times [\text{Mn}] + 44 - (\text{S1} + \text{S2})$ is 1.0 or more, and more preferably 2.0 or more. Preferably, $-10 \times [\text{Mn}] + 44 - (\text{S1} + \text{S2})$ is 10 or less, and more preferably 5.0 or less.

[Structure of steel sheet for quench hardening]

[0040] The structure of the steel sheet for quench hardening according to the present embodiment is described below.

[0041] Mn is poorly soluble in ferrite, so that too much formation of ferrite tends to cause segregation of Mn. Therefore, the area ratio of ferrite to the whole structure is preferably 50% or less. The area ratio of ferrite to the whole structure is more preferably less than 50%, even more preferably 45% or less, and even yet more preferably 30% or less. Additionally, the amount of ferrite is preferably smaller, and may be 0%. The area ratio of ferrite is measured by observing the position of 1/4 of the steel sheet thickness with an optical microscope or scanning electron microscope (SEM). Deposition of carbides may be found in ferrite particles, but in this case, the area ratio of ferrite including the carbides is measured, on the assumption that carbide is absent. More specifically, deposition of carbides will not change the area ratio of ferrite.

[0042] In the steel sheet for quench hardening, the main structure is preferably other than ferrite, and is preferably mainly composed of, for example, pearlite, bainite, and martensite (including auto-tempered martensite). As will be described later, the steel sheet for quench hardening is manufactured without tempering, so that tempered martensite is preferably 0%.

[Method for manufacturing steel sheet for quench hardening]

[0043] The method for manufacturing the steel sheet for quench hardening according to the present embodiment is described below.

[0044] Firstly, the steel having the above-described composition is hot-rolled. In the hot rolling, the steel sheet thus obtained is subjected to finish rolling in the austenite region, and then cooled at the average cooling rate [R] (°C/s) from the finish rolling temperature to the coiling temperature, and wound at the coiling temperature [T] (°C). After coiling, the steel sheet is kept at the temperature from the coiling temperature to the "coiling temperature - 50°C" for a period of [t] hour. The [R], [t], [T] must satisfy the following formula (2).

$$6.0 < 2 \times 10^4 \times (\ln[R] + 10) / ((\ln[t] + 70) \times [T]) \quad (2)$$

[0045] As the coiling temperature [T] increases, Mn tends to cause segregation. As the retention time [t] from the coiling temperature to the (coiling temperature - 50°C) increases, Mn tends to cause segregation. As the average cooling rate [R] from the finish rolling temperature to the coiling temperature decreases, Mn tends to cause segregation. The formula (2) was derived with reference to the relationship between the parameters [R], [t], and [T] and segregation of Mn, and the tempered parameter in continuous heating determined by the method described in "Toshihiro Tsuchiyama, Physical Meaning of Tempering Parameter and Its Application for Continuous Heating or Cooling Heat Treatment Process, Journal of The Japan society for heat treatment vol. 42, No. 3, P 163". The parameters in the formula (2) are described below in detail.

<Average cooling rate [R] (°C/s) from finish rolling temperature to coiling temperature>

[0046] When the cooling rate is low, ferrite is formed during cooling, and Mn which is poorly soluble in ferrite diffuses in untransformed austenite, which tends to cause segregation of Mn. Therefore, the average cooling rate [R] is preferably 10°C/s or more, and more preferably 15°C/s or more. The upper limit of the average cooling rate [R] is not particularly limited, but is industrially preferably 200°C/s or less, more preferably 100°C/s or less, and even more preferably 50°C/s or less.

[0047] The finish rolling temperature is not particularly limited as long as it is in the austenite region, but is preferably Ar_3 transformation temperature or higher, from the viewpoint of suppressing the increase in hot deformation resistance. In accordance with ordinary procedure, the temperature is preferably 950°C or lower, from the viewpoint of suppressing the occurrence of scales.

<Coiling temperature [T] (°C)>

[0048] If the coiling temperature is too high, untransformed austenite tends to occur, which promotes diffusion of Mn in the untransformed austenite, and can cause a nonuniform Mn concentration in the steel sheet. On the other hand, if the coiling temperature is too low, the steel sheet has too high strength, which impairs cold rolling properties. Therefore, the coiling temperature [T] is preferably 320°C or higher and 650°C or lower, and more preferably 350°C or higher and 600°C or lower.

<Retention time [t] (hour) from coiling temperature to "coiling temperature - 50°C">

[0049] Although depending on the coiling temperature, the retention time [t] in the above-described temperature range is preferably 15 hours or less, and more preferably 10 hours or less. If the retention time from the coiling temperature to "the coiling temperature - 50°C" tends to cause segregation of Mn. The lower limit of the retention time [t] is not particularly limited, but is industrially preferably 0.25 hours or more.

