(19) Europäisches Patentamt / European Patent Office / Office européen des brevets

(11) EP 4 549 606 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
07.05.2025 Bulletin 2025/19

(21) Application number: **22949154.3**

(22) Date of filing: **19.12.2022**

(51) International Patent Classification (IPC):
C22C 38/02 (2006.01) *C22C 38/04* (2006.01)
C22C 38/06 (2006.01) *C22C 38/42* (2006.01)
C22C 38/44 (2006.01) *C22C 38/46* (2006.01)
C22C 38/48 (2006.01) *C22C 38/50* (2006.01)
C21D 8/02 (2006.01) *C22C 33/04* (2006.01)

(86) International application number:
PCT/CN2022/139834

(87) International publication number:
WO 2024/001078 (04.01.2024 Gazette 2024/01)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
KH MA MD TN

(30) Priority: **29.06.2022 CN 202210747803**

(71) Applicants:
- **Shandong Iron And Steel Company Ltd.**
  Laiwu, Shandong 271104 (CN)
- **Laiwu Steel Yinshan Section Co., Ltd.**
  Jinan, Shandong 271104 (CN)

(72) Inventors:
- **MA, Heng**
  Jinan, Shandong 271104 (CN)
- **ZHANG, Qingpu**
  Jinan, Shandong 271104 (CN)
- **WANG, Zhongxue**
  Jinan, Shandong 271104 (CN)
- **WANG, Tengfei**
  Jinan, Shandong 271104 (CN)
- **ZHANG, Pei**
  Jinan, Shandong 271104 (CN)
- **HE, Kang**
  Jinan, Shandong 271104 (CN)
- **WANG, Yuexiang**
  Jinan, Shandong 271104 (CN)
- **QIN, Gang**
  Jinan, Shandong 271104 (CN)
- **LIU, Jungang**
  Jinan, Shandong 271104 (CN)
- **GAO, Zhibin**
  Jinan, Shandong 271104 (CN)

(74) Representative: **Bryn Aarflot AS**
Patent
Stortingsgata 8
0161 Oslo (NO)

(54) **80 MM THICK 690 MPA-GRADE ULTRA-HIGH STRENGTH AND TOUGHNESS MARINE STEEL PLATE AND PREPARATION METHOD THEREFOR**

(57) The present invention relates to an 80mm-thick 690MPa-grade ultra-high strength and toughness marine-engineering steel plate and the preparation method thereof, wherein the chemical composition of the steel plate, by mass percentage, is shown as follows: C: 0.08%~0.10%, Si: 0.20%~0.30%, Mn: 1.10%~1.25%, P ≤0.007%, S ≤0.002%, Nb: 0.020%~0.030%, Ti: 0.010%~0.020%, V: 0.030%~0.045%, Cr: 0.40%~0.60%, Ni: 1.40%~1.50%, Cu: 0.15%~0.25%, Mo: 0.25%~0.35%, Als: 0.015%~0.045%, and Pcm ≤0.33%, Ceq ≤0.64%, the rest are Fe and inevitable impurity elements. The 80mm-thick 690MPa-grade ultra-high strength and toughness marine-engineering steel plate according to the present invention has the performance indicators that meets all the certification requirements of China Classification Society for EH690 steel. Also, the saturated corrosion current density at -300mV (relative to Ag/AgCl reference electrode) is ≤1.90mA/cm^2; the corrosion-active inclusion has a density of ≤9/mm^2. The product has excellent characteristics such as high toughness, low temperature resistance, and corrosion resistance, etc.

EP 4 549 606 A1

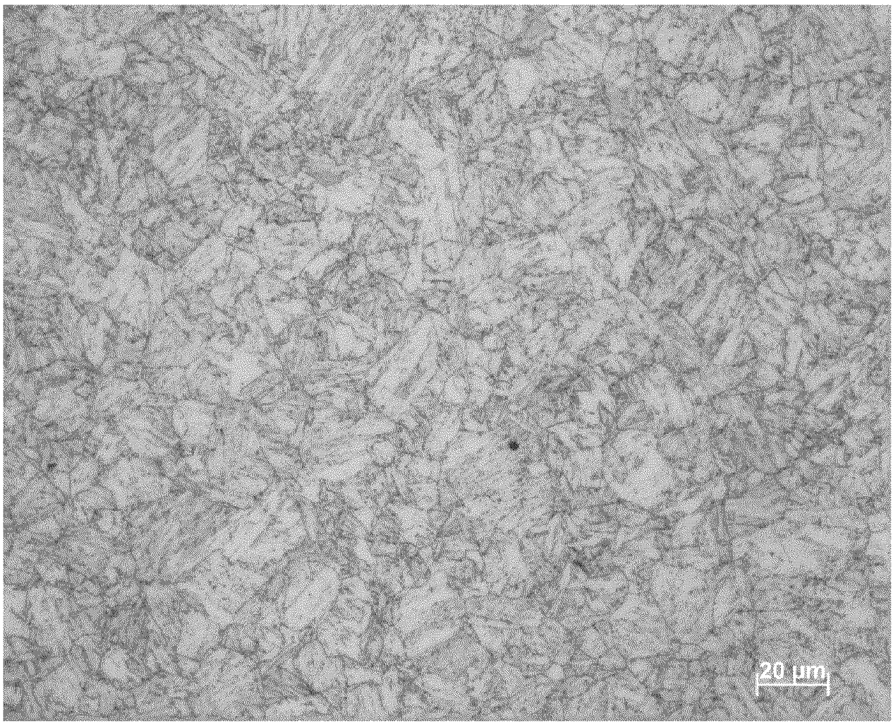

Figure 1

Description

Cross-Reference To Related Applications

[0001] The present application claims the priority right to Chinese patent application 2022107478038, titled "An 80mm-thick 690MPa-grade ultra-high strength and toughness marine-engineering steel plate and the preparation method thereof" and submitted on June 29, 2022, which is hereby incorporated by reference.

Technical field

[0002] The present invention involves the technical field of producing ultra-high strength marine-engineering steel, and specifically relates to an 80mm-ultra-thick 690MPa-grade ultra-high strength and toughness marine-engineering steel plate and the preparation method thereof.

Background Art

[0003] With the continuous exploration of the marine field, research and development, as well as production, of the ultra-thick steel that can be used for ship and marine engineering have become a top priority. Due to the complex and varied marine environment, such ultra-thick marine-engineering steel is required to have excellent properties such as high strength, high toughness, easy welding, and resistance to seawater corrosion, etc.

