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(54) STEEL FOR MARINE ENGINEERING HAVING CORROSION RESISTANCE TO HIGHLY HUMID AND HOT MARINE ATMOSPHERE AND FABRICATION METHOD THEREFOR

(57) The disclosure is directed to steel for marine engineering, comprising the following chemical elements by mass percentage: C: 0.01-0.05%, Si: 0.05-0.60%, Mn: 0.50-1.30%, Cr: 0.6-1.20%, Ni: 2.0-3.0%, Al: 0.01-0.06%, Ti: 0.005-0.012%, and Mg: 0.0005-0.0015%; $0<Ca\leq0.0045\%$,$0<Cu\leq0.5\%$, and $0<Mo\leq0.40\%$; and the remainder of Fe and inevitable impurities. The disclosure further discloses a manufacturing method for the steel for marine engineering, comprising the following steps: (1) smelting and continuous casting; (2) heating; (3) controlled rolling, the original austenite grain size after rolling being 20-25 μm; (4) air cooling; and (5) quenching and tempering, the austenite grain size after quenching being 20-25 μm. The steel for marine engineering according to the present disclosure may be applied to boats and marine engineering structures, and is especially suitable for highly humid and hot sea regions.

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Description

TECHNICAL FIELD

[0001] The present disclosure relates to steel and a manufacturing method therefor, and particularly relates to steel for marine engineering and a manufacturing method therefor.

BACKGROUND

[0002] As is well known, the South China Sea contains a large amount of energy and resources. In order to develop and apply the resources in the South China Sea, considerable human and material resources have been invested at present.

[0003] The environment of the South China Sea is special. Its highly humid and hot environment with strong radiation and high chlorine is liable to cause serious corrosion of steel materials, and prone to lead to saponification and aging of the paint film of the material, causing serious corrosion. Cl^- is easily adsorbed on the metal surface, leading to the occurrence of anodic dissolution and pitting corrosion, which can even develop into a cracking source, resulting in stress corrosion cracking under the combined action of hydrogen. These problems reduce the mechanical properties and service life of steel for marine platforms. In addition, as marine platforms have long service cycles and are far from sea coasts, regular repair and maintenance are very difficult, and therefore steel for marine platforms needs to have fairly high corrosion resistance.

[0004] In recent years, as China progressively exercises its sovereignty over the South China Sea and begins to develop and utilize resources in the South China Sea, in order to overcome the extreme environment of the South China Sea, there is an urgent need to develop corrosion-resistant steel suitable for highly humid and hot marine environments to meet the demand for marine engineering equipment construction.

[0005] At present, although many iron and steel enterprises around the world have developed weathering steel with atmospheric corrosion resistance and seawater corrosion resistant steel with seawater corrosion resistance. However, such steel is not ideal in applications and cannot be applied well in highly humid and hot marine environments.

[0006] In the production and development processes of the existing steel for marine engineering, the marine atmospheric corrosion resistance of steel plates was not fully considered, but the strength and impact properties of the steel were the main concern. In highly humid and hot regions such as the South China Sea, the marine atmospheric corrosion resistance of the existing steel for marine engineering is not excellent enough, so that the service life of steel plates is not long.

[0007] For example, Chinese patent publication No. CN106756476A which is published on May 31, 2017, and entitled "High-Strength Weathering Steel for Highly Humid and Hot Marine Atmospheric Environment and Manufacturing Method Therefor" discloses high-strength weathering steel for highly humid and hot marine atmospheric environment, which achieves the purpose of improving corrosion resistance by increasing Ni content, adding very few element Cr, adding Mo, Sn, Sb, RE and other micro-alloying elements in combination, and refining the grain structure by trace element of Nb. The highlight of this patent is the use of Sn and Sb to improve the corrosion resistance of steel plates. However, Sn and Sb are strictly controlled impurity elements in structural steel, and will undoubtedly adversely affect the comprehensive mechanical properties of the steel and adversely affect the safety of the marine engineering platform.

[0008] For another example, Chinese patent publication No. CN105132832Awhich is published on Dec. 9, 2015, and entitled "Steel Plate Having corrosion resistance to highly humid and hot marine atmosphere, and Manufacturing Method Therefor" discloses a steel plate having corrosion resistance to highly humid and hot marine atmosphere and a manufacturing method therefor, wherein the steel plate is added with 0.5-0.6% of Si, 0.5-0.7% of Mn, 0.5-0.6% of Cu, 0.5-0.6% of Ni, and 0.3-0.5% of Mo, and a high content of Cr (3.00-3.50%), and added with Sn (0.20-0.30%) and Sb (0.06-0.10%) in combination. This patent has the advantages that the corrosion resistance of weathering steel in a highly humid and hot, severe atmospheric corrosion environment of the South China Sea is improved substantially, and has relatively low production cost, which is economical and practical.

[0009] For another example, Chinese patent publication No. CN103741056A which is published on Apr. 23, 2014, and entitled "Corrosion-Resistant Steel Plate for Marine Environment in the South China Sea and Manufacturing Process Therefor" discloses a corrosion-resistant steel plate for a marine environment in the South China Sea, which adopts a low-carbon composition, and is added with much Si, Mn, Cu, Cr and Ni, and some element Sn. The steel plate has a single-phase polygonal ferrite structure, an average grain size of 10.17 μm, a steel grade yield strength of 355 MPa, a tensile strength of 490-630 MPa, and a Charpy impact energy at -40 °C of greater than 34 J.

[0010] In view of the above-mentioned shortcomings of the prior art, it is expected to obtain new steel for marine engineering, which has not only excellent strength and toughness, but also excellent anti-fracture and anti-crack properties and corrosion resistance to highly humid and hot marine atmosphere.

SUMMARY

[0011] One of the objectives of the present disclosure is to provide steel for marine engineering, which has not only excellent strength toughness, but also excellent anti-fracture and anti-crack properties and corrosion resistance to highly humid and hot marine atmosphere. The steel for marine engineering of the present disclosure can be applied to boats and marine engineering structures, especially marine atmospheric structural components of marine engineering structures, and can serve in different sea regions, especially suitable for highly humid and hot sea regions such as the South China Sea, which has broad application prospects.

[0012] In order to achieve the above objective, the present disclosure provides steel for marine engineering, comprising the following chemical elements by mass percentage:
C: 0.01-0.05%, Si: 0.05-0.60%, Mn: 0.50-1.30%, Cr: 0.6-1.20%, Ni: 2.0-3.0%, Al: 0.01-0.06%, Ti: 0.005-0.012%, and Mg: 0.0005-0.0015%, $0<Ca\leq 0.0045\%$, $0<Cu\leq 0.5\%$, and $0<Mo\leq 0.40\%$; and the remainder of Fe and inevitable impurities.