[0050] The above-described "retention" does not necessarily mean retention at the same temperature, and the temperature may vary within the above-described temperature range. For example, a constant temperature may be retained within the temperature range, or the temperature may change within this range, more specifically, the temperature may decrease, increase by heating, or increase by recuperation accompanied by transformation.

[0051] In the manufacturing method according to the present embodiment, the steel sheet is retained in the above-described temperature range for a predetermined time, and then cooled to room temperature. The cooling rate at that time is not particularly limited, and for example, air cooling may be used.

[Pickling, cold rolling]

[0052] After the hot rolling, the steel sheet is pickled as necessary, and cold-rolled at a cooling rate of about 30 to 80%.

[Plating]

[0053] After the hot rolling, the steel sheet may be subjected to plating, as long as the increase of the steel sheet temperature in the manufacturing process is 300°C or lower.

[Quench Hardened member]

[0054] A quench hardened member having a high intensity with hardness of 515 HV or more and marked T direction bendability is obtained by the manufacture using the steel sheet for quench hardening with suppressed segregation of Mn according to the present embodiment. Specifically, a quench hardened member having a high strength with hardness of 515 HV or more after quench hardening, and marked T direction bendability is obtained by quench hardening the steel sheet for quench hardening with suppressed segregation of Mn according to the present embodiment. The hardness of the quench hardened member is preferably 525 HV or more, and more preferably 535 HV or more. The upper limit of the hardness of the quench hardened member is not particularly limited, and, for example, 680 HV or less, preferably 650 HV or less, more preferably 600 HV or less, and even more preferably 570 HV or less.

[0055] For the quench hardened member, the value of the formula (5), which represents the relationship between the bend angle and the hardness, is preferably more than 0, and more preferably 5 or more. The bend angle is calculated by converting the displacement under the maximum load obtained in the bending test in T direction by the VDA standard (VDA238-100) defined by Verband der Automobilindustrie. When the value of the formula (5) is more than 0, it means that both of the hardness and the bend angle are high.

$$\text{Bend angle} - (-0.6 \times \text{hardness} + 376) \quad (5)$$

Generally, strength and bendability tend to be contrary to each other, and bendability decreases as the strength increases. However, the quench hardened member has high strength and high bendability.

[0056] The method for manufacturing a quench hardened member is described below.

[0057] For example, the method for manufacturing a quench hardened member when the steel sheet for quench hardening according to the present embodiment is used for hot press molding is not particularly limited, and may use a known method such as a die quench method. More specifically, the steel sheet for quench hardening is heated to a temperature to form an austenite single phase to increase the strength, and then subjected to press molding with a die with easier moldability. More specifically, the steel sheet for quench hardening according to the present embodiment is heated to a temperature of the A_{c3} point or more defined in the following formula (3), and then press molding of the steel sheet with a die is initiated. After initiation of the press molding, the steel sheet is cooled to the range of the M_s point defined by the formula (4) while keeping the average cooling rate of 20 to 300°C/s within the die.

$$A_{c3} (^{\circ}\text{C}) = 910 - 203 \times [\text{C}]^{1/2} + 44.7 \times [\text{Si}] - 30 \times [\text{Mn}] + 700 \times [\text{P}] + 400 \times [\text{Al}] + 400 \times [\text{Ti}] + 104 \times [\text{V}] - 11 \times [\text{Cr}] + 31.5 \times [\text{Mo}] - 20 \times [\text{Cu}] - 15.2 \times [\text{Ni}] \quad (3)$$

$$M_s (^{\circ}\text{C}) = 550 - 361 \times [\text{C}] - 39 \times [\text{Mn}] - 10 \times [\text{Cu}] - 17 \times [\text{Ni}] - 20 \times [\text{Cr}] - 5 \times [\text{Mo}] + 30 \times [\text{Al}] \quad (4)$$

[0058] The method for producing a quench hardened member when used for hot press molding is not particularly limited to the above-described method as long as the hardness of 515 HV or more is satisfied. For example, the steel sheet may be heated to a temperature at which an austenite single phase is formed, subjected to hot press molding, and then cooled such as air cooling.