[0004] There are many deficiencies in the current technology for producing ultra-thick 690MPa-grade steel plates. For instance, in the aspect of composition design, some preparation methods involve addition of a large amount of alloying elements, which increases production costs; while others may cause difficulties in the production process or subsequent processing and use of steel plates. And in terms of production process, there often exists problem of comprising a long heat treatment process.

[0005] Chinese patent CN 111304551B relates to an ultra-high-strength EH690 extra-thick steel plate and the manufacturing method thereof. In the patent, C: 0.10% ~ 0.17%, Si: 0.25% ~ 0.45%, Mn: 0.90% ~ 1.30%, S ≤0.003%, P≤0.010%, V: 0.041% ~ 0.076%; Als: 0.03% ~ 0.05%, N: 0.004% ~ 0.013%, Ni: 1.40% ~ 1.80%, Cr: 0.60% ~ 1.00%, Mo : 0.30% ~ 0.50%, Nb: 0.021% ~ 0.04%, Cu: 0.43% ~ 0.50%, Ti ≤ 0.02%, among which more V, Cr, Mo, Cu and other elements are added. In this patent, a heat treatment process of quenching, sub-temperature quenching and tempering is used after rolling.

[0006] The patent application with publication number CN110846577A relates to a 690MPa-grade medium manganese steel with a low yield ratio and the manufacturing method thereof, wherein the composition contains 4.1%-4.7% of Mn element. However, addition of a large amount of Mn element brought huge difficulties in steelmaking and continuous casting process, and the continuous casting production caused accidents easily. Although the medium manganese steel had higher low-temperature toughness, problems such as unqualified flaw inspection and corner cracks, etc. often occurred to the rolled steel plates.

[0007] The application with the publication number CN 112251670A and the patent CN 102965592B both relate to a method for preparing extra-thick 690MPa-grade marine-engineering steel, wherein 0.001% ~ 0.0015% and 0.001% ~ 0.003% of B element were added to the chemical composition respectively, to improve the strength of the steel plate. Addition of B element significantly increased the incidence of welding cracks in the steel plate, which is detrimental to subsequent processing. In these preparation technologies, in order to obtain the desired performance, it is necessary to perform a normalizing heat treatment at 890-920°C before quenching and high-temperature tempering heat treatment, or a low-temperature tempering heat treatment below 300°C after quenching and high-temperature tempering heat treatment, which does not meet the industry's need for improving production efficiency and reducing costs.

Summary of the Invention

[0008] In view of the shortcomings and defects of the existing technology, the present invention is to provide an 80 mm 690MPa-grade ultra-high strength and toughness marine-engineering steel plate and the preparation method thereof. The 80 mm 690MPa-grade ultra-high strength and toughness marine-engineering steel plate of the present invention possesses the performance indicators that meet the certification requirements of China Classification Society for EH690 steel. Also, the saturated corrosion current density at -300mV (relative to Ag/AgCl reference electrode) is ≤ 1.90mA/cm^2; the corrosion-active inclusion has a density of ≤ 9/mm^2. The product has excellent comprehensive characteristics such as high strength and toughness, low temperature resistance, and corrosion resistance, etc.

[0009] To achieve the objectives above, the first aspect of the present invention provides a composition design for an 80mm 690MPa-grade ultra-high strength and toughness marine-engineering steel plate, adopting the technical solution shown as follow:

An 80mm 690MPa-grade ultra-high strength and toughness marine-engineering steel plate, wherein, the chemical composition of the steel plate, by mass percentage, comprises: C: 0.08%~0.10%, Si: 0.20%~0.30%, Mn: 1.10% ~1.25%, P ≤ 0.007%, S ≤ 0.002%, Nb: 0.020%~0.030%, Ti: 0.010%~0.020%, V: 0.030%~0.045%, Cr: 0.40%~0.60%, Ni: 1.40%~1.50%, Cu: 0.15%~0.25%, Mo: 0.25%~0.35%, Als: 0.015%~0.045%, and the rest are Fe and inevitable impurity elements; and it is controlled that Pcm is ≤0.33% and Ceq is≤0.64%.

Among them, Ceq=C+Mn/6+(Cr+Mo+V)/5+(Ni+Cu)/15;

$$Pcm=C+Si/30+Mn/20+Cu/20+Ni/60+Cr/20+Mo/15+V/10+5B.$$

[0010] In the 80mm 690MPa-grade ultra-high strength and toughness marine-engineering steel plate mentioned above, as a preferred embodiment, the inevitable impurity elements comprise: H≤0.0002%, O≤0.003%, N≤0.004%, B≤0.0005%, As≤0.006%, Sb≤0.010%, Sn≤0.020%, Pb≤0.010%, Bi≤0.010%, by mass percentage。

[0011] The main alloys in said 80mm 690MPa-grade ultra-high strength and toughness marine-engineering steel plate exhibit the following functions:

Cr, as in extra-thick steel plates, can effectively improve hardenability to compensate for the strength loss caused by thickness, and also enhance the corrosion resistance of the steel plate. However, if Cr content is too high, Cr-Mn composite oxides with low melting point forms, which can easily cause surface cracks in the steel plate during heat treatment process and also deteriorate the welding performance. Therefore, the Cr content is controlled at 0.40% ~ 0.60% in the present invention.

[0012] Ni is an element that significantly improves the low-temperature toughness of extra-thick steel plates. Addition of appropriate Ni can reduce the stacking fault energy of crystals, facilitate the slip movement of dislocations, and improve impact toughness. Moreover, Ni can promote the formation of a protective dense rust layer on the surface of steel plates, and thus improve corrosion resistance of the steel plates. However, overhigh Ni content does not favor welding performance. Therefore, the Ni content is controlled at 1.40%~1.50% in the present invention.

[0013] Cu can enhance the corrosion resistance and strength of steel, and improve weldability and machinability, etc. However, overhigh Cu content will increase the thermal brittleness tendency of steel plates. Therefore, the Cu content is controlled at 0.15%~0.25% in the present invention.

[0014] Mo is an element that improves hardenability. It can expand the γ phase area, delay the formation of precipitated ferrite, effectively enhance the strength, and also significantly improve the stability of the strength and toughness properties in the thickness direction of extra-thick steel plates. However, overhigh Mo content will deteriorate the weldability of steel plates, therefore the Mo content is controlled at 0.25%~0.35% in the present invention.

[0015] Nb can effectively refine grain size and also enhance precipitation strengthening. However, due to the limitations of C and the influence of heating temperature, Nb in an overhigh content cannot be fully dissolved. Therefore, the Nb content is controlled at 0.020%~0.030% in the present invention.

[0016] Ti can also refine grain size and enhance precipitation strengthening, and it also significantly improves the low-temperature impact toughness of steel plates. However, when Ti content is too high, large TiN particles are easily formed, thus losing the function of refining grain size. Therefore, the Ti content is controlled at 0.010% ~0.020% in the present invention.