[0013] In an embodiment, the mass percentages of the chemical elements in the steel for marine engineering of the present disclosure are as follows:
C: 0.015-0.04%, Si: 0.15-0.60%, Mn: 0.50-1.30%, Cr: 0.6-0.90%, Ni: 2.0-2.85%, Al: 0.01-0.06%, Ti: 0.005-0.012%, and Mg: 0.0005-0.0015%, $0<Ca\leq 0.0045\%$, $0<Cu\leq 0.5\%$, and $0<Mo\leq 0.40\%$; and the remainder of Fe and inevitable impurities.

[0014] The steel for marine engineering of the present disclosure has ultra-low C, and is designed with a Mn, Nb, V and Ti micro-alloying and Cr-Ni-Mo-Cu alloying composition system. In the steel for marine engineering of the present disclosure, the design principles of the chemical elements are specifically described as follows:

C: the steel for marine engineering of the present disclosure adopts an ultra-low carbon design, which not only uses the interstitial strengthening effect of carbon to ensure suitable strength of the invented steel plate, but also can effectively prevent precipitation of excessive carbides and reduce the potential difference between the matrix and the carbide phase to obtain good corrosion resistance, while the steel plate has good low-temperature toughness and welding property. Therefore, in the steel for marine engineering of the present disclosure, the mass percentage of C is controlled to 0.01-0.05%.

Si: in the steel for marine engineering of the present disclosure, the element Si is a common weak deoxidizing element in steelmaking, and has certain solid solution strengthening effect. It is to be noted that under Cl^- conditions, element Si can form complex oxides of FeAlSiO in the rust layer of the steel and clog cavities and cracks, thereby playing a protective role for the steel. On this basis, in the steel for marine engineering of the present disclosure, the mass percentage of Si is controlled to 0.05-0.60%.

Mn: in the steel for marine engineering of the present disclosure, Mn is the most basic alloying element for a low-alloy high-strength steel type, and can improve the strength of the steel by solid solution strengthening and compensate for the loss of strength caused by the reduced content of the element C in the steel. However, it is to be noted that the content of the element Mn in the steel should not be too high. If the content of element Mn in the steel is too high, segregation is liable to occur in the center of the steel plate, which reduces the low-temperature toughness of the steel. On this basis, in the steel for marine engineering of the present disclosure, the mass percentage of Mn is controlled to 0.50-1.30%.

Cr: in the steel for marine engineering of the present disclosure, the element Cr can improve the passivation performance of the steel to facilitate the formation of a compact oxide film on the steel surface, and is likely to be enriched in the inner rust layer to refine alpha hydroxy iron oxide. However, it is to be noted that the content of the element Cr in the steel should not be too high. If too much Cr is added, under the Cl^- environment, the corrosion resistance of the steel will be worsened seriously in the late stage of corrosion. Therefore, considering the beneficial effects and adverse effects of the element Cr in combination, in the steel for marine engineering of the present disclosure, the mass percentage of the element Cr is controlled to 0.6-1.20%.

Ni: in the steel for marine engineering of the present disclosure, the element Ni can infinitely solid-solubilize with the iron matrix, which can improve the low-temperature toughness of the steel, especially the impact toughness of the central part of a thick steel plate, and can improve the anti-fracture and anti-crack properties of the steel plate. Furthermore, the increase of the content of the element Ni in the steel plays a great role in improving the corrosion resistance of the steel in the marine environment. Ni can slow down the corrosion development trend of the material over time, and inhibit the inverse effect of corrosion and the tendency of pitting corrosion. However, it is to be noted that the content of the element Ni in the steel should not be too high. If the content of the element Ni in the steel is too high, the slab surface is liable to generate highly viscous iron oxide scale, which is difficult to remove so that the surface quality and fatigue property of the steel plate will be affected. On this basis, in the steel for marine engineering of the present disclosure, the mass percentage of Ni is controlled to 2.0-3.0%.

Al: in the steel for marine engineering of the present disclosure, Al belongs to a grain refining element. The element Al is added to the steel for deoxidation. After complete deoxidation, the content of O in the material is reduced so that the aging property is improved. In addition, it is to be noted that adding an appropriate amount of Al in the steel is also conducive to refining grains and improving the strength and toughness property of the steel. Therefore, in the steel for marine engineering of the present disclosure, the mass percentage of the element Al is controlled to 0.01-0.06%.

Ti: in the steel for marine engineering of the present disclosure, the element Ti is a strong N-fixing element, which can effectively suppress the content of the element N in the steel and prevent adverse effects on the properties of the steel due to an excessively high content of N. Furthermore, a TiN precipitation phase formed by the elements Ti and N can inhibit excessive growth of grains in slabs and steel plates during heating. Therefore, in the steel for marine engineering of the present disclosure, the mass percentage of the added element Ti is controlled to 0.005-0.012%.

Mg: in the steel for marine engineering of the present disclosure, the element Mg can effectively improve sulfide morphology, refine inclusions, and enhance the corrosion resistance of the steel plate. The element Mg is an important element for implementing beneficial modification technology of inclusions in the present disclosure. If the content of the element Mg in the steel is too low, modification of inclusions cannot be realized. If the content of the element Mg in the steel is too high, it is liable to form MgO and MgS, which would clog the tundish nozzle. Therefore, in the steel for marine engineering described in the present invention, the mass percentage of the added element Mg is controlled to 0.0005-0.0015%.

Ca: in the steel for marine engineering of the present disclosure, by Ca treatment, the morphology of sulfides in the steel can be controlled, the anisotropy of the steel plate can be improved, and the low-temperature toughness can be increased. The element Ca is also an important element for implementing beneficial modification technology of inclusions in the present disclosure, and its content needs to match the content of Mg. Therefore, in the steel for marine engineering of the present disclosure, the mass percentage of the added element Ca is controlled to $0<\mathrm{Ca}\leq 0.0045\%$.

Cu: in the steel for marine engineering of the present disclosure, the element Cu can appropriately improve the hardenability of the steel, and can improve the atmospheric corrosion resistance of the steel. However, the content of the element Cu in the steel should not be too high. If the content of Cu in the steel is too high, the welding property of the steel will deteriorate. Therefore, in the steel for marine engineering of the present disclosure, the mass percentage of Cu can be preferably controlled to $0<\mathrm{Cu}\leq 0.5\%$.