[0059] Alternatively, the steel sheet for quench hardening according to the present embodiment is subjected to press molding other than hot pressing, and then quench hardened to make a quench hardened member. For example, when the steel sheet for quench hardening according to the present embodiment is subjected to hot press molding, the steel sheet is heated to about 200 to 700°C and hot-pressed, and then quench hardened with high frequency only in the portion requiring hardness, thus making a quench hardened member. When the steel sheet for quench hardening according to the present embodiment is subjected to cold press molding, the steel sheet is cold-pressed, and then quench hardened with high frequency only in the portion requiring hardness, thus making a quench hardened member.

[0060] The present specification discloses, as described above, techniques of various modes. Main techniques of them are summarized below.

[0061] One aspect of the present invention is a steel sheet for quench hardening having a composition satisfying, in terms of % by mass, C: more than 0.2% and 0.4% or less, Si: 0.8% or more and 1.4% or less, Mn: 1% or more and 3% or less, P: more than 0% and 0.02% or less, S: more than 0% and 0.002% or less, sol.Al: 0.02% or more and 0.06% or less, N: more than 0% and 0.01% or less, O: more than 0% and 0.01% or less, B: 0.0005% or more and 0.005% or less, and Ti: 0.005% or more and 0.1% or less, the balance being iron and unavoidable impurities, and the Mn concentration satisfying the following formula (1).

$$S1 + S2 < -10 \times [\text{Mn}] + 44(1)$$

[Mn]: Mn concentration in a steel sheet analyzed by inductively coupled plasma emission spectrography (% by mass)

S1: area % of the region where the Mn concentration analyzed by an electron beam microprobe analyzer in the structure at a position of 1/4 of the steel sheet thickness is two times or more the [Mn]

S2: area % of the region where the Mn concentration analyzed by an electron beam microprobe analyzer in the structure at a position of 1/4 of the steel sheet thickness is 0.5 times or less the [Mn]

[0062] In the steel sheet for quench hardening, the area ratio of ferrite at the position of 1/4 of the steel sheet thickness is preferably 0% or more and 50% or less.

[0063] The composition of the steel sheet for quench hardening preferably satisfies B: 0.001 % or more and 0.005% or less, in terms of % by mass.

[0064] The steel sheet for quench hardening preferably further contains at least one other element selected from the group consisting of Cr: more than 0% and 3% or less, Mo: more than 0% and 3% or less, Nb: more than 0% and 0.1% or less, and V: more than 0% and 0.1% or less, in terms of % by mass.

[0065] Another aspect of the present invention is a quench hardened member manufactured using the steel sheet for quench hardening, the quench hardened member having hardness of 515 HV or more and marked T direction bendability.

[0066] Another aspect of the present invention is a method for manufacturing the steel sheet for quench hardening, including finish rolling the steel sheet in the austenite region, followed by a process which satisfies the following formula (2).

$$6.0 < 2 \times 10^4 \times (\ln[R] + 10) / ((\ln[t] + 70) \times [T]) \quad (2)$$

[R]: average cooling rate from "finish rolling temperature" to "coiling temperature" (°C/s)

[t]: retention time (h) from "coiling temperature" to "coiling temperature - 50°C"

[T]: "coiling temperature" (°C)

[0067] In the method for manufacturing steel sheet for quench hardening, the average cooling rate R is preferably 10°C/s or more and 200°C/s or less.

[0068] In the method for manufacturing steel sheet for quench hardening, the retention time t is preferably 0.25 hours or more and 15 hours or less.

[0069] In the method for manufacturing steel sheet for quench hardening, the coiling temperature T is preferably 320°C or higher and 650°C or lower.

[0070] According to the present invention, the use of the steel sheet for quench hardening allows to provide a quench hardened member having marked T direction bendability, even if the hardness after quench hardening is in a high strength region of 515 HV or more.

Examples

[0071] The present invention is further specifically described below with reference to examples, but the present invention is not limited to the following examples, and may be appropriately modified within the range which complies with the above- and below-described scopes, and such modification is included in the technical range of the present invention.

[Experiment No. 1]

[0072] The steel having the composition given in Table 1 (the balance is composed of iron and unavoidable impurities, the empty sections in Table 1 indicate no addition of an element) is ingoted, subjected to the below-described hot rolling, thus obtaining a hot rolled steel sheet. Thereafter, the surface of the steel sheet was ground, thus obtaining a steel sheet for quench hardening having a thickness of 1.4 mm.

