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

(72) Inventors:
- **CHEN, Mengxiao**
Shanghai 201900 (CN)
- **ZHONG, Yong**
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) HIGH-PLASTICITY 1500-MPA-GRADE ULTRAHIGH-STRENGTH STEEL AND PREPARATION METHOD THEREFOR

(57) High-plasticity 1500-MPa-grade ultrahigh-strength steel and a manufacturing method therefor. The steel comprises the following components in percentages by weight: 0.35-0.40% of C, 1.0-1.8% of Si, 1.5-2.0% of Mn, 0.3-0.6% of Cr, 0.02-0.05% of Al, 0.02-0.05% of Ti, and 0.002-0.02% of B, with the balance being Fe and other inevitable impurities. Moreover, the steel also satisfies: the carbon equivalent Ceq1 of a peritectic reaction zone is greater than 0.17%, and C_{eq1}=C-0.03Mn-0.06Si-0.222S-0.04P; and the carbon equivalent C_{eq2} for welding is smaller than or equal to 0.56%, and C_{eq2}=C+Mn/20+Si/30+2P+4S. The ultra-high-strength steel of the present invention has a yield strength of 1000-1300 MPa, a tensile strength of greater than or equal to 1500 MPa, and an elongation at break of greater than or equal to 18%, has a good surface quality, and is particularly suitable for manufacturing structural members and safety members of vehicles with complex shapes and high requirements for a forming performance, such as A/B pillars, side impact beams, longitudinal beams, and bumpers.

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Description

Technical Field

[0001] The present disclosure relates to the technology for manufacturing high-strength steel, and in particular to a high-plasticity 1500MPa-grade ultra-high strength steel and a method for manufacturing the same.

Background Art

[0002] In recent years, in order to achieve the goals of reducing vehicle weight, saving energy, reducing emissions, improving collision safety and reducing manufacturing costs, advanced high-strength steel for automobiles has been widely used in the automobile manufacturing industry. Advanced high-strength steel is currently a material that has the highest overall competitiveness for lightweight vehicle bodies because the increased steel sheet strength allows for reducing the steel sheet thickness while maintaining excellent forming performance.

[0003] Currently, the ultra-high-strength martensitic steel having a strength up to the 1500MPa grade and used in a large amount has an elongation of about 5%, which can no longer meet the dual requirements in the automotive field for automobile safety and forming performance during the manufacturing process. Another type of steel used in a large amount is hot-formed steel. However, the forming process of the hot-formed steel has high requirements on heating equipment and cooling capacity. The process is complicated, and the elongation of this steel is basically within 10%. The third generation high-strength steel for automobiles has attracted extensive attention because of its high strength, high plasticity and low cost, and its strength-elongation product can reach 20-30GPa%.

[0004] Chinese Patent CN103667884B discloses "a method for preparing 1400MPa-grade low-yield-ratio high-elongation cold-rolled ultra-high strength automobile steel", whose composition is: C 0.14%-0.16%, Si 1.31%-1.51%, Mn 2.7%-2.9%, S≤0.005%, P≤0.009%, Al 0.11%-0.51%, RE 0.005-0.20%, and a balance of Fe and unavoidable impurities. The composition of this patented steel is designed simply to include C, Si, Mn, Al and a small amount of rare earth elements, and the manufacturing process involves conventional casting-hot rolling-cold rolling-continuous annealing. The finished steel structure comprises 70-85% of martensite, 5-20% of retained austenite and a small amount of ferrite. However, the tensile strength of the invented steel is at the 1400MPa grade, the elongation is greater than or equal to 8%, and the yield strength is relatively low.

[0005] Chinese Patent CN106244918B discloses "a 1500MPa-grade automobile steel having a high strength-elongation product and a manufacturing method for the same". The composition of this patented steel is: C 0.1-0.3%, Si 0.1-2.0%, Mn 7.5-12%, Al 0.01-2.0%, and the chemical elements further include at least one of Nb 0.01-0.07%, Ti 0.02-0.15%, V 0.05-0.20%, Cr 0.15-0.50%, Mo 0.10-0.50%, wherein the balance is iron and other unavoidable impurities. The manufacturing method comprises the following steps: 1) smelting and casting; 2) hot rolling; 3) bell furnace annealing, wherein the annealing temperature is 600-700°C, and the annealing time is 1-48h; 4) cold rolling; 5) first annealing after cold rolling, wherein the annealing temperature is between the Ac1 and Ac3 temperatures, and the annealing time is more than 5min; 6) second annealing after cold rolling, wherein the annealing temperature is 750-850°C, and the annealing time is 1-10min; 7) tempering, wherein the tempering temperature is 200-300°C, and the tempering time is not less than 3min. The microstructure of the 1500MPa-grade automobile steel having a high strength-elongation product is austenite+martensite+ferrite or austenite+martensite, and its strength-elongation product is not less than 30GPa%. Although this patent can achieve a better match between strength and plasticity, the manufacturing process is extremely complicated, and the high Mn content in the composition also makes it difficult to manufacture the steel.

[0006] Chinese Patent CN106917055B discloses "a third generation high strength-and-toughness automobile steel and its preparation method". The composition of the steel is: C 0.40-0.60%, Si 1.00-2.00%, Mn 1.5-3.0%, Ni 0-0.60%, Cr 0.50-1.50%, Mo 0.30-0.60%, V 0-0.20%, Co 0-1.50%, Al 0-1.50%, and a balance of Fe and unavoidable impurities. After vacuum smelting, casting is carried out, and then hot rolling is carried out with a total reduction rate of 80%-95%. The resulting hot-rolled sheet is heated to 900-970°C at a rate of 5-20°C/s for 10-20 minutes of austenitization, and then air-cooled to 250-320°C and held for 2-12 hours. The material has a yield strength of more than 1000 MPa, a tensile strength of more than 1500 MPa, and an elongation after fracture of more than 20%. This patent mainly involves an ultra-high strength bainitic steel with a complex composition containing a number of alloying elements. At the same time, the heat treatment process is inefficient, the austenitizing temperature is too high, and the low-temperature treatment time is too long.

