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(54) **MARTENSITE-BASED STAINLESS STEEL MATERIAL AND METHOD FOR PRODUCING SAME**

(57) A martensite-based stainless steel material has a composition containing: 0.30 to 0.60% by mass of C; 0.05 to 1.00% by mass of Si; 0.05 to 1.50% by mass of Mn; 0.040% by mass or less of P; 0.030% by mass or less of S; 13.0 to 18.0% by mass of Cr; 0.01 to 0.30% by mass of Ni; 0.01 to 1.00% by mass of Mo; 0.030% by mass or less of Al; 0.010 to 0.350% by mass of N; 0.0001

to 0.0030% by mass of Ca; and 0.001 to 0.010% by mass of O; 2.5C + N being 1.10% or more, and the balance being Fe and impurities. The martensite-based stainless steel material has an average grain diameter of carbides of 0.50 μm or less. Also, the number of the carbides having a size of 10 μm or more is 0.20/cm² or less.

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Description

FIELD OF THE INVENTION

5 **[0001]** The present invention relates to a martensite-based stainless steel material and a method for producing the same.

BACKGROUND OF THE INVENTION

10 **[0002]** Stainless steel materials used for various cutting tools such as shavers, scissors, and kitchen knives require high hardness. Therefore, a martensite-based stainless steel material having a higher C content is used (for example, Patent Literature 1).

[0003] However, the higher C content results in production of carbides with alloy elements such as Cr, which tend to be deposited as coarse eutectic carbides during the production step. Complete solutionizing of the eutectic carbides is difficult even by an annealing step or the like, which will decrease a solid solution amount of C during quenching and cause excessive softening. Further, the eutectic carbides serve as starting points for corrosion, resulting in a decrease in corrosion resistance and causing nicks and irregular patterns during processing.

[0004] Therefore, Patent Literature 2 proposes a martensite-based stainless steel material for cutlery, wherein the martensite-based stainless steel material contains 0.40 to 0.50% by mass of C; 0.05 to 0.60% by mass of Si; 0.5 to 1.5% by mass of Mn; 0.035 % or less of P; 0.010% or less of S; 11.0 to 15.5% by mass of Cr; 0.01 to 0.30% by mass of Ni; 0.01 to 0.30% by mass of Cu; 0.01 to 0.30% by mass of Mo; 0.01 to 0.10% by mass of V; 0.02% or less by mass of Al; 0.002 to 0.10% by mass of Sn; 0.010 to 0.035% by mass of N; 0.0001 to 0.0010% by mass of Ca; 0.001 to 0.01% by mass of O, the balance being Fe and unavoidable impurities, and wherein the martensite-based stainless steel material satisfies $Cu + Ni + Mo = 0.05$ to 0.30%, and wherein the number of inclusions having a size of 10 μm or more is 0.2/cm² or less.

[0005] Further, Patent Literature 3 propose a method for producing a grain-refined martensite-based stainless steel material, the method comprising the steps of: preparing a substrate having a composition comprising 13.0 to 14.0% by weight of Cr; 1.15 to 1.35% by weight of Mo; 0.35 to 0.55% by weight of C; 0.20 to 0.50% by weight of Si; 0.20 to 0.50% by weight of Mn; 0.025% by weight or less of P; 0.020% by weight or less of S, the balance being Fe and unavoidable impurity elements; subjecting the substrate to at least one of a high-density dislocation generation process and an ultra-rapidly solidification process, followed by annealing to obtain a ferrite steel having a fine structure; subjecting the ferrite steel to cold rolling, annealing, and optionally plastic working into a predetermined shape, followed by quenching to obtain a grain-refined martensite-based stainless steel material.

PRIOR ART

Patent Literatures

[0006]

[Patent Literature 1] Japanese Patent Application Publication No. 2000-2735877 A

[Patent Literature 2] Japanese Patent Application Publication No. 2018-9231 A

[Patent Literature 3] Japanese Patent Application Publication No. 2003-313612 A

SUMMARY OF THE INVENTION

Problem to be Solved by the Invention

50 **[0007]** However, in the martensite-based stainless steel material as described in Patent Literature 2, an average grain diameter of inclusions (especially carbides) is not controlled, so that workability may be insufficient and irregular patterns may be generated.

[0008] Further, the martensite-based stainless steel material as described in Patent Literature 3 is not suitable for mass production because special steps such as the high-density dislocation generation process and the ultra-rapidly solidification process are introduced. Furthermore, this martensite-based stainless steel material has a higher Mo content and is expensive.

[0009] Such conventional martensite-based stainless steel materials with a reduced C content have the above problems.

[0010] The present invention has been made to solve the above problems. An object of the present invention is to

provide a martensite-based stainless steel material, which has good workability, has higher hardness and corrosion resistance after quenching or quenching and tempering, and can suppress generation of irregular patterns, and a method for producing the same.

5 Means for Solving the Problem

[0011] As a result of intensive studies for martensite-based stainless steel materials, the inventors of the present invention have found that among inclusions, in particular, carbides are closely related to corrosion resistance, workability, and irregular patterns, and that all of the above problems can be solved by controlling the number of carbides having a size of 10 μm or more and the average grain diameter of the carbides, and they have completed the present invention.

[0012] Thus, the present invention relates to a martensite-based stainless steel material having a composition comprising: 0.30 to 0.60% by mass of C; 0.05 to 1.00% by mass of Si; 0.05 to 1.50% by mass of Mn; 0.040% by mass or less of P; 0.030% by mass or less of S; 13.0 to 18.0% by mass of Cr; 0.01 to 0.30% by mass of Ni; 0.01 to 1.00% by mass of Mo; 0.030% by mass or less of Al; 0.010 to 0.350% by mass of N; 0.0001 to 0.0030% by mass of Ca; and 0.001 to 0.010% by mass of O; 2.5C + N being 1.10% or more, and the balance being Fe and impurities,

wherein the martensite-based stainless steel material has an average grain diameter of carbides of 0.50 μm or less, and

wherein the number of the carbides having a size of 10 μm or more is 0.20/cm² or less.

[0013] The present invention also relates to a method for producing a martensite-based stainless steel material, wherein the method comprises a hot rolling step of subjecting a slab to a heat treatment at a temperature equal to or higher than T represented by the following equation (1) for 1 to 5 hours, and then subjecting the slab to hot rolling:

$$T [^{\circ}\text{C}] = 6500 / (4 - \log C [\%]) - 273 \quad (1),$$

wherein the slab has a composition comprising: 0.30 to 0.60% by mass of C; 0.05 to 1.00% by mass of Si; 0.05 to 1.50% by mass of Mn; 0.040% by mass or less of P; 0.030% by mass or less of S; 13.0 to 18.0% by mass of Cr; 0.01 to 0.30% by mass of Ni; 0.01 to 1.00% by mass of Mo; 0.030% by mass or less of Al; 0.010 to 0.350% by mass of N; 0.0001 to 0.0030% by mass of Ca; and 0.001 to 0.010% by mass of O; 2.5C + N being 1.10% or more, and the balance being Fe and impurities.

