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

(11) EP 4 578 982 A1

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

(43) Date of publication:
02.07.2025 Bulletin 2025/27

(21) Application number: **23856622.8**

(22) Date of filing: **22.08.2023**

(51) International Patent Classification (IPC):
C22C 38/02 *(2006.01)* ***C22C 38/04*** *(2006.01)*
C22C 38/06 *(2006.01)* ***C22C 38/14*** *(2006.01)*
C22C 38/12 *(2006.01)* ***C21D 8/02*** *(2006.01)*
C21D 1/26 *(2006.01)*

(52) Cooperative Patent Classification (CPC):
C21D 1/26; C21D 8/02; C22C 38/02; C22C 38/04; C22C 38/06; C22C 38/12; C22C 38/14

(86) International application number:
PCT/CN2023/114258

(87) International publication number:
WO 2024/041533 (29.02.2024 Gazette 2024/09)

(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: **23.08.2022 CN 202211011693**

(71) Applicant: **BAOSHAN IRON & STEEL CO., LTD.**
Shanghai 201900 (CN)

(72) Inventors:
- **LI, Wei**
  Shanghai 201900 (CN)
- **ZHU, Xiaodong**
  Shanghai 201900 (CN)
- **WANG, Li**
  Shanghai 201900 (CN)

(74) Representative: **Kuhnen & Wacker**
Patent- und Rechtsanwaltsbüro PartG mbB
Prinz-Ludwig-Straße 40A
85354 Freising (DE)

(54) 100-KG-GRADE COLD-ROLLED LOW-ALLOY ANNEALED DUAL-PHASE STEEL AND MANUFACTURING METHOD THEREFOR

(57) Disclosed in the present invention is a 100-kg-grade cold-rolled low-alloy annealed dual-phase steel, which comprises Fe and inevitable impurities, and further comprises the following chemical elements in percentages by mass: 0.1 %<C≤0.13%, Si: 0.5-0.8%, Mn: 1.6-1.8%, Al: 0.01-0.03%, Nb: 0.01-0.03%, Ti: 0.01-0.03%, and B: 0.0020-0.0030%, wherein Mo and Cr are not included in the chemical elements thereof. The microstructure of the 100-kg-grade cold-rolled low-alloy annealed dual-phase steel is martensite + ferrite. Accordingly, further disclosed in the present invention is a manufacturing method for the 100-kg-grade cold-rolled low-alloy annealed dual-phase steel. A 100-kg-grade cold-rolled low-alloy annealed dual-phase steel obtained by using the manufacturing method not only has good economical performance, but also has high strength, a good ratio of elongation and good bending performance.

EP 4 578 982 A1

Description

Technical Field

[0001] The present disclosure relates to a metal material and a manufacturing method thereof, in particular to a 100-kg grade cold-rolled low-alloy annealed dual-phase steel and a manufacturing method thereof.

Background Art

[0002] In recent years, with the intensification of the global energy crisis and environmental problems, energy conservation and safety have become the main development direction of the automobile manufacturing industry, among which reducing vehicle weight is one of the measures to save energy and reduce emissions. In the actual application process, due to the good mechanical properties and use properties of high-strength dual-phase steel, it can be effectively applied to the production and manufacturing of vehicle structural parts.

[0003] At present, with the development of ultra-high-strength steel and the changes in the current market, the market and users generally expect high-strength steel to have good economy and better performance. At present, 980MPa grade low-alloy steel is still the mainstream steel in application, accounting for 20% of the total amount of low-alloy steel, and is widely used in various types of structural parts and safety parts. However, with the continuous development of the trend of weight reduction and energy saving in the automotive industry, and the rapid progress of the level of domestic and foreign steel mills, especially the domestic steel mills, the development of dual-phase steel in the future will inevitably be based on low-cost and high overall performance.

[0004] In the current prior art, researchers have conducted a lot of research on 980MPa grade steel and have achieved certain research results.

[0005] For example, a Chinese patent document with a publication number of CN109280854A, a publication date of January 29, 2019, and a title of "980MPa grade low-carbon cold-rolled dual-phase steel and production method thereof" discloses a 980MPa grade low-carbon cold-rolled dual-phase steel. The technical problem to be solved by this technical solution is that the existing 980MPa grade cold-rolled dual phase steel has high production cost and production difficulty. Its chemical composition in mass percentage is as follows: C: 0.05~0.10%, Si: 0.30~0.70%, Mn: 2.00~2.50%, Cr: 0.40~0.80%, Al: 0.01~0.06%. The 980MPa grade low-carbon cold-rolled dual phase steel is obtained by controlling the molten iron V content in the converter, followed by hot rolling, acid rolling, annealing process. The dual phase steel prepared by this technical solution has excellent mechanical properties and forming performance, and its cost advantage is obvious. However, the technical solution uses the noble alloy Cr in the design of the steel, and at the same time contains a high content of Mn, which will not only lead to the increase of alloy cost, but also cause serious banded structure, resulting in non-uniformity of mechanical properties.

[0006] For another example, a Chinese patent document with a publication number of CN111455285A, a publication date of July 28, 2020, and a title of "Low-cost and easy-to-produce cold-rolled dual-phase steel with a tensile strength of 980 MPa and production method thereof" discloses a cold-rolled dual-phase steel with a tensile strength of 980 MPa and production method thereof. The chemical composition is as follows: C 0.080~0.095%, Si 0.4~0.6%, Mn 2.1~2.3%, Als 0.06~0.08%, Cr 0.2~0.4%, Nb 0.03~0.05%, Ti 0.01~0.02%, Ca 0.0015~0.0040%, P≤0.012%, S≤0.005%, N≤0.005%, with a balance of Fe and unavoidable impurities.