[0007] Chinese Patent Application CN108018484A discloses "a cold-rolled high strength steel with a tensile strength of at least 1500MPa and excellent formability and a method for manufacturing the same". The composition of the steel in this patent application is: C 0.25-0.40%, Si 1.50-2.50%, Mn 2.0-3.0%, Al 0.03-0.06%, P≤0.02%, S≤0.01%, N≤0.01% and at least one of 0.1-1.0% Cr and 0.1-0.5% Mo, and it also comprises at least one of 0.01-0.1% Nb, 0.01-0.2% V and 0.01-0.05% Ti, wherein the balance is Fe and other unavoidable impurities. The manufacturing method includes the following steps: 1) smelting and casting; 2) hot rolling; 3) pickling; 4) cold rolling; 5) continuous annealing: heating the strip steel to a soaking temperature in the range of 800-900°C, holding for at least 60 seconds, then cooling to 150-300°C at a rate of 30-80°C/s, then reheating to 350-440°C, holding for 30-300 seconds, and finally cooling to room temperature. The product has a microstructure of 5-20% retained austenite and 70-90% martensite, a tensile strength of at least 1500MPa and excellent formability.

[0008] There are relatively few related patents focusing on the field of short-process technology for 1500MPa-grade ultra-high strength steel.

[0009] Chinese Patent CN111455282B discloses a "quenched and partitioned steel with a tensile strength ≥1500MPa produced using a short process and a method therefor". The composition of this steel comprises: C 0.26-0.34%, Si 1.9-2.7%, Mn 2.6-3.4%, Ti 0.02-0.07%, Als 0.02-0.05%, P≤0.018%, S≤0.004%, N≤0.006%, O≤30ppm. The manufacturing process comprises: desulfurization of molten iron, smelting, argon blowing, LF refining, soft blowing, RH vacuum treatment, continuous casting to form a slab, soaking of the cast slab, descaling, seven-pass finishing rolling, laminar cooling, coiling, temper rolling, pickling, and continuous annealing. The steel strip has an Rel in the range of 1000-1200 MPa, an Rm of ≥ 1500 MPa, and an elongation of ≥ 15%. The method is one for producing a 1500MPa-grade quenched and partitioned steel using a short process. The composition of this patented steel is designed simply to include C, Si, Mn, Al, and Ti. Although this patent can achieve a good match between high strength and high plasticity, the use of a high Si and high Mn composition system causes a series of problems, such as steel leakage during thin slab continuous casting, slab surface cracking, and a high risk of generation of scrap steel during rolling thin-gauge steel, which increases the difficulty in and cost of producing ultra-high strength steel in a short process.

[0010] Chinese Patent Application CN114012056A discloses "a 1500MPa-grade hot-formed steel and a method for preparing the same". The composition of the steel comprises: C 0.19-0.26%, Si 0.05-1.3%, Mn 0.9-2.1%, P<0.015%, S≤0.002%, Alt 0.02-0.12%, B 0.002-0.020%, Cr 0.15-2.0%, Ti 0.02-0.15%, N≤0.006%, V+Nb≤0.15%, and a balance of Fe and unavoidable impurities. The molten steel is smelted and continuously cast, then subjected to soaking treatment, descaling prior to rough rolling, rough rolling, electromagnetic induction heating, descaling prior to finishing rolling, finishing rolling, laminar cooling, coiling, air cooling to room temperature and pickling. After the pickled sheet is obtained, it is hot stamped to obtain a 1500MPa-grade hot-formed steel with an elongation within 10%. This patent application also adopts a method for producing a hot-formed steel using a short process. The composition designed for this steel is relatively complex, comprising a number of alloying elements. Although the process is relatively simple, the manufacturing method pertains to the field of hot-formed ultra-high strength steel, and the elongation of the material is insufficient.

Summary

[0011] One of the objects of the present disclosure is to provide a high-plasticity 1500MPa-grade ultra-high strength steel and a method for manufacturing the same. The ultra-high strength steel has excellent strength and plasticity, excellent surface quality, good welding performance, and a relatively simple composition without excessive alloying elements, and the manufacturing process is simple and efficient. The steel has a yield strength of 1000-1300MPa, a tensile strength of ≥1 500MPa, and an elongation at break of ≥18%. It has good application prospects in automotive safety structural parts, and is particularly suitable for manufacturing vehicle structural parts and safety parts having complex shapes and high requirements on forming performance, such as A/B pillars, door anti-collision bars, girders, bumpers, etc. As used herein, "1500 MPa grade" and "ultra-high strength" refer to a tensile strength of ≥1500 MPa; and "high plasticity" refers to an elongation at break of ≥18%.

[0012] To achieve the above object, the technical solution of the present disclosure is as follows:
A high-plasticity 1500MPa-grade ultra-high strength steel, comprising the following components in weight percentage:

C: 0.35-0.40%;
Si: 1.0~1.8%;
Mn: 1.5~2.0%;
Cr: 0.3~0.6%;
Al: 0.02~0.05%;
Ti: 0.02~0.05%;
B: 0.002~0.02%;
a balance comprising Fe and other unavoidable impurities, wherein the following is satisfied:

carbon equivalent in peritectic reaction zone C_{eq1}>0.17%, C_{eq1}=C-0.03Mn-0.06Si-0.222S-0.04P; and
welding carbon equivalent C_{eq2}≤0.56%, C_{eq2}=C+Mn/20+Si/30+2P+4S.

[0013] Preferably, the balance is Fe and other unavoidable impurities.
[0014] Preferably, the C content is 0.36-0.38 wt%.
[0015] Preferably, the Si content is 1.4-1.7 wt%.
[0016] Preferably, the Mn content is 1.7-2.0 wt%.

[0017] Preferably, the Cr content is 0.4-0.6 wt%.

[0018] Preferably, among the other unavoidable impurities: P is ≤0.015wt%, S is ≤0.002wt%, O is ≤0.002wt%, N is ≤0.004wt%.

[0019] The ultra-high strength steel of the present disclosure has a yield strength of 1000-1300 MPa, a tensile strength of ≥1500 MPa, and an elongation at break of ≥18%.

[0020] In some embodiments, the yield strength of the ultra-high strength steel of the present disclosure is 1000 MPa, 1050 MPa, 1100 MPa, 1150 MPa, 1200 MPa, 1250 MPa, 1300 MPa, or within a range consisting of any two of the foregoing values.

[0021] In some embodiments, the tensile strength of the ultra-high strength steel of the present disclosure is 1500 MPa, 1520 MPa, 1540 MPa, 1560 MPa, 1580 MPa, 1600 MPa, or within a range consisting of any two of the foregoing values.

[0022] In some embodiments, the elongation at break of the ultra-high strength steel of the present disclosure is 18%, 19%, 20%, 21%, 22%, 23%, 24%, 25% or within a range consisting of any two of the foregoing values.

[0023] In the design of the composition of the ultra-high strength steel of the present disclosure:

The present disclosure makes full use of the influence of the C, Si and Mn elements on the phase transformation of the material. At the same time, for the purpose of improving the process stability of thin slab continuous casting and rolling, and helping the carbon equivalent of the composition to avoid the peritectic reaction zone so as to improve the surface quality of the hot-rolled sheet, Cr and B are used to match with low Si and low Mn to increase the strength, and an ultra-high strength steel sheet product with excellent strength, plasticity and surface quality is finally achieved.

