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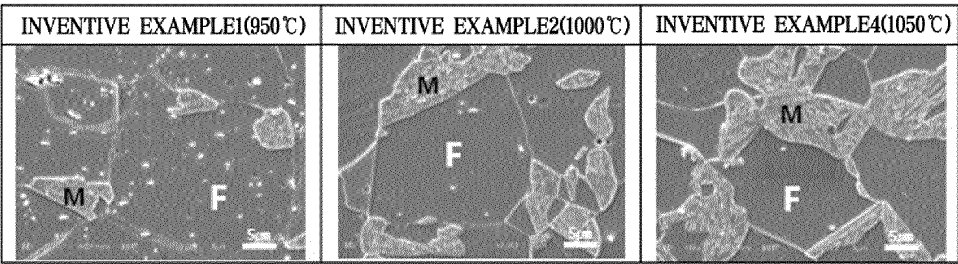
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(54) **HIGH CORROSION RESISTANCE AND HIGH STRENGTH STAINLESS STEEL AND METHOD FOR MANUFACTURING SAME**

(57) A high corrosion resistance and high strength stainless steel, according to one example of the present invention, comprises, in wt%, 0.01-0.1% of C, 0.01-0.1% of N, 0.01-1.0% of Si, 0.01-3.0% of Mn, 10.0-20.0% of Cr, 0.001-1.0% of Al, at most 0.05% of P, at most 0.01% of S, and the remainder in Fe and other unavoidable impurities, wherein the distribution of carbides with a diameter of at least 0.5 μm is at most 7/100 μm^2 per unit area, and the microstructure is dual phase with a martensite phase and a ferrite phase and the martensite phase is at least 20% in area ratio.

[FIG. 4]



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Description

[Technical Field]

- 5 **[0001]** The present disclosure relates to a high corrosion resistance and high strength stainless steel having a martensite-ferrite dual phase after cold annealing heat treatment and a method for manufacturing the same.

[Background Art]

- 10 **[0002]** High functionality such as high strength and light weight has been required in ferritic stainless steel products which are widely used in various kitchenware, home appliances, and automotive parts. Particularly, extreme cost reduction as well as improvement of energy efficiency via light weight by decreasing weight with a reduced thickness due to high strength is required. However, there is a limit to improvement in strength by grain refinement because phase transformation is not accompanied in conventional ferritic stainless steels.
- 15 **[0003]** To solve this, a cold-rolled steel sheet with an excellent appearance may be obtained by reducing roping that may be caused during a cold rolling process by forming a martensite phase during a hot annealing process, but distribution of the martensite phase during a hot annealing process may increase strength to cause problems such as cracks or tearing of the steel sheet during a cold rolling process due to rolling loads. To solve this, a reduction ratio per pass may be reduced during the cold rolling, but the number of passes may be increased thereby, resulting in economic loss. There is a need for a
- 20 stainless steel having strength without reducing corrosion resistance.

[Disclosure]

[Technical Problem]

- 25 **[0004]** The present disclosure has been proposed to solve the above-described problems, and provided are a high corrosion resistance and high strength stainless steel obtained by controlling distribution of a carbide and forming a martensite phase in a cold annealing process and a method of manufacturing the same.
- 30 **[0005]** However, the technical problems to be solved by the present disclosure are not limited to the aforementioned problems, and any other technical problems not mentioned herein will be clearly understood from the following description by those skilled in the art to which the present disclosure pertains.

[Technical Solution]

- 35 **[0006]** According to an embodiment of the present disclosure, a high corrosion resistance and high strength stainless steel includes, in percent by weight (wt%), 0.01 to 0.1% of C, 0.01 to 0.1% of N, 0.01 to 1.0% of Si, 0.01 to 3.0% of Mn, 10.0 to 20.0% of Cr, 0.001 to 1.0% of Al, 0.05% or less of P, 0.01% or less of S, and the remainder of Fe and other unavoidable impurities, wherein distribution of carbides with a diameter of 0.5 μm or more is 7/100 μm^2 or less per unit area, a microstructure is a dual phase of a martensite phase and a ferrite phase, and the martensite phase is 20% or more in an
- 40 area ratio.
- [0007]** In the high corrosion resistance and high strength stainless steel, Expression (1) below is satisfied: Expression (1): $420\text{C}+470\text{N}+23\text{Ni}+10\text{Mn}+180-(11.5\text{Cr}+11.5\text{Si}+52\text{Al}) \geq 10$. In Expression (1) C, N, Ni, Mn, Cr, Si and Al represent weight percentages (wt%) of respective elements.
- 45 **[0008]** In the high corrosion resistance and high strength stainless steel, a pitting potential is 70 mV or more, and a yield strength may be 350 MPa or more.
- [0009]** In the high corrosion resistance and high strength stainless steel, a tensile strength may be 500 MPa or more.
- [0010]** In the high corrosion resistance and high strength stainless steel, a hardness may be 200 Hv or more.
- [0011]** In the high corrosion resistance and high strength stainless steel, a hardness of the martensite phase may be 400 Hv or more.
- 50 **[0012]** In the high corrosion resistance and high strength stainless steel, an aspect ratio of a ferrite crystal grain may be 2.0 or less.
- [0013]** According to an embodiment of the present disclosure, a method for manufacturing a high corrosion resistance and high strength stainless steel includes: reheating a slab including, in percent by weight (wt%), 0.01 to 0.1% of C, 0.01 to 0.1% of N, 0.01 to 1.0% of Si, 0.01 to 3.0% of Mn, 10.0 to 20.0% of Cr, 0.001 to 1.0% of Al, 0.05% or less of P, 0.01% or less of S, and the remainder of Fe and other unavoidable impurities at 1050 to 1250°C; hot rolling and hot annealing the slab; and cold rolling and cold annealing the slab at 950 to 1100°C, wherein the high corrosion resistance and high strength stainless steel satisfies Expression (1) below and has a dual phase microstructure of a martensite phase and a ferrite phase: Expression (1): $420\text{C}+470\text{N}+23\text{Ni}+10\text{Mn}+180-(11.5\text{Cr}+11.5\text{Si}+52\text{Al}) \geq 10$. In Expression (1), C, N, Ni, Mn, Cr, Si and Al
- 55

represent weight percentages (wt%) of respective elements.

[0014] In the method for manufacturing a high corrosion resistance and high strength stainless steel, distribution of carbides with a diameter of 0.5 μm or more may be 7/100 μm^2 or less per unit area.

[0015] In the method for manufacturing a high corrosion resistance and high strength stainless steel, the hot annealing may be performed at 750 to 900°C.

[0016] In the method for manufacturing a high corrosion resistance and high strength stainless steel, the martensite phase after cold annealing may be 20% or more in an area ratio, and a hardness of the martensite phase after cold annealing may be 400 Hv or more.