[0007] For another example, a Chinese patent document with a publication number of CN107043888A, a publication date of August 15, 2017, and a title of "980 MPa-grade cold rolled dual-phase steel plate with excellent cold bending performance and preparation method thereof" discloses a 980 MPa-grade cold rolled dual-phase steel plate, which has a chemical composition in weight percentage as follows: C 0.10~0.12%; Si 0.45~0.65%; Mn 2.4~2.6%; Cr 0.35~0.45%; Nb 0.05~0.075%; Ti 0.06~0.10%; Als 0.055~0.075%; P≤0.008%; S≤0.002%; N≤0.003%, with a balance of Fe and unavoidable impurities. Although the dual phase steel plate prepared by this technical solution has excellent mechanical properties, the content of Cr, Nb and Ti elements added to the steel is relatively high.

[0008] It can be seen that although some of the existing patented technologies of 1000MPa dual phase steel involve better forming properties, these technical solutions either use high C content and high Si content, or contain more alloy content such as Cr, Nb and Ti, which is not only not conducive to the weldability, surface quality and phosphating properties of steel, but also leads to an increase in cost. In addition, although some steels with high Si content have high hole expansion ratio and good bending performance, they have a high yield ratio and reduced stamping performance.

[0009] Therefore, in order to meet the current market demand, the present disclosure expects to develop a 100 kg grade cold-rolled low-alloy annealed dual-phase steel with both economy and excellent mechanical properties.

Summary

[0010] One of the objects of the present disclosure is to provide a 100 kg grade cold-rolled low-alloy annealed dual-phase steel, wherein the 100 kg grade cold-rolled low-alloy annealed dual-phase steel has both economy and excellent mechanical properties, and it still has high strength and excellent elongation and bending performance under the premise of not adding Mo, Cr elements. It has a yield strength of ≥ 550Mpa, a tensile strength of ≥ 1T000MPa, a gauge-length elongation at break A_{50} of ≥12%, a 90° bending performance R/t of ≤1.0, and has a very good promotion prospect and application value. In the present disclosure, 100 kg grade refers to a tensile strength of steel ≥980MPa, and 1000MPa grade refers to a tensile strength of steel ≥1000MPa.

[0011] In order to achieve the above purpose, the present disclosure provides a 100 kg grade cold-rolled low-alloy annealed dual-phase steel, which comprises Fe and unavoidable impurity elements, and also comprises the following chemical elements in mass percentages as follows:

0.1%< C≤0.13%, Si: 0.5%~0.8%, Mn: 1.6%~1.8%, Al: 0.01%~0.03%, Nb: 0.01~0.03%, Ti: 0.01~0.03%, B: 0.0020~0.0030%;
Its chemical elements do not comprise Mo or Cr;

[0012] The microstructure of the 100 kg grade cold-rolled low-alloy annealed dual-phase steel is martensite + ferrite.

[0013] Further, in the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure, the mass percentage of each chemical element is:
0.1%< C≤0.13%, Si: 0.5%~0.8%, Mn: 1.6%~1.8%, Al: 0.01%~0.03%, Nb: 0.01~0.03%, Ti: 0.01~0.03%, B: 0.0020~0.0030%, with a balance of Fe and other unavoidable impurities.

[0014] In the present disclosure, the inventors adopt a C-Si-Mn based composition system to ensure that the obtained cold-rolled low-alloy annealed dual-phase steel can reach 1000MPa grade strength. In the chemical composition design, the dual-phase steel does not comprise precious alloying elements such as Mo and Cr, which can effectively ensure the economy. In addition, the present disclosure also adds and utilizes a trace amount of element B having high hardenability in the design of chemical composition, so as to play the effect of further reducing Mn content. In addition, trace amounts of Nb and Ti are added to the steel to inhibit the growth of austenite grains, so as to effectively refine the grains.

[0015] In the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure, the design principle of each chemical element is specifically described as follows:

[0016] C: in the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure, the addition of C element can improve the strength of the steel and improve the hardness of martensite. If the mass percentage of C in the steel is less than 0.1%, the strength of the steel plate will be affected, and it is not conducive to the formation of austenite in a desired amount and the stability thereof. When the mass percentage of C element in the steel is higher than 0.13%, it will cause an overly high martensite hardness and a coarse grain size, which are not conducive to the forming performance of the steel plate, and at the same time an overly high carbon equivalent, which is not conducive to welding. Therefore, in order to ensure the performance of the steel, in the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure, the mass percentage of C element is specifically controlled to be 0.1%< C ≤0.13%, for example, the mass percentage of C element can be 0.101%, 0.105%, 0.11%, 0.115%, 0.12%, 0.125%, 0.13% or within the range of any two values mentioned above.

[0017] Si: in the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure, the addition of Si element to the steel can improve the hardenability of the steel, and the solid dissolved Si in the steel can affect the interaction of dislocations, thereby increasing the work hardening rate, which can appropriately improve the elongation of the dual-phase steel, and is beneficial to better formability. However, it should be noted that the content of Si element in the steel should not be too high, and when the mass percentage of Si element in the steel is too high, it will not be conducive to the control of the surface quality of the steel plate. Therefore, in order to give full play to the beneficial effect of Si element, in the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure, the mass percentage of Si element is controlled to be 0.5%~0.8%, for example, the mass percentage of Si element can be 0.5%, 0.55%, 0.6%, 0.65%, 0.7%, 0.75%, 0.8% or within the range of any two values mentioned above.

[0018] Mn: in the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure, the addition of Mn element is not only conducive to improving the hardenability of the steel, but also can effectively improve the strength of the steel plate. When the mass percentage of Mn in the steel is less than 1.6%, the strength of the steel plate is insufficient. When the mass percentage of Mn in the steel is higher than 1.8%, the strength of the steel plate is too high, which will reduce its forming performance. Therefore, considering the beneficial effect of Mn element, in the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure, the mass percentage of Mn element is controlled to be 1.6%~1.8%, for example, the mass percentage of Mn element can be 1.6%, 1.63%, 1.65%, 1.68%, 1.7%, 1.73%, 1.75%, 1.78%, 1.8% or within the range of any two values mentioned above.