[0024] C: C is the most important solid solution strengthening element and is extremely critical for ensuring strength. A higher mass percentage of the C element in the steel leads to a higher fraction of retained austenite and higher enrichment of C in the retained austenite during partitioning, which is beneficial to enhancing the stability of the retained austenite, producing the TRIP effect, and improving the ductility of the material. However, too high a C content in the steel will lead to reduced weldability of the steel. When the mass percentage of C in the steel exceeds 0.40%, more twin crystals are likely to appear after quenching, thereby increasing crack sensitivity. In view of the above, in the present disclosure, the C content is controlled in the range of 0.35-0.40 wt%, for example, 0.36 wt%, 0.37 wt%, 0.38 wt%, 0.39 wt%, preferably in the range of 0.36-0.38 wt%.

[0025] Si: Si can strongly suppress formation of cementite during the partitioning process, and promote the enrichment of carbon into the retained austenite, thereby improving the stability of the retained austenite. The Si content required to effectively suppress the formation of cementite is at least 1.0%. It should be noted that if the content of the Si element in the steel is too high, the high-temperature plasticity of the steel will be reduced, and the risk of slab cracking and even steel leakage during thin slab continuous casting will be increased greatly. At the same time, when the Si content is too high, stable oxides will form on the surface of the steel sheet, which will have an adverse effect on the subsequent pickling process. In view of the above, in the present disclosure, the Si content is controlled in the range of 1.0-1.8 wt%, for example, 1.1 wt%, 1.2 wt%, 1.3 wt%, 1.4 wt%, 1.5 wt%, 1.6 wt%, 1.7 wt%, preferably in the range of 1.4-1.7 wt%.

[0026] Mn: Mn can expand the austenite phase zone, reduce the Ms and Mf points, and improve austenite stability and steel hardenability. At the same time, Mn is also a relatively important solid solution strengthening element, having a great influence on steel strength. However, it should be noted that too high a Mn content in the steel will lead to increased latent heat of solidification; especially for thin slab continuous casting, it will lead to limited heat transfer and too thin a slab shell, such that the risk of slab cracking and even steel leakage during thin slab continuous casting will be increased greatly, affecting the production stability of the ultra-high strength steel in a short process. At the same time, too high a Mn content will deteriorate the corrosion resistance and the welding performance. In view of the above, in the present disclosure, the Mn content is controlled in the range of 1.5-2.0 wt%, for example, 1.6 wt%, 1.7 wt%, 1.8 wt%, 1.9 wt%, preferably in the range of 1.7-2.0 wt%.

[0027] Cr: Cr also acts to contribute to the strength. Especially, in the present disclosure, since the Si and Mn contents need to be controlled to ensure stable proceeding of the thin slab continuous casting and rolling process, Cr is a key element for supplementing the strength. Cr can improve the hardenability of the steel and reduce the martensite transformation temperature, while helping to refine the austenite grains and improve the strength during rolling. When the Cr content is lower than 0.3wt%, it is difficult to guarantee the strength, while when it is higher than 0.6wt%, it will affect the welding performance of the material. In view of the above, in the present disclosure, the Cr content is controlled in the range of 0.3-0.6 wt%, for example, 0.4 wt%, 0.5 wt%, preferably in the range of 0.4-0.6 wt%.

[0028] Al: When the Al element exists in a state of solid solution, it can inhibit precipitation of cementite and transformation from γ to martensite, and improve the stability of austenite. In addition, the Al element can form fine and dispersed insoluble particles with C and N, which can refine the grains. However, if the mass percentage of the Al element in the steel is too high, a large amount of oxide inclusions will form easily, which is not conducive to the cleanliness of the molten steel. Therefore, in the present disclosure, the Al content is controlled in the range of 0.02-0.05 wt%, for example, 0.03 wt%, 0.04 wt%.

[0029] Ti: Ti can fix nitrogen in the steel to form stable compounds, thereby improving the slab quality and eliminating the edge crack defects. It can also form fine carbides to prevent growth of austenite grains and refine the grains. However, if its content is higher than 0.05wt% as defined in the present disclosure, it will be disadvantageous for the enrichment of C in the retained austenite and the stabilization of the retained austenite; if its content is lower than 0.02wt% as defined in the present disclosure, the crack occurrence rate will increase. Therefore, the Ti content in the present disclosure needs to be controlled in the range of 0.02-0.05wt%, for example, 0.03wt%, 0.04wt%.

[0030] B: Its main function is to improve the hardenability and strength of the steel. B tends to segregate at the austenite grain boundaries and delay the transformation of austenite to ferrite. The effects are significant at a low content. At the same time, B has a good grain boundary purification effect, which can impede segregation of harmful elements at the grain boundaries to a certain extent, thereby improving the deformation coordination of the material. However, too high a mass percentage of B will cause the steel strength to increase, which is not conducive to obtaining good plasticity. Therefore, the B content in the present disclosure needs to be controlled in the range of 0.002-0.02wt%, for example, 0.005wt%, 0.01 wt%, 0.015wt%.

[0031] Among the other unavoidable impurities in the present disclosure: P is ≤0.015wt%, S is ≤0.002wt%, O is ≤0.002wt%, N is ≤0.004wt%.

[0032] In the above solution, the P, S, O, and N elements are all impurity elements. Among them, although P can play a role in solid solution strengthening, inhibit formation of carbides, and is beneficial to improving the stability of retained austenite, too high a mass percentage of P will weaken the grain boundaries, increase the brittleness of the material, and deteriorate the welding performance. In other words, the positive effect of the P element is weaker than its negative effect. Therefore, it is preferred to control the mass percentage of P to be P≤0.015wt%. As for N, because an unduly high mass percentage of N will make steelmaking and continuous casting difficult, and is not conducive to inclusion control, the mass percentage of N is preferably controlled to be N≤0.004wt%. Accordingly, if the S content in the steel is too high, the plasticity of the material will be deteriorated significantly. For the ultra-high strength steel, the S content should be controlled more strictly. Therefore, the S content is controlled to be S≤0.002wt%. The line defects and peeling defects on the surface of the ultra-high strength steel are mainly caused by the presence of Al_2O_3 and other types of inclusions under the skin of the continuous casting slab. Therefore, in order to improve the surface quality of the finished strip steel, it is necessary to reduce the inclusions generated by deoxidation in the steel and control the O content in steelmaking. Therefore, in the present disclosure, the O content is controlled to be O≤0.002wt%.