[Table 1]

Steel type	C	Si	Mn	P	S	sol.Al	N	O	B	Cr	Ti	Nb	V
A1	0.265	1.21	2.23	0.0010	0.0014	0.039	0.0044	0.0005	0.0018		0.020		
A2	0.266	1.18	2.25	0.0030	0.0015	0.041	0.0039	0.0005	0.0020		0.020	0.048	
A3	0.269	1.21	2.26	0.0040	0.0014	0.040	0.0034	0.0004	0.0021		0.049		
A4	0.268	1.20	2.27	0.0020	0.0015	0.039	0.0034	0.0005	0.0013		0.020		0.053
A5	0.264	1.21	2.28	0.0005	0.0013	0.039	0.0049	0.0004	0.0017		0.020		
A6	0.266	1.19	1.21	0.0040	0.0012	0.041	0.0035	0.0005	0.0018		0.020		
A7	0.267	1.21	1.24	0.0040	0.0011	0.040	0.0040	0.0006	0.0022	0.63	0.020		
A8	0.268	0.02	1.21	0.0020	0.0012	0.039	0.0044	0.0012	0.0020	0.23	0.020		
A9	0.268	0.20	1.22	0.0030	0.0013	0.041	0.0040	0.0006	0.0018	0.23	0.020		
B1	0.315	1.24	1.20	0.0030	0.0010	0.041	0.0041	0.0006	0.0015		0.021		
B2	0.326	1.21	1.21	0.0040	0.0010	0.041	0.0045	0.0009	0.0017		0.020		
B3	0.297	1.21	1.79	0.0020	0.0010	0.040	0.0039	0.0005	0.0016		0.020		
B4	0.323	1.21	1.49	0.0040	0.0010	0.040	0.0041	0.0006	0.0016		0.020		

[Hot rolling]

[0073] A slab was heated to 1250°C, and hot-rolled to a sheet thickness of 2.3 mm at a rolling reduction rate of 90% and the "finish rolling temperature (°C)" given in Table 2. Thereafter, the steel sheet thus obtained was cooled from the above-described temperature to the "coiling temperature (°C)" given in Table 2 at the "average cooling rate (°C/s)" given in Table 2, wound, and then kept at the temperature from "the coiling temperature - 50(°C)" to "coiling temperature (°C)" for a period of "retention time (h)" given in Table 2. Subsequently, the steel sheet was air-cooled to room temperature, thus manufacturing a hot rolled steel sheet.

[Experiment Nos. 6, 11, 17, and 22]

[0074] A steel sheet for quench hardening was obtained in the same manner as in Experiment No. 1, except that the composition, finish rolling temperature, average cooling rate, coiling temperature, and retention time were changed to the conditions given in Tables 1 and 2.

[Experiment Nos. 2 to 5, 7 to 10, 12 to 16, 18 to 21, and 23 to 26]

[0075] A hot rolled steel sheet was obtained in the same manner as in Experiment No. 1, except that the composition, finish rolling temperature, average cooling rate, coiling temperature, and retention time were changed to the conditions given in Tables 1 and 2. Thereafter, the hot rolled steel sheet thus obtained was pickled to remove scales from the surface, and then cold-rolled, thus manufacturing a cold rolled steel sheet having a sheet thickness of 1.4 mm, and obtaining a steel sheet for quench hardening.

[0076] The steel sheets for quench hardening of Experiment Nos. 1 to 26 were, as specified below, measured for the metal structures and the Mn concentration. Additionally, the steel sheets for quench hardening of Experiment Nos. 1 to 26 were subjected to the below-described quench hardening test to obtain quench hardened members, and these quench hardened members were evaluated for various mechanical properties as specified below, and the results are given in Table 2.

[Area ratio of ferrite]

[0077] The steel sheet for quench hardening was polished at the cross section in the L direction (parallel to rolling direction), and then corroded with nital. Thereafter, the position at 1/4 of the steel thickness was observed in three visual fields with an optical microscope at a magnification of 1000 times (100 μm × 100 μm size/field), the area ratio of ferrite was measured by the point counting at a lattice spacing of 5 μm and a lattice point number of 20 × 20, and the average of the three visual fields was calculated.

[Concentration distribution of Mn]

[0078] The concentration distribution of Mn was rated using the formula (1) based on the following criterion, and those rated A were passed, and those rated as B were rejected. The method for measuring [Mn] and the method for calculating S1 + S2 are as described below.

$$S1 + S2 < -10 \times [Mn] + 44 \quad (1)$$

[Mn]: Mn concentration in a steel sheet analyzed by inductively coupled plasma emission spectrography (% by mass)
 S1: area % of the region where the Mn concentration analyzed by an electron beam microprobe analyzer in the structure at a position of 1/4 of the steel sheet thickness is two times or more the [Mn]
 S2: area % of the region where the Mn concentration analyzed by an electron beam microprobe analyzer in the structure at a position of 1/4 of the steel sheet thickness is 0.5 times or less the [Mn]

(Evaluation criteria)

[0079]