Mo: in the steel for marine engineering of the present disclosure, the element Mo can effectively improve the pitting corrosion resistance of the steel, but too high a content of Mo increases the cold cracking tendency of the steel plate. Therefore, in the steel for marine engineering of the present disclosure, the mass percentage of the element Mo can be controlled to $0<\mathrm{Mo}\leq 0.40\%$.

[0015] In an embodiment, the steel for marine engineering of the present disclosure further comprises at least one of the following chemical elements: $0<\mathrm{Nb}\leq 0.04\%$, $0<\mathrm{V}\leq 0.05\%$, and $0<\mathrm{B}\leq 0.0005\%$.

[0016] In the above technical solution of the present disclosure, the elements Cu, Mo, Nb, V and B can all further improve the performance of the steel for marine engineering of the present disclosure.

[0017] Nb: in the steel for marine engineering of the present disclosure, Nb is a strong carbonitride forming element with a strong grain refining effect. Adding an appropriate amount of Nb to the steel to obtain a uniform grain size can effectively prevent some of the grains from excessive growth and form mixed crystal structure during heating, which would otherwise deteriorate the strength and toughness properties and the corrosion performance. Therefore, in the steel for marine engineering of the present disclosure, the mass percentage of the element Nb can be controlled to $0<\mathrm{Nb}\leq 0.04\%$.

[0018] V: in the steel for marine engineering of the present disclosure, the element V can contribute to the strengthening of the steel by forming VN or V(CN) fine precipitated particles with C and N. Furthermore, the element V is beneficial to improving the stability of hardness after quenching and tempering. However, it is to be noted that the content of the element V in the steel should not be too high. If the content of the element V in the steel is too high, the cost will be increased significantly. Therefore, in the steel for marine engineering of the present disclosure, the mass percentage of the element V can be controlled to $0<\mathrm{V}\leq 0.05\%$.

[0019] B: in the steel for marine engineering of the present disclosure, the element B can improve the hardenability of the steel and influence the cold cracking property of the steel. Therefore, in the steel for marine engineering of the present disclosure, the mass percentage of the element B can be controlled to $0<B\leq0.0005\%$.

[0020] It is to be noted that the addition of the elements Cu, Mo, Nb, V and B mentioned above will increase the cost of the material. Therefore, considering the performance and cost control in combination, in the technical solution of the present disclosure, it is preferred to add at least one of the above elements.

[0021] In an embodiment, in the steel for marine engineering of the present disclosure, among the inevitable impurities, $P\leq0.015\%$, and/or $S\leq0.0040\%$.

[0022] In the above technical solution, both P and S are impurity elements in the steel. Therefore, in order to achieve better performance and better quality of the steel, the content of impurity elements in the steel should be reduced as much as possible where technical conditions permit. If the content of the elements P and S in the steel is too high, defects such as segregation and inclusion are liable to occur, which deteriorate the welding property, impact toughness and HIC resistance of the steel plate.

[0023] Therefore, preferably, in the steel for marine platforms of the present disclosure, it is controlled that $P\leq0.015\%$ and $S\leq0.0040\%$. More preferably, beneficial modification technology of inclusions is used to spheroidize the inclusions, refine their size and achieve their uniform distribution, thereby reducing the influence of inclusions on toughness and corrosiveness.

[0024] In an embodiment, the mass percentages of the chemical elements in the steel for marine engineering of the present disclosure further satisfy at least one of:

$1.8\leq\alpha\leq2.0$, wherein $\alpha=1.2\mathrm{Cr}+5\mathrm{Ni}-\mathrm{Cr}^2-\mathrm{Ni}^2-4.61$;

$4.2\leq\beta\leq7.9$, wherein $\beta=40\mathrm{Al}+60\mathrm{Ti}+20\sqrt{\mathrm{Nb}+\mathrm{V}+\mathrm{Ti}}$; and

$35\leq\gamma\leq65$, wherein $\gamma=10\mathrm{Si}+30\sqrt{\mathrm{Mo}}+57\sqrt{\mathrm{Cu}}$.

[0025] For each chemical element, the value before the percent symbol of the mass percentage of the chemical element is substituted into the formula.

[0026] In the above technical solution, while controlling the mass percentages of individual elements in the steel for marine engineering of the present disclosure, it is also preferred to control the mass percentages of the chemical elements in the steel to satisfy at least one of: $1.8\leq\alpha\leq2.0$, $4.2\leq\beta\leq7.9$ and $35\leq\gamma\leq65$, so as to ensure a balance among the alloying element contents, so that the steel achieves good resistance to highly humid and hot corrosion, as well as balanced and improved strength and toughness.

[0027] In an embodiment, the microstructure of the steel for marine engineering of the present disclosure is tempered bainite with a phase ratio of greater than or equal to 95%.

[0028] In the above technical solution, the microstructure of the steel for marine engineering of the present disclosure is a tempered bainite structure, and the phase ratio of the tempered bainite is 95% or more, so that the steel has more balanced and improved strength and toughness.

[0029] In an embodiment, the steel for marine engineering of the present disclosure has a yield strength of 355 MPa or more, a tensile strength of 500-650 MPa, an elongation rate of 22% or more, an impact energy at -60°C of 100 J or more, a crack tip opening displacement (CTOD) at -60°C of 0.8 mm or more, a nil ductility transition temperature (NDTT) of -65°C or less, and a corrosion rate in a highly humid and hot atmospheric environment of 0.85 $g/(m^2*h)$ or less.

[0030] Correspondingly, another objective of the present disclosure is to provide a manufacturing method for steel for marine engineering. The manufacturing method is simple to perform. Steel for marine engineering manufactured by the method has not only excellent strength and toughness, but also excellent anti-fracture and anti-crack properties as well as corrosion resistance to highly humid and hot marine atmosphere.

[0031] In an embodiment, the steel for marine engineering prepared by the manufacturing method of the present disclosure has a yield strength of 355 MPa or more, a tensile strength of 500-650 MPa, an elongation rate of 22% or more, an impact energy at -60°C of 100 J or more, a CTOD at -60°C of 0.8 mm or more, an NDTT of -65°C or more, and a corrosion rate in a highly humid and hot atmospheric environment of 0.85 $g/(m^2*h)$ or less. The steel for marine engineering manufactured by the method of the present disclosure can be used for boats and marine engineering structures and has broad application prospects.

[0032] To achieve the above objective, the present disclosure provides a manufacturing method for steel for marine engineering, comprising the following steps:

(1) smelting and casting;
(2) heating;

(3) controlled rolling, the original austenite grain size after rolling being 20-25 μm;
(4) air cooling; and
(5) quenching and tempering, the austenite grain size after quenching being 20-25 μm.