[0033] In addition, the contents of the components of the ultra-high strength steel according to the present disclosure should also meet the following requirements:

carbon equivalent in peritectic reaction zone C_{eq1}>0.17%, C_{eq1}=C-0.03Mn-0.06Si-0.222S-0.04P; and
welding carbon equivalent C_{eq2}≤0.56%, C_{eq2}=C+Mn/20+Si/30+2P+4S.

[0034] The reason is as follows: when the carbon equivalent of the molten steel is in the peritectic reaction zone and the peritectic reaction occurs, the liquid phase of the molten steel reacts with the δ phase to generate the γ phase. During this process, the solidification of the molten steel will lead to a very obvious volume shrinkage (about 4.7%). This makes it easier for the thin slab continuous casting to produce defects such as surface cracks on the casting slab, and in severe cases it may even cause steel leakage. The carbon equivalent C_{eq1} in the peritectic reaction zone ranges from 0.08% to 0.17%. For high-carbon ultra-high strength steel, the composition needs to be designed so that the carbon equivalent C_{eq1} is higher than 0.17 to avoid the peritectic reaction. At the same time, from the empirical formula, the increase in the contents of the Si and Mn elements makes it easier for the composition to enter the peritectic reaction zone, thereby affecting the surface quality of the final product.

[0035] In addition, in the present disclosure, it has been discovered by extensive research that when the mass percentages of C, Si, Mn, P and S satisfy the welding carbon equivalent C_{eq2}≤0.56%, the welding performance of the high-strength steel obtained is better; and at the same time, the solid solution and structure strengthening effects of the material with such a composition are better, and the material strength is higher. On the contrary, when the welding carbon equivalent C_{eq2} is >0.56%, the welding performance of the material will be deteriorated notably.

[0036] The microstructure of the ultra-high strength steel of the present disclosure is 10%-15% by volume of ferrite + 70%-80% by volume of martensite + retained austenite.

[0037] In some embodiments, in the microstructure of the ultra-high strength steel of the present disclosure, the volume fraction of ferrite is 10%, 11%, 12%, 13%, 14%, 15% or within a range consisting of any two of the foregoing values.

[0038] In some embodiments, in the microstructure of the ultra-high strength steel of the present disclosure, the volume fraction of martensite is 70%, 72%, 74%, 76%, 78%, 80% or within a range consisting of any two of the foregoing values.

[0039] In some embodiments, in the microstructure of the ultra-high strength steel of the present disclosure, the volume fraction of retained austenite is 10%, 11%, 12%, 13%, 14%, 15% or within a range consisting of any two of the foregoing values.

[0040] In the ferrite in the microstructure of the ultra-high strength steel, the number of grains with a grain size of ≤5 μm accounts for 90% or more, and the number of grains with a grain size of ≤3 μm accounts for 60% or more.

[0041] The average grain size of the retained austenite in the microstructure of the ultra-high strength steel is ≤2 μm;

and/or the average C content C(ra) in the retained austenite satisfies: 1.2wt%≤C(ra)≤2.0wt%.

[0042] In some embodiments, in the microstructure of the ultra-high strength steel of the present disclosure, the average grain size of the retained austenite is ≤1.6 μm.

[0043] In some embodiments, in the microstructure of the ultra-high strength steel of the present disclosure, the average grain size of the retained austenite is 0.5 μm, 0.6 μm, 0.8 μm, 1.0 μm, 1.2 μm, 1.4 μm, 1.6 μm, 1.8 μm, 2.0 μm, or within a range consisting of any two of the foregoing values.

[0044] In some embodiments, in the microstructure of the ultra-high strength steel of the present disclosure, the average C content C(ra) in the retained austenite satisfies: 1.2wt%≤C(ra)≤1.8wt%.

[0045] The reason is that the presence of a certain amount of retained austenite in the structure of the material enables phase transformation into martensite during the deformation process, resulting in the TRIP effect, so that the material has good plasticity while having a tensile strength of the 1500MP grade. The presence of a certain amount of fine-grained ferrite allows, to a certain extent, the steel to have better ductility among the materials of the same grade of strength, and at the same time, contributes part of the material strength due to the strengthening effect of the fine grains. However, if its content exceeds 15%, the tensile strength of the material is insufficient; and if the content is less than 10%, it is difficult to meet the requirement for high plasticity.

[0046] Martensite exists as the major hard phase in the material to guarantee the strength. When its content is lower than 70%, the tensile strength of the material is insufficient; and when the content is higher than 80%, it is difficult to ensure the presence of sufficient retained austenite and ferrite to guarantee plasticity. For ferrite grains, it is necessary to ensure that the grains are small enough to fully exert the strengthening effect of the fine grains. At the same time, the uniformity of the ferrite structure must be ensured to avoid the appearance of abnormally large grains to improve the plasticity of the material. Therefore, the number of grains with a grain size of ≤5μm should be controlled to account for 90% or more, and the number of grains with a grain size of ≤3μm should account for 60% or more.

[0047] At the same time, for the retained austenite grains, the factors that influence the stability of the retained austenite during material deformation mainly include the size of the retained austenite grains and the average C content in the retained austenite. When the retained austenite grain size is > 2 μm, the retained austenite is rather large and unstable, which makes it easy to complete the TRIP effect in the early stage of deformation, resulting in insufficient plasticity of the material.

[0048] On the other hand, when the average C content in the retained austenite is < 1.2wt%, the stability of the retained austenite is insufficient, and the retained austenite is prone to martensitic transformation in the early stage of the deformation process, so that the TRIP effect is insufficient, and the formability of the steel sheet cannot be improved significantly. When the average C content in the retained austenite is > 2wt%, the retained austenite is too stable to undergo martensitic transformation during the deformation process, so that the TRIP effect is also insufficient, and the formability of the steel sheet cannot be improved either.

[0049] In some embodiments, the ultra-high strength steel of the present disclosure has a thickness of 0.8-2.0 mm.

[0050] The method for manufacturing the ultra-high strength steel according to the present disclosure is aimed to address the problems encountered by the prior art ultra-high strength steel, especially 1500MPa-grade ultra-high strength steel in the cold rolling process, i.e. the difficulty in thickness accuracy control and sheet shape control of a hard rolled sheet, and the stringent requirement on the rolling force of a cold rolling unit for rolling the ultra-high strength steel. In the present disclosure, the 1500MPa-grade ultra-high strength steel is creatively subjected to thin slab continuous casting and rolling to obtain a hot-rolled coil with a finished thickness directly, and then the hot coil is subjected to treatment in an insulation cover, so that the uniformity of the structure and properties of the hot coil is improved greatly, and the internal stress of the material is also eliminated to avoid abnormal brittle fracture in subsequent steps. After the treatment in the insulation cover, pickling is carried out, and then the final continuous annealing treatment is carried out directly, omitting the step of cold rolling which is a bottleneck in the conventional process. At the same time, due to the use of the thin slab continuous casting technology, inherent advantages in terms of structure uniformity and segregation control are observed. Also, due to the characteristic of hot delivery of the billet obtained by the thin slab continuous casting, a small amount of fine-grained ferrite can be maintained in the structure, so that the elongation of the resulting ultra-high strength steel can be improved significantly under the same strength conditions.