[0019] Al: in the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure, the addition of Al element can play the role of deoxidation and grain refinement. On the other hand, the lower the content of Al in the steel, the more conducive to the castability of smelting. Therefore, in order to give play to the beneficial effects of Al element, in the present disclosure, the mass percentage of Al element is controlled to be 0.01%~0.03%, for example, the mass percentage of Al element can be 0.01%, 0.015%, 0.02%, 0.025%, 0.03% or within the range of any two values mentioned above.

[0020] Nb: in the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure, Nb element is an important element for refining the grain. After adding a small amount of strong carbide-forming element Nb to the microalloy steel, in the process of controlled rolling, it can lead to a strain-induced precipitation phase to significantly reduce the recrystallization temperature of deformed austenite through particle pinning and subgrain boundaries, provide nucleation particles, and have a significant effect on grain refinement.. In addition, in the process of continuous annealing austenitization, the soaking of insoluble carbide and nitride particles will prevent the coarsening of soaked austenite grains through the particle pinning grain boundary mechanism, so as to effectively refine the grains. Based on this, in order to give full play to the beneficial effect of Nb element, in the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure, the mass percentage of Nb element is specifically controlled to be 0.01~0.03%, for example, the mass percentage of Nb element can be 0.01%, 0.015%, 0.02%, 0.025%, 0.03% or within the range of any two values mentioned above.

[0021] Of course, in some preferred embodiments, in order to achieve better implementation effects, the mass percentage of Nb elements can be further preferably controlled to be 0.015~0.025%.

[0022] Ti: in the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure, the added strong carbide-forming element Ti also shows a strong effect of inhibiting the growth of austenite grains at high temperatures, and the addition of Ti elements also helps to refine the grains. Therefore, in order to exert the beneficial effect of Ti element, in the present disclosure, the mass percentage of Ti element is specifically controlled to be 0.01~0.03%, for example, the mass percentage of Ti element can be 0.01%, 0.015%, 0.02%, 0.025%, 0.03% or within the range of any two values mentioned above.

[0023] Of course, in some preferred embodiments, in order to achieve better implementation effects, the mass percentage of Ti element can be further preferably controlled to be 0.015~0.025%.

[0024] B: in the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure, the addition of B element is not only conducive to improving the hardenability of the steel, but also can effectively improve the strength of the steel plate. When the mass percentage of B element in the steel is less than 0.0020%, it will also cause an insufficient strength of the steel plate. When the mass percentage of B element in the steel is higher than 0.0030%, it will also lead to an excessively high strength of the steel plate and reduce its forming performance. Therefore, in the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure, the mass percentage of B element is controlled to be 0.0020~0.0030%, for example, the mass percentage of B element can be 0.0020%, 0.0023%, 0.0025%, 0.0028%, 0.0030% or within the range of any two values mentioned above.

[0025] In the above-mentioned component design, this dual-phase steel designed by the present disclosure is not added with precious alloying elements such as Mo, Cr, etc., and it has very excellent economy. At the same time, in order to ensure that the 1000 MPa grade tensile strength of dual-phase steel can be obtained at the normal continuous annealing gas cooling rate of 40-100 °C/s, the chemical composition design needs to ensure the alloy addition content of C, Mn and B to provide sufficient hardenability. However, the upper limit of the content of C, Mn and B alloying elements in the dual-phase steel also needs to be controlled to ensure excellent welding and forming properties, and to avoid the strength from exceeding the upper limit.

[0026] Further, in the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure, among the unavoidable impurities, P is ≤ 0.012%, S is ≤0.0025%, N is ≤ 0.005%.

[0027] In the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure, P element, S element and N element are all impurity elements in the steel, and the lower the content of P, N and S elements in the steel, the better the implementation effect. Specifically, MnS formed by S element will seriously affect the formability of the steel, while the N element will easily cause cracks or bubbles on the surface of the slab. Therefore, if the technical conditions permit, in order to obtain the steel of better performance and better quality, the content of impurity elements in the steel should be reduced as much as possible, and P, S and N elements in the steel should be specifically controlled to be: P≤0.012%, S≤0.0025%, N ≤0.005%. In some embodiments, in the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure, the mass percentage of P element is 0.001~0.012%, and/or the mass percentage of S element is 0.001 ~0.0025%, and/or the mass percentage of N element is 0.001~0.005%.

[0028] Further, in the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure, the mass percentage of each chemical element satisfies at least one of the following items:

Nb: 0.015~0.025%,
Ti: 0.015~0.025%.

[0029] Further, in the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure, the volume percentage of martensite is ≥60%, for example, the volume percentage of martensite can be 60%, 65%, 70%, 75%, 80%, 85%, 90% or within the range of any two values mentioned above.

[0030] Further, in the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure, its hardenability factor Y_Q satisfies: $2.0 \le Y_Q \le 2.4$, wherein Y_Q=Mn+200xB, and each chemical element in the formula represents the numerical value before the mass percent sign. In some embodiments, the hardenability factor Y_Q is 2.0, 2.1, 2.2, 2.3, 2.4 or within the range of any two values mentioned above.

[0031] In this 100 kg grade cold-rolled low-alloy annealed dual-phase steel designed by the present disclosure, the combination effect of B element and Mn element can make the steel achieve a better strength effect. In order to make the final strength of the steel meet the requirements, the present disclosure can further control the mass percentage content of Mn and B to meet $2.0 \le Y_Q \le 2.4$, wherein Y_Q=Mn+200xB, while controlling the mass percentage content of a single chemical element.

[0032] However, it should be noted that in the alloy design, the Mn content is the maximum parameter that affects the overall cost, so the present disclosure uses the comprehensive hardenability of Mn-B, and by adding an appropriate amount of B, the alloy design amount of Mn can be further reduced, thereby helping to reduce the cost and improving the manufacturability of on-site production at the same time.