[0033] In an embodiment, in the manufacturing method of the present disclosure, in step (1), hot metal pretreatment, converter smelting, LF refining, RH refining, inclusions beneficial treatment and continuous casting are performed successively, wherein in the inclusions beneficial treatment stage, composite inclusions with $MgO+Al_2O_3$ as the core which coated with CaS and MnS are formed, the size of the composite inclusions is 0.2 to 2.5 μm, and the number of composite inclusions in this size range accounts for more than 95% of the total number of inclusions.

[0034] In an embodiment, in the manufacturing method of the present disclosure, in step (1), in the stage of converter smelting, slag cutoff tapping is performed, with the thickness of a slag layer being controlled to be smaller than 30 mm; in the stage of LF refining, the sum of the mass percentages of FeO and MnO in the slag is controlled to be smaller than 1%, and a formula is satisfied: $(CaO+MgO+MnO)/(SiO_2+P_2O_5)\geq 9$, with the mass percentages of the substances being substituted into the formula; in the stage of inclusions beneficial treatment, Mg treatment or Mg and Ca composite treatment is performed; and when Mg and Ca composite treatment is performed, Ca and Mg need to be fed at the same time with a wire feeding speed of 150-250 m/min.

[0035] In the above technical solution, in step (1) of the manufacturing method of the present disclosure, in the stage of converter smelting, performing slag cutoff tapping, with the thickness of a slag layer being controlled to be smaller than 30 mm, can reduce the oxidation of slag in the ladle, prevent the increase of oxygen activity and rephosphorization of molten steel, and is conducive to subsequent production of white slag and inclusions modification treatment.

[0036] In the above technical solution, controlling $(CaO+MgO+MnO)/(SiO_2+P_2O_5)$ to be greater than 9 in the stage of LF refining can ensure good dephosphorization and desulfurization ability of the slag. In the process of producing white slag from the ladle, the sum of the mass percentages of FeO and MnO in the slag is controlled to be smaller than 1% so as to ensure the reduction of the slag and full desulfurization, reducing the content of inclusions in molten steel, and improving the strength and toughness as well as corrosion resistance of the steel.

[0037] In an embodiment, in the manufacturing method of the present disclosure, in step (2), it is controlled that a slab heating temperature $T_h=1150+600C+120\sqrt{Nb+Ti+V}$, with a unit being °C; and for each chemical element, the value before the percent symbol of the mass percentage of the chemical element is substituted into the formula.

[0038] In the above technical solution, in step (2) of the manufacturing method of the present disclosure, the purpose of controlling the slab heating temperature to the above value is to ensure sufficient solid solution of micro-alloyed carbonitrides, and facilitate homogenization of alloying elements, mitigate macroscopic and microscopic segregation in the steel, reduce the formation of corrosion primary cells due to different phases and potential differences between components, and improve the corrosion resistance of the steel plate.

[0039] In an embodiment, in the manufacturing method of the present disclosure, in step (3), it is controlled that an initial rolling temperature $T_{sr}=0.92T_h-0.96T_h$; it is controlled that a final rolling temperature $T_{fr}=1100-199C-98\sqrt{Mn}-42\sqrt{Ni}-21Cr$; units of the initial rolling temperature and the final rolling temperature are both °C; and for each chemical element, the value before the percent symbol of the mass percentage of the chemical element is substituted into the formula.

[0040] In the above technical solution, the purpose of controlling that the initial rolling temperature $T_{sr}=0.92T_h-0.96T_h$ is mainly to ensure that the steel plate is rolled at a relatively high temperature in a recrystallization zone to fully recrystallize and form uniform equiaxed austenite grains.

[0041] In the above technical solution, controlling the final rolling temperature to satisfy $T_{fr}=1100-199C-98\sqrt{Mn}-42\sqrt{Ni}-21Cr$ can ensure that the steel plates are rolled at a temperature above the non-static recrystallization temperature to prevent the occurrence of mixed crystals and uneven grains; secondly, it can be ensured that there is sufficient temperature drop space in the rolling process.

[0042] In an embodiment, in the manufacturing method of the present disclosure, in step (3), rolling reduction in a single pass is 8-12%, and cumulative rolling reduction is 60% or more.

[0043] In the above technical solution of the present disclosure, the purpose of controlling rolling reduction of a single pass to 8-12% is mainly to ensure that the steel plate has sufficient recrystallization driving force in each pass, while the number of the rolling passes are sufficient enough to achieve grain homogenization of the steel plate, so as to maintain the original austenite grain size after rolling to 20-25 μm. Moreover, in step (3) of the present disclosure, the purpose of controlling cumulative rolling reduction to be 60% or more is mainly to achieve sufficient recrystallization and sufficient homogenization at the core of the steel plate to ensure the strength and toughness, and anti-fracture and anti-crack properties of the core.

[0044] Further, in the manufacturing method of the present disclosure, in step (5), it is controlled that a quenching temperature $T_q=955-11C-14Mn-17\sqrt{Cr}+16\sqrt{Mo}$; and/or it is controlled that a tempering temperature $T_t=710-203\sqrt{C}-15.2Ni+44.7Si+104V+31.5Mo$; units of the quenching temperature and the tempering temperature are both °C; and for each chemical element, the value before the percent symbol of the mass percentage of the chemical element is substituted into the formula.

[0045] In the above technical solution of the present disclosure, the purpose of setting the above-mentioned quenching temperature is firstly to ensure complete austenitization of the steel plate; and secondly, by austenitization at a relatively high temperature, sufficient solid solution of carbonitrides can be achieved, uniform distribution of alloy in the steel can be facilitated, and microscopic electrochemical corrosion caused by segregation can be mitigated. Furthermore, the quenching temperature will not be too high, which would otherwise cause part of austenite grains to grow rapidly, resulting in mixed crystals. Subsequently, water quenching can be performed, the purpose of which is to obtain a high cooling rate and form a unitary martensitic structure, so as to ensure that the austenite grain size after quenching is maintained at 20-25 μm.

[0046] In the above technical solution of the present disclosure, in step (5) of the present disclosure, the purpose of setting the above-mentioned tempering temperature is firstly to ensure that the steel plate has good mechanical properties and anti-fracture and anti-crack properties, secondly to eliminate quenching stress within the steel plate by tempering, so as to prevent corrosion caused by different forces at various positions inside the steel plate, and finally to obtain tempered bainite structure after the steel plate is tempered, thereby reducing microscopic galvanic corrosion caused by multiple phases.

[0047] It is to be noted that in the present disclosure, if the tempering temperature is too high, a ferrite structure will be formed in the steel, which will reduce the strength and impact property of the steel plate; and if the tempering temperature is too low, the strength of the steel plate is too high and the impact toughness is relatively low.