Effects of Invention

[0014] According to the present invention, it is possible to provide a martensite-based stainless steel material, which has good workability, has higher hardness and corrosion resistance after quenching or quenching and tempering, and can suppress generation of irregular patterns, and a method for producing the same.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] FIG. 1 is a graph showing a relationship between 2.5C + N and hardness in Examples and Comparative Examples.

DETAILED DESCRIPTION OF THE INVENTION

[0016] Hereinafter, embodiments of the present invention will be specifically described. It is to understand that the present invention is not limited to the following embodiments, and those which have appropriately added changes, improvements and the like to the following embodiments based on knowledge of a person skilled in the art without departing from the spirit of the present invention fall within the scope of the present invention.

[0017] It should be noted that, as used herein, the expression "%" in relation to any component means "% by mass", unless otherwise specified.

[0018] A martensite-based stainless steel material according to an embodiment of the present invention has a composition containing: 0.30 to 0.60% by mass of C; 0.05 to 1.00% by mass of Si; 0.05 to 1.50% by mass of Mn; 0.040% by mass or less of P; 0.030% by mass or less of S; 13.0 to 18.0% by mass of Cr; 0.01 to 0.30% by mass of Ni; 0.01 to 1.00% by mass of Mo; 0.030% by mass or less of Al; 0.010 to 0.350% by mass of N; 0.0001 to 0.0030% by mass of Ca; and 0.001 to 0.010% by mass of O; 2.5C + N being 1.10% or more, and the balance being Fe and impurities.

[0019] As used herein, the term "steel material" means materials having various shapes such as steel sheets. Further,

the term "steel sheet" is a concept including a steel strip. Furthermore, the term "impurities" refers to components contaminated due to various factors of raw materials such as ores and scraps, and the production steps, during the industrial production of stainless steel materials, which are permissible within a range that does not adversely affect the present invention. Examples of the impurities include Zn, Pb, Se, Sb, H, Ga, Ta, Mg, Zr, and the like. When these elements are contained as impurities, $Zn \leq 100$ ppm, $Pb \leq 100$ ppm, $Se \leq 100$ ppm, $Sb \leq 500$ ppm, $H \leq 100$ ppm, $Ga \leq 500$ ppm, $Ta \leq 500$ ppm, $Mg \leq 120$ ppm, and $Zr \leq 120$ ppm.

[0020] Further, the martensite-based stainless steel material according to the embodiment of the present invention may further contain at least one of: 0.50% or less of V; 0.30% or less of Nb; 0.3% or less of Ti; 4.0% or less of Cu; 0.100% or less of Sn; 0.0050% or less of B; and 0.30% or less of Co.

[0021] Each component will be described in detail below.

<0.30 to 0.60% of C>

[0022] C is an essential element for obtaining a predetermined hardness (Vickers hardness) after quenching or quenching and tempering. In order to stably obtain a hardness of 500 HV or more, the C content should be 0.30% or more. Excessive addition of C promotes sensitization during quenching and impairs corrosion resistance, and non-solid solution carbonitrides also reduce toughness after quenching or tempering. Therefore, the C content should be 0.6% or more. In view of a decrease in hardness and toughness due to variations in heating conditions during quenching or quenching and tempering, the C content preferably has a lower limit of 0.32% and an upper limit of 0.58%.

<0.05 to 1.00% of Si>

[0023] Si is required for deoxidization during melting and refining, as well as Si is also a useful element for suppressing the formation of oxide scales during quenching. Further, when the Si content is lower, deoxidation tends to be insufficient and more carbides are generated, which may be the starting points for rusting, resulting in a decrease in corrosion resistance. Therefore, the Si content should be 0.05% or more. On the other hand, Si narrows an austenite single-phase temperature range and impairs quenching stability. Therefore, the Si content should be 1.00% or less. From the viewpoint of stably obtaining the above effects of Si, the Si content preferably has a lower limit of 0.07% and an upper limit of 0.98%.

<0.05 to 1.50% of Mn>

[0024] Mn is an element added as a deoxidizing agent, and also expands the austenite single-phase region to contributes to improvement of hardenability. If sufficient Mn is not added, two-phase region expands and an alpha phase increases. As a result, Cr carbonitrides also increase, and Cr-deficient layers are formed around them, so that they tend to be starting points for rusting and decrease corrosion resistance. Therefore, the Mn content should be 0.05% or more. From the standpoint of stably obtaining the above effects of Mn, the Mn content preferably have a lower limit of 0.07%. On the other hand, excessive Mn decreases the corrosion resistance, promotes the formation of oxide scales during quenching, and increases the subsequent polishing load. Therefore, the Mn content should be 1.50% or less. In view of the deterioration of corrosion resistance due to granules such as MnS, the Mn content is preferably 1.45% or less.

<0.040% or less of P>

[0025] P is an element contained as an impurity in a main raw material such as a molten iron and ferrochromium. It is an element harmful to the toughness and corrosion resistance of hot-rolled annealed sheets and quenched materials. Therefore, the P content should be 0.040% or less, and preferably 0.038% or less. On the other hand, the lower limit of the P content is not particularly limited. However, excessive reduction causes problems that the use of high-purity raw materials is required, leading to an increase in costs. Therefore, the lower limit of the P content is preferably 0.010%.

<0.030% or less of S>

[0026] S forms sulfide inclusions and deteriorates general corrosion resistance of steel (general corrosion and pitting corrosion). Moreover, S decreases hot workability and increases susceptibility to edge cracking of a hot-rolled sheet. Therefore, the S content should be 0.030% or less, and preferably 0.025% or less. The lower limit of the S content is not particularly limited, but a lower S content provides a better the corrosion resistance, while it increases a desulfurization load to increase the production cost. Therefore, the lower limit of the S content is preferably 0.001%.

<13.0 to 18.0% of Cr>

[0027] Cr is an element for maintaining the corrosion resistance required for the main application of the martensite-based stainless steel material. Therefore, the Cr content should be 13.0% or more. On the other hand, from the viewpoint of suppressing the formation of retained austenite after quenching, the Cr content should be 18.0% or less. From the viewpoint of stably obtaining the above effects of Cr, the Cr content preferably has a lower limit of 13.1% and an upper limit of 17.8%.