[0033] Further, in the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure, neither of the particle size of martensite and the particle size of ferrite is more than 5 microns. For example, the particle size of martensite can be 3.5 microns, 3.8 microns, 4 microns, 4.2 microns, 4.5 microns, 4.8 microns, 5 microns, or within the range of any two values mentioned above, and the particle size of ferrite can be 3.5 microns, 3.8 microns, 4 microns, 4.2 microns, 4.5 microns, 4.8 microns, 5 microns, or within the range of any two values mentioned above.

[0034] Further, in the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure, the difference in microhardness between martensite and ferrite is $\triangle HV \le 150$. In some embodiments, the difference in microhardness between martensite and ferrite $\triangle HV$ is 90, 100, 110, 120, 130, 140, 150, or within the range of any two values mentioned above.

[0035] Further, in the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure, it is characterized in that it has a yield strength of ≥ 550MPa, a tensile strength of ≥ 1000MPa, a gauge-length elongation at break A_{50} of ≥12%, and a 90° bending performance R/t of ≤1.0. In some embodiments, the yield strength of the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure is 550MPa, 600MPa, 650MPa, 700MPa or within the range of any two values mentioned above. In some embodiments, the tensile strength of the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure is 1000MPa, 1020MPa, 1040MPa, 1060MPa, 1080MPa, 1100MPa or within the range of any two values mentioned above. In some embodiments, the gauge-length elongation at break A_{50} of the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure is 12%, 13%, 14%, 15%, 16%, 17% or within the range of any two values mentioned above. In some embodiments, the 90° bending performance R/t of the 100 kg grade cold-rolled low-alloy annealed dual-phase steel described in the present disclosure is 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 or within the range of any two values mentioned above.

[0036] Correspondingly, another object of the present disclosure is to provide the manufacturing method of the 100 kg grade cold-rolled low-alloy annealed dual-phase steel. The manufacturing method is convenient and simple to implement, and the 100 kg grade cold-rolled low-alloy annealed dual-phase steel prepared by the manufacturing method has high strength and excellent elongation and bending performance, wherein it has a yield strength of ≥ 550MPa, a tensile strength of ≥1000MPa, a gauge-length elongation at break A_{50} of ≥12%, and a 90° bending performance R/t of ≤1.0.

[0037] In order to achieve the above purpose, the present disclosure proposes a manufacturing method of the above-mentioned 100 kg grade cold-rolled low-alloy annealed dual-phase steel, which comprises steps:

(1) smelting and casting;
(2) hot rolling: wherein a continuously cast product is first heated to 1160~1190 °C, held for not less than 150 min, for example, 150~250min, then final rolling of hot rolling is carried out at 850~890 °C, and quick cooling is carried out at a rate of 30~80 °C/s after rolling; then coiling is carried out at a coiling temperature of 500~540°C; then air cooling is carried out after coiling;
(3) cold rolling;
(4) annealing: wherein the annealing soaking temperature is 825~855 °C, the annealing time is 40~200s, and then the steel plate is cooled to the starting temperature of quick cooling at a rate of 3~5 °C/s, and then quickly cooled at a rate of 40~100 °C/s, wherein the starting temperature of quick cooling is 735~760 °C, and the end temperature of quick cooling is 265~290 °C;
(5) tempering;
(6) temper rolling.

[0038] Further, in the manufacturing method described in the present disclosure, in step (4), the annealing soaking temperature is 830~840 °C.

[0039] In this technical solution designed by the present disclosure, in some preferred embodiments, in order to obtain a better implementation effect, i.e. the obtained grain size is fine, the mechanical properties of the obtained steel are moderate, and the forming performance is better, the annealing soaking temperature can be further preferably controlled to be 830-840 °C.

[0040] Further, in the manufacturing method of the present disclosure, in step (3), the reduction rate of cold rolling is controlled to be 50~70%.

[0041] Further, in the manufacturing method described in the present disclosure, in step (5), the tempering temperature is controlled to be 265~290 °C, and the tempering time is 100~400s.

[0042] Further, in the manufacturing method of the present disclosure, in step (6), the reduction rate of temper rolling is controlled to be ≤ 0.3%, such as 0.1~0.3%.

[0043] Compared with the prior art, the 100 kg grade cold-rolled low-alloy annealed dual-phase steel and manufacturing method thereof of the present disclosure have the advantages and beneficial effects described below:
The present disclosure develops a new 100 kg grade cold-rolled low-alloy annealed dual-phase steel, which can obtain a steel plate with a tensile strength greater than 1000MPa and a martensite + ferrite dual phase structure without the addition of alloy elements of Mo, Cr, through rational chemical composition design and optimized manufacturing process. The fine and uniform martensite + ferrite dual phase structure can further ensure that the steel has excellent elongation and bending performance, and has good formability.

[0044] The 100 kg grade cold-rolled low-alloy annealed dual-phase steel designed and prepared by the present disclosure has good economy and at the same time has the characteristics of high strength and excellent elongation and bending performance. It has a yield strength of ≥ 550MPa, a tensile strength of ≥ 1000MPa, a gauge-length elongation at break A_{50} of ≥12%, a 90° bending performance R/t of ≤1.0. The 100 kg grade cold-rolled low-alloy annealed dual-phase steel is simple to produce and manufacture, and has a very good promotion prospect and application value, which can effectively meet the needs of the market and users.

Detailed Description

[0045] The 100 kg grade cold-rolled low-alloy annealed dual-phase steel and its manufacturing method will be further interpreted and explained below in conjunction with specific embodiments of the present disclosure, but the interpretation and explanation do not constitute an undue limitation to the technical solution of the present disclosure.

Example 1-6 and Comparative Example 1-14

[0046] Table 1-1 lists the mass percentage of each chemical element designed for the 100 kg grade cold-rolled low-alloy annealed dual-phase steels of Example 1-6 and the comparative steels of Comparative Example 1-14.