[0017] V is an element that refine grain size in steel, and also has the effect of precipitation strengthening. When less than 0.02% of V is added, the effect is not significant; when more than 0.05% of V is added, the toughness and weldability of the steel are reduced. Therefore, the V content is controlled at 0.030%~0.045% in the present invention.

[0018] Al can immobilize the free N in the steel, and improve the low-temperature toughness of the steel plate and welded HAZ. Moreover, the dispersion and precipitation of AlN inhibits the growth of austenite grains during the heating process, uniformly refine the austenite grain size, and improve the impact toughness. However, overhigh Al content will increase the number and size of inclusions in the steel, and reduce the internal quality of the steel plate, thus affecting the heat processing performance, welding performance and cutting performance of the steel. Therefore, the Al content is controlled at 0.020% ~ 0.050% in the present invention.

[0019] Ceq: Controlling of carbon equivalent index is beneficial to ensuring the strength and weldability of the steel plate. In the present invention, Ceq content is controlled to be ≤ 0.64%.

[0020] Pcm: Controlling of cold crack sensitivity coefficient is beneficial to ensuring the welding performance of the product. In the present invention, Pcm content is controlled to be ≤ 0.33%.

[0021] Impurity elements in steel, such as S, P, etc., will increase the segregation level of the continuous casting billets and reduce the uniformity of structural properties in the thickness direction of the steel plate. Therefore, the S and P contents are controlled to be no more than 0.005% and 0.010%, respectively. B is easily enriched at grain boundaries, which reduces the low-temperature impact performance and fatigue performance of the steel plate, and also significantly increases the tendency of welding cracks. Therefore, the B content is controlled to be ≤ 0.0005%. And the contents of other inevitable impurity elements are controlled as follows: As ≤ 0.006%, Sb ≤ 0.010%, Sn ≤ 0.020%, Pb ≤ 0.010%, Bi ≤ 0.010%, H ≤ 0.0002%, O ≤ 0.003%, N ≤ 0.004%.

[0022] The second aspect of the present invention provides a method for preparing the 80mm 690MPa-grade ultra-high strength and toughness marine-engineering steel plate described above, comprising steps of converter smelting, LF+RH double refining, continuous casting, casting billet heating, rolling, and heat treatment. Specifically:

(1) Converter smelting

[0023] KR-treated molten iron is used; in the molten iron, S is ≤0.008%. nickel plates, copper plates, and ferromolybdenum are added along with scrap steel. A double-slag deep dephosphorization process is used for smelting and the alkalinity is controlled at R=3.0-4.0 in the final slag, so as to achieve early slag transformation in the initial stage, good slag transformation during the process, and complete slag transformation in the final stage. Metal manganese, ferroniobium, ferrovanadium, low-carbon ferrochromium, and ferrosilicon are used for alloying. The alloy is added when 1/4 of the steel is loaded until 3/4 of molten steel is discharged. Aluminum ferromanganese is added, according to 3-3.5 kg/t steel, for deoxidation.

(2) LF+RH refining

[0024] Argon is blown at the bottom and stirred throughout the entire process. Aluminum particles, calcium carbide, and silicon carbide are used to adjust the slag. Titanium wire is used to adjust the Ti component, and aluminum wire is used to adjust the Al component. The alkalinity of the final slag is controlled to be 2.5 and above, and the LF refining period is ≥ 50min, with a soft blowing period of ≥10min.

[0025] The present processing mode is used in RH refining. It is ensured that the vacuum degree is within 30Pa and the pure degassing period is ≥5 min. After RH treatment, the calcium-aluminum wire is fed according to 1-1.5 m/t, the soft blowing period is ≥14min, and the RH smelting period is ≥50min.

(3) Continuous casting

[0026] Whole-process protective casting is adopted, wherein peritectic steel protecting slag is used; the liquidus temperature is 1510~1520°C; the superheat level is controlled within 20°C; 300mm-thick continuous casting billet is used and pulled at a speed of 0.70-0.90m/min; and light pressing technology is used at the solidification end of the fan-shaped billet. The billet is slowly cooled for at least 72 hours after entering the pit and stacking.

(4) Casting billet heating

[0027] The billet is cold loaded into the furnace; a multi-stage heating process is adopted; the soaking section temperature is 1190-1240°C, the soaking period is ≥ 60 min; the tapping temperature is 1200-1230°C; and the total heating period is 290-310min. On one hand, the casting billet is ensured to be burned evenly and thoroughly; and on the other hand, excessive growth of austenite grains is prevented. A high-pressure water cold loaded treatment is carried out before the hot cast billet is rolled.

(5) Rolling

[0028] The rolling process comprises two stages of rolling, i.e. rough rolling and precision rolling. The rough rolling is a recrystallization rolling process with no more than 5 rough rolling passes, and the reduction rates (thickness reduction in a single pass/entry thickness, the same below) of at least 2 passes are ensured to be ≥19%. The high reduction rates enable the austenite grains to be fully refined, which provides structural guarantee for improving the strength and toughness of thick steel plates. After rough rolling, the intermediate billet has a thickness of 120-130mm. The precision rolling is a un-recrystallization rolling process with an initial temperature of 835-865°C and no more than 7 precision rolling passes. Preferably, the precision rolling passes are conducted for 5 times. By use of the deformation accumulation effect between passes and the forced phase transformation mechanism induced by defects within the deformed austenite grains, a large number of deformation bands, twins, and dislocations appearance in the austenite grains, thus creating conditions for ferrite deformation nucleation and improving the strength and toughness of the steel plate. The thickness of the intermediate billet obtained after rough rolling is controlled, so as to allocate reduction between the rough rolling and the precision rolling reasonably and improve the performance of the steel plate, especially the core impact toughness and the performance uniformity in the thickness direction.

[0029] After rolling, the cooling process is controlled to increase the ferrite nucleation rate and form fine and dispersed precipitates, thus further improving the strength and toughness of the steel plate. The initial cooling temperature is

800~820°C; the final cooling temperature is 550~590°C; and the cooling speed is controlled at 6~10°C/s. After that, the steel plate is moved into a slow cooling pit or stacked for slow cooling, to ensure sufficient phase transformation and improve the structural uniformity of the thick steel plate. The slow cooling period is ≥ 48 hours.

(6) Heat treatment

[0030] A quenching and high-temperature tempering process is used.