<0.01 to 0.30% of Ni>

[0028] As with Mn, Ni is an austenite stabilizing element and also has an effect of improving the toughness after quenching or quenching and tempering. On the other hand, when a large amount of Ni is contained, a press formability of a hot-rolled annealed sheet may be deteriorated due to solid-solution strengthening, and the production cost increases since Ni is an expensive element. Therefore, the Ni content should be 0.30% or less. On the other hand, Ni is an element effective for suppressing the progression of pitting corrosion. From the viewpoint of stably obtaining the above effects of Ni, the Ni content preferably has a lower limit of 0.02% and an upper limit of 0.27%.

<0.01 to 1.00% of Mo>

[0029] Mo is an element effective for improving the corrosion resistance of the martensite structure containing δ ferrite. From the viewpoint of obtaining the effect, the Mo content should be 0.01% or more. On the other hand, Mo is an element for stabilizing the ferrite phase, and excessive addition narrows the austenite single-phase temperature range, thereby impairing the hardenability. Therefore, the Mo content should be 1.00% or less. From the viewpoint of stably obtaining the above effects of Mo, the Mo content preferably has a lower limit of 0.02% and an upper limit of preferably 0.50%, and more preferably 0.30%.

<0.030% or less of Al>

[0030] In addition to being added as a deoxidizing element, Al is an element that improves oxidation resistance. However, when a large amount of Al is contained, the carbides tend to become large. Therefore, the Al content should be 0.030% or less, and preferably 0.025% or less, and more preferably 0.020% or less. On the other hand, the lower limit of the Al content is not particularly limited, and Al may not be contained. However, from the viewpoint of obtaining the above effects of Al, the lower limit of Al is preferably 0.001%. Here, Al is T. Al.

<0.010 to 0.350% of N>

[0031] As with C, N is an essential element for obtaining a predetermined hardness (Vickers hardness) after quenching or quenching and tempering. Particularly, in an embodiment of the present invention, the content of C is reduced, and so it is necessary to contain N in place of C. Further, when N is in solid solution, it also has an effect of improving corrosion resistance. From the viewpoint of obtaining these effects, the N content should be 0.010% or more. However, N may form Cr nitrides and cause a Cr depleted layer, and in this case, it may reduce corrosion resistance. On the other hand, excessive addition of N leads to a difficulty to control in the steelmaking stage, so that defects caused by bubbles tend to be formed. When the defects caused by bubbles are formed, they tend to become starting points for rusting, so that they may decrease the corrosion resistance as well as reduce the yield. Therefore, the N content should be 0.350% or less. From the viewpoint of stably obtaining the above effects of N, the lower limit of the N content is preferably 0.020%, and more preferably 0.025%, and still more preferably 0.036%, and the upper limit is preferably 0.300%, and more preferably 0.290%.

<0.0001 to 0.0030% of Ca>

[0032] Ca is added to adjust the composition at the steelmaking stage, and it acts as a strong deoxidizing agent and has an effect of promoting deoxidation. However, since Ca is a powerful deoxidizing element, most of it floats to a surface as inclusions in molten steel and a little Ca remains in the steel. However, when a large amount of Ca is added, inclusions generated during the steelmaking contain CaO, which is highly likely to become a starting point for rusting, thereby deteriorating corrosion resistance. Therefore, the Ca content should be 0.0030% or less, and preferably 0.0010% or less. On the other hand, since it is impossible to remove even fine inclusions, it is difficult to reduce the Ca content to less than 0.0001% in terms of the production steps. Therefore, the content of Ca should be 0.0001% or more.

<0.001 to 0.010% of O>

[0033] In order to reduce the inclusions, O is an important element together with Al and Ca. If a large amount of O is added, the number of large inclusions (especially carbides) remaining in the steel increases, which adversely affects corrosion resistance. Therefore, the O content should be 0.010% or less. Further, it is preferable to reduce O as much as possible, but since excessive reduction leads to an increase in cost, the content of O should be 0.001% or more. From the viewpoint of the balance between the cost and the corrosion resistance, the O content preferably has a lower limit of 0.002% and an upper limit of 0.009%.

<2.5C + N being 1.10% or more>

[0034] As described above, C and N are essential elements for obtaining a predetermined hardness (Vickers hardness) after quenching or quenching and tempering. In an embodiment of the invention, N is contained as an alternative to reducing the C content, and C contributes to the hardness at 2.5-fold of N. Therefore, from the viewpoint of obtaining a predetermined hardness, 2.5C + N should be 1.10% or more, and preferably 1.25% or more. Although the upper limit of 2.5C + N is not particularly limited, it is preferably 1.80%, and more preferably 1.70%, and still more preferably 1.60%.

<0.50% or less of V>

[0035] V is an element that forms fine carbonitrides and contributes to improvement of corrosion resistance, and is optionally added. However, excessive addition of V may lead to coarsening of deposits, resulting in a decrease in toughness after quenching. Therefore, the V content is 0.50% or less, and preferably 0.30% or less, and more preferably 0.20% or less. Although the lower limit of the content of V is not particularly limited, V may be contaminated in the alloy raw material as an unavoidable impurity and may be difficult to remove it in the refining step. From the viewpoint of obtaining the above effects, the lower limit of the V content is preferably 0.01%, and more preferably 0.02%, and even more preferably 0.03%.

<0.30% or less of Nb>

[0036] Nb is an element that forms carbonitrides and suppresses sensitization and deterioration of corrosion resistance due to deposition of Cr carbonitrides, and is optionally added. However, excessive addition of Nb results in an unstable martensite phase and reduction of hardness. Therefore, the Nb content is 0.30% or less, and preferably 0.28% or less, and more preferably 0.25% or less. Although the lower limit of the Nb content is not particularly limited, it is preferably 0.01%, and more preferably 0.05%, from the viewpoint of obtaining the above effects.

<0.3% or less of Ti>

[0037] Ti is an element that forms carbonitrides and suppresses sensitization and deterioration of corrosion resistance due to deposition of Cr carbonitrides, and is optionally added. However, excessive addition of Ti forms coarse TiN, leading to the generation of hot rolling defects and a decrease in toughness. Therefore, the Ti content should be 0.3% or less, and preferably 0.25% or less. Although the lower limit of the Ti content is not particularly limited, it is preferably 0.01%, and more preferably 0.06%, and still more preferably 0.10%, from the viewpoint of obtaining the above effects.

<4.0% or less of Cu>

[0038] Cu is an element that is effective for improving the corrosion resistance of the martensite structure containing δ ferrite and contributes to improvement of hardenability as an austenite stabilizing element, and is optionally added. However, excessive addition of Cu leads to a decrease in hot workability and an increase in raw material costs. Therefore, the Cu content should be 4.0% or less, and preferably 3.8% or less, and more preferably 3.5% or less. Although the lower limit of the Cu content is not particularly limited, it is preferably 1.0%, and more preferably 1.3%, and still more preferably 1.5%, from the viewpoint of obtaining the above effects.