[0017] In the method for manufacturing a high corrosion resistance and high strength stainless steel, an aspect ratio of a ferrite crystal grain may be 2.0 or less.

[Advantageous Effects]

[0018] According to an embodiment of the present disclosure, provided are a stainless steel having a dual phase of martensite and ferrite and satisfying both high corrosion resistance and high strength after cold annealing heat treatment and a method of manufacturing the same.

[Description of Drawings]

[0019]

FIG. 1 shows images of microstructures of comparative examples according to cold annealing temperature.

FIG. 2 shows images of microstructures of inventive examples according to cold annealing temperature.

FIG. 3 shows images of microstructures and carbides of comparative examples according to cold annealing temperature .

FIG. 4 shows images of microstructures and carbides of inventive examples according to cold annealing temperature.

[Best Mode]

[0020] A high corrosion resistance and high strength stainless steel according to an embodiment may include, in percent by weight (wt%), 0.01 to 0.1% of C, 0.01 to 0.1% of N, 0.01 to 1.0% of Si, 0.01 to 3.0% of Mn, 10.0 to 20.0% of Cr, 0.001 to 1.0% of Al, 0.05% or less of P, 0.01% or less of S, and the remainder of Fe and other unavoidable impurities, wherein distribution of carbides with a diameter of 0.5 μm or more is 7/100 μm^2 or less per unit area, a microstructure is a dual phase of a martensite phase and a ferrite phase, the martensite phase is 20% or more in an area ratio.

[Modes of the Invention]

[0021] Hereinafter, embodiments of the present disclosure will be described. The embodiments of the present disclosure may, however, be embodied in many different forms and should not be construed as being limited to the embodiments set forth herein. Rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the concept of the invention to those skilled in the art.

[0022] The terms used herein are merely used to describe particular embodiments. An expression used in the singular encompasses the expression of the plural, unless otherwise indicated. Throughout the specification, the terms such as "including" or "having" are intended to indicate the existence of features, numbers, operations, components, parts, or combinations thereof disclosed in the specification, and are not intended to preclude the possibility that one or more other features, numbers, operations, components, parts, or combinations thereof may exist or may be added.

[0023] Meanwhile, unless otherwise defined, all terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. Thus, these terms should not be interpreted in an idealized or overly formal sense unless expressly so defined herein. As used herein, the singular forms are intended to include the plural forms as well, unless the context clearly indicates otherwise.

[0024] In addition, the terms "about", "substantially", etc. used throughout the specification means that when a natural manufacturing and a substance allowable error are suggested, such an allowable error corresponds the value or is similar to the value, and such values are intended for the sake of clear understanding of the present disclosure or to prevent an unconscious infringer from illegally using the disclosure of the present disclosure.

[0025] The present disclosure is configured to improve strength in accordance with a fraction of martensite formed in a ferrite matrix by forming a ferrite-martensite dual phase in a final product by improving stability of an austenite phase in the ferrite matrix and conducting phase transformation into the martensite phase during cooling via cold annealing heat treatment at a temperature where the austenite phase is formed. In addition, in order to avoid loads, cracks, or fractures

during a cold rolling process, the hot annealing is performed directly below Ac1 temperature, i.e., the ferrite single-phase domain, to form a soft ferrite single phase. Upon completion of the cold rolling, a cold annealing is performed at a temperature where the austenite phase is formed, so as to induce phase transformation into martensite during cooling to improve strength.

[0026] A solid solution of $M_{23}C_6$ type carbides precipitated on the ferrite phase in a matrix may be formed by performing heat treatment at a temperature where the austenite phase is formed in the cold annealing process. The present disclosure may provide a stainless steel having strength without deteriorating corrosion resistance by controlling distribution of the carbides, and a method for manufacturing the same.

[0027] Also, the present disclosure may provide a stainless steel without deteriorating forming quality of a final product by controlling an aspect ratio of ferrite crystal grains and a method for manufacturing the same.

[0028] A high corrosion resistance and high strength stainless steel according to an embodiment of the present disclosure may include, in percent by weight (wt%), 0.01 to 0.1% of C, 0.01 to 0.1% of N, 0.01 to 1.0% of Si, 0.01 to 3.0% of Mn, 10.0 to 20.0% of Cr, 0.001 to 1.0% of Al, 0.05% or less of P, 0.01% or less of S, and the remainder of Fe and other unavoidable impurities. Hereinafter, reasons for numerical limitations on the contents of alloying elements will be described.

[0029] The content of C may be from 0.01% to 0.1%.

[0030] C, as an austenite-stabilizing element, has an effect on enlarging an austenite phase region, so as to increase strength of a steel by forming hard martensite during cooling. To obtain such an effect, 0.01% or more of C is required. Preferably, 0.02% or more of C is required to sufficiently enlarge the austenite region to obtain a certain degree of strength.

However, with the C content exceeding 0.1%, the steel sheet hardens causing a significant decrease in ductility, and formability cannot be obtained in the case of excessive formation of martensite. In addition, a large amount of Cr carbide products caused by addition of excessive C may cause a decrease in Cr resulting in deterioration of corrosion resistance. Therefore, the C content may be in the range of 0.01 to 0.1%. Preferably, the C content may be in the range of 0.02 to 0.1%.

[0031] The content of N may be from 0.01 to 0.1%.

[0032] Like C and Mn, N, as an austenite-stabilizing element, has an effect on enlarging an austenite phase region. To obtain such an effect, 0.01% or more of N is required. However, with the N content exceeding 0.1%, ductility rapidly decreases due to a solid solution strengthening effect and a decrease in Cr is caused due to precipitation of Cr nitrides, thereby deteriorating corrosion resistance. Therefore, the N content may be in the range of 0.01 to 0.1%. Preferably, the N content may be in the range of 0.02 to 0.1%, more preferably, in the range of 0.01 to 0.07%.

[0033] The content of Si may be from 0.01 to 1.0%.

[0034] Si is an element serving as a deoxidize while dissolving a steel. To obtain such an effect, 0.01% or more Si is required. However, with the Si content exceeding 1.0%, the steel sheet hardens to increase a rolling load during hot rolling and surface defects such as sticking may be caused. In addition, an excess of Si, as a ferrite-stabilizing element, may deteriorate stability of austenite. Therefore, the Si content may be in the range of 0.01 to 1.0%. Preferably, the Si content may be in the range of 0.20 to 0.50%.

[0035] The content of Mn may be from 0.01 to 3.0%.

[0036] Like C, Mn, as an austenite phase-stabilizing element, has an effect on enlarging an austenite phase region. To obtain such an effect, 0.01% or more of Mn is required. However, with the Mn content exceeding 3.0%, the amount of produced MnS increases to deteriorate corrosion resistance. Therefore, the Mn content may be in the range of 0.01 to 3.0%. Preferably, the Mn content may be 0.2 to 1.0%.

[0037] The content of Cr may be from 10.0 to 20.0%.