A: the formula (1) is satisfied (the value of $S1 + S2$ is less than the value of $-10 \times [Mn] + 44$)

B: the formula (1) is not satisfied (the value of $S1 + S2$ is not less than the value of $-10 \times [Mn] + 44$)

(Method for measuring [Mn])

[0080] A sample with a dimension of 30 mm $\times$ 100 mm was cut out from the center portion in the width direction of the steel sheet for quench hardening. The sample thus cut out was pulverized, the powder thus obtained was dissolved in a mixed acid solution composed of hydrochloric acid and nitric acid, and then the solution was chemically analyzed by coupled plasma emission spectroscopy using an inductively coupled plasma emission spectrometer (ICPV-1017, SHIMADZU CORPORATION), thus obtaining [Mn].

(Method for calculating $S1 + S2$)

[0081] The steel sheet for quench hardening was cut at the cross section in the L direction and embedded in a resin, and the cross section was polished. Thereafter, at the position of 1/4 of the steel sheet thickness, the Mn concentration was measured in the region of about 120 $\mu\text{m} \times 95 \mu\text{m}$ using an electron beam microprobe analyzer (electron probe micro analyzer: EPMA, JXA-8100 Series, manufactured by JEOL Ltd.) under conditions that the beam diameter was about 5 μm . The specific setting in the EPMA apparatus was as follows.

[0082] Measurement area X: 300 point Y: 240 point

Feed: 0.4 μm

Beam diameter setting: zero

Fetching time: 20 msec/point

Electron beam accelerating voltage: 15 kV

Irradiation current: $1 \times 10^{-6}\text{A}$ (1 μA)

[0083] Subsequently, the Mn concentration at each point measured in the above-described conditions was divided by [Mn], and the number of points where the Mn concentration is two times or more the [Mn] and the number of points where the Mn concentration is 0.5 times or less the [Mn] were determined. Additionally, the total of the number of points where the Mn concentration is two times or more the [Mn] and the number of points where the Mn concentration is 0.5 times or less the [Mn] was divided by the total number of measured points (300 $\times$ 240 points), thus calculating $S1 + S2$ (area %).

[Quench Hardening test]

[0084] The quench hardening test was carried out under the following conditions by a die quench method using a simulated die.

[0085] Steel temperature of steel sheet for quench hardening: 900°C

Heating time: 100 seconds

Cooling time: about 15 seconds

Die quenching initiation temperature: 700°C

Die quenching load: 2000 kgf

Retention time of bottom dead center of molding: 30 seconds

[Evaluation of scale adhesion]

[0086] The molded article (quench hardened member) after the quench hardening test was cooled naturally to ordinary temperature with the molded article evacuated from the die, the surface of the quench hardened member was observed visually, and the presence or absence of peeling of scales was examined. In the present examples, the proportion of the area with scale peeling to the surface area of the quench hardened member was calculated, and evaluated by the following criterion.

(Evaluation criteria)

[0087] Pass (○): the area with scale peeling was less than 15% of the surface area of quench hardened member
Failure (×): the area with scale peeling was not less than 15% of the surface area of quench hardened member

[Hardness]

[0088] The Vickers hardness (HV) of the quench hardened member was measured by the method described in JIS Z 2244.

[Evaluation of T direction bendability in consideration of hardness]

[0089] T direction bendability of the quench hardened member was evaluated under the following measurement conditions based on the VDA standard (VDA 238-100) defined in Verband der Deutschen Automobilindustrie. In the present Examples, the displacement under the maximum load obtained in the bending test was converted to an angle based on the VDA standard, thus obtaining the bend angle. In general, there is a correlation that the bend angle decreases as the hardness of the quench hardened member increases, so that the T direction bendability was evaluated based on the size of the bend angle to the hardness of the quench hardened member. Specifically, the T direction bendability was rated by the value of the formula (5) based on the following criterion, and those rated as A were passed (○), and those rated as B were rejected (×). The relationship between the hardness [hardness (HV) after quench hardening] and the bend angle [bend angle (°) after quench hardening] of each quench hardened member is given in Fig. 1.

$$\text{Bend angle} = (-0.6 \times \text{hardness} + 376) \quad (5)$$

(Evaluation criteria)

[0090]

A: the value of the formula (5) is more than 0 (the value of the bend angle is more than the value of $-0.6 \times \text{hardness} + 376$)

B: the value of the formula (5) is 0 or less (the value of the bend angle is not more than the value of $-0.6 \times \text{hardness} + 376$)

(Measurement conditions)

[0091] Test method: roll support, punch push-in

Roll diameter: ϕ 30 mm

Punch shape: tip R = 0.4 mm

Distance between rolls: 3.5 mm

Push-in speed: 20 mm /min

Test piece dimension: 60 mm $\times$ 60 mm

Bend direction: right angle to rolling direction

Testing machine: AUTOGRAPH 20 kN manufactured by SHIMADZU CORPORATION.