[0031] According to the composition design, the Ac3 temperature of the steel plate of the present invention is about 850°C. To ensure the formation of fine and uniform austenite grains, thus obtaining a fine martensite structure after quenching and reducing the content of the low-hardness ferrite phase in the quenching structure, quenching heating temperature should be 30~50°C higher than Ac3. Considering that the composition contains strong carbide-forming elements such as Nb, V, and Ti, etc., which can increase the coarsening temperature of austenite grains, the quenching temperature is set to 920±5°C, to accelerate the dissolution of alloy carbides, enhance the stability of undercooled austenite, and improve the hardenability of steel. The heating period is 1.3~1.6min/mm×plate thickness; and the holding time is 30± 3min. After the heating period and holding time, the steel plate is loaded into the quenching machine for quenching treatment. In the present invention, the ultra-wide integral slit type quenching machine designed by North-eastern University is used. The high-pressure water spray system of its cooling water system includes 2 sets of slit nozzles and 4 sets of high-density Type I nozzles, having a length of 3640mm. The low-pressure water spray system includes 18 sets of high-density Type II nozzles, having a length of 12600mm. The water pressure in the high-pressure section is 0.7~0.9bar, and the water pressure in the low-pressure section is 0.3~0.4bar. Based on the principle of "low roller speed + large water volume quenching", the roller speed of the quenching machine is 1.6-1.8m/min, the water volume in the high-pressure section is 5376-6067m^3/h, and the water volume in the low-pressure section is 3499-3888m^3/h. Preferably, The roller speed of the quenching machine is 1.6m/min, the water volume in the high-pressure section is 5376m^3/h, and the water volume in the low-pressure section is 3888m^3/h; the roller speed of the quenching machine is 1.8m/min, the water volume in the high-pressure section is 6067 m^3/h, and the water volume in the low-pressure section is 3499 m^3/h. The ratio of the water volume from the upper nozzle to the water volume from the lower nozzle is approximately 1:1.4, to ensure the symmetry and uniformity of the steel plate during the quenching process. In this way, through cooling of the high-pressure section, the steel plate is fully quenched and all phase transformations are completed. The heat conducted from the inside to the surface of the steel plate is further taken away in the low-pressure section, to prevent residual heat tempering, so that the steel plate is cooled down to the room temperature ultimately.

[0032] High-temperature tempering can eliminate the complex internal stress of the steel plate after rapid cooling quenching and endow the steel plate with excellent comprehensive mechanical properties. In the present invention, the tempering heating temperature is 600±5°C, the heating period is 2~2.5min/mm*plate thickness, and the holding time is 30 ±3min. After released from the furnace, the steel plates are cooled down to room temperature by blowing cold air on the cooling bed. It is necessary to avoid stacking and storing the steel plates within a short period after being released from the furnace to prevent high-temperature tempering brittleness.

[0033] In this way, an 80mm 690MPa-grade ultra-high strength and toughness marine-engineering steel plate is obtained. Its major performance indicators include that: yield strength is ≥690MPa, tensile strength is 770~940MPa, elongation at break is ≥16%, lateral impact energy at the core and at -40°C is ≥100J, -40°C CTOD is ≥0.15mm, saturated corrosion current density at -300mV (relative to Ag/AgCl reference electrode) is ≤1.90 mA/cm^2 , corrosion-active inclusion has a density of ≤9/mm^2.

[0034] Compared with prior art, the present invention has advantages shown as follows:

(1) Good performance uniformity

[0035] The present invention provides high-quality casting billet raw materials through controlling the composition, purity and gas content in the steelmaking process. By scientifically designing the heating, rolling, and controllable post-rolling cooling processes, as well as adopting large reduction in the rough rolling stage and reasonably allocating the reduction amounts between the two stages, the deformation is penetrated into the core of the steel plate. The heat treatment process is optimized to obtain a high strength and toughness structure throughout the thickness section, excellent performances in many aspects, such as mechanical properties, lateral and longitudinal impact, aging impact and cold bending, and uniform performance in the thickness direction. The certification requirements of China Classification Society for EH690 steel are fully satisfied.

(2) Low cost, high production efficiency

[0036] Through optimizing the composition design, adopting suitable controlled rolling and cooling processes, integrating plastic deformation and post-rolling cooling with solid-state phase transformation, and fully enabling the effects of solid solution strengthening, precipitation strengthening, and grain refinement strengthening, the effects of alloy elements have been fully exerted. By optimizing the roller speed of the quenching machine, the design of the water volume of the high-pressure and low-pressure sections and the upper and lower water ratio, the heat treatment effect of thick steel plates has been improved. After quenching and high-temperature tempering treatment, high-performance steel plates can be obtained without further heat treatment processes, which shortens the production process and reduces production costs.

(3) Excellent corrosion resistance

[0037] This invention utilizes high-clean molten steel smelting technology, high-penetration rolling technology and optimized heat treatment processes to obtain a low-inclusion, highly homogeneous structure with good corrosion resistance, greatly improving the corrosion potential of the steel plate matrix itself. Moreover, the addition of Cr+Cu+Ni alloy element can effectively promote the formation of a dense, protective rust layer with good adhesion on the surface of the steel plate, which hinders corrosive media such as H_2O, O_2, Cl^-, etc. from penetrating into the steel matrix, thus ensuring the safety of the products that serve in highly corrosive marine environment.

Description of Drawings

[0038]

Figure 1 shows the 500x metallographic structure near the surface of the steel plate prepared in Example 1 of the present invention;

Figure 2 shows the 500x metallographic structure at the 1/4 thickness position of the steel plate prepared in Example 1 of the present invention;

Figure 3 shows the 500x metallographic structure at the 1/2 thickness position of the steel plate prepared in Example 1 of the present invention;

Figure 4 shows the -300mV (vs. Ag/AgCl) potentiostatic polarization curve of the steel plate prepared in Example 1 of the present invention; and

Figure 5 shows the corrosion-active inclusions in the steel plate prepared in Example 1 of the present invention under a 50x field of view.

Specific Modes for Carrying out the Invention

[0039] The present invention will be further illustrated in detail with reference to the drawings and specific Examples.