<0.100% or less of Sn>

[0039] Sn is an element effective for improving corrosion resistance after quenching or quenching and tempering, and is optionally added. However, excessive addition of Sn promotes edge cracking during hot rolling. Therefore, the Sn content should be 0.100% or less, and preferably 0.090% or less. Although the lower limit of the Sn content is not particularly limited, it is preferably 0.002%, and preferably 0.050%, from the viewpoint of obtaining the above effects.

<0.0050% or less of B>

[0040] B is an element effective for improving hot workability and is optionally added. However, excessive addition of B may reduce hardenability due to combined deposition of borides and carbides. Therefore, the B content should be 0.0050% or less, and preferably 0.0045% or less. Although the lower limit of the content of B is not particularly limited, it is preferably 0.0002% from the viewpoint of obtaining the above effects.

<0.30% or less of Co>

[0041] Co is an element that improves heat resistance and is optionally added. However, since Co is expensive, an excessive Co content leads to an increase in production costs. Therefore, the Co content should be 0.30% or less, and preferably 0.10% or less, and more preferably 0.05% or less. Although the lower limit of the Co content is not particularly limited, it is preferably 0.01% from the viewpoint of obtaining the above effects.

[0042] The martensite-based stainless steel material according to an embodiment of the present invention has an average grain diameter of carbides of 0.50 μm or less, and preferably 0.48 μm or less. By controlling the average grain diameter of the carbides to such a range, the workability of the martensite-based stainless steel material is improved to suppress a nicked edge of cutlery during production of cutlery (especially during a cutlery edging process), and also suppress generation of irregular patterns. Although the lower limit of the average grain diameter of the carbides is not particularly limited, it is preferably 0.01 μm , and more preferably 0.05 μm , and still more preferably 0.10 μm .

[0043] Here, the carbides for which the average grain diameter is defined include both eutectic carbides generated during casting and deposited carbides generated during the rolling step.

[0044] Further, the average grain diameter of the carbides can be calculated by observing cross sections of the martensite-based stainless steel material with an SEM, measuring a circle equivalent diameter of each carbide in the observation fields, and calculating the average value.

[0045] In the martensite-based stainless steel material according to the embodiment of the present invention, the number of carbides having a size of 10 μm or more is 0.20/cm² or less, and preferably 0.19/cm² or less. Since the carbides having a size of 10 μm or more tend to form starting points for rusting, the control of the number of the carbides having a size of 10 μm or more to such a range can lead to suppression of rusting, thereby improving corrosion resistance. Although the number of the carbides having a size of 10 μm or more is preferably as low as possible, the number is not particularly limited, but it is generally 0.01/cm² or more.

[0046] Here, the carbides having a size of 10 μm or more for which the number is defined are mainly targeted to eutectic carbides generated during casting. Further, the size of the carbide refers to (long diameter + short diameter) / 2 of the carbide.

[0047] The number of the carbides having a size of 10 μm or more is calculated by observing cross sections of the martensite-based stainless steel material with an optical microscope to determine the number of the carbides having a size of 10 μm or more, and dividing the number by the area of the measurement region.

[0048] The martensite-based stainless steel material according to an embodiment of the present invention has a hardness (Vickers hardness) of 500 HV or more after quenching or quenching and tempering. In particular, when the martensite-based stainless steel material is used for cutlery, it is preferable that the hardness is 550 HV or more. Although the upper limit of the hardness is not particularly limited, it is preferably 900 HV, and more preferably 800 HV.

[0049] Here, the quenching is carried out at 1000 to 1100°C. The tempering is carried out at 100 to 400°C. A sub-zero treatment at -200 to -50°C is preferably carried out after the quenching.

[0050] In addition, the hardness means a value measured at room temperature (25°C) using a Vickers hardness tester.

[0051] Although the martensite-based stainless steel material according to the embodiment of the present invention is not particularly limited, it is preferably a hot-rolled sheet, a hot-rolled annealed sheet, a cold-rolled sheet, or a cold-rolled annealed sheet.

[0052] The method for producing the martensite-based stainless steel material according to an embodiment of the present invention includes a hot rolling step of subjecting a slab having the same composition as that of the martensite-based stainless steel material as described above to a heat treatment at a temperature equal to or higher than T represented by the following equation (1) for 1 to 5 hours, and then subjecting it to a hot rolling. By performing the hot rolling step, a hot-rolled sheet can be obtained.

$$T [^{\circ}\text{C}] = 6500 / (4 - \log C [\%]) - 273 \quad (1)$$

[0053] By performing the heat treatment under such conditions, the eutectic carbides generated during casting can be completely solutionized, so that the average grain diameter of the carbides and the number of the carbides having a size of 10 μm or more can be controlled within the above range.

[0054] The hot rolling conditions are not particularly limited, but it is preferable to finish the sheet to a thickness of 2 to 8 mm by rough rolling and finish rolling.

[0055] After the hot rolling, the hot-rolled sheet is wound at a coiling temperature of 800°C to 900°C. The wound hot-rolled sheet is in a form of a coil.

[0056] After the hot rolling step, the coiled-like hot-rolled sheet is subjected to a softening step of performing annealing at a temperature of Ac1 point to (Ac1 point - 50°C) for 1 to 5 hours. A hot-rolled annealed sheet can be obtained by performing the softening step. Further, since the coarsening of the carbides is suppressed by performing the annealing under such conditions, it is possible to stably control the average grain diameter of the carbides and the number of the carbides having a size of 10 μm or more to the above ranges. The annealing is performed by maintaining the coiled-like hot-rolled sheet in a heated state at a temperature of Ac1 point to (Ac1 point - 50°C). Therefore, it should be noted that the annealing is not performed by reheating the coil-like hot-rolled sheet to that temperature after once cooling it. Also, the annealing is performed in a batch annealing furnace.

[0057] Here, the Ac1 point is calculated by the following equation (2):

$$Ac1 = -250C + 73Si - 66Mn - 115Ni + 35Cr + 60Mo - 18Cu + 620Ti + 750Al - 280N + 410 \quad (2)$$

[0058] In the equation, the symbol of each element is % by mass of each element.

[0059] The hot-rolled annealed sheet obtained in the softening step may be optionally washed with an acid.

[0060] After the softening step, the hot-rolled annealed sheet which has been optionally washed with an acid is subjected to cold rolling. A cold-rolled sheet can be obtained by performing the cold rolling step.

[0061] The conditions for the cold rolling are not particularly limited, but they may be appropriately adjusted according to required cold-rolled sheets.