[0038] Cr is an element forming a passivated layer on the surface of a steel sheet providing an effect on improving corrosion resistance. This effect may be obtained at a Cr content of 10.0% or more, and corrosion resistance is improved as the Cr content increases. In addition, Cr, as a ferrite-stabilizing element, has an effect on preventing formation of the austenite phase. With a Cr content less than 10.0%, the austenite phase is excessively formed, failing to obtain a certain degree of formability. Therefore, the Cr content is controlled to 10.0% or more. However, in the case where the Cr content exceeds 20.0%, the austenite phase is not formed, failing to obtain a desired fraction of the martensite phase. Therefore, the Cr content may be in the range of 10.0 to 20.0%. Preferably, the Cr content may be in the range of 12.0 to 18.0%.

[0039] The content of Al may be from 0.001 to 1.0%.

[0040] Like Si, Al is an element serving as a deoxidizer. To obtain such an effect, 0.001% or more of Al is required. However, with an Al content exceeding 1.0%, Al inclusions such as Al_2O_3 increase easily causing deterioration in surface appearance. Therefore, the Al content may be in the range of 0.001 to 1.0%. Preferably, the Al content may be in the range of 0.001 to 0.1%.

[0041] The content of Ni may be from 0.01% to 1.0%.

[0042] Ni, as a representative austenite-stabilizing element, is expensive resulting in an increase in manufacturing costs. In addition, although corrosion resistance is improved thereby, an excessive amount may cause an increase in impurities, thereby deteriorating elongation. Therefore, the present disclosure may optionally include Ni in an amount of 0.01 to 1.0%. Preferably, the Ni content may be 0.5% or less.

[0043] The content of P may be 0.05% or less.

[0044] P is an element segregated in grain boundaries to promote destruction of the grain boundaries and regarded as an unavoidable impurity whose content should be controlled as low as possible. Therefore, the P content may be 0.05 or less. Preferably, the P content may be 0.03% or less.

[0045] The content of S may be 0.01% or less.

[0046] S is an element present as a sulfide-based inclusion such as MnS and deteriorates ductility or corrosion resistance. Particularly, an S content exceeding 0.01% causes significant adverse effects. Therefore, S is regarded as an unavoidable impurity whose content should be controlled as low as possible. Therefore, the S content may be 0.01% or less. More preferably, the S content may be 0.005% or less.

[0047] The remaining component of is iron (Fe). However, unintended impurities may be inevitably incorporated from raw materials or surrounding environments during a common manufacturing process, and thus addition of other alloying elements is not excluded. These impurities are known to any person skilled in the art of manufacturing and details thereof are not specifically mentioned in the present disclosure.

[0048] Hereinafter, a high corrosion resistance and high strength stainless steel according to an embodiment of the present disclosure having the above-described composition of alloying elements will be described.

[0049] In the high corrosion resistance and high strength stainless steel according to an embodiment of the present disclosure, distribution of carbides with a diameter of 0.5 μm or more may be 7/100 μm^2 or less per unit area. With the distribution of carbides more than 7/100 μm^2 per unit area, corrosion resistance and high strength cannot be obtained simultaneously.

[0050] In the high corrosion resistance and high strength stainless steel according to an embodiment of the present disclosure, a microstructure is a dual phase of a martensite phase and a ferrite phase, wherein an area ratio of the martensite phase may be 20% or more. With the area ratio of the martensite phase less than 20%, high strength cannot be obtained.

[0051] In the high corrosion resistance and high strength stainless steel according to an embodiment of the present disclosure, in the case where the distribution of carbides with a diameter of 0.5 μm or more is 7/100 μm^2 or less due to a formation of a solid solution of the carbides in a matrix, a decrease in corrosion resistance caused by precipitation of the carbides may be prevented, and at the same time, in the case where the area ratio of the martensite phase is 20% or more, high strength may be obtained, and thus the stainless steel may satisfy both high corrosion resistance and high strength.

[0052] The high corrosion resistance and high strength stainless steel according to an embodiment of the present disclosure may have a value of Expression (1) of 10 or more.

$$\text{Expression (1): } 420\text{C}+470\text{N}+23\text{Ni}+10\text{Mn}+180-(11.5\text{Cr}+11.5\text{Si}+52\text{Al})$$

[0053] In Expression (1), C, N, Ni, Mn, Cr, Si and Al represent weight percentages (wt%) of respective elements.

[0054] In the case where the value of Expression (1) is less than 10, phase transformation of the austenite phase may not occur vigorously due to low stability of the austenite phase so that the austenite phase may not be transformed into martensite. Therefore, the value of Expression (1) may be controlled to be 10 or more, preferably, 30 or more. In this case, the austenite phase formed at a high temperature may be easily transformed into the martensite phase during cooling, so that the area ratio of the martensite phase may be 20% or more.

[0055] The high corrosion resistance and high strength stainless steel according to an embodiment of the present disclosure may have a pitting potential of 70 mV or more and a yield strength of 350 MPa or more satisfying both corrosion resistance and strength.

[0056] In addition, the high corrosion resistance and high strength stainless steel according to an embodiment of the present disclosure may have a tensile strength of 500 MPa or more and a hardness of 200 Hv or more. In addition, the martensite phase may have a hardness of 400 Hv or more.

[0057] In addition, in the high corrosion resistance and high strength stainless steel according to an embodiment of the present disclosure, the ferrite crystal grain may have an aspect ratio of 2.0 or less. The aspect ratio of the ferrite crystal grain refers to a ratio obtained by dividing a length of the ferrite crystal grain in the rolling direction by a length of the ferrite crystal grain in the thickness direction. This is represented by Expression (2) below in the present disclosure.

$$\text{Expression (2): } Ar = Dr/Dt$$

[0058] In this regard, Ar refers to an aspect ratio of the ferrite crystal grain, Dr refers to a length of the ferrite crystal grain in the rolling direction, and Dt refers to a length of the ferrite crystal grain in the thickness direction.

[0059] The ferrite crystal grains are approximately 30 to 50 μm in size, and in the case where non-recrystallized ferrite

crystal grains elongated in the rolling direction are distributed, there is a high possibility that inferior forming quality such as ridging may occur. Therefore, it is desirable to distribute the ferrite phase that does not undergo phase transformation as equiaxed recrystallized grains as much as possible to prevent deterioration in forming quality of final products. Therefore, the aspect ratio of the ferrite crystal grain may be controlled to 2.0 or less in the present disclosure to obtain excellent forming quality.

[0060] Hereinafter, a method for manufacturing a high corrosion resistance and high strength stainless steel according to an embodiment of the present disclosure including the above-described composition of alloying elements will be described.

[0061] The high corrosion resistance and high strength stainless steel of the present disclosure may be manufactured by performing reheating - hot rolling - finish rolling - hot annealing - cold rolling - cold annealing processes on a slab including the above-described composition of alloying elements.