[0048] Compared with the prior art, the steel for marine engineering and the manufacturing method therefor of the present disclosure have the following advantages and beneficial effects as described below:
by composition design, structure regulation, and condition control of production process and the like, the steel plate of the present disclosure achieves suitable strength property, excellent impact toughness, good anti-fracture and anti-crack properties, and excellent corrosion resistance to highly humid and hot marine atmosphere.

[0049] Compared with the prior art, the manufacturing method of the present disclosure uses unique composition design technology, pure steel smelting technology, inclusions beneficial control technology, steel homogenization technology, grain size control and microstructure regulation technology, so as to produce steel types with strength requirements of 355 MPa level, good low-temperature impact toughness, good anti-fracture and anti-crack properties and excellent resistance to highly humid and hot atmospheric corrosion. The steel plate manufactured by the method of the present disclosure differs greatly from the existing steel plates in structure, composition and process design.

[0050] The steel for marine engineering of the present disclosure can achieve: a yield strength of 355 MPa or more, a tensile strength of 500-650 MPa, an elongation rate of 22% or more, an impact energy at -60°C of 100 J or more, a CTOD at -60°C of 0.8 mm or more, an NDTT of -65°C or less, and a corrosion rate in a highly humid and hot atmospheric environment of 0.85 $g/(m^2*h)$ or less.

[0051] The steel for marine engineering of the present disclosure can be used for key components of boats and marine engineering structures, meets the current development demand for steel for boats and marine engineering equipment in China, and has broad application prospects.

DETAILED DESCRIPTION

[0052] Specific implementation modes of the present invention will be further explained and described below in conjunction with specific embodiments. However, the explanation and description do not limit technical solutions of the present invention.

Examples 1-6 and Comparative Example 1

[0053] Both steel for marine engineering in Examples 1-6 and comparative steel in Comparative Example 1 are prepared by the following steps:

(1) performing smelting and casting according to the chemical compositions shown in Table 1-1 and Table 1-2 below, wherein hot metal pretreatment, converter smelting, LF refining, RH refining, inclusions beneficial treatment

and continuous casting are performed successively, wherein at the stage of inclusions beneficial treatment, composite inclusions with $MgO+Al_2O_3$ as the core which coated with CaS and MnS are formed. The size of the composite inclusions is 0.2-2.5μm, and the number of the composite inclusions within the size range accounts for 95% or above of the total number of inclusions.

[0054] At the stage of converter smelting, slag cutoff tapping is performed, with the thickness of a slag layer being controlled to be smaller than 30 mm; at the stage of LF refining, the sum of the mass percentages of FeO and MnO in the slag is controlled to be smaller than 1%, and $(CaO+MgO+MnO)/(SiO_2+P_2O_5)$ is controlled to be greater than 9, with the mass percentages of the substances being substituted into the relationship; at the stage of inclusions beneficial treatment, Mg treatment or Mg and Ca composite treatment is performed; and when Mg and Ca composite treatment is performed, Ca and Mg need to be fed at the same time with a wire feeding speed of 150-250 m/min.

[0055] (2) heating: it is controlled that the slab heating temperature T_h=1150+600C+ $120\sqrt{Nb+Ti+V}$, with a unit being °C.

[0056] (3) controlled rolling: the original austenite grain size after rolling is maintained at 20-25 μm; it is controlled that the initial rolling temperature T_{sr}=0.92T_h-0.96T_h; it is controlled that the final rolling temperature $T_{fr}=1100-199C-98\sqrt{Mn}-42\sqrt{Ni}-21Cr$; units of the initial rolling temperature and the final rolling temperature are both °C; and the rolling reduction of a single pass is 8-12%, and cumulative rolling reduction is 60% or more.

[0057] (4) air cooling.

[0058] (5) quenching+tempering: it is controlled that the quenching temperature $T_q=955-11C-14Mn-17\sqrt{Cr}+16\sqrt{Mo}$, and it is controlled that the tempering temperature $Tt=710-203\sqrt{C}-15.2Ni+44.7Si+104V+31.5Mo$; and the austenite grain size after quenching is maintained at 20-25 μm.

[0059] It is to be noted that in Examples 1-6 of the present disclosure, 6 different chemical compositions are designed and combined with suitable production processes to manufacture steel plates having different thickness specifications. The chemical composition designs of the steel for marine engineering in Examples 1-6 and the related processes all meet the design specification requirements of the present disclosure.

[0060] Tables 1-1 and 1-2 list the mass percentages of the chemical elements of the steel for marine engineering in Examples 1-6 and the comparative steel in Comparative Example 1.

Table 1-1 (wt.%, the remainder being Fe and other inevitable impurities except P and S)

Serial Number	Chemical element														
	C	Si	Mn	P	S	Cr	Ni	Al	Ti	Mg	Ca	Cu	Mo	Nb	V	B
Example 1	0.015	0.55	1.3	0.015	0.003	0.60	2.20	0.01	0.008	0.0010	0.0001	0.5	0.4	0.01	0.05	0.0003
Example 2	0.020	0.45	1.2	0.012	0.002	0.90	2.40	0.05	0.009	0.0005	0.0006	0.4	0.1	0.015	0.03	0.0002
Example 3	0.030	0.35	1.1	0.012	0.003	0.90	2.25	0.04	0.012	0.0012	0.0001	0.4	0	0.016	0.01	0.0001
Example 4	0.030	0.45	1.0	0.010	0.002	0.70	2.50	0.03	0.012	0.0008	0.0002	0.3	0.4	0.016	0	0.0004
Example 5	0.040	0.15	0.8	0.008	0.002	0.60	2.75	0.02	0.011	0.0015	0.0010	0.1	0.3	0.02	0	0.0001
Example 6	0.020	0.60	0.5	0.012	0.003	0.80	2.85	0.06	0.008	0.0005	0.0045	0.2	0.2	0	0	0
Comparative Example 1	***0.12***	0.15	***1.35***	0.002	0.003	***0***	***0***	0.02	***0***	***0***	***0***	0	0	0.015	0	0

Table 1-2

Serial Number	α	β	γ
Example 1	1.91	6.1	64.78
Example 2	1.90	7.2	50.04
Example 3	1.85	6.2	39.55
Example 4	1.99	5.3	54.69
Example 5	1.94	5.0	35.96
Example 6	1.84	4.7	44.91
Comparative Example 1	-4.61	3.2	1.50
Note: In Table 1-2 above, $\alpha=1.2Cr+5Ni-Cr^2-Ni^2-4.61$, $\beta=40Al+60Ti+20\sqrt{Nb+V+Ti}$, and $\gamma=10Si+30\sqrt{Mo}+57\sqrt{Cu}$; for each chemical element, the value before the percent symbol of the mass percentage of the chemical element is substituted into the formula.			