[0062] After the cold rolling step, the cold-rolled sheet is subjected to an annealing step of heating the cold-rolled sheet in the temperature range from 100°C to Ac1 point to (Ac1 point - 50°C) at a heating rate of 50°C/second or more, preferably 100°C/second or more. It should be noted that the annealing can be started with a state where the cold-rolled sheet is in a temperature range of room temperature (25°C) or more and less than 100°C. A cold-rolled annealed sheet can be obtained by performing the annealing step. Further, since the coarsening of the carbides is suppressed by performing the annealing step under such conditions, it is possible to stably control the average grain diameter of the carbides and the number of the carbides having a size of 10 μm or more to the above ranges.

[0063] The martensite-based stainless steel material according to the embodiment of the present invention produced as described above has, in addition to the controlled steel composition, the number of the carbides having a size of 10 μm or more and the average grain diameter of the carbides controlled to the predetermined ranges. Therefore, it has good workability, higher hardness and higher corrosion resistance after quenching or quenching and tempering, and can suppress the generation of irregular patterns.

EXAMPLES

[0064] While the present invention will be described below in detail with reference to Examples, the present invention is not construed as being limited thereto.

[0065] A steel having each steel composition as shown in Table 1 was melted and cast into a slab having a thickness of 200 mm. The slab was subjected to a heat treatment at each temperature for each time as shown in Table 2, and then subjected to hot rolling (rough rolling and finish rolling) to obtain a hot-rolled sheet having a thickness of 3 mm, which was wound into a coil at a coiling temperature of 850 °C. The coil-like hot-rolled sheet was transferred to a batch annealing furnace, and a softening step was performed at each temperature for each time as shown in Table 2. Subsequently, the hot-rolled annealed sheet obtained in the softening step was then subjected to cold rolling, and then subjected to an annealing step by heating it in the temperature range from 100 °C to each temperature as shown in Table 2 at each heating rate as shown in Table 2. It should be noted that the annealing was started with a state where the cold-rolled sheet was at room temperature (25°C). Subsequently, the sheet was washed with an acid. The resulting cold-rolled annealed sheets (martensite-based stainless steel materials) were evaluated as follows:

[Table 1]

Steel Nos.	Steel Composition (% by mass)													
	C	Si	Mn	P	S	Cr	Ni	Mo	Al	N	Ca	O	2.5C + N	Others
A 1	0.58	0.56	0.28	0.018	0.002	14.5	0.15	0.30	0.014	0.111	0.0003	0.004	1.56	--
A 2	0.34	0.48	0.50	0.012	0.001	15.8	0.08	0.29	0.013	0.266	0.0004	0.003	1.13	--
A 3	0.45	0.95	0.28	0.016	0.001	14.6	0.13	0.50	0.013	0.174	0.0006	0.005	1.30	--
A 4	0.45	0.07	0.65	0.018	0.002	15.8	0.11	0.48	0.005	0.132	0.0006	0.003	1.26	Sn:0.08
A 5	0.49	0.36	1.42	0.012	0.001	15.5	0.15	0.06	0.010	0.059	0.0005	0.006	1.28	--
A 6	0.46	0.33	0.08	0.015	0.001	14.2	0.12	0.46	0.009	0.142	0.0006	0.005	1.29	Ti:0.22 B:0.004
A 7	0.44	0.63	0.35	0.036	0.001	15.2	0.10	0.46	0.009	0.197	0.0003	0.003	1.30	--
A 8	0.45	0.39	0.31	0.018	0.024	13.9	0.11	0.15	0.013	0.198	0.0005	0.006	1.32	--
A 9	0.44	0.36	0.68	0.020	0.002	17.8	0.08	0.06	0.007	0.179	0.0006	0.003	1.28	--
A 10	0.49	0.36	0.36	0.012	0.001	13.1	0.09	0.46	0.011	0.136	0.0005	0.004	1.36	Cu:2.8
A 11	0.47	0.42	0.33	0.011	0.002	13.9	0.26	0.22	0.005	0.154	0.0005	0.006	1.33	--
A 12	0.46	0.48	0.71	0.020	0.001	14.7	0.03	0.28	0.006	0.116	0.0003	0.003	1.27	--
A 13	0.45	0.36	0.49	0.020	0.001	15.3	0.12	0.28	0.009	0.195	0.0006	0.004	1.32	--
A 14	0.44	0.27	0.37	0.012	0.001	14.1	0.07	0.02	0.007	0.161	0.0006	0.005	1.26	--
A 15	0.43	0.45	0.48	0.014	0.002	13.9	a 15	0.41	0.018	0.202	0.0005	0.006	1.28	--
A 16	0.46	0.40	0.57	0.019	0.001	15.1	0.14	0.16	0.009	0.284	0.0003	0.005	1.43	Nb:0.24
A 17	0.52	0.26	0.78	0.012	0.001	14.6	0.09	0.45	0.005	0.027	0.0004	0.004	1.33	--
A 18	0.46	0.36	0.32	0.013	0.001	14.5	0.05	0.21	0.007	0.157	0.0025	0.004	1.31	--
A 19	0.45	0.52	0.38	0.018	0.002	15.2	0.15	0.28	0.005	0.127	0.0002	0.004	1.25	Ti:0.12
A 20	0.46	0.26	0.43	0.017	0.002	14.8	0.07	0.17	0.012	0.120	0.0004	0.003	1.27	--
A 21	0.44	0.34	0.28	0.018	0.002	14.5	0.14	0.49	0.012	0.152	0.0003	0.002	1.25	--
A 22	0.50	0.51	0.37	0.015	0.002	14.7	0.06	0.51	0.010	0.026	0.0005	0.005	1.27	V:0.1 Co:0.02
A 23	0.42	0.51	0.37	0.010	0.000	14.5	0.06	0.60	0.010	0.216	0.0005	0.003	1.27	--
B 1	0.81	0.55	0.46	0.018	0.013	13.5	0.08	0.35	0.012	0.186	0.0005	0.005	2.21	--

(continued)