[0062] The method for manufacturing the high corrosion resistance and high strength stainless steel of the present disclosure may include: reheating a slab including, in percent by weight (wt%), 0.01 to 0.1% of C, 0.01 to 0.1% of N, 0.01 to 1.0% of Si, 0.01 to 3.0% of Mn, 10.0 to 20.0% of Cr, 0.001 to 1.0% of Al, 0.05% or less of P, 0.01% or less of S, and the remainder of Fe and other unavoidable impurities; hot rolling and hot annealing the slab; and cold rolling and cold annealing the slab.

[0063] The slab having the above-described composition of alloying elements may satisfy a value of Expression (1) of 10 or more.

$$\text{Expression (1): } 420C + 470N + 23Ni + 10Mn + 180 - (11.5Cr + 11.5Si + 52Al)$$

[0064] In Expression (1), C, N, Ni, Mn, Cr, Si and Al represent weight percentages (wt%) of respective elements.

[0065] In the case where the value of Expression (1) is less than 10, phase transformation of the austenite phase may not occur vigorously due to low stability of the austenite phase so that the austenite phase may not be transformed into martensite. Therefore, the value of Expression (1) may be controlled to be 10 or more, preferably, 30 or more. Therefore, after forming the austenite phase at a high temperature, phase transformation into the martensite phase occurs easily during cooling.

[0066] The slab having the above-described composition of alloying elements may be reheated at 1050 to 1250°C and hot rolled. A finish rolling temperature may be 700 to 950°C.

[0067] In addition, the hot annealing may be performed at 750°C to 900°C corresponding to directly below Ac1 temperature, i.e., the ferrite single-phase domain, preferably 800°C to 850°C, to form a soft ferrite single phase.

[0068] The hot-rolled steel sheet formed of a soft ferrite single phase may be cold rolled at room temperature. Upon completion of cold rolling, cold annealing may be performed. The cold annealing may be performed at 950 to 1100°C. By performing the cold annealing at 950°C or higher, that is higher than the temperature for forming the austenite phase, i.e., 900°C or higher, phase transformation into martensite may be induced during cooling, thereby improving strength. However, in the case of performing annealing at a temperature higher than 1100°C, ferrite crystal grains may coarsen to deteriorate formability or the orange peel phenomenon and the like may occur on the surface of a bent portion due to coarsening of crystal grains in severely bent portions, and therefore, it is preferable to perform the heat treatment at 1100°C or less.

[0069] In addition, according to the method for manufacturing the high corrosion resistance and high strength stainless steel according to the present disclosure, the cold annealing temperature may be maintained at a temperature where the austenite phase is formed such that $M_{23}C_6$ type carbides precipitated on the ferrite phase may form a solid solution in a matrix.

[0070] According to the method for manufacturing the high corrosion resistance and high strength stainless steel according to the present disclosure, cold annealing heat treatment may be performed at a temperature where the austenite phase is formed such that the carbides form a solid solution in a matrix and the distribution of carbides with a diameter of 0.5 μm or more is 7/100 μm^2 or less per unit area.

[0071] According to the method for manufacturing the high corrosion resistance and high strength stainless steel according to the present disclosure, the martensite phase may have a hardness of 400 Hv or more after cold annealing. Carbon obtained by decomposition of the carbides increases stability of the austenite phase to form the austenite phase, and the martensite phase having a BCT structure with high hardness may be formed during cooling.

[0072] According to the method for manufacturing the high corrosion resistance and high strength stainless steel according to the present disclosure, the area ratio of the martensite phase after cold annealing may be 20% or more. In the case of performing cold annealing heat treatment at a temperature where the austenite phase is formed, the area ratio of the martensite phase increases as the temperature is raised, and accordingly, yield strength and tensile strength may be improved.

[0073] In the case where the distribution of carbides with a diameter of 0.5 μm or more is 7/100 μm^2 or less per unit area due to formation of a solid solution of the carbides in a matrix, a decrease in corrosion resistance caused by precipitation of the carbides may be prevented, and at the same time, a martensite phase with high hardness may be formed and the area ratio of the martensite phase increases, thereby obtaining strength.

[0074] A stainless steel manufactured by the method of manufacturing a high corrosion resistance and high strength stainless steel according to an embodiment of the present disclosure may have a pitting potential of 70 mV or more and a yield strength of 350 MPa or more satisfying both corrosion resistance and strength.

[0075] In addition, a stainless steel manufactured by the method of manufacturing a high corrosion resistance and high strength stainless steel according to an embodiment of the present disclosure may have a tensile strength of 500 MPa or more and a hardness of 200 Hv or more.

[0076] In addition, a stainless steel manufactured by the method of manufacturing a high corrosion resistance and high strength stainless steel according to an embodiment of the present disclosure may satisfy an aspect ratio of the ferrite crystal grain, represented by Expression (2), of 2.0 or less, resulting in excellent forming quality of final products. Expression (2) is defined by $Ar = Dr/Dt$, wherein Ar is an aspect ratio of the ferrite crystal grain, Dr is a length of the ferrite crystal grain in the rolling direction, and Dt is a length of the ferrite crystal grain in the thickness direction.

[0077] Hereinafter, the present disclosure will be described in more detail through examples. However, it is necessary to note that the following examples are only intended to illustrate the present disclosure in more detail and are not intended to limit the scope of the present disclosure. This is because the scope of the present disclosure is determined by matters described in the claims and able to be reasonably inferred therefrom.

{Example}

[0078] A slab including, in percent by weight (wt%), 0.035% of C, 0.038% of N, 0.32% of Si, 0.5% of Mn, 16.3% of Cr, 0.003% of Al, 0.09% of Ni, 0.02% or less of P, 0.004 % or less of S, and the remainder of Fe and other unavoidable impurities was processed by reheating - hot rolling - finish rolling - hot annealing - cold rolling - cold annealing in a temperature range of the present disclosure to manufacture a cold-annealed material. Particularly, in order to evaluate effects according to cold annealing heat treatment temperature in the present disclosure, different cold annealing heat treatment temperatures were applied to the slabs prepared within the scope of the present disclosure, as shown in Table 1.

[0079] Table 1 below shows fractions of the martensite phase of examples according to cold annealing heat treatment temperature.

Table 1

	Cold annealing temperature ($^{\circ}\text{C}$)	Martensite phase fraction (%)
Comparative Example 1	820	0
Comparative Example 2	890	0
Comparative Example 3	910	0
Comparative Example 4	930	0
Inventive Example 1	950	26.5
Inventive Example 2	1000	37.3
Inventive Example 3	1030	40.1
Inventive Example 4	1050	42.5

[0080] FIGS. 1 and 2 show images of microstructures of examples according to cold annealing heat treatment temperature. Changes in the microstructures were observed by using a scanning electron microscope (SEM). It may be confirmed that Comparative Examples 1 to 4 are formed of the ferrite phase. With regard to Inventive Examples 1 to 4, a white phase area corresponds to the ferrite phase, and a black phase area corresponds to the martensite phase in FIG. 2. Increases in fractions of the martensite phase in the ferrite matrix may be confirmed as the cold annealing heat treatment temperature increases in Table 1 and FIGS. 1 and 2.