Table 1-1. (wt%, the balance is Fe and other unavoidable impurities except P, S and N)

No.	Chemical element									
	C	Si	Mn	B	Al	P	S	N	Nb	Ti
Ex. 1	0.108	0.55	1.63	0.0024	0.025	0.008	0.0025	0.0035	0.015	0.018
Ex. 2	0.122	0.62	1.68	0.0022	0.012	0.012	0.0019	0.0037	0.017	0.015
Ex. 3	0.118	0.66	1.75	0.0022	0.024	0.009	0.0018	0.0042	0.016	0.023
Ex. 4	0.125	0.74	1.78	0.0024	0.015	0.011	0.0022	0.0028	0.022	0.016
Ex. 5	0.104	0.71	1.65	0.0029	0.018	0.012	0.002	0.0028	0.023	0.024
Ex. 6	0.126	0.68	1.70	0.0025	0.022	0.011	0.0023	0.0033	0.028	0.029
CEx. 1	**0.093**	0.56	1.74	0.0023	0.019	0.01	0.0014	0.0044	0.020	0.016
CEx. 2	**0.138**	0.77	1.73	0.0021	0.021	0.009	0.0024	0.0033	0.018	0.021
CEx. 3	0.111	0.58	**1.56**	0.0026	0.023	0.011	0.0017	0.0027	0.016	0.016
CEx. 4	0.104	0.55	**1.88**	0.0027	0.016	0.009	0.0023	0.0037	0.019	0.023
CEx. 5	0.123	0.72	1.77	**0.0012**	0.027	0.012	0.0015	0.0028	0.02	0.02
CEx. 6	0.116	0.69	1.61	**0.0032**	0.017	0.011	0.0018	0.003	0.018	0.019
CEx. 7-14	0.107	0.58	1.69	0.0025	0.016	0.007	0.0017	0.0021	0.024	0.018

[0047] Table 1-2 lists the values of the hardenability factor Y_Q of the 100 kg grade cold-rolled low-alloy annealed dual-phase steels of Example 1-6 and the comparative steels of Comparative Example 1-14.

Table 1-2.

No.	Hardenability factor Y_Q
Ex. 1	2.11
Ex. 2	2.12
Ex. 3	2.19
Ex. 4	2.26
Ex. 5	2.23
Ex. 6	2.20
CEx. 1	2.20
CEx. 2	2.15
CEx. 3	2.08
CEx. 4	**2.42**
CEx. 5	2.01
CEx. 6	2.25
CEx. 7-14	2.19
Note: in Table 1-2 above, Y_Q=Mn+200×B, and each chemical element in the formula represents the value before the mass percentage sign.	

[0048] The 100 kg grade cold-rolled low-alloy annealed dual-phase steels of Example 1-6 of the present disclosure and the comparative steels of Comparative Example 1-14 were prepared by adopting the following steps:

(1) Smelting and casting were carried out according to the chemical composition design shown in Table 1-1 and Table 1-2 to prepare a continuously cast product.
(2) Hot rolling: the continuously cast product was first heated to 1160~1190 °C, held for not less than 150min, and then final rolling of hot rolling was carried out at 850~890 °C, and quick cooling was carried out at a rate of 30~80 °C/s after rolling; then coiling was carried out, and the coiling temperature was controlled to be 500~540°C; and air cooling was carried out after coiling.
(3) Cold rolling: the steel coil was cold rolled, and the reduction rate of cold rolling was controlled to be 50~70%.
(4) Annealing: the annealing soaking temperature was controlled to be 825~855 °C, which could also be preferably controlled to be 830~840 °C, the annealing time was controlled to be 40~200s, and then cooled to the starting temperature of quick cooling at a rate of 3~5 °C/s, and then quickly cooled at a rate of 40~100 °C/s, wherein the starting temperature of quick cooling was 735~760 °C, and the end temperature of quick cooling was 265~290 °C.
(5) Tempering: the tempering temperature was controlled to be 265~290°C, and the tempering time was 100~400s.
(6) Temper rolling: the reduction rate of temper rolling was controlled to be ≤ 0.3% to obtain the finished dual-phase steel.

[0049] In this technical solution designed by the present disclosure, the chemical composition design and related process of 100 kg grade cold-rolled low-alloy annealed dual-phase steels prepared above in Example 1-6 of the present disclosure meet the requirements of the design specification of the present disclosure.

[0050] Correspondingly, although the comparative steels in Comparative Example 1-14 also adopted the composition of Table 1-1 and Table 1-2 in combination with the above-mentioned process flow to prepare, in order to highlight the superiority of the technical solution of the present disclosure, the designed comparative steels in Comparative Example 1-14 had parameters that did not meet the design requirements of the present disclosure in the chemical composition and/or related manufacturing processes.

[0051] Specifically, the chemical composition of comparative steels in Comparative Example 1-6 had parameters that failed to meet the design requirements of the present disclosure; and the chemical composition of comparative steels in Comparative Example 7-14 satisfied the design requirements of the present disclosure, but the relevant process parameters all had the parameters that failed to meet the design specifications of the present disclosure.

[0052] Table 2-1 and Table 2-2 list the specific process parameters of the 100 kg grade cold-rolled low-alloy annealed dual-phase steels of Example 1-6 and the comparative steels in Comparative Example 1-14 in the above process steps (1)-(6).

Table 2-1.