[0051] Specifically, the method for manufacturing the high-plasticity 1500MPa-grade ultra-high strength steel of the present disclosure comprises the following steps:

1) Smelting and casting

[0052] Smelting and casting the above composition into a slab, preferably by thin slab continuous casting, wherein a slab thickness at a continuous casting outlet is controlled to be 55-60 mm, and a continuous casting withdrawl speed is controlled to be 2-5 m/min;

2) Slab heating

[0053] Heating temperature: 1200-1300°C, furnace time: 25-40min;

3) Hot rolling and cooling

[0054] Performing high-pressure descaling first, controlling a rolling-end temperature at 860-930°C, and then performing laminar cooling to 500-600°C with a cooling rate controlled at 20-40°C/s, followed by coiling;

4) Slow cooling treatment

[0055] After the coiling of a hot-rolled coil, laying down the coil and sealing it in-situ with an insulation cover, or transferring it into a sealed insulation cover for slow cooling; and after treatment in the insulation cover for ≥4h, opening the cover and taking out the hot-rolled coil; preferably, after the coiling of the hot-rolled coil, allowing it to stay on a reel for ≥3min, and then sealing it in-situ with an insulation cover, or transferring it into a sealed insulation cover for slow cooling;

5) Pickling

[0056] Controlling a pickling speed at 60-150m/min;

6) Annealing

[0057] Performing continuous annealing at an annealing temperature of 820-900°C; slow cooling to 690-760°C at a cooling rate of 3-10°C/s to obtain a certain proportion of ferrite; then rapid cooling to 150-250°C at a cooling rate of 50-100°C/s to partially transform austenite into martensite; then reheating to 360-460°C, holding for 100-400s, and finally cooling to room temperature.

[0058] Preferably, in step 1), the steel leakage rate during the thin slab continuous casting is controlled to be ≤1%, and the substandard rate due to cracks is controlled to be ≤1.2%.

[0059] Preferably, in the annealing process in step 6), the annealing temperature is 840-870°C, followed by slow cooling to 700-730°C at a cooling rate of 3-10°C/s, rapid cooling to 170-230°C; and then reheating to 400-430°C after the rapid cooling, and holding for 150-300s.

[0060] Preferably, the volume content of hydrogen in the reducing atmosphere in the continuous annealing furnace is controlled to be 10-15%.

[0061] Preferably, in step 3), during the high-pressure descaling, the water pressure of the first descaling pass is controlled to be not less than 260 bar, and the water pressure of the second descaling pass is controlled to be not less than 340 bar.

[0062] Preferably, a U-shape coiling mode is used for the coiling in step 3). That is, the coiling temperature is controlled at 550-650°C within a distance of ≤30 m from the head to the tail of the steel strip.

[0063] In the method for manufacturing the ultra-high strength steel of the present disclosure:

Thin slab continuous casting is preferably utilized for the continuous casting described in the present disclosure. The contents of the alloying elements in the ultra-high strength steel are relatively high, and the continuous casting process is not stable enough. Especially, the solidification latent heat is high, and the slab shell is thin. Therefore, the withdrawl speed in the thin slab continuous casting process needs to be controlled at a low level. When the withdrawl speed exceeds 5m/min, problems such as liquid level fluctuation and steel leakage are prone to occur during the continuous casting process. However, the withdrawl speed cannot be too low to affect the production efficiency. Therefore, it is desirable to control it at 2-5m/min.

[0064] At the same time, due to the use of the thin slab continuous casting, the rough rolling process can be omitted, and the hot rolling deformation rate can be reduced, so that the final product specifications can be satisfied more easily. The thin slab continuous casting enables full use of the heat of the slab by charging the hot slab into the heating furnace directly without waiting for the slab to completely cool to room temperature, thereby reducing the energy consumption required for heating. At the same time, due to the absence of phase transformation caused by cooling and then heating, the high-temperature structure in a hot-rolled state is more uniform, and the ferrite or ferrite + pearlite structure obtained after hot rolling is more uniform, which is beneficial to maintaining a small amount of fine-grained ferrite in the microstructure of the finished product during annealing, thereby improving the uniformity of the structure, and helping to improve plasticity.

[0065] In the step of slab heating, the slab obtained by the thin slab continuous casting is first heated at high temperature in the full austenite zone for a period of time to soften the material and allow the components to diffuse fully and evenly. Moreover, it's desirable to perform the treatment at a temperature as high as possible for a period of time as short as possible to both obtain a uniform composition of the ultra-high strength steel and avoid an excessive thickness of the iron oxide scale. The heating temperature should not exceed 1300°C; otherwise, the problem of overfiring at grain boundaries may occur. At this time, the heating time can be shortened to 25 minutes, which is beneficial to the control of the iron oxide scale. On the other hand, if the heating temperature is lower than 1200°C, it will take a long time to achieve a uniform composition, which is not conducive to the subsequent control of the iron oxide scale.

[0066] For descaling of the slab, after the slab is removed from the heating furnace, it is first subjected to two passes of high-pressure water descaling to remove the fluffy iron oxide scale on the surface of the cast slab as much as possible. After further rolling to the required thickness by finishing rolling, a uniform and fine structure of the recrystallized material is formed. When the rolling-end temperature of the finishing rolling is lower than 860°C, ferrite will precipitate at the end of the rolling, which may render the strength in the hot-rolled state insufficient and affect the subsequent cold rolling annealing performance. With the upper limit control of the slab heating temperature as well as the temperature drop during rolling taken into account, the rolling-end temperature of the finishing rolling generally does not exceed 930°C. The purpose of controlling the cooling rate at 20-40°C/s during the laminar cooling is to avoid formation of excessive bainite or even martensite during the cooling process, so as to ensure that the structure in the hot-rolled coiled state is mainly uniform ferrite + pearlite. The coiling temperature of the hot-rolled steel sheet is one of the most critical process parameters that influence the performances in the hot-rolled state. When the coiling temperature is higher than 600°C, internal oxidation of Si and Mn is likely to occur on the surface of the steel sheet, and a broken surface layer will be generated by pickling, which affects the surface quality of the final product. Nevertheless, since the fine-grained ferrite structure needs to be maintained in the structure in the hot-rolled state, the coiling temperature should not be too low, and must be controlled to be 500°C or higher. The main reason for using the U-shape coiling mode in the coiling process to increase the coiling temperature at the head and tail is that the temperature drop at the head and tail of the ultra-high strength steel is large, so that phase transformation is prone to occur at the head and tail, leading to higher strength than at the middle of the coil. At the same time, increasing the coiling temperature is also conducive to reducing the strength of the strip head, making it easier to coil.