[0081] In Comparative Examples 1 to 4 in which the cold annealing heat treatment temperatures are below the range of the present disclosure, only the ferrite phase was observed, and although the martensite phase may be present as the temperature increases, the martensite phase was only in a trace amount that cannot be measured. On the contrary, in Inventive Examples 1 to 4 satisfying the range according to the present disclosure, the cold annealing heat treatment temperature satisfies the range of 950 $^{\circ}\text{C}$ or higher, and it may be confirmed that the fraction of the martensite phase was 20% or more in the ferrite matrix.

[0082] Table 2 below shows the numbers of $M_{23}C_6$ type carbides per unit area according to the cold annealing heat treatment temperature.

Table 2

	Cold annealing temperature (°C)	Number of carbides (No./100 μm^2)
Comparative Example 1	820	10.6
Comparative Example 3	910	8.2
Inventive Example 1	950	6.5
Inventive Example 2	1000	0.8
Inventive Example 4	1050	0.3

[0083] FIGS. 3 and 4 show images of microstructures of examples and number of $M_{23}C_6$ type carbides (No./100 μm^2) according to cold annealing heat treatment temperature. Changes in the microstructures and carbides were observed by using an SEM. In FIGS. 3 and 4, the martensite phase was expressed as M, and the ferrite phase was expressed as F. It may be confirmed that a large number of carbides were present at a hot annealing temperature below 950°C in Comparative Examples 1 and 3.

[0084] Referring to FIG. 4, it may be confirmed that the martensite phase is formed at a temperature of 950°C or higher, and it may also be confirmed that the distribution of carbides gradually decreased due to formation of a solid solution thereof. It may be confirmed, based on Table 2 and FIGS. 3 and 4, that the fraction of the martensite phase increases in the ferrite matrix, and the number of the carbides per unit area decreases as the cold annealing heat treatment temperature increases.

[0085] It may be confirmed that the number of the carbides per unit area exceeds 7 in the comparative examples that do not satisfy the cold annealing heat treatment temperature range of present disclosure. On the contrary, it may be confirmed that the number of the carbides per unit area is reduced to 7 or less in the inventive examples because the cold annealing heat treatment temperature satisfied 950°C or higher corresponding to the range of the present disclosure.

[0086] Table 3 below shows pitting potential, yield strength, tensile strength, elongation, and hardness of the examples.

Table 3

	Pitting potential (mV/100 μA)	Yield strength (MPa)	Tensile strength (MPa)	Hardness of steel (Hv)
Comparative Example 1	106.8	305.3	479.0	143.7
Comparative Example 2	61.7	327.9	478.5	145.5
Comparative Example 3	50.3	333.4	477.2	148.4
Comparative Example 4	58.2	338.5	484.0	148.1
Inventive Example 1	78.1	367.5	609.7	204.7
Inventive Example 2	123.0	391.7	700.4	210.7
Inventive Example 3	141.4	410.7	723.6	219.8
Inventive Example 4	93.3	451.8	736.0	255.1

[0087] Referring to Table 3, in the case where the area ratio of the martensite phase is 20% or more and the number of the carbides per unit area is 7 or less by satisfying the cold annealing heat treatment temperature of the present disclosure, the pitting potential is 70 mV or more and the yield strength is 350 MPa or more indicating that a stainless steel having high strength without deteriorating corrosion resistance may be obtained. The pitting potential is measured at a temperature of 30°C in a 3.5% NaCl solution at 0.333 mV/sec.

[0088] In the case of Comparative Examples 2 to 4 in which a trace amount of martensite begins to be formed due to an increase in the cold annealing temperature, it may be confirmed that the yield strength and tensile strength are higher than those of Comparative Example 1. In the case of Inventive Examples 1 to 4 corresponding to the cold annealing temperature of the present disclosure or higher, it may be confirmed that the martensite fraction increases to 20% or more, thereby obtaining excellent strength with a yield strength of 350 MPa or more and a tensile strength of 500 MPa or more.

[0089] In addition, in the case of Inventive Examples 1 to 4 corresponding to the cold annealing temperature of 950°C or

higher, in which a solid solution of carbides is formed, the number of the carbides per unit area in the ferrite matrix is 7 or less indicating that a reduction in pitting potential caused by consumption of Cr in accordance with precipitation of carbides may be prevented. Accordingly, the pitting potential of 70 mV or more is obtained indicating that excellent corrosion resistance may be obtained.

[0090] In the case of Comparative Examples 2 to 4, the pitting potential is less than 70 mV, indicating that the cold annealing temperature corresponds to a temperature at which the solid solution of carbides is not formed and the carbides are precipitated, so that Cr is consumed due to precipitation of carbides.

[0091] However, in the case of Comparative Example 1, although the pitting potential satisfies the range of 70 mV or more, the yield strength is low, so that strength is not obtained although the corrosion resistance is obtained.

[0092] In addition, hardness of steels is measured as an average value measured 10 times with a load of 1 kg using a micro Vickers hardness tester. The hardness measured in Comparative Examples 1 to 4 in which the martensite phase does not exist is about 140 Hv indicating inferior hardness. On the contrary, the hardness measured in Inventive Examples 1 to 4 in which 20% or more of the martensite phase exists is 200 Hv or more indicating high hardness.

[0093] In the present disclosure, transformation into the martensite phase is performed in the cold annealing process after cold rolling at a temperature where a solid solution the carbides is formed and transformation into martensite is induced during cooling by cold annealing heat treatment in a temperature range where the austenite phase is formed, and thus, the number of the carbides per unit area is controlled to 7 or less and the area ratio of the martensite phase of 20% or more is obtained, thereby providing stainless steel satisfying both corrosion resistance and strength.

[0094] Table 4 below shows hardness of the martensite phase and the ferrite phase.

[Table 4]

	Hardness of martensite phase (Hv)	Hardness of ferrite phase (Hv)
Comparative Example 1	x	154.0
Comparative Example 3	x	155.0
Inventive Example 1	428.7	157.6
Inventive Example 2	535.7	164.4
Inventive Example 4	546.7	159.9

[0095] Hardness of the martensite phase and the ferrite phase is measured by a micro hardness meter (load: 5 g). Based thereon, the hardnesses of the ferrite phase of the inventive examples are about 150 to 160 Hv similar to those of the comparative examples, and the hardnesses of the martensite phase were higher than 400 Hv that is high. That is, with regard to the hardness of the steels of inventive examples, $M_{23}C_6$ type carbides precipitated on the ferrite phase may form a solid solution in a matrix in the austenite region by cold annealing heat treatment, and in this case, carbon obtained by decomposition of the carbides increases stability of the austenite phase to form the austenite phase, and the martensite phase having a BCT structure with high hardness may be formed during cooling, so as to obtain high hardness.