No.	Step (2)					Step (3)
	Heating temperature (°C)	Holding time (min)	Final temperature of hot rolling (°C)	Cooling rate (°C/s)	Coiling temperature (°C)	Reduction rate of cold rolling (%)
Ex. 1	1168	155	858	62	511	55
Ex. 2	1179	165	877	52	525	67
Ex. 3	1166	200	890	78	534	58
Ex. 4	1174	185	865	66	505	70
Ex. 5	1169	190	875	46	520	54
Ex. 6	1187	220	854	34	536	62
CEx. 1	1172	195	885	72	528	65
CEx. 2	1180	205	855	50	540	54
CEx. 3	1183	170	882	30	533	50
CEx. 4	1188	158	850	64	506	66
CEx. 5	1190	184	890	49	515	55
CEx. 6	1166	179	884	76	525	62
CEx. 7	**1154**	169	876	54	516	58
CEx. 8	**1203**	204	870	55	537	68
CEx. 9	1177	158	868	59	**484**	64
CEx. 10	1174	173	885	60	**562**	52
CEx. 11	1164	182	873	70	535	55
CEx. 12	1186	194	875	77	506	63
CEx. 13	1175	169	858	69	537	59
CEx. 14	1166	175	866	53	524	60

Table 2-2.

No.	Step (4)						Step (5)		Step (6)
	Annealing soaking temperatur e (°C)	Annealing time (s)	Cooling rate(°C/s)	Starting temperature of quick cooling (°C)	Cooling rate of quick cooling (°C/s)	End temperatur e of quick cooling (°C)	Tempering temperatur e (°C)	Tempering time (s)	Reduction rate of temper rolling (%)
Ex. 1	834	80	3	735	55	275	275	150	0.2
Ex. 2	845	120	3	747	54	268	268	320	0.2
Ex. 3	838	112	4	750	85	270	270	250	0.3
Ex. 4	836	170	3	740	72	272	272	270	0.1
Ex. 5	828	190	5	745	60	288	288	195	0.3
Ex. 6	850	65	4	755	96	273	273	375	0.1
CEx. 1	840	160	5	748	48	285	285	330	0.1
CEx. 2	839	70	3	736	65	279	279	200	0.2
CEx. 3	844	115	4	742	75	275	275	180	0.2
CEx. 4	828	180	5	746	82	266	266	110	0.3
CEx. 5	833	75	3	742	67	283	283	280	0.2
CEx. 6	846	84	5	753	90	288	288	140	0.1
CEx. 7	829	130	4	743	50	276	276	330	0.3
CEx. 8	845	125	3	738	85	269	269	225	0.3
CEx. 9	827	99	4	751	44	280	280	195	0.2
CEx. 10	848	140	5	752	76	290	290	280	0.1
CEx. 11	**818**	125	5	744	55	285	285	390	0.2
CEx. 12	**862**	65	3	738	66	270	270	180	0.1
CEx. 13	837	135	4	750	59	**245**	**245**	300	0.2
CEx. 14	841	156	4	747	72	**299**	**299**	200	0.3

[0053] It should be noted that in the above table 2-2, the end temperature of quick cooling in each example and comparative example was the same as the tempering temperature, which was because, in the actual process operation, the tempering operation was carried out after the end of the quick cooling operation.

[0054] Correspondingly, after completing the above-mentioned manufacturing process, the inventors sampled the dual-phase steel of each example and comparative example for the finished dual-phase steels prepared in Example 1-6 and Comparative Example 1-14, respectively, so as to obtain the corresponding steel plate samples, and the microstructure of the steel plate sample of each example and comparative example was observed and analyzed by optical microscope, and it was observed that the microstructures of the 100-kg cold-rolled low-alloy annealed dual-phase steels of Example 1-6 and the comparative steel plates of Comparative Example 1-14 were martensite +ferrite.

[0055] To this end, the inventors further analyzed the microstructure of the steel plate of each example and comparative example to obtain the test results of the phase proportion of martensite, the particle size of martensite, the particle size of ferrite and the difference in microhardness between martensite and ferrite △HV in the microstructure of the steel plate of Example 1-6 and Comparative Example 1-14, and the relevant test results are specifically listed in Table 3 below. In the present disclosure, phase proportion refers to the proportion of each phase in the structure measured by the area method; particle size refers to the grain size of each structure, which is based on the average values of the transverse and longitudinal directions. The phase proportion and particle size were observed by an optical microscope, and the phase proportion and particle size were measured with the help of the analysis software that comes with the optical microscope. Microhardness was measured using a Wechsler microhardness tester.

Table 3.

No.	Phase proportion of martensite (%)	Particle size of martensite (μm)	Particle size of ferrite (μm)	Difference in microhardness between martensite and ferrite △HV
Ex. 1	68	4.5	4.0	115
Ex. 2	70	4.3	4.5	100
Ex. 3	77	3.9	4.1	105
Ex. 4	82	4.4	4.5	110
Ex. 5	62	4.7	4.6	95
Ex. 6	75	4.2	4.5	110
CEx. 1	**45**	**5.2**	5.0	90
CEx. 2	86	4.3	4.6	135
CEx. 3	**47**	4.9	**5.1**	95
CEx. 4	75	4.6	4.2	100
CEx. 5	**46**	**5.5**	**5.6**	90
CEx. 6	78	4.8	4.6	125
CEx. 7	**44**	**5.8**	**6.0**	90
CEx. 8	80	4.3	4.2	120
CEx. 9	79	4.6	4.5	115
CEx. 10	**42**	**6.2**	**6.0**	85
CEx. 11	**48**	**5.5**	**5.5**	90
CEx. 12	84	4.3	4.6	115
CEx. 13	85	4.0	4.2	120
CEx. 14	**47**	**5.6**	**5.6**	90

[0056] As can be seen from the above Table 3, in the present disclosure, the microstructure of the 100 kg grade cold-rolled low-alloy annealed dual-phase steels prepared in Example 1-6 was martensite + ferrite, and the volume percentage (phase proportion) of the martensite was between 62% and 82%, the particle size of martensite is between 3.9μm and 4.7μm, the particle size of ferrite was between 4.0μm and 4.6μm, and the difference in microhardness between martensite and ferrite △HV was between 95 and 115.