[0061] Table 2 lists specific process parameters for fabricating the steel for marine engineering in Embodiments 1-6 and the comparative steel in Comparative Example 1.

Table 2

Serial Number	Plate thickness	Step (1)	Step (2)	Step (3)				Step (5)	
		Wire feeding speed (m/min)	Slab heating temperature (°C)	Initial rolling temperature (°C)	Final rolling temperature (°C)	Rolling reduction of a single pass (%)	Cumulative rolling reduction (%)	Quenching temperature (°C)	Tempering temperature (°C)
Example 1	20	150	1190	1119	910	8	94	934	694
Example 2	40	170	1190	1118	905	9	89	927	671
Example 3	60	190	1191	1120	909	10	83	923	657
Example 4	80	210	1188	1117	915	11	78	937	670
Example 5	100	230	1195	1123	922	12	72	939	644
Example 6	120	250	1173	1102	939	12	67	940	671
Comparative Example 1	60	-	1120	1020	760	5-13	83	-	-

[0062] The obtained steel for marine engineering in Examples 1-6 and the obtained comparative steel in Comparative Example 1 are sampled, respectively, a tensile test, a Charpy V-notch impact test, a CTOD test (an index to check the fracture toughness of steel plates), an NDTT property checking test (an important index to measure the crack arrest properties of steel plates) and a corrosion test under highly humid and hot conditions are performed on finished plates in the Examples and the Comparative Example, respectively. The test results of the Examples and the Comparative Example are listed in Table 3, respectively.

Testing methods are described below:

[0063] Tensile test: according to GB/T 228.1, full-thickness plate-like tensile test specimens are used for steel plates with a thickness of smaller than 50 mm, and rod-like tensile test specimens are used for steel plates with a thickness of greater than 50 mm, then the room-temperature tensile properties of the steel plates are measured.

[0064] Charpy V-notch impact test: according to GB/T 229, Charpy V-notch impact test specimens are used to measure the impact properties of the material plates at a position of t/4 of thicknesses at -60°C.

[0065] CTOD test: according to BS7448-1, full-thickness CTOD test specimens are used to measure the fracture toughness of the materials at -60°C.

[0066] NDTT property checking test: according to GB/T 6803-2008, P3 test specimens are used to measure the nil-ductility transition temperature of the materials.

[0067] Corrosion test under highly humid and hot conditions: it is controlled that the test process uses 5% NaCl solution with a temperature of 35 °C, and a pH of 6.5-7.2, an average sedimentation rate of salt spray is controlled to 1.5mL/(80cm^2·h), and an RH (relative humidity) is controlled to 95%-100%.

[0068] Table 3 lists the test results of the steel for marine engineering in Embodiments 1-6 and the comparative steel in Comparative Example 1.

Table 3

Serial Number	Yield Strength ReH (MPa)	Tensile strength RM (MPa)	Elongation rate A (%)	Impact energy KV2 at -60°C (J)	CTOD value at -60°C (J)	NDTT (°C)	Corrosion rate under highly humid and hot conditions g/(m^2*h)
Example 1	541	595	25	300	2.0	-80	0.83
Example 2	532	587	24	305	1.8	-75	0.72
Example 3	508	580	25	298	1.6	-75	0.79
Example 4	488	570	23	268	1.5	-70	0.6
Example 5	450	551	22	258	1.1	-70	0.8
Example 6	423	532	22	270	0.8	-65	0.78
Comparative Example 1	420	523	22	220	0.5	-45	1.21

[0069] As can be seen from Table 3, the overall performance of the steel for marine engineering in Examples 1-6 is significantly superior to that of the comparative steel in Comparative Example 1. In a highly humid and hot atmospheric environment, the corrosion rates of the steel for marine engineering in Examples 1-6 are significantly smaller than the corrosion rate of the steel in Comparative Example 1. As can be seen, the steel for marine engineering in Examples 1-6 has better resistance to highly humid and hot corrosion, compared with the comparative steel in Comparative Example 1.

[0070] As shown in Table 3, the steel for marine engineering in Examples 1-6 has excellent strength and toughness properties, anti-fracture and anti-crack properties, and resistance to highly humid and hot corrosion, compared with the comparative steel in Comparative Example 1. The steel for marine engineering in Examples 1-6 all has a yield strength of 423 MPa or more, a tensile strength of 532-595 MPa, an impact energy at -60°C of 270 J or more, an elongation rate of 22% or more, a CTOD at -60°C of 0.8 mm or more, an NDTT of -65°C or less, and a corrosion rate in a highly humid and hot atmospheric environment of 0.83 g/(m^2*h) or less.

[0071] In summary, as can be seen, by reasonable chemical composition design in combination with an optimized process, the steel for marine engineering of the present disclosure achieves suitable strength properties, excellent impact toughness, good anti-fracture and anti-crack properties and excellent corrosion resistance to highly humid and hot marine atmosphere at the same time. The steel for marine engineering of the present disclosure can be effectively used for manufacturing key components of boats and marine engineering structures, offshore wind power platforms, sea island buildings, etc. The steel meets the current development demand for steel for boats and marine engineering equipment in China, and has broad application prospects.

[0072] In addition, combinations of various technical features in the present disclosure are not limited to combinations described in the claims or embodiments. All technical features in the present disclosure can be freely combined or incorporated in any way, unless contradictions are generated therebetween.

[0073] It also needs to be noted that the embodiments listed above are only specific implementations of the present disclosure. Obviously, the present disclosure is not limited to the above embodiments, and similar changes or modifications thereto can be directly obtained or easily conceived from the disclosure of the present disclosure by those skilled in the art, and should all fall within the protection scope of the present disclosure.

Claims

1. Steel for marine engineering, comprising the following chemical elements by mass percentage:
   C: 0.01-0.05%, Si: 0.05-0.60%, Mn: 0.50-1.30%, Cr: 0.6-1.20%, Ni: 2.0-3.0%, Al: 0.01-0.06%, Ti: 0.005-0.012%, and Mg: 0.0005-0.0015%; $0<Ca\leq 0.0045\%$, $0<Cu\leq 0.5\%$, and $0<Mo\leq 0.40\%$; and the remainder of Fe and inevitable impurities.