[0096] Table 5 below shows aspect ratios of ferrite crystal grains.

[Table 5]

	Region	Average aspect ratio ferrite crystal grain in each region	Average aspect ratio of ferrite crystal grain in entire region
Comparative Example 1	1 (1t/5)	1.562	2.066
	2 (2t/5)	1.892	
	3 (3t/5)	2.136	
	4 (4t/5)	2.108	
	5 (5t/5)	1.632	
Inventive Example 2	1 (1t/5)	1.485	1.490
	2 (2t/5)	1.480	
	3 (3t/5)	1.493	
	4 (4t/5)	1.508	
	5 (5t/5)	1.483	

(continued)

	Region	Average aspect ratio ferrite crystal grain in each region	Average aspect ratio of ferrite crystal grain in entire region
5 10	Inventive Ex-ample 3	1 (1t/5)	1.556
		2 (2t/5)	
		3 (3t/5)	
		4 (4t/5)	
		5 (5t/5)	
15	Inventive Ex-ample 4	1 (1t/5)	1.559
		2 (2t/5)	
		3 (3t/5)	
		4 (4t/5)	
		5 (5t/5)	

[0097] The aspect ratio of the ferrite crystal grain according to an embodiment of the present disclosure may be 2.0 or less. The aspect ratio of the ferrite crystal grain refers to a ratio obtained by dividing a length of the ferrite crystal grain in the rolling direction by a length of the ferrite crystal grain in the thickness direction. In the present disclosure, this is represented by Expression (2), $Ar = Dr/Dt$. In this regard, Ar refers to an aspect ratio of the ferrite crystal grain, Dr refers to a length of the ferrite crystal grain in the rolling direction, and Dt refers to a length of the ferrite crystal grain in the thickness direction. According to the present disclosure, in order to measure the aspect ratio of the ferrite crystal grain, the steel sheet was divided into a total of 5 regions from the upper surface layer to the lower surface layer opposite thereto in a cross-section thickness direction of the rolling direction of the steel sheet, and aspect ratios of 1000 ferrite crystal grains of each region were measured to obtain an average value of each region, and the average value was calculated to calculate an aspect ratio of the entire region. This may be regarded as an aspect ratio of the ferrite crystal grain and may be controlled to 2.0 or less. It may be confirmed that deterioration in forming quality may be prevented by controlling the aspect ratio of the ferrite crystal grain to 2.0 or less according to an embodiment of the present disclosure.

[0098] As a result, it may be confirmed that the present disclosure may provide a stainless steel having both corrosion resistance and strength and a method of manufacturing the same by obtaining a 20% or more of a fraction of the martensite phase and controlling the number of the carbides per unit area to 7 or less by inducing phase transformation into martensite and inducing formation of a solid solution of carbides during cooling, by controlling a reheating temperature, a finish rolling temperature, a hot annealing temperature, and a cold annealing temperature, particularly, by performing cold annealing heat treatment at 950°C or higher where the austenite phase is formed in the stainless steel where the austenite phase is formed.

[0099] It may be confirmed that a stainless steel satisfying both high corrosion resistance and high strength with excellent yield strength, tensile strength and hardness with no inferior corrosion resistance with a pitting potential of 70 mV or more and a method of manufacturing the same may be provided.

[0100] In addition, the effect of preventing deterioration in forming quality may be obtained by controlling the aspect ratio of the ferrite crystal grain to 2.0 or less.

[0101] While the present disclosure has been particularly described with reference to exemplary embodiments, it should be understood by those of skilled in the art that various changes and modifications in form and details may be made without departing from the spirit and scope of the present disclosure.

[Industrial Applicability]

[0102] According to an embodiment of the present disclosure, a stainless steel satisfying high corrosion resistance and high strength and having a dual phase of martensite and ferrite after cold annealing heat treatment and a method for manufacturing the same may be provided, and thus the present disclosure has industrial applicability.

Claims

1. A high corrosion resistance and high strength stainless steel comprising, in percent by weight (wt%), 0.01 to 0.1% of C, 0.01 to 0.1% of N, 0.01 to 1.0% of Si, 0.01 to 3.0% of Mn, 10.0 to 20.0% of Cr, 0.001 to 1.0% of Al, 0.05% or less of P,

0.01% or less of S, and the remainder of Fe and other unavoidable impurities,

wherein distribution of carbides with a diameter of 0.5 μm or more is 7/100 μm^2 or less per unit area,
a microstructure is a dual phase of a martensite phase and a ferrite phase, and
the martensite phase is 20% or more in an area ratio.

2. The high corrosion resistance and high strength stainless steel according to claim 1, wherein Expression (1) below is satisfied:

$$\text{Expression (1): } 420\text{C}+470\text{N}+23\text{Ni}+10\text{Mn}+180-(11.5\text{Cr}+11.5\text{Si}+52\text{Al}) \geq 10$$

(in Expression (1) C, N, Ni, Mn, Cr, Si and Al represent weight percentages (wt%) of respective elements).

3. The high corrosion resistance and high strength stainless steel according to claim 1, wherein a pitting potential is 70 mV or more, and a yield strength is 350 MPa or more.

4. The high corrosion resistance and high strength stainless steel according to claim 1, wherein a tensile strength is 500 MPa or more.

5. The high corrosion resistance and high strength stainless steel according to claim 1, wherein a hardness is 200 Hv or more.

6. The high corrosion resistance and high strength stainless steel according to claim 1, wherein a hardness of the martensite phase is 400 Hv or more.

7. The high corrosion resistance and high strength stainless steel according to claim 1, wherein an aspect ratio of a ferrite crystal grain is 2.0 or less.

8. A method for manufacturing a high corrosion resistance and high strength stainless steel, the method comprising:

reheating a slab including, in percent by weight (wt%), 0.01 to 0.1% of C, 0.01 to 0.1% of N, 0.01 to 1.0% of Si, 0.01 to 3.0% of Mn, 10.0 to 20.0% of Cr, 0.001 to 1.0% of Al, 0.05% or less of P, 0.01% or less of S, and the remainder of Fe and other unavoidable impurities at 1050 to 1250°C;

hot rolling and hot annealing the slab; and

cold rolling and cold annealing the slab at 950 to 1100°C,

wherein the high corrosion resistance and high strength stainless steel satisfies Expression (1) below and has a dual phase microstructure of a martensite phase and a ferrite phase:

$$\text{Expression (1): } 420\text{C}+470\text{N}+23\text{Ni}+10\text{Mn}+180-(11.5\text{Cr}+11.5\text{Si}+52\text{Al}) \geq 10$$

(in Expression (1), C, N, Ni, Mn, Cr, Si and Al represent weight percentages (wt%) of respective elements).