[0057] Correspondingly, after completing the above observation and analysis, in order to verify the performance of steel in each example and comparative example, the 100-kg cold-rolled low-alloy annealed dual-phase steels prepared in Example 1-6 and the comparative steels prepared in Comparative Example 1-14 were sampled, and the corresponding steel plate samples were obtained. And the steel plate samples obtained in Example 1-6 and Comparative Example 1-14 were tested to obtain the mechanical property data of the steels in Example 1-6 and Comparative Example 1-14, and the relevant test results are listed in the following Table 4.

[0058] The relevant mechanical property test methods were as follows:

Tensile test: the GB/T228-2010 Metallic materials-Tensile testing-Method of test at ambient temperature was used to detect the yield strength, tensile strength and gauge-length elongation at break A_{50} of the steels in Example 1-6 and Comparative Example 1-14, wherein, the gauge-length elongation at break A_{50} represents: the elongation at break of the tensile specimen having parallel length * width of 50mm * 25mm.

[0059] Bending performance test: the GB/T232-2010 Metallic materials-bending experiment was used to detect the 90° bending performance R/t of the steels in Example 1-6 and Comparative Example 1-14.

[0060] Table 4 lists the mechanical property test results of the 100 kg grade cold-rolled low-alloy annealed dual-phase steels in Example 1-6 and the comparative steels in Comparative Example 1-14.

Table 4.

No.	Yield strength (MPa)	Tensile strength (MPa)	A_{50} gauge-length elongation at break (%)	Kilogram force (kg/cm^2)	90° bending performance R/t
Ex. 1	585	1010	14.3	103	0.6
Ex. 2	602	1020	13.8	104	0.7
Ex. 3	611	1032	13.5	105	1.0
Ex. 4	655	1054	12.7	108	0.8
Ex. 5	577	1002	15.5	101	0.7
Ex. 6	643	1045	13.0	107	0.9
CEx. 1	552	**969**	16.7	99	0.6
CEx. 2	724	1089	**11.4**	111	**1.5**
CEx. 3	563	**977**	15.6	100	0.6
CEx. 4	735	1074	**11.2**	110	**0.9**
CEx. 5	**545**	**974**	16.3	99	0.7
CEx. 6	740	1088	**10.8**	111	**1.1**
CEx. 7	**543**	**966**	16.7	99	0.8
CEx. 8	729	1077	**11.5**	110	**0.9**
CEx. 9	733	1090	**10.8**	111	**1.1**
CEx. 10	**548**	**959**	15.9	98	0.6
CEx. 11	555	**974**	16.0	99	0.7
CEx. 12	727	1094	**10.5**	112	**1.4**
CEx. 13	740	1101	**10.1**	112	**1.6**
CEx. 14	**548**	**975**	15.8	99	0.6
Note: Kilogram force, or kg force, is a common unit of force, and the SI unit of force is Newton. 1 kg force refers to the gravitational force (i.e. 9.8N) exerted on a 1 kg object. So 1 kgf = 9.8 Newtons.					

[0061] It can be seen from Table 4 that in the present disclosure, the 100 kg grade cold-rolled low-alloy annealed dual-phase steels of Example 1-6 prepared by this technical solution designed by the present disclosure has quite excellent mechanical properties, and its yield strength is between 585MPa and 655MPa, its tensile strength is between 1002MPa and 1054MPa, and its gauge-length elongation at break A_{50} is between 12.7% and 15.5%, and the 90°bending performance R/t is between 0.6 and 1.0. The tensile strength of more than 1000MPa is obtained under the premise of not adding precious alloying elements such as Mo and Cr into the dual-phase steel of each example, and the steels are all 100 kg grade cold-rolled low-alloy annealed dual-phase steels, and have good elongation and bending performance at the same time.

[0062] Compared with the 100 kg grade cold-rolled low-alloy annealed dual-phase steels of Example 1-6, the comprehensive performances of the comparative steels in Comparative Example 1-14 are obviously inferior because the comparative steels in Comparative Example 1-14 do not meet the parameters required by the present disclosure in the chemical composition design and/or related manufacturing process.

[0063] To sum up, it can be seen that in the present disclosure, a dual phase steel with both low cost and excellent mechanical properties is obtained through a reasonable chemical composition design combined with an optimized process. It has a tensile strength of greater than 1000MPa, and has good elongation and bending performance at the same time.

[0064] It should be noted that the combination of various technical features in this case is not limited to the combination mode recorded in the claims of this case or the combination mode recorded in the specific embodiment, and all the technical features recorded in this case can be freely combined or combined in any way, unless there is a contradiction between them.

[0065] It should also be noted that the examples listed above are only specific examples of the present disclosure. Obviously, the present disclosure is not limited to the above examples, and similar changes or deformations made thereby are directly derived or easily associated by those skilled in the art from the contents disclosed in the present disclosure, and should belong to the scope of protection of the present disclosure.

Claims

1. A 100 kg grade cold-rolled low-alloy annealed dual-phase steel, which comprises Fe and unavoidable impurity elements, wherein it further comprises the following chemical elements in mass percentages as follows:

   0.1%<C≤0.13%, Si: 0.5%~0.8%, Mn: 1.6%~1.8%, Al: 0.01%~0.03%, Nb: 0.01~0.03%, Ti: 0.01~0.03%, B: 0.0020~0.0030%;
   and its chemical elements do not comprise Mo or Cr;
   the microstructure of the 100 kg grade cold-rolled low-alloy annealed dual-phase steel is martensite + ferrite.

2. The 100 kg grade cold-rolled low-alloy annealed dual-phase steel of claim 1, wherein the mass percentage of each chemical element is:
   0.1%<C≤0.13%, Si: 0.5%~0.8%, Mn: 1.6%~1.8%, Al: 0.01%~0.03%, Nb: 0.01~0.03%, Ti: 0.01~0.03%, B: 0.0020~0.0030%, with a balance of Fe and other unavoidable impurities.

3. The 100 kg grade cold-rolled low-alloy annealed dual-phase steel of claim 1 or 2, wherein among the unavoidable impurities, P is ≤ 0.012%, S is ≤0.0025%, N is ≤ 0.005%.