<u>Example 1</u>

[0040] According to the chemical composition shown in Table 1, high-clean molten steel was obtained through converter smelting and LF+RH double refining in accordance with the above smelting process, and a 300mm-thick continuous casting billet was obtained through casting. The casting billet was heated; the tapping temperature was 1210°C; the furnace period was 300 minutes; rough rolling was conducted for 5 passes (The 5^{th} pass was empty); the reduction rates of the 3^{rd} and 4^{th} passes were 19.3% and 23.7% respectively; and the intermediate billet obtained after the rough rolling had a thickness of 130mm. Once the temperature reached 845°C, the precision rolling stage began and was conducted for 7 passes (The 7^{th} pass was empty). Controlled cooling was performed at a speed of about 8°C/s, with an initial cooling temperature of 815°C and a final cooling temperature of 590°C. After rolling, slow cooling was carried out in a slow-cooling pit for 48 hours and longer. The quenching temperature was raised to 920°C and held for 30 minutes. The roller speed of the quenching machine was 1.8m/min. The water volume in the high-pressure section was 6067m^3/h. The water volume in the low-pressure section was 3499m^3/h. The ratio of the water volume from the upper nozzle to the water volume from the lower nozzle was 1:1.4. The tempering heating temperature was 600°C and the temperature was held for 30 minutes. As shown in Figures 1 to 3, the near-surface structure was mainly composed of tempered martensite; while toward the core, the contents of dispersed granular bainite, ferrite, and pearlite increased gradually. The inspection was carried out in accordance with the test methods and requirements in Materials and Welding Rules (2021) of China Classification Society. The main tensile properties and impact performance indicators are shown in Table 2, and the corrosion resistance performance indicators are shown in Table 3.

Example 2

[0041] According to the chemical composition shown in Table 1, high-clean molten steel was obtained through converter smelting and LF+RH double refining in accordance with the above smelting process, and a 300mm-thick continuous casting billet was obtained through casting. The continuous casting billet was heated; the tapping temperature was 1230°C; the furnace period was 290 minutes; rough rolling was conducted for 5 passes; the reduction rates of the 4^{th} and the 5^{th} passes were 19.1% and 22.3% respectively; and the intermediate billet obtained after the rough rolling had a thickness of 120mm. Once the temperature reached 860°C, the precision rolling stage began and was conducted for 5 passes. Controlled cooling was performed at a speed of about 10°C/s, with an initial cooling temperature of 803°C and a final cooling temperature of 559°C. After rolling, slow cooling was carried out in a slow-cooling pit for 48 hours and longer. The quenching temperature was raised to 920°C and held for 30 minutes. The roller speed of the quenching machine was 1.6m/min. The water volume in the high-pressure section was $5376m^3/h$. The water volume in the low-pressure section was $3888m^3/h$. The ratio of the water volume from the upper nozzle to the water volume from the lower nozzle was 1:1.4. The tempering heating temperature was 600°C and the temperature was held for 30 minutes.

Comparative Example:

[0042] In order to illustrate the influence of quenching machine parameters on the performance of steel plates, one embodiment of adjusting the quenching machine was used as a comparative example in the present invention. In the Comparative Example, smelting and casting were carried out through methods that were same as those in Example 2. The continuous casting billet was heated; the tapping temperature was 1230°C; the furnace period was 290 minutes; rough rolling was conducted for 5 passes; the reduction rates of the 4^{th} and the 5^{th} passes were 20.0% and 21.6% respectively; and the intermediate billet obtained after the rough rolling had a thickness of 120mm. Once the temperature reached 850°C, the precision rolling stage began and was conducted for 5 passes. Controlled cooling was performed at a speed of about 10°C/s, with an initial cooling temperature of 805°C and a final cooling temperature of 562°C. After rolling, slow cooling was carried out in a slow-cooling pit for 48 hours and longer. The quenching temperature was raised to 920°C and held for 30 minutes. The roller speed of the quenching machine was 2.0m/min. The water volume in the high-pressure section was $6255m^3/h$. The water volume in the low-pressure section was $3287m^3/h$. The ratio of the water volume from the upper nozzle to the water volume from the lower nozzle was 1:1.4. The tempering heating temperature was 600°C and the temperature was held for 30 minutes.

[0043] Table 2 shows the tensile and impact properties of the steel plates obtained from the Examples and the Comparative Example. For the steel plate prepared according to the method of the present invention, the yield strength was ≥690MPa, the tensile strength was 770-940MPa, and the elongation at break was ≥16%; the lateral impact energy at -40°C was ≥100J, and the uniformity performance in the thickness direction was good. However, the strength and toughness of the product in Comparative Example were significantly lower than those of the product in Examples, especially the impact performance at 1/4 of thickness and at the core cannot meet the performance requirements for E690 steel.

[0044] Table 3 shows the corrosion resistance performance indicators of the steel plates obtained from the Examples and the Comparative Examples. The saturated corrosion current density was measured using the Autolab electrochemical workstation, wherein a three-electrode system with Ag/AgCl electrode as the reference electrode and Pt electrode as the auxiliary electrode was used. A sample with an exposed area of $1cm^2$ was taken from the steel plate and used as the working electrode. The sample was subjected to anodic polarization at a constant potential of -300mV in artificial seawater solution (with the composition shown in Table 4), and the polarization current change and its corrosion current density after stabilization were recorded. Figure 4 shows the - 300mV (vs. Ag/AgCl) potentiostatic polarization curve of the steel plate prepared in Example 1. To measure the density of corrosion-active inclusions, a sample in a size of 10mm*10mm*5mm was taken from the steel plate, polished, and soaked in artificial seawater for 20 minutes. After removed, the sample was rinsed with alcohol, dried with cold air, and placed under a 50x microscope to take several consecutive photos and calculate the density of the corrosion-active inclusions. Figure 5 shows the corrosion-active inclusions in the steel plate prepared in Example 1 under a 50x field of view.

Table 1. Chemical composition (wt%) of the steel plates in Examples and Comparative Examples of the present invention

No.	Furnace Number	C	Si	Mn	P	S	Nb	Ti	V	Cr	Ni	Cu	Mo	Al
Example 1	H212-08 914	0.095	0.22	1.20	0.007	0.001	0.025	0.012	0.032	0.43	1.44	0.18	0.275	0.026
Example 2	H214-08 856	0.088	0.28	1.13	0.006	0.001	0.024	0.018	0.035	0.55	1.44	0.22	0.286	0.030
Comparative Example	H214-08 856	0.088	0.28	1.13	0.006	0.001	0.024	0.018	0.035	0.55	1.44	0.22	0.286	0.030

Table 2. Performance of the steel plates in Examples and Comparative Examples of the present invention

No.	Thickness /mm	Sampling location	Tensile properties			Lateral impact energy at -40°C			
			Yield strength /MPa	Tensile strength /MPa	Elongation at break /%	Measurement value 1	Measurement value 2	Measurement value 3	Average value
Example 1	80	Near surface	/	/	/	223	215	228	222
		At 1/4 of thickness	760	819	18.0	220	182	230	211
		At 1/2 of thickness	745	805	18.0	222	216	26.6	155
Example 2	80	Near surface	/	/	/	236	233	228	232
		At 1/4 of thickness	756	810	17.0	207	263	165	212
		At 1/2 of thickness	743	798	18.0	160	131	208	166
Comparative Example	80	Near surface	/	/	/	227	269	248	248
		At 1/4 of thickness	722	784	17.5	62.8	50	55.1	56
		At 1/2 of thickness	709	774	16.0	59	52.2	11.6	41