[Table 2]

Experiment No.	Steel type	Finish-rolling temperature (°C)	Average cooling rate [R] (°C/s)	Coiling temperature [T] (°C)	Retention time [t] (h)	Formula (2) right side	S1 + S2 (area %) (formula (1) left side)	Formula (1) right side	Formula (1) right side left side	ferrite (area %)	Hardness after quench hardening (HV)	Bend test angle (°)	Value of formula (5)	Bendability	Scale adhesion
1	A1	925	30	350	0.5	11.0	20.7	21.7	1.0	0	563	47.1	8.9	○	○
2	A1	880	15	650	3	5.5	24.5	21.7	-2.8	56	538	45.6	-7.6	×	○
3	A1	840	15	600	10	5.9	22.5	21.7	-0.8	48	545	40.8	-8.2	×	○
4	A1	880	15	586	3	6.1	19.5	21.7	2.2	45	551	52.6	7.2	○	○
5	A2	920	30	658	0.5	5.9	27.7	21.5	-6.2	55	552	37.6	-7.2	×	○
6	A2	900	30	395	0.5	9.8	20.6	21.5	0.9	12	553	45.6	1.4	○	○
7	A2	928	15	680	3	5.3	28.9	21.5	-7.2	61	532	52.5	-4.3	×	○
8	A3	924	30	420	0.5	9.2	17.1	21.4	4.3	33	554	53.0	9.4	○	○
9	A3	880	40	648	0.5	6.1	20.8	21.4	0.6	50	529	62.8	4.2	○	○
10	A4	900	30	655	0.5	5.9	22.0	21.3	-0.7	55	531	47.1	-10.3	×	○
11	A4	914	30	350	0.5	11.0	19.0	21.3	2.3	38	542	52.7	1.9	○	○
12	A5	870	30	658	0.5	5.9	23.4	21.2	-2.2	60	550	40.3	-5.7	×	○
13	A6	890	30	650	0.5	5.9	33.7	31.9	-1.8	78	529	52.0	-6.6	×	○
14	A6	930	15	550	5	6.5	30.8	31.9	1.1	44	535	62.9	7.9	○	○
15	A6	935	15	450	10	7.8	30.8	31.9	1.1	23	543	55.8	5.6	○	○
16	A7	912	30	651	0.5	5.9	32.2	31.6	-0.6	33	536	53.6	-0.8	×	○
17	A7	916	30	331	0.5	11.7	30.6	31.6	1.0	0	545	56.5	7.5	○	○
18	A7	915	20	600	3	6.1	28.5	31.6	3.1	19	536	60.2	5.8	○	○
19	A8	930	20	600	0.5	6.3	33.7	31.9	-1.8	38	511	63.0	-6.4	×	×
20	A8	940	30	540	0.5	7.2	30.7	31.9	1.2	24	489	63.6	-19.0	×	×
21	A9	894	20	600	0.5	6.3	31.8	31.8	0.0	28	506	64.1	-8.3	×	×
22	A9	892	30	380	0.5	10.2	30.0	31.8	1.8	0	490	68.2	-13.8	×	×

(continued)

Experiment No.	Steel type	Finish-rolling temperature (°C)	Average cooling rate [R] (°C/s)	Coiling temperature [T] (°C)	Retention time [t] (h)	Formula (2) right side	S1 + S2 (area %) (formula (1) left side)	Formula (1) right side	Formula (1) right side left side	ferrite (area %)	Hardness after quench hardening (HV)	Bend test angle (°)	Value of formula (5)	Bendability	Scale adhesion
23	B1	920	30	625	3	6.0	27.1	32.0	4.9	29	565	49.5	12.2	○	○
24	B2	920	30	600	5	6.2	27.9	31.9	4.0	37	598	44.4	27.0	○	○
25	B3	920	30	625	3	6.0	24.5	26.1	1.6	25	558	47.8	6.5	○	○
26	B4	920	30	625	3	6.0	26.2	29.1	2.9	11	582	45.4	18.4	○	○

[0092] Tables 1 and 2 allow the following discussions.