[0067] Controlling the thickness of the oxide scale on the surface of the hot-rolled steel strip to be ≤6 μm and ($FeO+Fe_3O_4$) in the oxide scale on the surface of the hot-rolled steel strip to be ≤30 wt% facilitates the proceeding of subsequent step (5), and has an important influence on the performances of the steel sheet obtained after continuous annealing. The reason is as follows: in the technical solution of the present disclosure, FeO and Fe_3O_4 are more difficult to pickle than Fe_2O_3, so controlling the thickness of the oxide scale on the surface of the hot-rolled steel strip of the present disclosure and ($FeO+Fe_3O_4$)≤30wt% in the oxide scale on the surface of the hot-rolled steel strip can improve the pickling effect, and a pickled sheet surface that can be used directly for continuous annealing can be obtained. Since the pickled sheet can be subjected directly to continuous annealing, the deformation rate of the hot-rolled structure is small, and the structure of the steel sheet is mainly ferrite and pearlite or bainite. Therefore, under the same continuous annealing conditions, the material strength can be reduced, the structure is made more uniform, and excellent ductility is obtained.

[0068] After coiling, the steel coil is allowed to stay on the reel for at least 3 minutes before removing it from the reel. The main purpose for this is to allow the bainitic transformation to complete in the inner layers of the steel coil to prevent the hot coil from flattening after removing it from the reel. The reason is that, for ultra-high-strength steel, the temperature of the inner layers drops faster during coiling, so that the temperature gradually enters the bainite temperature range during the coiling process, and the bainitic transformation occurs, leading to volume expansion. At this time, due to the different temperature drop rates of the inner and outer layers, the expansion caused by the bainitic transformation is also different. Thus, it is necessary to allow the steel coil to stay on the reel for at least 3 minutes to allow the bainitic transformation to complete, so that the volume change of the entire steel coil can be homogenized effectively under the support of the reel, thereby avoiding flattening of the hot coil after it is removed from the reel.

[0069] After hot rolling, the steel coil as a whole may be cooled slowly by the treatment in an insulation cover to improve the uniformity of the performances and structure. At the same time, the slow cooling process is also a process of releasing the thermal stress in the material, which is beneficial to the stability of the material in subsequent processing, so as to avoid extreme situations such as brittle fracture. The treatment time has to be at least 4 hours to completely release the internal stress, but the time should not be too long to affect the rhythm of production.

[0070] In the manufacturing method of the present disclosure, if the pickling speed is too fast, under-pickling will be resulted, and the inner oxide layer of the steel sheet cannot be cleaned thoroughly, leading to color difference. If it is too slow, over-pickling will be resulted, and the surface quality of the pickled sheet and the production efficiency will be affected. Therefore, it is desirable to control the pickling speed in the range of 60-150m/min.

[0071] In the manufacturing method of the present disclosure, the annealing temperature of the continuous annealing is controlled at 820-900°C to form a homogenized structure of austenite or austenite + ferrite. Then, the material is slowly cooled to 690-760°C at a cooling rate of 3-10°C/s to further adjust the ferrite content in the structure and improve the plasticity of the material. Then, the material is cooled to 150-250°C (i.e., between the Ms and Mf temperatures) at a rate of 50-100°C/s, because the critical cooling rate needs to be no less than 50°C/s in order to ensure that only martensitic transformation occurs during the cooling process, while the production cost will increase significantly if the cooling rate exceeds 100°C/s. At this time, austenite is mostly transformed into martensite, ensuring that the steel has high strength. Then, the material is heated to 360-460°C and held for 100-400s to allow carbon to be partitioned in martensite and austenite, forming a certain amount of carbon-rich retained austenite which is stably maintained till room temperature. Due to the TRIP effect, the work hardening ability and formability of the steel can be improved significantly, and an ultra-high strength steel sheet with excellent plasticity is thus obtained. The above partitioning process is set this way for the following reason: when the reheating temperature is lower than 360°C or the reheating time is less than 100s, the stabilization process of the retained austenite in the steel is insufficient, and the content of retained austenite finally obtained at room temperature will be insufficient; when the reheating temperature is higher than 460°C or the reheating time is more than 400s, obvious temper softening occurs in the steel, which will cause a significant decrease in the final material strength.

[0072] Preferably, in the continuous annealing process of step 6) in the present disclosure, the annealing temperature is 840-870°C. The material is cooled slowly to 700-730°C at a cooling rate of 3-10°C/s, then cooled rapidly to 170-230°C, and then heated to 400-430°C after the rapid cooling and held for 150-300s, wherein the volume content of hydrogen in the reducing atmosphere in the continuous annealing furnace is controlled to be 10-15%.

[0073] Due to the high C content and the alloying components of Mn, Si, Cr, and B designed for the ultra-high strength steel of the present disclosure as well as the ferrite grain refinement mechanism, during the continuous annealing process, the nucleation points of the reverse austenitic transformation increase while the size is further reduced. The average grain size of the retained austenite stably maintained till room temperature can be ≤2μm; and the average C content in the retained austenite is ≥1.2wt%. In addition, since the material still contains a certain amount of Si, the martensite formed during the rapid cooling substantially does not decompose during the partitioning process, thereby ensuring the martensite content in the structure and thus ensuring the strength of the steel.

[0074] Compared with the prior art, the present disclosure has the following advantages:

1. The composition design of the ultra-high strength steel of the present disclosure is unique, based on different ideas than those for the composition designs of the existing patents.

[0075] The composition designs of the existing patents are mostly complex, involving more alloying elements (such as Mo, V, Nb, Ni and even rare earth elements, etc.), and mostly showing the characteristics of a high Si and high Mn composition.

[0076] The composition design of the present disclosure is simple and unique, and it makes full use of the influence of the C, Si and Mn elements on the phase transformation of the material. At the same time, the process stability of thin slab continuous casting and rolling is improved. The carbon equivalent of the composition is controlled to avoid the peritectic reaction zone so as to improve the surface quality, and the welding carbon equivalent is controlled to obtain excellent welding performance. In addition, Cr and B are used to match with low Si and low Mn to increase the strength. Finally, an ultra-high strength steel sheet product with excellent strength, plasticity, surface quality and welding performance is achieved.