Table 3. Corrosion resistance performance indicators of the steel plates in Examples of the present invention

No.	Thickness/mm	Sampling location	Saturated corrosion current density /(mA/cm^2)	Density of corrosion- active inclusions /(Number/mm^2)
Example 1	80	Near surface	1.80	4.11
		At 1/4 of thickness	1.85	5.85
		At 1/2 of thickness	1.87	7.69
Example 2	80	Near surface	1.78	3.36
		At 1/4 of thickness	1.82	6.47
		At 1/2 of thickness	1.88	8.95

Table 4. Composition of the artificial seawater

Composition	NaCl	Na_2SO_4	$NaHCO_3$	KCl	$MgCl_2 \cdot 6H_2O$	$CaCl_2$	KBr
Content (g/L)	24.53	4.09	0.201	0.695	11.1	1.16	0.101

[0045] The method of the present invention can be implemented using the upper and lower limits and the interval values of the processing parameters (such as temperature, time, etc.) of the present invention, and the embodiments will not be listed herein.

[0046] Any content not described in detail in the present invention can be based on conventional technical knowledge in this field.

[0047] Finally, it should be noted that the Examples above are only for illustrating, but not for limiting, the technical solution of the present invention. Although the present invention has been described in detail with reference to the Examples, those skilled in the art should understand that any modification or equivalent substitution of the technical solution of the present invention does not depart from the spirit and scope of the technical solution of the present invention, and should be included in the scope of the claims of the present invention.

Claims

1. An 80mm-thick 690MPa-grade ultra-high strength and toughness marine-engineering steel plate, wherein, the chemical composition of the steel plate, by mass percentage, comprises: C: 0.08%~0.10%, Si: 0.20%~0.30%, Mn: 1.10%~1.25%, P≤0.007%, S≤0.002%, Nb: 0.020%~0.030%, Ti: 0.010%~0.020%, V: 0.030%~0.045%, Cr: 0.40%~0.60%, Ni: 1.40%~1.50%, Cu: 0.15%~0.25%, Mo: 0.25%~0.35%, Als: 0.015%~0.045%, and Pcm≤0.33%, Ceq≤0.64%; and the rest are Fe and inevitable impurity elements.

2. The 80mm-thick 690MPa-grade ultra-high strength and toughness marine-engineering steel plate according to claim 1, wherein, the content of each component in the inevitable impurity elements is shown as follow: H is ≤0.0002%, O is ≤0.003%, N is ≤0.004%, B is ≤0.0005%, As is ≤0.006%, Sb is ≤0.010%, Sn is ≤0.020%, Pb is ≤0.010%, Bi is ≤0.010%, by mass percentage.

3. The 80mm-thick 690MPa-grade ultra-high strength and toughness marine-engineering steel plate according to claim 1 or 2, wherein, the major performance indicators of the ultra-high strength and toughness marine-engineering steel plate include that: yield strength is ≥690MPa; tensile strength is 770-940MPa; elongation at break is ≥16%; lateral impact energy at the core and at -40°C is ≥100J; CTOD at -40°C is ≥0.15mm; saturated corrosion current density at -300mV, relative to Ag/AgCl reference electrode, is ≤ 1.90mA/cm^2; corrosion-active inclusion has a density of ≤9/mm^2.

4. A method for preparing the 80mm-thick 690MPa-grade ultra-high strength and toughness marine-engineering steel plate according to any one of claims 1-3, comprising the steps of converter smelting, LF+RH double refining, continuous casting, casting billet heating, rolling, and heat treatment.

5. The method according to claim 4, wherein, in the step of converter smelting, KR-treated molten iron is used; in the molten iron, S is ≤0.008%; nickel plates, copper plates, and ferromolybdenum are added along with scrap steel; a double-slag deep dephosphorization process is used for smelting; metal manganese, ferroniobium, ferrovanadium, low-carbon ferrochromium, and ferrosilicon are used for alloying; and aluminum ferromanganese is added, according to 3-3.5 kg/t steel, for deoxidation.

6. The method according to claim 4, wherein, in the step of LF+RH double refining, argon is blown at the bottom throughout the LF refining process; the refining period is ≥50 min, and the soft blowing period is 10-15 min; in the RH refining process, the vacuum degree is ensured within 30 Pa, the pure degassing period is ≥5min; after RH treatment, the calcium-aluminum wire is fed according to 1-1.5 m/t, the soft blowing period is 15-20 min, and the RH smelting period is ≥50min.

7. The method according to claim 4, wherein, in the step of continuous casting, whole-process protective casting is adopted; the superheat level is controlled within 20°C; 300mm-thick continuous casting billet is used and pulled at a speed of 0.70-0.90m/min; and the obtained casting billet is cooled down slowly for 72 hours and longer.

8. The method according to claim 4, wherein, in the step of casting billet heating, a multi-stage heating process is adopted; the temperature is 1190-1240°C in the soaking section; the soaking period is ≥60 min; the tapping temperature is 1200-1230°C; and the total heating period is 290-310min.

9. The method according to claim 4, wherein, the step of rolling comprises two stages of rolling, i.e. rough rolling and precision rolling; the rough rolling is a recrystallization rolling process with no more than 5 rough rolling passes, the reduction rates of at least 2 passes are ensured to be ≥19%, and the intermediate billet obtained after rough rolling has a thickness of 120-130mm; the precision rolling is a un-recrystallization rolling process with an initial rolling temperature of 835-865°C and no more than 7 precision rolling passes; after rolling, the initial cooling temperature of the rapid cooling process is 800~820°C, the final cooling temperature is 550~590°C, and the cooling rate is 6~10°C/s.

10. The method according to claim 4, wherein, in the step of heat treatment, a quenching and high-temperature tempering process is used; the quenching temperature is 920±5°C, heating period is 1.3~1.6min/mm×plate thickness, the holding time is 30± 3min; the water pressure in the high-pressure section and the low-pressure section of the quenching machine is 0.7~0.9bar and 0.3~0.4bar, respectively; the roller speed is 1.6-1.8m/min, the water volume in the high-pressure section is 5376-6067m^3/h, and the water volume in the low-pressure section is 3499-3888m^3/h; the ratio of the water volume from the upper nozzle to the water volume from the lower nozzle is about 1:1.4, the tempering heating temperature is 600±5°C, the heating period is 2~2.5min/mm*plate thickness, the holding time is 30±3min, and the product is air-cooled after being discharged from the furnace.