9. The method according to claim 8, wherein distribution of carbides with a diameter of 0.5 μm or more is 7/100 μm^2 or less per unit area.

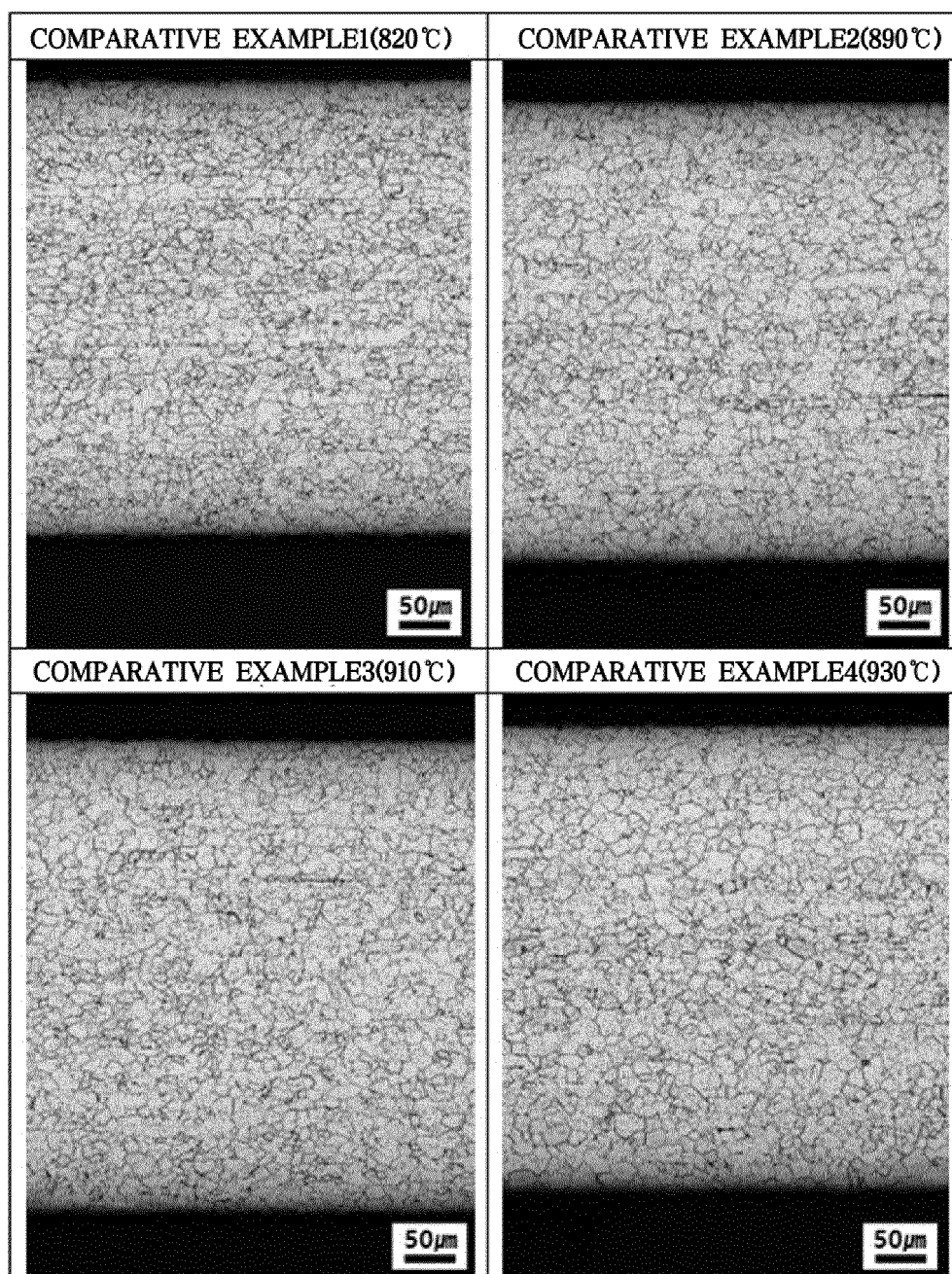
10. The method according to claim 8, wherein the hot annealing is performed at 750 to 900°C.

11. The method according to claim 8, wherein the martensite phase after cold annealing is 20% or more in an area ratio.

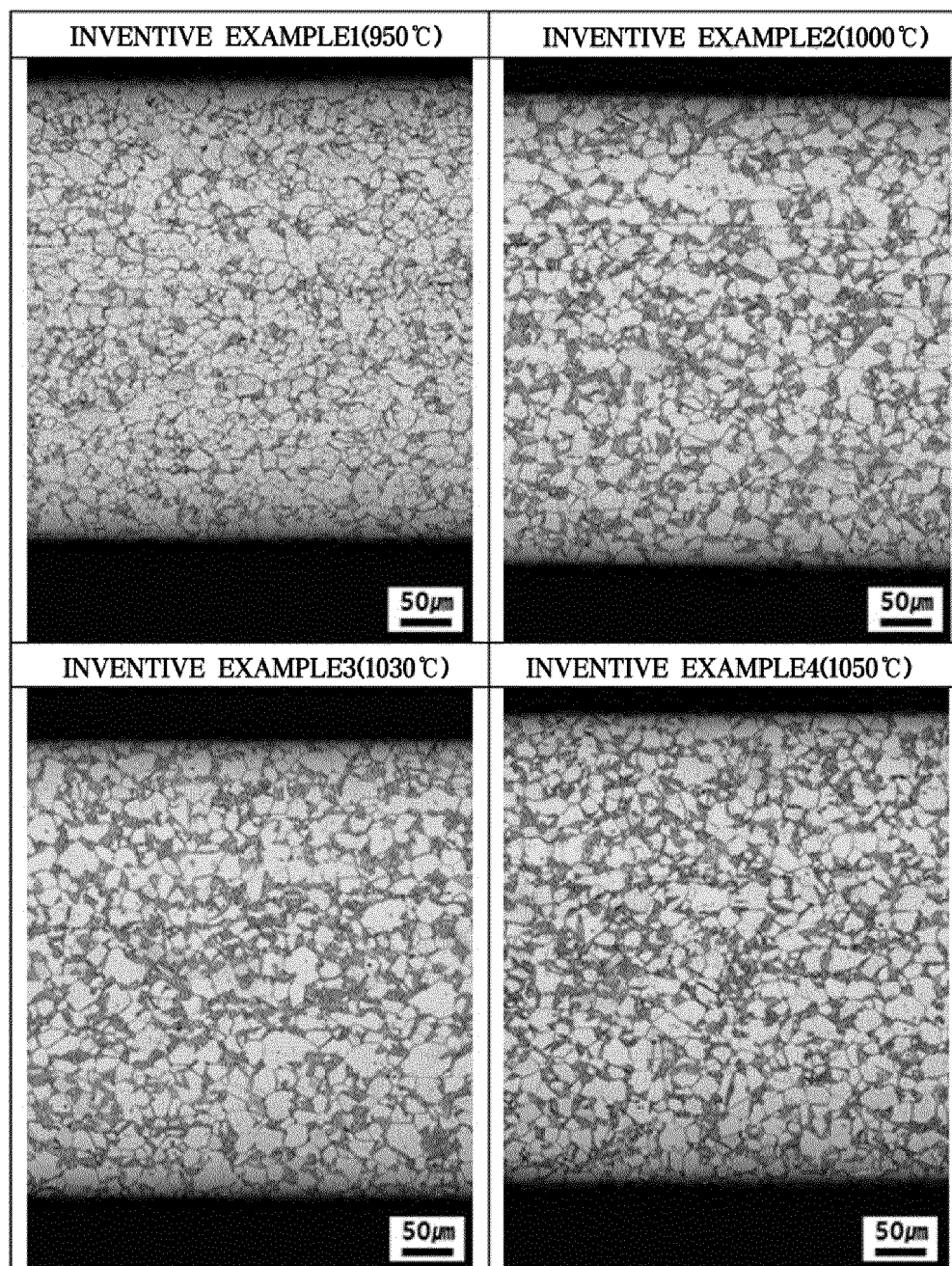
12. The method according to claim 8, wherein a hardness of the martensite phase after cold annealing is 400 Hv or more.