[0077] 2. The manufacturing method of the present disclosure is also unique, based on different ideas than those for the manufacturing methods of the existing patents.

[0078] A conventional production process including continuous casting + hot rolling + pickling + cold rolling + continuous annealing/bell-type annealing is used in most of the existing patents. The process flow is lengthy, and for ultra-high-strength steel, there are problems with respect to cold-rolled sheet shape and thickness accuracy.

[0079] The present disclosure creatively proposes using an efficient process flow including thin slab continuous casting + precision hot rolling + slow cooling treatment + pickling + continuous annealing. This process flow enables elimination of the step of cold rolling which is a bottleneck for ultra-high strength steel, and at the same time, this process flow has inherent advantages in terms of structure uniformity, segregation control and manufacturing cost. Due to the characteristic of hot delivery of the billet obtained by the thin slab continuous casting, a small amount of fine-grained ferrite can be maintained in the structure, so that the elongation of the resulting ultra-high strength steel can be improved significantly under the same strength conditions. In addition, during the continuous annealing process, the nucleation points of the reverse austenitic transformation increase, and the size is further reduced. Finally, a very fine and uniform mixed structure of martensite, ferrite and retained austenite is obtained. This structure is notably advantageous in plasticity over products of the same grade while ensuring strength.

[0080] The ultra-high strength steel obtained according to the present disclosure has good application prospects in automobile safety and structural parts. It is especially suitable for manufacturing vehicle structural parts and safety parts having complex shapes and high requirements on formability, such as A/B pillars, door anti-collision bars, girders, bumpers, etc.

Description of the Drawings

[0081]

FIG. 1 is a photograph showing the microstructure of the ultra-high strength steel in Example 4 according to the present disclosure.

FIG. 2 is an electron backscatter diffraction (EBSD) photograph of the phase composition of the ultra-high strength steel in Example 4 according to the present disclosure.

Detailed Description

[0082] The present disclosure will be further illustrated below with reference to the Examples and drawings.

[0083] Table 1 lists the compositions of the steels in the Examples according to the present disclosure and the Comparative Examples, with the balance comprising Fe and other unavoidable impurities except P, S, O and N.

[0084] The method for manufacturing the steels in the Examples according to the present disclosure comprises the following steps:

1) Smelting and casting

[0085] The composition was smelted, and cast into a slab by thin slab continuous casting. The slab thickness at the continuous casting outlet was controlled to be 55-60 mm, and the continuous casting withdrawl speed was controlled to be 2-5 m/min;

2) Slab heating

[0086] The heating temperature was 1200-1300°C, and the furnace time was 25-40min;

3) Hot rolling and cooling

[0087] First, high-pressure descaling was performed. The rolling-end temperature was controlled at 860-930°C. Then, laminar cooling was performed. The cooling rate was controlled at 20-40°C/s. After cooling to 500-600°C, coiling was performed using a U-shape coiling mode;

4) Slow cooling treatment

[0088] After the coiling of the hot-rolled coil was finished, it was allowed to stand on the reel for ≥3 minutes. Then, it was removed from the reel and transferred into a sealed insulation cover for slow cooling treatment. After the treatment in the insulation cover for ≥4 hours, the cover was opened to take out the hot-rolled coil;

5) Pickling

[0089] The pickling speed was controlled at 60-150m/min;

6) Annealing

[0090] Continuous annealing was performed at an annealing temperature of 820-900°C. The coil was slowly cooled to 690-760°C at a cooling rate of 3-10°C/s to obtain a certain proportion of ferrite; then rapidly cooled to 150-250°C at a cooling rate of 50-100°C/s to partially transform austenite into martensite; then heated to 360-460°C, held for 100-400s, and finally cooled to room temperature.

[0091] Table 2 and Table 3 show the manufacturing process parameters for the steels in the Examples according to the present disclosure and the Comparative Examples.

[0092] The steels in Comparative Examples 1-3 were manufactured using the same steps of the manufacturing method according to the present disclosure, except that the components and/or manufacturing process parameters didn't meet the design requirements of the present disclosure.

[0093] The C content in Comparative Example 1 was lower than the lower limit of the range designed according to the present disclosure, and its peritectic reaction carbon equivalent fell in the peritectic reaction zone; the Si and Mn contents in Comparative Example 2 were both higher than the upper limit of the range designed according to the present disclosure, and neither its peritectic reaction carbon equivalent nor its welding carbon equivalent met the design requirements of the present disclosure; although the peritectic reaction carbon equivalent and welding carbon equivalent in Comparative Example 3 both met the requirements, the Si and Cr contents were both lower than the lower limit of the range designed according to the present disclosure, leading to insufficient material performances.

[0094] The Comparative Examples in Table 2 were different from the Examples mainly in continuous casting withdrawl speed, slab heating temperature and time, rolling-end temperature and coiling temperature, as well as treatment time in the insulation cover.

[0095] The Comparative Examples in Table 3 were different from the Examples mainly in pickling rate, annealing process, rapid cooling rate, partitioning temperature and time.

[0096] Table 4 lists the mechanical performance test results of the ultra-high strength steels with excellent plasticity in Examples 1-20 and the comparative steels in Comparative Examples 1-3, as well as the steel leakage rate during the thin slab continuous casting process and substandard rate due to cracks under the conditions of the corresponding Examples and Comparative Examples, wherein the mechanical performances were tested according to IS06892:1998 (Metallic materials - Tensile testing at ambient temperature) using P14 (A50) standard tensile test pieces.

[0097] As it can be seen from Table 4, the ultra-high strength steels with excellent plasticity in Examples 1-20 according to the present disclosure achieved excellent control of ductility, stability of the continuous casting process, and surface quality of the cast billet while ensuring strength, exhibiting a yield strength YS of 1000-1300MPa, a tensile strength TS of ≥1500MPa, and an elongation at break of ≥18%. At the same time, the steel leakage rate during the thin slab continuous casting process was controlled to be ≤1%, and the substandard rate due to cracks was controlled to be ≤1.2%. As used herein, the steel leakage rate during continuous casting and the substandard rate due to cracks are the ratios of the number of slabs suffering from steel leakage and the number of cracked slabs to the total number of slabs in the batch, respectively.