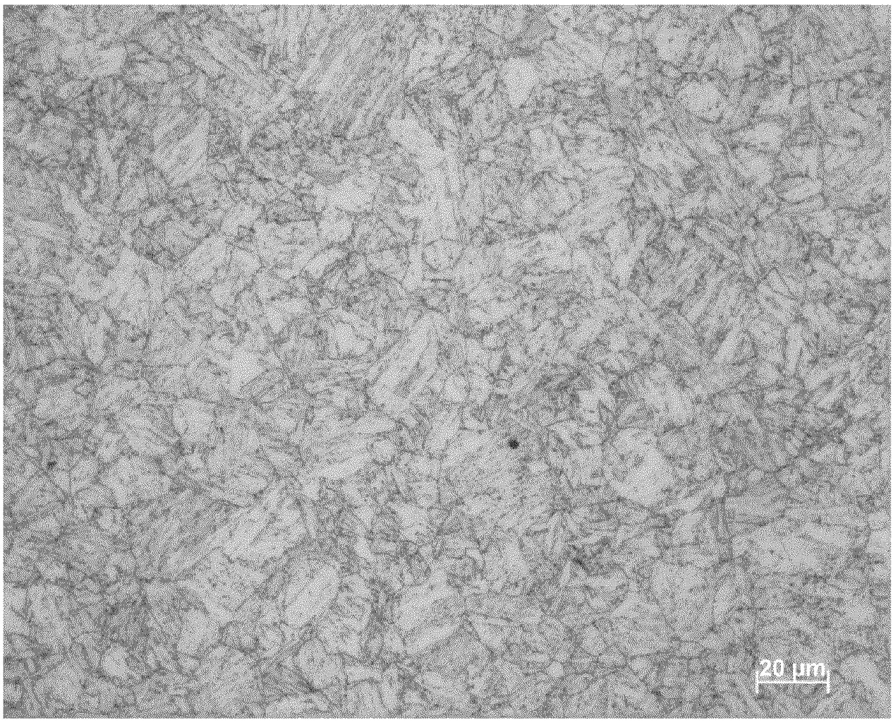

Figure 1

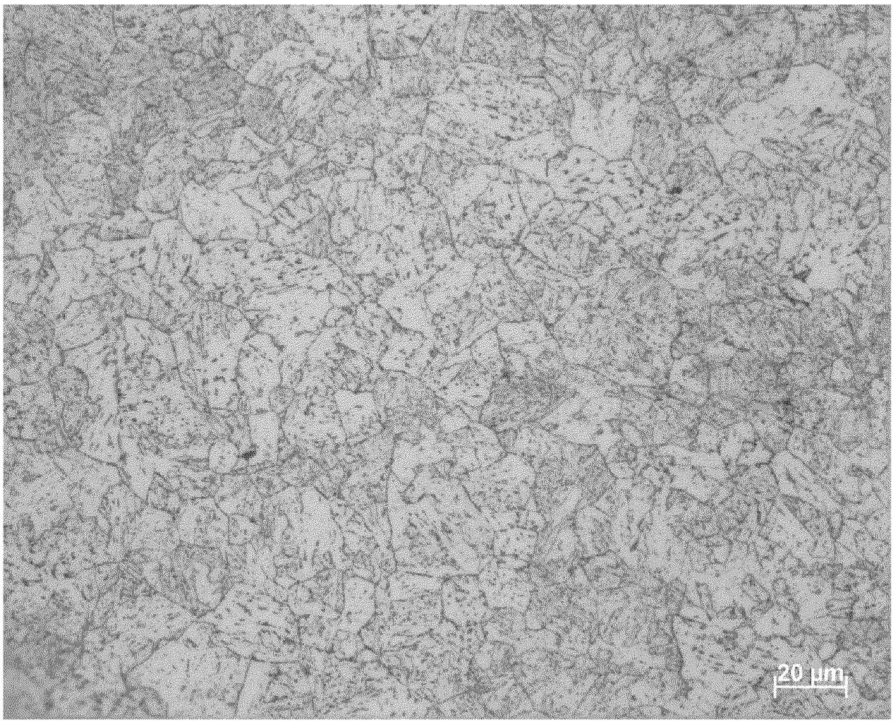

Figure 2

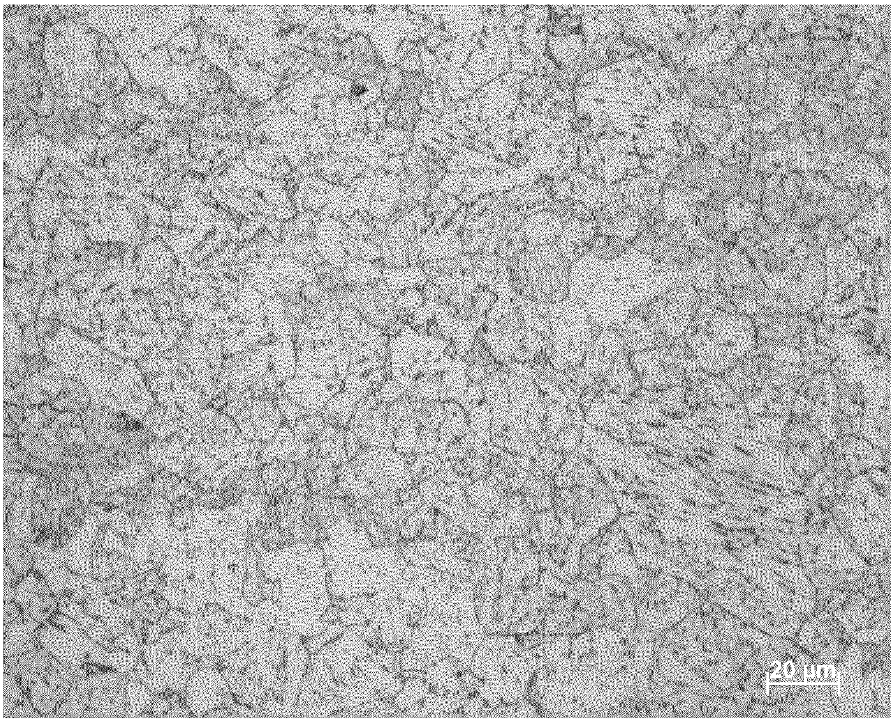

Figure 3

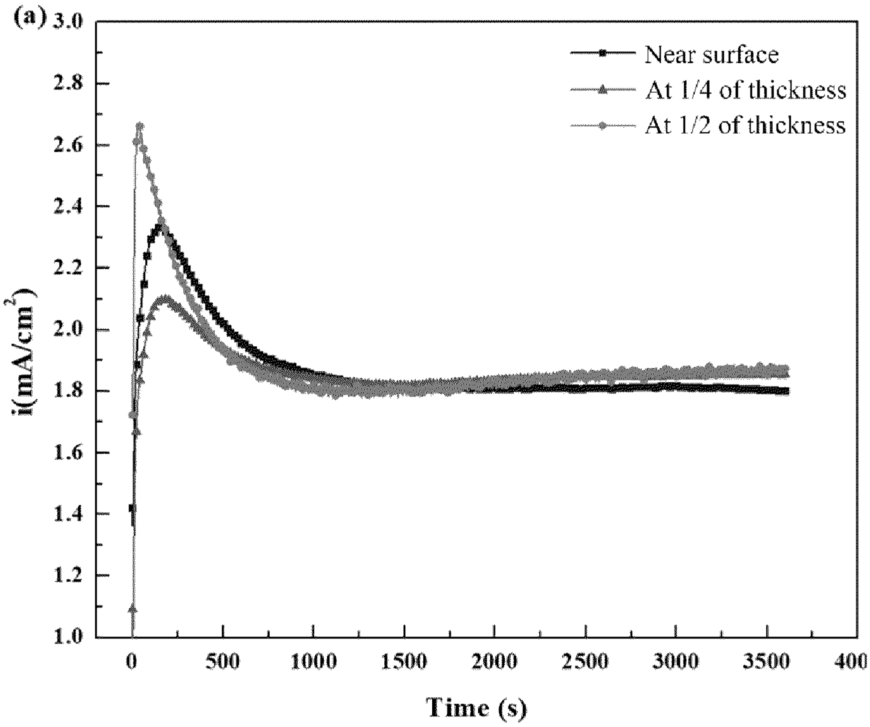

Figure 4

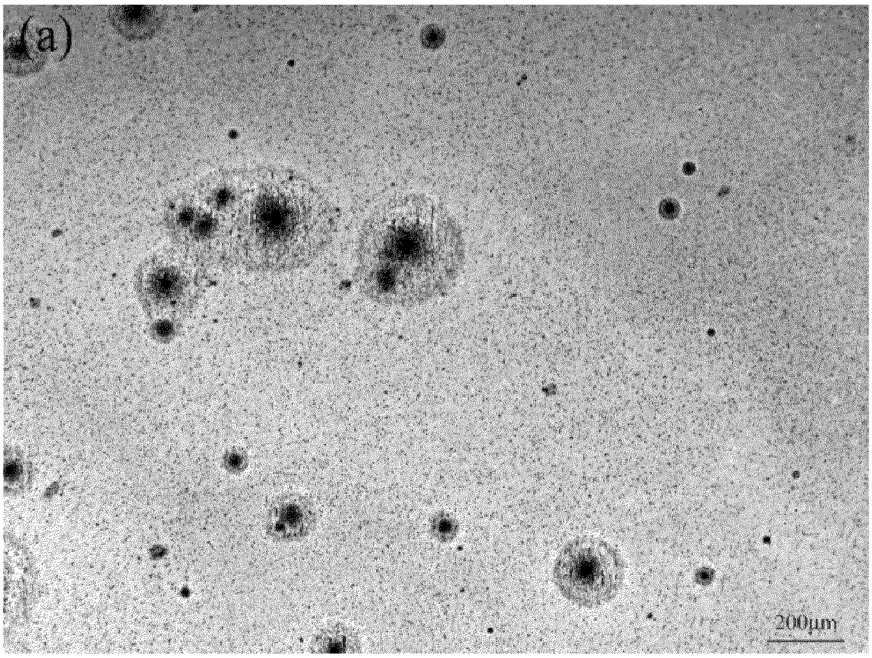

Figure 5

INTERNATIONAL SEARCH REPORT

International application No. **PCT/CN2022/139834**

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/02(2006.01)i;C22C 38/04(2006.01)i;C22C 38/06(2006.01)i;C22C 38/42(2006.01)i;C22C 38/44(2006.01)i;C22C 38/46(2006.01)i;C22C 38/48(2006.01)i;C22C 38/50(2006.01)i;C21D8/02(2006.01)i;C22C 33/04(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)

IPC:C22C; 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, WPABS, CNKI: 钢, 船舶, 海洋, 精炼, 铸, 轧制, 铌, 钛, 钒, 铬, 镍, 铜, 钼, 铝, 690, 80kg, steel, ship+, ocean, mari+, refin+, cast+, roll+, Nb, Niobium, Ti, Titanium, V, vanadium, Cr, chrom+, Ni, nickel, Cu, Copper, Mo, molybdenum, Al, Aluminum

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PX	CN 115094322 A (SHANDONG IRON AND STEEL COMPANY LTD.; LAIWU IRON AND STEEL GROUP YINSHAN SECTION STEEL CO., LTD.) 23 September 2022 (2022-09-23) claims 1-10	1-10
X	CN 102851622 A (NANJING IRON & STEEL CO., LTD.) 02 January 2013 (2013-01-02) description, paragraphs 8 and 20-24	1-10
X	CN 109161791 A (BAOSHAN IRON & STEEL CO., LTD.) 08 January 2019 (2019-01-08) description, paragraphs 12, 29-51, and 60, and table 3	1-10
A	CN 110791713 A (NANJING IRON & STEEL CO., LTD.) 14 February 2020 (2020-02-14) entire document	1-10