13. The method according to claim 8, wherein an aspect ratio of a ferrite crystal grain is 2.0 or less.

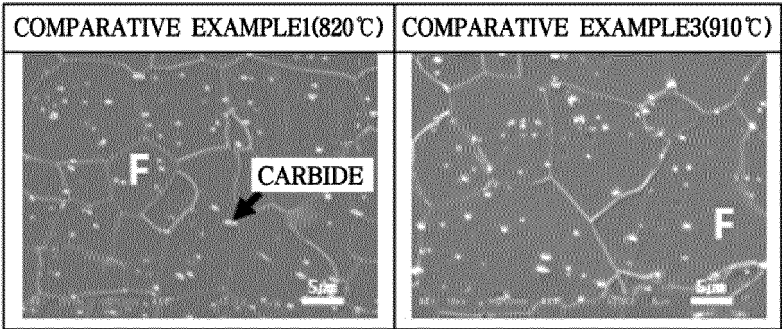
[FIG. 1]



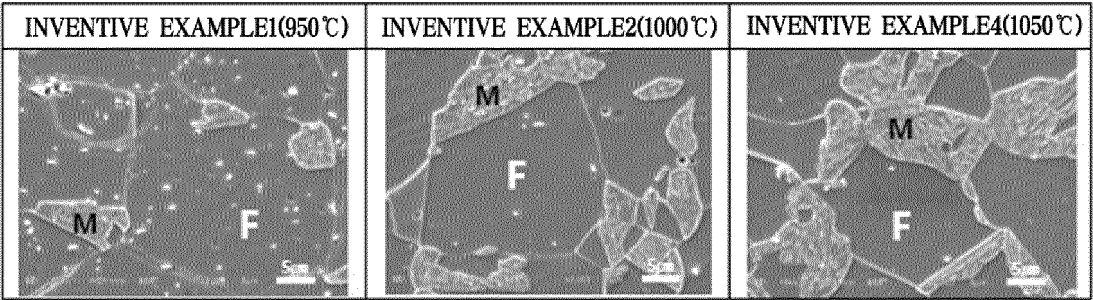
[FIG. 2]



[FIG. 3]



[FIG. 4]



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2023/003277

A. CLASSIFICATION OF SUBJECT MATTER**C22C 38/38**(2006.01)i; **C22C 38/02**(2006.01)i; **C22C 38/06**(2006.01)i; **C21D 8/02**(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)

C22C 38/38(2006.01); B21B 3/02(2006.01); C21D 6/00(2006.01); C21D 8/02(2006.01); C21D 9/46(2006.01);
C22C 38/00(2006.01)

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

Korean utility models and applications for utility models: IPC as above
Japanese utility models and applications for utility models: IPC as above

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

eKOMPASS (KIPO internal) & keywords: 스테인리스(stainless), 탄화물(carbide), 마르텐사이트(martensite), 페라이트
(ferrite), 소둔(annealing), 경도(hardness)**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 10-2016-0113179 A (JFE STEEL CORPORATION) 28 September 2016 (2016-09-28) See paragraphs [0085]-[0086], [0095] and [0097], claims 1 and 7 and table 2.	1-13
A	JP 2000-109957 A (SUMITOMO METAL IND. LTD. et al.) 18 April 2000 (2000-04-18) See paragraph [0030] and claim 1.	1-13
A	WO 2021-205876 A1 (NIPPON STEEL STAINLESS STEEL CORPORATION et al.) 14 October 2021 (2021-10-14) See claims 1 and 6.	1-13
A	JP 2000-282147 A (NISSHIN STEEL CO., LTD.) 10 October 2000 (2000-10-10) See paragraph [0016] and claim 1.	1-13
A	US 2020-0270718 A1 (APERAM) 27 August 2020 (2020-08-27) See claims 1 and 4.	1-13

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

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/KR2023/003277

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
KR 10-2016-0113179 A	28 September 2016	CN 106414783 A	15 February 2017
		CN 106414783 B	22 January 2019
		EP 3098330 A1	30 November 2016
		EP 3098330 B1	22 April 2020
		ES 2803573 T3	28 January 2021
		JP 5888476 B2	22 March 2016
		JP WO2015-111403 A1	23 March 2017
		TW 201533250 A	01 September 2015
		TW I527910 B	01 April 2016
		US 10000824 B2	19 June 2018
JP 2000-109957 A	18 April 2000	US 2016-0369368 A1	22 December 2016
		WO 2015-111403 A1	30 July 2015
		DE 69929017 T2	03 August 2006
		EP 0994199 A1	19 April 2000
		EP 0994199 B1	21 December 2005
		KR 10-0385342 B1	27 May 2003
		KR 10-2000-0028813 A	25 May 2000
		SG 82645 A1	21 August 2001
		US 6277215 B1	21 August 2001
WO 2021-205876 A1	14 October 2021	CN 115244207 A	25 October 2022
		EP 4134461 A1	15 February 2023
		KR 10-2022-0134780 A	05 October 2022
		TW 202138586 A	16 October 2021
JP 2000-282147 A	10 October 2000	None	
US 2020-0270718 A1	27 August 2020	BR 112020008649 A2	27 October 2020
		BR 112020008649 B1	10 January 2023
		CN 111902551 A	06 November 2020
		EP 3704280 A1	09 September 2020
		EP 3704280 B1	13 April 2022
		JP 2021-503545 A	12 February 2021
		KR 10-2020-0077583 A	30 June 2020
		WO 2019-086934 A1	09 May 2019

Form PCT/ISA/210 (patent family annex) (July 2022)