2. The steel for marine engineering according to claim 1, wherein the mass percentages of the chemical elements are as follows:
   C: 0.015-0.04%, Si: 0.15-0.60%, Mn: 0.50-1.30%, Cr: 0.6-0.90%, Ni: 2.0-2.85%, Al: 0.01-0.06%, Ti: 0.005-0.012%, and Mg: 0.0005-0.0015%; $0<Ca\leq 0.0045\%$, $0<Cu\leq 0.5\%$, and $0<Mo\leq 0.40\%$; and the remainder of Fe and inevitable impurities.

3. The steel for marine engineering according to claim 1 or 2, wherein the steel further comprises at least one of the following chemical elements: $0<Nb\leq 0.04\%$, $0<V\leq 0.05\%$, and $0<B\leq 0.0005\%$.

4. The steel for marine engineering according to claim 1 or 2, wherein in the inevitable impurities, $P\leq 0.015\%$, and/or $S\leq 0.0040\%$.

5. The steel for marine engineering according to claim 1 or 2, wherein the mass percentages of the chemical elements further satisfy at least one of the following relationships:

   $1.8\leq\alpha\leq 2.0$, wherein $\alpha=1.2Cr+5Ni-Cr^2-Ni^2-4.61$; and

   $35\leq\gamma\leq 65$, wherein $\gamma=10Si+30\sqrt{Mo}+57\sqrt{Cu}$.

6. The steel for marine engineering according to claim 1 or 2, wherein the steel has a microstructure of tempered bainite with a phase ratio of 95% or more.

7. The steel for marine engineering according to claim 3, wherein the mass percentages of the chemical elements further satisfy: $4.2\leq\beta\leq 7.9$, wherein $\beta=40Al+60Ti+20\sqrt{Nb+V+Ti}$.

8. The steel for marine engineering according to claim 1 or 2, wherein the steel has a yield strength of 355 MPa or more, a tensile strength of 500-650 MPa, an elongation rate of 22% or more, an impact energy at -60°C of 100 J or more, a CTOD at -60°C of 0.8 mm or more, an NDTT of -65°C or less, and a corrosion rate in a highly humid and hot atmospheric environment of 0.85 $g/(m^2*h)$ or less.

9. A manufacturing method for the steel for marine engineering according to any one of claims 1-8, comprising the following steps:

   (1) smelting and continuous casting;
   (2) heating;
   (3) controlled rolling, an original austenite grain size after rolling being 20-25 μm;
   (4) air cooling; and
   (5) quenching and tempering, an austenite grain size after quenching being 20-25 μm.

10. The manufacturing method according to claim 9, wherein in step (1), hot metal pretreatment, converter smelting, LF refining, RH refining, inclusions beneficial treatment and continuous casting are performed successively, wherein in the stage of inclusions beneficial treatment, composite inclusions having a size of 0.2-2.5μm are formed, and the composite inclusion comprises $MgO+Al_2O_3$ coated with CaS and MnS as its core and a number of the composite inclusions within the size range accounting for 95% or more of a total number of inclusions.

11. The manufacturing method according to claim 10, wherein in step (1), at the stage of converter smelting, slag cutoff tapping is performed, with a thickness of a slag layer being controlled to be smaller than 30 mm; at the stage of LF refining, a sum of the mass percentages of FeO and MnO in slag is controlled to be smaller than 1%, and a formula is satisfied: $(CaO+MgO+MnO)/(SiO_2+P_2O_5)>9$, in the formula, each substances represents their corresponding mass percentages; at the stage of inclusions beneficial treatment, Mg treatment or Mg and Ca composite treatment is performed; and when Mg and Ca composite treatment is performed, Ca and Mg are fed at the same time with a wire feeding speed of 150-250 m/min.

12. The manufacturing method according to claim 10, wherein in step (2), a slab heating temperature T_h satisfies $T_h=1150+600C+120\sqrt{Nb+Ti+V}$, with a unit being °C.

13. The manufacturing method according to claim 12, wherein in step (3), an initial rolling temperature T_{sr} satisfies $T_{sr}=0.92T_h-0.96T_h$; a final rolling temperature T_{fr} satisfies $T_{fr}=1100-199C-98\sqrt{Mn}-42\sqrt{Ni}-21Cr$, with a unit being °C.

14. The manufacturing method according to claim 12, wherein in step (3), rolling reduction in a single pass is 8-12%, and cumulative rolling reduction is 60% or more.

15. The manufacturing method according to claim 12, wherein in step (5), a quenching temperature T_q satisfies $T_q=955-11C-14Mn-17\sqrt{Cr}+16\sqrt{Mo}$, and/or a tempering temperature T_t satisfies $T_t=710-203\sqrt{C}-15.2Ni+44.7Si+104V+31.5Mo$, with a unit being °C.

Amended claims under Art. 19.1 PCT

1. Steel for marine engineering, comprising the following chemical elements by mass percentage:
C: 0.01-0.05%, Si: 0.05-0.60%, Mn: 0.50-1.30%, Cr: 0.6-1.20%, Ni: 2.0-2.85%, Al: 0.01-0.06%, Ti: 0.005-0.012%, and Mg: 0.0005-0.0015%; $0<Ca\leq0.0045\%$, $0<Cu\leq0.5\%$, and $0<Mo\leq0.40\%$; and the remainder of Fe and inevitable impurities.

2. The steel for marine engineering according to claim 1, wherein the mass percentages of the chemical elements are as follows:
C: 0.015-0.04%, Si: 0.15-0.60%, Mn: 0.50-1.30%, Cr: 0.6-0.90%, Ni: 2.0-2.85%, Al: 0.01-0.06%, Ti: 0.005-0.012%, and Mg: 0.0005-0.0015%; $0<Ca\leq0.0045\%$, $0<Cu\leq0.5\%$, and $0<Mo\leq0.40\%$; and the remainder of Fe and inevitable impurities.

3. The steel for marine engineering according to claim 1 or 2, wherein the steel further comprises at least one of the following chemical elements: $0<Nb\leq0.04\%$, $0<V\leq0.05\%$, and $0<B\leq0.0005\%$.

4. The steel for marine engineering according to claim 1 or 2, wherein in the inevitable impurities, $P\leq0.015\%$, and/or $S\leq0.0040\%$.

5. The steel for marine engineering according to claim 1 or 2, wherein the mass percentages of the chemical elements further satisfy at least one of the following relationships:

$1.8\leq\alpha\leq2.0$, wherein $\alpha=1.2Cr+5Ni-Cr^2-Ni^2-4.61$; and

$35 \leq \gamma \leq 65$, wherein $\gamma = 10\mathrm{Si} + 30\sqrt{\mathrm{Mo}} + 57\sqrt{\mathrm{Cu}}$.