[0093] The experiments in Table 2 manufactured under the manufacturing conditions which satisfy the formula (2) using the steel types A1 to A7 and B1 to B4 in Table 1 which satisfy the composition of the present invention (Experiment Nos. 1, 4, 6, 8, 9, 11, 14, 15, 17, 18, and 23 to 26) satisfy the formula (1), and the quench hardened members had marked T direction bendability even they had a high strength of 515 HV or more, and also had marked scale adhesion.

[0094] On the other hand, the steel sheets other than the above-described ones did not satisfy the composition nor manufacturing conditions defined in the present invention as described below in detail, and did not achieve desired properties.

[0095] Experiment Nos. 2, 3, 5, 7, 10, 12, 13, and 16 manufactured under the manufacturing conditions which does not satisfy the formula (2) did not satisfy the formula (1), and had poor T direction bendability of the quench hardened member.

[0096] In the steel types A8 and A9 in Table 1, the Si content was less than the lower limit (0.8%) defined in the present invention, so that Experiment Nos. 19 to 22 gave insufficient hardness of the quench hardened member, and T direction bendability of the quench hardened member and scale adhesion were also poor.

[0097] The present application is based on Japanese Patent Application No. 2016-037635 filed on February 29, 2016 and Japanese Patent Application No. 2016-207673 filed on October 24, 2016, and these contents are included in the present application.

[0098] In order to describe the present invention, the present invention is appropriately and thoroughly described above with reference to drawings throughout the embodiments, but it should be appreciated that these embodiments can be altered and/or improved by those skilled in the art. Accordingly, as long as the altered embodiments or improved embodiments made by those skilled in the art are not on the level at which the embodiments departs from the scope of claims, the altered embodiments or improved embodiments are interpreted as included in the scope of claims.

Industrial Applicability

[0099] According to the present invention, a quench hardened member having marked T direction bendability is provided by the use of the above-described steel sheet for quench hardening, even if the hardness after quench hardening is in a high strength region of 515 HV or more.

Claims

1. A steel sheet for quench hardening, the steel sheet having a composition of, in terms of % by mass,
C: more than 0.2% and 0.4% or less,
Si: 0.8% or more and 1.4% or less,
Mn: 1% or more and 3% or less,
P: more than 0% and 0.02% or less,
S: more than 0% and 0.002% or less,
sol.Al: 0.02% or more and 0.06% or less,
N: more than 0% and 0.01% or less,
O: more than 0% and 0.01% or less,
B: 0.0005% or more and 0.005% or less, and
Ti: 0.005% or more and 0.1% or less,
a balance being iron and unavoidable impurities, and a Mn concentration satisfying the following formula (1):

$$S1 + S2 < -10 \times [Mn] + 44 \quad (1)$$

where

[Mn] is Mn concentration in a steel sheet analyzed by inductively coupled plasma emission spectrography (% by mass),

S1 is an area % of the region where the Mn concentration analyzed by an electron beam microprobe analyzer in structure at a position of 1/4 of the steel sheet thickness is two times or more the [Mn],

S2 is an area % of the region where the Mn concentration analyzed by an electron beam microprobe analyzer in structure at a position of 1/4 of the steel sheet thickness is 0.5 times or less the [Mn].

2. The steel sheet for quench hardening according to claim 1, wherein an area ratio of ferrite at a position of 1/4 of the steel sheet thickness is 0% or more and 50% or less.
3. The steel sheet for quench hardening according to claim 1, wherein the composition satisfies
B: 0.001% or more and 0.005% or less, in terms of % by mass.
4. The steel sheet for quench hardening according to claim 1, wherein the composition further comprises at least another element selected from the group consisting of
Cr: more than 0% and 3% or less,
Mo: more than 0% and 3% or less,
Nb: more than 0% and 0.1% or less, and
V: more than 0% and 0.1% or less, in terms of % by mass.
5. A quench hardened member manufactured using the steel sheet for quench hardening according to any one of claims 1 to 4, the quench hardened member having hardness of 515 HV or more and marked T direction bendability.
6. A method for manufacturing steel sheet for quench hardening according to any one of claims 1 to 4, the method comprising
finish rolling in an austenite region to carry out a process satisfying the following formula (2):