Steel Nos.	Steel Composition (% by mass)													
	C	Si	Mn	P	S	Cr	Ni	Mo	Al	N	Ca	O	2.5C + N	Others
B 2	<u>0.25</u>	0.53	0.42	0.019	0.013	13.5	0.08	0.35	0.011	0.199	0.0005	0.005	<u>0.82</u>	--
B, 3	0.46	<u>1.13</u>	0.49	0.009	0.015	14.3	0.03	0.15	0.005	0.182	0.0004	0.003	1.33	--
B 4	0.47	0.39	<u>1.62</u>	0.009	0.012	14.8	0.07	0.31	0.017	0.091	0.0006	0.006	1.27	--
B 5	0.48	0.60	0.52	0.019	0.007	<u>19.3</u>	0.18	0.20	0.015	0.143	0.0006	0.005	1.34	--
B 6	0.49	0.45	0.46	0.026	0.013	<u>12.7</u>	0.14	0.38	0.014	0.147	0.0004	0.005	1.37	--
B 7	0.45	0.44	0.20	0.016	0.010	<u>14.4</u>	0.41	0.04	0.013	0.134	0.0003	0.003	1.26	--
B 8	0.46	0.49	0.52	0.013	0.004	148	0.15	<u>1.52</u>	0.008	0.103	0.0005	0.005	1.25	--
B 9	0.44	0.41	0.57	0.013	0.006	13.5	0.05	0.38	<u>0.103</u>	0.179	0.0003	0.005	1.28	--
B 10	0.46	0.36	0.43	0.009	0.008	153	0.15	0.24	0.015	<u>0.006</u>	0.0003	0.006	1.16	--
B 11	0.43	0.51	a as	0.007	0.014	157	0.18	0.31	0.007	0.224	0.0038	0.003	1.30	--
B 12	0.49	0.60	0.56	0.015	0.013	156	0.18	0.14	0.005	0.180	0.0006	<u>0.016</u>	1.41	--
B 13	0.31	0.51	0.41	0.019	0.013	13.6	0.08	0.42	0.013	0.197	0.0005	0.005	<u>0.97</u>	--
B 14	0.36	0.57	0.46	0.013	0.013	14.9	0.10	0.07	0.007	0.146	0.0004	0.006	<u>1.05</u>	--
The balance is Fe and impurities. Underlines indicate that they are outside the scope of the present invention.														

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[Table 2]

5		Steel Nos.	Hot Rolling Step/Slab Heating			Softening Step				Annealing Step	
			T (°C) / Eq. (1)	Temp. (°C)	Time (h)	Ac1 Point (°C)	Ac1 Point-50 (°C)	Temp. (°C)	Time (h)	Temp. (°C)	heating Rate (°C/s)
10	Ex. 1	A 1	1261	1270	1	775	725	750	1	750	100
	Ex. 2	A 2	1183	1200	1	823	773	800	1	800	150
	Ex. 3	A 3	1222	1230	1	835	785	800	1	800	150
	Ex. 4	A 4	1222	1230	1	796	746	750	1	750	150
15	Ex. 5	A 5	1235	1240	1	740	690	700	2	700	150
	Ex. 6	A 6	1226	1230	1	928	878	900	1	880	150
	Ex. 7	A 7	1219	1230	1	823	773	800	1	800	150
	Ex. 8	A 8	1222	1230	1	743	693	700	1	700	150
20	Ex. 9	A 9	1219	1220	1	854	804	850	1	800	150
	Ex. 10	A 10	1235	1240	1	686	636	680	2	680	150
	Ex. 11	A 11	1229	1240	1	732	682	700	2	700	150
	Ex. 12	A 12	1226	1230	1	783	733	750	1	750	150
25	Ex. 13	A 13	1222	1230	1	782	732	750	1	750	150
	Ex. 14	A 14	1219	1230	1	142	692	700	2	700	150
	Ex. 15	A 15	1216	1220	1	754	704	750	1	750	150
	Ex. 16	A 16	1226	1230	1	736	686	700	2	700	150
30	Ex. 17	A 17	1244	1250	1	771	721	750	1	750	150
	Ex. 18	A 18	1226	1230	1	776	726	750	1	750	150
	Ex. 19	A 19	1222	1230	1	885	835	850	1	850	150
	Ex. 20	A 20	1226	1230	1	781	731	750	1	750	150
35	Ex. 21	A 21	1219	1230	1	794	744	750	1	750	150
	Ex. 22	A 22	1237	1250	1	844	794	800	1	800	150
	Ex. 23	A 23	1212	1220	1	803	753	800	1	780	100
	Comp. 1	<u>B 1</u>	1316	1320	1	659	609	650	2	650	150
45	Comp. 2	<u>B 2</u>	1139	1150	1	796	746	150	1	750	150
	Comp. 3	<u>B 3</u>	1226	1230	1	804	754	800	1	800	150
	Comp. 4	<u>B 4</u>	1229	1230	1	730	680	700	2	700	150
	Comp. 5	<u>B 5</u>	1232	1240	1	937	887	900	1	880	150
55	Comp. 6	<u>B 6</u>	1235	1240	1	711	661	700	2	700	150

(continued)

	Steel Nos.	Hot Rolling Step/Slab Heating			Softening Step				Annealing Step	
		T (°C) / Eq. (1)	Temp. (°C)	Time (h)	Ac1 Point (°C)	Ac1 Point-50 (°C)	Temp. (°C)	Time (h)	Temp. (°C)	heating Rate (°C/s)
Comp. 7	<u>B 7</u>	1222	1230	1	748	698	700	2	700	150
Comp. 8	<u>B 8</u>	1226	1230	1	866	816	850	1	<u>800</u>	150
Comp. 9	<u>B 9</u>	1219	1230	1	809	759	800	1	<u>750</u>	150
Comp. 10	<u>B 10</u>	1226	1230	1	835	785	800	1	800	150
Comp. 11	<u>B 11</u>	1216	1220	1	804	754	800	1	800	150
Comp. 12	<u>B 12</u>	1235	1240	1	781	731	750	1	750	150
Comp. 13	<u>B 13</u>	1169	1170	1	789	739	750	1	750	150
Comp. 14	<u>B 14</u>	1190	1190	1	810	760	800	1	800	150
Underlines indicate that they are outside the scope of the present invention.										

(Hardness)

[0066] Each of the resulting cold-rolled annealed sheets was quenched by heating to 1000 to 1100°C, and then surface-polished with #80, and the JIS surface hardness (quenching hardness) was measured with a Vickers hardness tester. The measurement temperature was room temperature (25°C). A hardness of 500 HV or more was considered to be acceptance.

(Corrosion Resistance)

[0067] Each of the resulting cold-rolled annealed sheet was quenched by heating to 1000 to 1100°C, then surface-polished with #600 and subjected to a salt spray test in accordance with JIS Z 2371: 2015 "Methods of salt spray testing" for 24 hours to measure a rust area percentage. In the evaluation, a rust area percentage of less than 10% was determined to be acceptance (O), and a rust area percentage of 10% or more was determined to be nonacceptance (x).