A	JP S6326339 A (NIPPON KOKAN K. K.) 03 February 1988 (1988-02-03) entire document	1-10
A	CN 103014541 A (SHOUGANG CO., LTD.) 03 April 2013 (2013-04-03) entire document	1-10

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

* Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevance
- "D" document cited by the applicant in the international application
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "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	Date of mailing of the international search report
17 March 2023	**22 March 2023**

Name and mailing address of the ISA/CN	Authorized officer
China National Intellectual Property Administration (ISA/CN) **China No. 6, Xitucheng Road, Jimenqiao, Haidian District, Beijing 100088**	
Facsimile No. **(86-10)62019451**	Telephone No.

Form PCT/ISA/210 (second sheet) (July 2022)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2022/139834

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
CN	115094322	A	23 September 2022	None	
CN	102851622	A	02 January 2013	None	
CN	109161791	A	08 January 2019	None	
CN	110791713	A	14 February 2020	None	
JP	S6326339	A	03 February 1988	None	
CN	103014541	A	03 April 2013	None	

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

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- CN 2022107478038 **[0001]**
- CN 111304551 B **[0005]**
- CN 110846577 A **[0006]**
- CN 112251670 A **[0007]**
- CN 102965592 B **[0007]**

Non-patent literature cited in the description

- Materials and Welding Rules. China Classification Society, 2021 **[0040]**