6. The steel for marine engineering according to claim 1 or 2, wherein the steel has a microstructure of tempered bainite with a phase ratio of 95% or more.

7. The steel for marine engineering according to claim 3, wherein the mass percentages of the chemical elements further satisfy: $4.2 \leq \beta \leq 7.9$, wherein $\beta = 40\mathrm{Al} + 60\mathrm{Ti} + 20\sqrt{\mathrm{Nb} + \mathrm{V} + \mathrm{Ti}}$.

8. The steel for marine engineering according to claim 1 or 2, wherein the steel has a yield strength of 355 MPa or more, a tensile strength of 500-650 MPa, an elongation rate of 22% or more, an impact energy at -60°C of 100 J or more, a CTOD at -60°C of 0.8 mm or more, an NDTT of -65°C or less, and a corrosion rate in a highly humid and hot atmospheric environment of 0.85 $\mathrm{g/(m^2{*}h)}$ or less.

9. A manufacturing method for the steel for marine engineering according to any one of claims 1-8, comprising the following steps:

(1) smelting and continuous casting;
(2) heating;
(3) controlled rolling, an original austenite grain size after rolling being 20-25 μm;
(4) air cooling; and
(5) quenching and tempering, an austenite grain size after quenching being 20-25 μm.

10. The manufacturing method according to claim 9, wherein in step (1), hot metal pretreatment, converter smelting, LF refining, RH refining, inclusions beneficial treatment and continuous casting are performed successively, wherein in the stage of inclusions beneficial treatment, composite inclusions having a size of 0.2-2.5μm are formed, and the composite inclusion comprises $MgO+Al_2O_3$ coated with CaS and MnS as its core and a number of the composite inclusions within the size range accounting for 95% or more of a total number of inclusions.

11. The manufacturing method according to claim 10, wherein in step (1), at the stage of converter smelting, slag cutoff tapping is performed, with a thickness of a slag layer being controlled to be smaller than 30 mm; at the stage of LF refining, a sum of the mass percentages of FeO and MnO in slag is controlled to be smaller than 1%, and a formula is satisfied: $(CaO+MgO+MnO)/(SiO_2+P_2O_5)>9$, in the formula, each substances represents their corresponding mass percentages; at the stage of inclusions beneficial treatment, Mg treatment or Mg and Ca composite treatment is performed; and when Mg and Ca composite treatment is performed, Ca and Mg are fed at the same time with a wire feeding speed of 150-250 m/min.

12. The manufacturing method according to claim 10, wherein in step (2), a slab heating temperature T_h satisfies $T_h = 1150 + 600\mathrm{C} + 120\sqrt{\mathrm{Nb} + \mathrm{Ti} + \mathrm{V}}$, with a unit being °C.

13. The manufacturing method according to claim 12, wherein in step (3), an initial rolling temperature T_{sr} satisfies $T_{sr} = 0.92T_h\text{-}0.96T_h$; a final rolling temperature T_{fr} satisfies $T_{fr} = 1100 - 199\mathrm{C} - 98\sqrt{\mathrm{Mn}} - 42\sqrt{\mathrm{Ni}} - 21\mathrm{Cr}$, with a unit being °C.

14. The manufacturing method according to claim 12, wherein in step (3), rolling reduction in a single pass is 8-12%, and cumulative rolling reduction is 60% or more.

15. The manufacturing method according to claim 12, wherein in step (5), a quenching temperature T_q satisfies $T_q = 955 - 11\mathrm{C} - 14\mathrm{Mn} - 17\sqrt{\mathrm{Cr}} + 16\sqrt{\mathrm{Mo}}$, and/or a tempering temperature Tt satisfies $T_t = 710 - 203\sqrt{\mathrm{C}} - 15.2\mathrm{Ni} + 44.7\mathrm{Si} + 104\mathrm{V} + 31.5\mathrm{Mo}$, with a unit being °C.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2022/071240

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/02(2006.01)i; C22C 38/00(2006.01)i; C21D 9/52(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; C21D

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

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

CNTXT; ENTXTC; DWPI; CJFD; CNKI: 硅, 锰, 铬, 镍, 铝, 钛, 镁, 钙, 贝氏体, 淬火, 回火, Si, Silicon, Silicium, Silicone, Mn, Manganese, Manganous, Manganum, Mangan, Cr, Chromium, Chrome, Chrom, Ni, Nickel, Al, Aluminium, Aluminum, Mg, Magnesium, Ca, calcium, Ti, Titanium, Titanic, Bainite, hard+, quench+, temper+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2017160512 A (NIPPON STEEL & SUMITOMO METAL CORP.) 14 September 2017 (2017-09-14) description paragraphs 0012-0015, 0023-0024, 0034, 0046 and 0047, figures 1-4	1-15
A	CN 103320692 A (BAOSHAN IRON & STEEL CO., LTD.) 25 September 2013 (2013-09-25) entire document	1-15
A	CN 105008574 A (JFE STEEL CORPORATION) 28 October 2015 (2015-10-28) entire document	1-15
A	JP 2002332536 A (NIPPON STEEL CORP.) 22 November 2002 (2002-11-22) entire document	1-15
A	JP 2016180163 A (JFE STEEL CORP.) 13 October 2016 (2016-10-13) entire document	1-15

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

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

Date of the actual completion of the international search **30 March 2022**	Date of mailing of the international search report **13 April 2022**
Name and mailing address of the ISA/CN **China National Intellectual Property Administration (ISA/CN)** **No. 6, Xitucheng Road, Jimenqiao, Haidian District, Beijing 100088, China** Facsimile No. **(86-10)62019451**	Authorized officer Telephone No.

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

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
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Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 2017160512 A	14 September 2017	None	
CN 103320692 A	25 September 2013	JP 2016524653 A	18 August 2016
		WO 2014201887 A1	24 December 2014
		US 2016122844 A1	05 May 2016
		ES 2790421 T3	27 October 2020
		EP 3012340 A1	27 April 2016
		CA 2914441 A1	24 December 2014
		KR 20150143838 A	23 December 2015
		BR 112015027406 B1	17 March 2020
CN 105008574 A	28 October 2015	US 2016040274 A1	11 February 2016
		EP 2975148 A1	20 January 2016
		KR 20150119285 A	23 October 2015
		WO 2014141632 A1	18 September 2014
		JP 5618036 B1	05 November 2014
JP 2002332536 A	22 November 2002	None	
JP 2016180163 A	13 October 2016	None	

Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- CN 106756476 A **[0007]**
- CN 105132832 A **[0008]**
- CN 103741056 A **[0009]**