(Average Grain Diameter of Carbides)

[0068] Cross sections parallel to a rolling direction and a sheet thickness direction of each of the resulting cold-rolled annealed sheets were observed with SEM, and among carbides observed in the observation fields, all carbide grains except for carbide grains having a circle equivalent diameter of less than 0.10 μm and carbide grains partially protruding from the observation field were used as the measurement subjects to measure the circle equivalent diameter (μm), and a value obtained by dividing the sum of equivalent circle diameters of the carbide grains as the measurement subjects by the total number of the carbide grains as the measurement subjects was determined to be the average grain diameter (μm) of the carbides. However, the total number of the carbide grains as the measurement subjects was set to 100 or more by randomly selecting a plurality of non-overlapping observation fields. The circle equivalent diameter of the carbide grains was calculated from areas of the carbide grains obtained by processing the SEM images with image processing software.

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(Number of Carbides Having Size of 10 μm or more)

[0069] For each of the cross sections parallel to the rolling direction and the sheet thickness direction of the resulting cold-rolled annealed sheets, 20 areas each having 50 mm $\times$ 50 mm were visually observed using an optical microscope at magnifications of $\times$ 50 to determine an average number of observation areas, which was divided by the areas of the observation regions to calculate the number of the carbides.

(Workability)

[0070] Each of the resulting cold-rolled annealed sheets was punched into a cutlery shape to collect a steel material, which was quenched by heating at 1000 to 1100°C. The surface of the steel material was then ground, and one end face in the longitudinal direction was further subjected to wet grinding to subject it to cutlery edging, thereby obtaining a test material (cutlery). When no nicked edge of cutlery was generated during the cutlery edging, it was determined to be acceptance (O), and when a nicked edge(s) of cutlery was/were generated, it was determined to be nonacceptance (X).

(Irregular Patterns)

[0071] A test material (cutlery) was obtained by the same method as for the workability. The appearance of the test material was visually observed, and the cutlery surface having no irregular patterns was determined to be acceptance (O), and the cutlery surface having irregular patterns was determined to be nonacceptance (X).

[0072] Table 3 shows the above evaluation results.

[Table 3]

	Hardness (HV)	Corrosion Resistance	Average Grain Diameter of Carbides (μm)	Carbides Having 10 μm or more (Number/ cm^2)	Workability	Irregular Patterns
Ex. 1	701	○	0.47	0.17	○	○
Ex. 2	522	○	0.38	0.04	○	○
Ex. 3	645	○	0.22	0.09	○	○
Ex. 4	551	○	0.27	0.07	○	○
Ex. 5	600	○	0.21	0.10	○	○
Ex. 6	616	○	0.38	0.06	○	○
Ex. 7	618	○	0.23	0.10	○	○
Ex. 8	658	○	0.23	0.08	○	○
Ex. 9	622	○	0.27	0.18	○	○
Ex. 10	650	○	0.29	0.07	○	-
Ex. 11	628	○	0.24	0.15	○	○
Ex. 12	556	○	0.21	0.11	○	○
Ex. 13	639	○	0.30	0.15	○	○
Ex. 14	599	○	0.45	0.12	○	○
Ex. 15	580	○	0.29	0.12	○	○
Ex. 16	650	○	0.26	0.16	○	○
Ex. 17	639	○	0.37	0.11	○	○
Ex. 18	600	○	0.40	0.14	○	○
Ex. 19	583	○	0.27	0.10	○	○
Ex. 20	581	○	0.24	0.09	○	○
Ex. 21	600	○	0.40	0.07	○	○

(continued)

	Hardness (HV)	Corrosion Resistance	Average Grain Diameter of Carbides (μm)	Carbides Having 10 μm or more (Number/ cm^2)	Workability	Irregular Patterns
Ex. 22	580	○	0.29	0.09	○	○
Ex. 23	573	○	0.33	0.13	○	○
Comp. 1	762	○	<u>1.65</u>	<u>2.12</u>	×	×
Comp. 2	411	○	0.40	0.11	○	○
Comp. 3	475	○	0.29	0.12	○	○
Comp. 4	425	○	0.34	0.06	○	○
Comp. 5	465	○	<u>0.78</u>	<u>1.34</u>	×	×
Comp. 6	411	×	0.32	0.10	○	○
Comp. 7	403	○	0.26	0.07	○	-
Comp. 8	451	○	0.43	0.09	○	○
Comp. 9	435	○	0.35	0.05	○	-
Comp. 10	489	×	0.34	0.13	○	○
Comp. 11	611	×	0.34	0.12	○	○
Comp. 12	581	×	0.29	0.05	○	○
Comp. 13	432	×	0.31	0.11	○	○
Comp. 14	475	×	0.20	0.13	○	○
Underlines indicate that they are outside the scope of the present invention.						

[0073] As shown in Table 3, each of the cold-rolled annealed sheets (martensite-based stainless steel materials) according to Examples 1 to 23 had good hardness and corrosion resistance after quenching. Further, these cold-rolled annealed sheets have a smaller average grain diameter of the carbides and a smaller number of the carbides having a size of 10 μm or more, so that no nicked edge of cutlery was generated during the cutlery edging, and workability was good, and the generation of irregular patterns was also suppressed.

[0074] On the other hand, in the cold-rolled annealed sheets according to Comparative Examples 1 to 14, any of the steel composition, the average grain diameter of the carbides, and the number of the carbides having a size of 10 μm or more was outside the predetermined range, so that the hardness after quenching or the corrosion resistance was not sufficient. In particular, those having the larger average grain diameter of the carbides and the larger number of the carbides having a size of 10 μm or more generate nicked edges of cutlery during the cutlery edging, so that the workability was not sufficient and irregular patterns on the surface of the cutlery were generated.

[0075] Here, FIG. 1 shows a graph showing the relationship between $2.5C + N$ and the hardness in the above Examples and Comparative examples. As shown in FIG. 1, it was found that there is a proportional relationship between $2.5C +$

N and the hardness, and that an increase in $2.5C + N$ tends to increase the hardness. In particular, it was found that the control of $2.5C + N$ to 1.10% or more can provide the hardness of 500HV or more.

[0076] As can be seen from the above results, according to the present invention, it is possible to provide a martensite-based stainless steel material, which has good workability, has higher hardness and corrosion resistance after quenching or quenching and tempering, and can suppress generation of irregular patterns, and a method for producing the same.

Claims

1. A martensite-based stainless steel material having a composition comprising: 0.30 to 0.60% by mass of C; 0.05 to 1.00% by mass of Si; 0.05 to 1.50% by mass of Mn; 0.040% by mass or less of P; 0.030% by mass or less of S; 13.0 to 18.0% by mass of Cr; 0.01 to 0.30% by mass of Ni; 0.01 to 1.00% by mass of Mo; 0.030% by mass or less of Al; 0.010 to 0.350% by mass of N; 0.0001 to 0.0030% by mass of Ca; and 0.001 to 0.010% by mass of O; $2.5C + N$ being 1.10% or more, and the balance being Fe and impurities,

wherein the martensite-based stainless steel material has an average grain diameter of carbides of 0.50 μm or less, and

wherein the number of the carbides having a size of 10 μm or more is 0.20/ cm^2 or less.