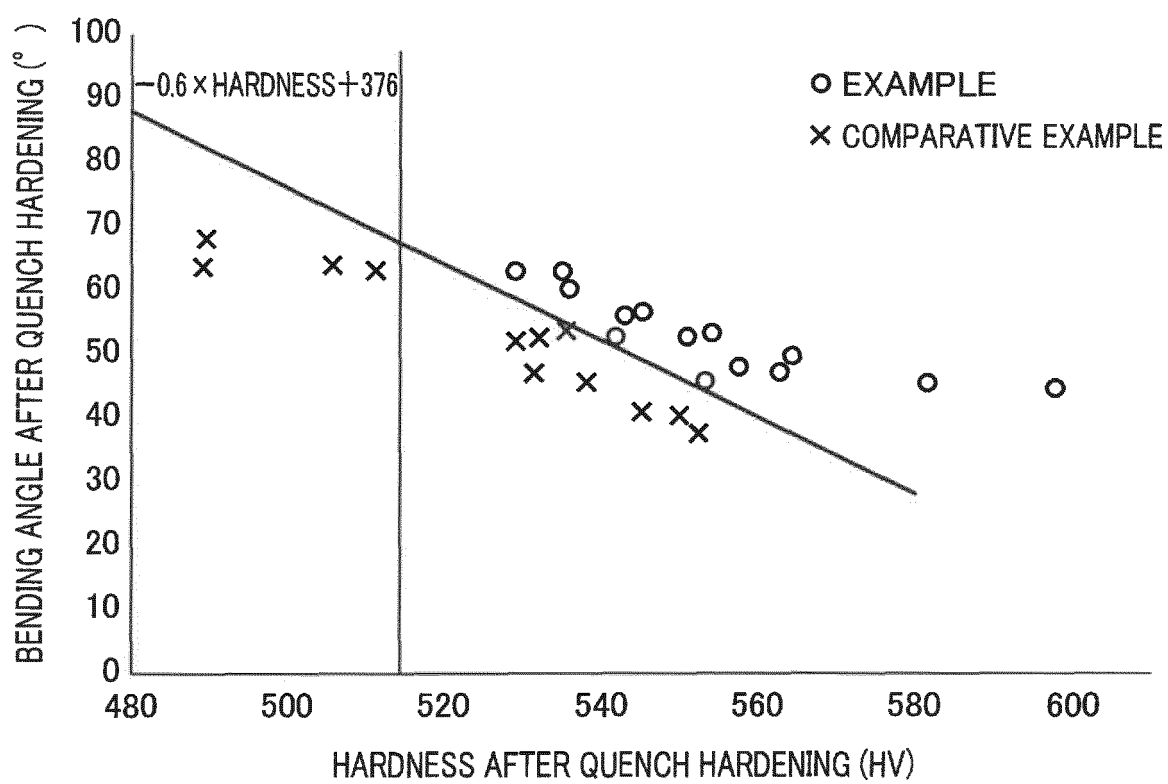
$$6.0 < 2 \times 10^4 \times (\ln[R] + 10) / ((\ln[t] + 70) \times [T]) \quad (2)$$

where

[R] is average cooling rate from "finish rolling temperature" to "coiling temperature" (°C/s),
[t] is retention time (h) from "coiling temperature" to "coiling temperature - 50°C",
[T] is "coiling temperature" (°C).

7. The method for manufacturing steel sheet for quench hardening according to claim 6, wherein the average cooling rate is 10°C/s or more and 200°C/s or less.
8. The method for manufacturing steel sheet for quench hardening according to claim 6, wherein the retention time is 0.25 hours or more and 15 hours or less.
9. The method for manufacturing steel sheet for quench hardening according to claim 6, wherein the coiling temperature is 320°C or higher and 650°C or lower.

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2017/002186

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/00(2006.01)i, C21D9/46(2006.01)i, C22C38/14(2006.01)i, C22C38/38(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, C21D9/46, C22C38/14, C22C38/38

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 1996-2017
Kokai Jitsuyo Shinan Koho 1971-2017 Toroku Jitsuyo Shinan Koho 1994-2017

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2013-185243 A (Kobe Steel, Ltd.), 19 September 2013 (19.09.2013), claims; examples & US 2015/0090377 A1 claims; examples & WO 2013/133165 A1 & EP 2824204 A1 & CN 104160051 A	1-9
X	JP 2013-185247 A (Kobe Steel, Ltd.), 19 September 2013 (19.09.2013), claims; examples (Family: none)	1-9
A	JP 2008-169475 A (Kobe Steel, Ltd.), 24 July 2008 (24.07.2008), & US 2010/0080728 A1 & WO 2008/072600 A1 & EP 2105514 A1 & CN 101541992 A	1-9

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

* Special categories of cited documents:

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search
28 February 2017 (28.02.17)

Date of mailing of the international search report
14 March 2017 (14.03.17)

Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2017/002186

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	JP 2009-263685 A (Nippon Steel Corp.), 12 November 2009 (12.11.2009), (Family: none)	1-9

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

REFERENCES CITED IN THE DESCRIPTION

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- JP 2016207673 A [0097]

Non-patent literature cited in the description

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