4. The 100 kg grade cold-rolled low-alloy annealed dual-phase steel of claim 1 or 2, wherein the mass percentage of each chemical element satisfies at least one of the following items:

   Nb: 0.015~0.025%,
   Ti: 0.015~0.025%.

5. The 100 kg grade cold-rolled low-alloy annealed dual-phase steel of claim 1 or 2, wherein the volume percentage of martensite is ≥ 60%.

6. The 100 kg grade cold-rolled low-alloy annealed dual-phase steel of claim 1 or 2, wherein the hardenability factor Y_Q satisfies: $2.0 \leq Y_Q \leq 2.4$, wherein $Y_Q = Mn + 200 \times B$, and each chemical element in the formula represents the numerical value before the mass percent sign.

7. The 100 kg grade cold-rolled low-alloy annealed dual-phase steel of claim 1 or 2, wherein neither of the particle size of martensite and the particle size of ferrite is more than 5 microns.

8. The 100 kg grade cold-rolled low-alloy annealed dual-phase steel of claim 1 or 2, wherein the difference in microhardness between martensite and ferrite △HV is ≤150.

9. The 100 kg grade cold-rolled low-alloy annealed dual-phase steel of claim 1 or 2, wherein it has a yield strength of ≥ 550Mpa, a tensile strength of ≥ 1000MPa, a gauge-length elongation at break A_{50} of ≥12%, and a 90° bending performance R/t of ≤1.0.

10. A manufacturing method of the 100 kg grade cold-rolled low-alloy annealed dual-phase steel of any one of claims 1-9, which comprises steps:

(1) smelting and casting;
(2) hot rolling: wherein a continuously cast product is first heated to 1160~1190 °C, held for not less than 150 min, then final rolling of hot rolling is carried out at 850~890 °C, and quick cooling is carried out at a rate of 30~80 °C/s after rolling; then coiling is carried out at a coiling temperature of 500~540°C; and air cooling is carried out after coiling;
(3) cold rolling;
(4) annealing: wherein the annealing soaking temperature is 825~855 °C, the annealing time is 40~200s, and then the steel plate is cooled to the starting temperature of quick cooling at a rate of 3~5 °C/s, and then quickly cooled at a rate of 40~100 °C/s, wherein the starting temperature of quick cooling is 735~760 °C, and the end temperature of quick cooling is 265~290 °C;
(5) tempering;
(6) temper rolling.

11. The manufacturing method of claim 10, wherein in step (4), the annealing soaking temperature is 830~840 °C.

12. The manufacturing method of claim 10, wherein in step (3), the reduction rate of cold rolling is controlled to be 50~70%.

13. The manufacturing method of claim 10, wherein in step (5), the tempering temperature is controlled to be 265~290 °C, and the tempering time is 100~400s.

14. The manufacturing method of claim 10, wherein in step (6), the reduction rate of temper rolling is controlled to be ≤ 0.3%.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2023/114258

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/02(2006.01)i; C22C38/04(2006.01)i; C22C38/06(2006.01)i; C22C38/14(2006.01)i; C22C38/12(2006.01)i; C21D8/02(2006.01)i; C21D1/26(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)

CNABS, CNTXT, ENTXTC, VEN, WPABSC, WPABS, DWPI, CJFD, 超星读秀, DUXIU, CNKI: 宝山钢铁, 宝钢, 李伟, 王利, 朱晓东, C, 碳, Si, 硅, Mn, 锰, B, 硼, Al, 铝, Ti, 钛, Nb, 铌, 马氏体, 铁素体, 双相, 两相, 复相, 冷轧, 100公斤级, 980MPa级, 淬透性因子, carbon, silicon, manganese, boron, aluminum, aluminium, titanium, niobium, martensite, ferrite, two phase, two-phase, dual phase, dual-phase, cold rolling

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 113737087 A (BAOSHAN IRON & STEEL CO., LTD.) 03 December 2021 (2021-12-03) description, paragraphs 0008-0050	1-14
A	CN 113737086 A (BAOSHAN IRON & STEEL CO., LTD.) 03 December 2021 (2021-12-03) description, paragraphs [0008]-[0058]	1-14
A	CN 113061812 A (ANGANG STEEL COMPANY LIMITED) 02 July 2021 (2021-07-02) description, paragraphs 0031-0086	1-14
A	CN 1940108 A (BAOSHAN IRON & STEEL CO., LTD.) 04 April 2007 (2007-04-04) description, page 3, paragraph 2 to page 5, paragraph 2	1-14
A	JP 2015113475 A (JFE STEEL CORP.) 22 June 2015 (2015-06-22) entire document	1-14
A	KR 102200227 B1 (POSCO) 08 January 2021 (2021-01-08) entire document	1-14

☐ 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
11 October 2023	**01 November 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**	Telephone No.

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

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2023/114258

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
CN	113737087	A	03 December 2021	CA	3180467	A1	02 December 2021
				WO	2021238916	A1	02 December 2021
				CN	113737087	B	19 July 2022
				IN	202247071018	A	06 January 2023
				EP	4159886	A1	05 April 2023
				JP	2023527389	A	28 June 2023
				US	2023227930	A1	20 July 2023
CN	113737086	A	03 December 2021	CA	3180469	A1	02 December 2021
				WO	2021238917	A1	02 December 2021
				IN	202247070792	A	30 December 2022
				EP	4159885	A9	21 June 2023
				EP	4159885	A1	05 April 2023
				US	2023203611	A1	29 June 2023
				JP	2023527390	A	28 June 2023
CN	113061812	A	02 July 2021	CN	113061812	B	19 July 2022
CN	1940108	A	04 April 2007	CN	100430505	C	05 November 2008
JP	2015113475	A	22 June 2015	JP	6048382	B2	21 December 2016
KR	102200227	B1	08 January 2021	None			

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

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- CN 109280854 A **[0005]**
- CN 111455285 A **[0006]**
- CN 107043888 A **[0007]**