2. The martensite-based stainless steel material according to claim 1, further comprising at least one of: 0.50% by mass or less of V; 0.30% by mass or less of Nb; 0.3% by mass or less of Ti; 4.0% by mass or less of Cu; 0.100% by mass or less of Sn; 0.0050% by mass or less of B; and 0.30% by mass or less of Co.

3. The martensite-based stainless steel material according to claim 1 or 2, wherein the martensite-based stainless steel material has a hardness of 500 HV or more after quenching or quenching and tempering.

4. The martensite-based stainless steel material according to any one of claims 1 to 3, wherein the martensite-based stainless steel material is for cutlery.

5. A method for producing a martensite-based stainless steel material, wherein the method comprises a hot rolling step of subjecting a slab to a heat treatment at a temperature equal to or higher than T represented by the following equation (1) for 1 to 5 hours, and then subjecting the slab to hot rolling:

$$T [^{\circ}\text{C}] = 6500 / (4 - \log C [\%]) - 273 \quad (1),$$

wherein the slab has a composition comprising: 0.30 to 0.60% by mass of C; 0.05 to 1.00% by mass of Si; 0.05 to 1.50% by mass of Mn; 0.040% by mass or less of P; 0.030% by mass or less of S; 13.0 to 18.0% by mass of Cr; 0.01 to 0.30% by mass of Ni; 0.01 to 1.00% by mass of Mo; 0.030% by mass or less of Al; 0.010 to 0.350% by mass of N; 0.0001 to 0.0030% by mass of Ca; and 0.001 to 0.010% by mass of O; $2.5C + N$ being 1.10% or more, and the balance being Fe and impurities.

6. The method for producing a martensite-based stainless steel material according to claim 5, wherein the slab further comprises at least one of: 0.50% by mass or less of V; 0.30% by mass or less of Nb; 0.3% by mass or less of Ti; 4.0% by mass or less of Cu; 0.100% by mass or less of Sn; 0.0050% by mass or less of B; and 0.30% by mass or less of Co.

7. The method for producing a martensite-based stainless steel material according to claim 5 or 6, wherein the method further comprises a softening step of performing annealing at a temperature of Ac1 point to (Ac1 point - 50°C) for 1 to 5 hours, after winding a hot-rolled sheet at a coiling temperature of 800°C to 900°C in the hot rolling step.

8. The method for producing a martensite-based stainless steel material according to claim 7, further comprising:

a cold rolling step of subjecting a hot-rolled annealed sheet obtained in the softening step to cold rolling; and an annealing step of heating a cold-rolled sheet obtained in the cold rolling step in a temperature range from 100°C to Ac1 point to (Ac1 point - 50°C) at a heating rate of 50°C/second or more.

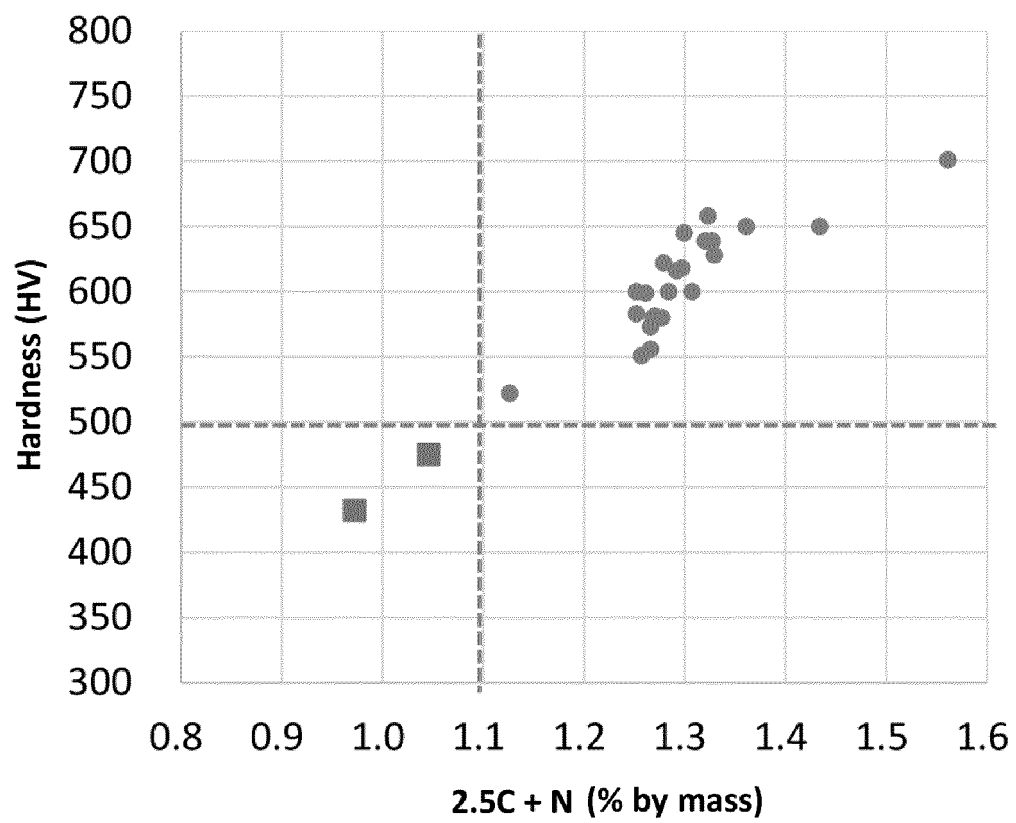


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2021/046879

A. CLASSIFICATION OF SUBJECT MATTER

C21D 9/18(2006.01)i; *C21D 9/46*(2006.01)i; *C22C 38/00*(2006.01)i; *C22C 38/44*(2006.01)i; *C22C 38/54*(2006.01)i
 FI: C22C38/00 302Z; C21D9/46 Q; C22C38/44; C22C38/54; C21D9/18

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)

C21D9/18; C21D9/46; C22C38/00; C22C38/44; C22C38/54

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

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2022
 Registered utility model specifications of Japan 1996-2022
 Published registered utility model applications of Japan 1994-2022

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 2020-094275 A (HITACHI METALS, LTD) 18 June 2020 (2020-06-18)	1-8
A	JP 2019-014916 A (NACHI FUJIKOSHI CORP) 31 January 2019 (2019-01-31)	1-8
A	US 2002/0162614 A1 (BOHLER EDELSTAHL GMBH) 07 September 2002 (2002-09-07)	1-8
P, A	WO 2021/124511 A1 (NIPPON STEEL STAINLESS STEEL CORP) 24 June 2021 (2021-06-24)	1-8

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

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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