[0098] Table 5 shows the observation results of the microstructures of the ultra-high strength steels with excellent plasticity in Examples 1-20 according to the present disclosure. The specific test methods are as follows:

1) The fraction of the retained austenite phase was quantitatively determined by XRD after taking a 10*10 mm sample from a steel sheet, grinding and polishing it;
2) The fraction of the martensite phase was quantitatively determined by EBSD after taking a 10*10 mm sample from a steel sheet, grinding and polishing it;
3) The ferrite grain size, fraction and the average size of retained austenite were obtained by statistical analysis performed when the standardized IQ values were processed during the EBSD quantitative analysis;
4) Test method for the C content in retained austenite: Assuming that the Mn and Al concentrations in each phase in the steel sheet structure had not changed, the lattice constant a_γ was read using the diffraction peak data of retained austenite in XRD, and the following empirical formula was used for calculation: $a_\gamma=0.3556+0.00452x_C+0.000095x_{Mn}+0.00056x_{Al}$, wherein X_C, X_{Mn}, and X_{Al} represented the C, Mn, and Al concentrations in retained austenite, respectively.

[0099] As it can be seen from Table 4 and Table 5, the microstructure of the 1500 MPa-grade ultra-high strength steel with excellent plasticity in each of Examples 1-20 according to the present disclosure was 10%-15% by volume of ferrite + 70%-80% by volume of martensite + retained austenite, wherein the number of grains with a grain size ≤5 μm in the ferrite accounted for 90% or more, the number of grains with a grain size ≤3 μm accounted for 60% or more, the average grain size of the retained austenite was ≤2 μm, and the average C content in the retained austenite was: 1.2wt%≤C(ra)≤2.0wt%.

[0100] This shows that the 1500MPa-grade ultra-high strength steel with excellent plasticity in each Example according to the present disclosure had a certain amount of fine-grained ferrite and sufficient retained austenite, as well as good structure uniformity. Therefore, the steel in each Example had excellent plasticity while ensuring high strength.

[0101] FIG. 1 and FIG. 2 are, respectively, the photograph of the typical microstructure and the EBSD photograph of the phase composition of the ultra-high strength steel in Example 4 according to the present disclosure. As it can be seen from these figures, the structure of the ultra-high strength steel according to the present disclosure is uniform and fine, and contains a large amount of fine dispersed retained austenite.

[0102] In summary, the composition design of the ultra-high strength steel according to the present disclosure is simple. Carbon-silicon-manganese steel is used as a basis, and only Cr and B are added as alloy strengthening elements. In addition, due to the compositional characteristic of low Si and low Mn, the peritectic reaction can be avoided in the continuous casting process, thereby greatly improving the stability of the continuous casting process, and the product obtained has excellent surface quality.

[0103] At the same time, the present disclosure creatively proposes using an efficient process flow including thin slab continuous casting + precision hot rolling + slow cooling treatment + pickling + continuous annealing. This process flow enables elimination of the step of cold rolling which is a bottleneck for ultra-high strength steel, and has inherent advantages in terms of structure uniformity, segregation control and manufacturing cost. The ultra-high strength steel obtained has a significantly higher elongation under the same strength conditions, and has good application prospects in automobile safety and structural parts. It is especially suitable for manufacturing vehicle structural parts and safety parts having complex shapes and high requirements on formability, such as A/B pillars, door anti-collision bars, girders, bumpers, etc. The short process technology of thin slab continuous casting and rolling can be used to directly provide a hot-rolled coil with the required finished product thickness (0.8-2.0mm), and the cold rolling process can be omitted accordingly, which greatly promotes energy saving, consumption reduction and production efficiency.

[0104] It should be noted that the prior art in the protection scope of the present disclosure is not limited to the Examples set forth in the present application file. All prior art that does not contradict the technical solution of the present disclosure, including but not limited to prior patent documents, prior publications, prior public uses, etc., can be included in the protection scope of the present disclosure.

[0105] In addition, combinations of the various technical features in the present disclosure are not limited to the combinations described in the claims in the present disclosure or the combinations described in the specific Examples. All technical features recorded in the present disclosure can be combined freely or associated in any way unless a contradiction occurs.

[0106] It should also be noted that the Examples listed above are only specific embodiments of the present disclosure. Obviously, the present disclosure is not limited to the above Examples, and changes or modifications made thereto can be directly derived from the present disclosure or easily conceived of by those skilled in the art, all of which fall within the protection scope of the present disclosure.

Table 1 unit: weight percent)

No.	Steel type	C	Si	Mn	Cr	Al	Ti	B	P	S	0	N	C_{eq1}	Ceq2
Exs. 1-4	A	0.35	1.8	2.0	0.50	0.03	0.04	0.020	0.014	0.0018	0.0019	0.0038	0.181	0.541
Exs. 5-8	B	0.37	1.7	1.8	0.60	0.05	0.05	0.010	0.013	0.0015	0.0017	0.0040	0.213	0.549
Exs. 9-12	C	0.38	1.6	1.7	0.55	0.04	0.05	0.0050	0.015	0.0020	0.0018	0.0034	0.231	0.556
Exs. 13-16	D	0.39	1.3	1.6	0.30	0.02	0.02	0.0030	0.012	0.0013	0.0015	0.0025	0.263	0.543
Exs. 17-20	E	0.40	1.0	1.5	0.40	0.04	0.03	0.0020	0.010	0.0009	0.0013	0.0030	0.294	0.532
Comp. Exs. 1	a	<u>0.33</u>	1.8	2.0	0.50	0.04	0.05	0.02	0.013	0.0017	0.0018	0.0035	<u>0.161</u>	0.523
Comp. Exs. 2	b	0.36	<u>1.9</u>	<u>2.8</u>	-	0.05	0.05	-	0.014	0.0020	0.0019	0.0037	<u>0.161</u>	<u>0.599</u>
Comp. Exs. 3	C	0.38	<u>0.9</u>	1.8	<u>0.20</u>	0.03	0.04	0.0020	0.013	0.0020	0.0017	0.0038	0.271	0.534
Note: C_{eq1}=C-0.03Mn-0.06Si-0.222S-0.04P, C_{eq2}=C+Mn/20+Si/30+2P+4S.														

Table 2

	Steel type	Product thickness (mm)	Slab thickness (mm)	Continuous casting withdrawl speed (m/min)	Slab heating temperature (°C)	Furnace time (min)	Oxide scale thickness (μm)	$(FeO+Fe_3O_4)$ content (wt%)	Rolling-end temperature (°C)	Average coiling temperature (°C)	Laminar cooling rate (°C/s)	Insulation cover treatment time (h)
Ex. 1	A	0.8	55	2.0	1200	40	3.1	22.7	903	576	20	4
Ex. 2	A	0.9	55	2.2	1235	38	3.5	23.3	910	590	22	4
Ex. 3	A	1.0	55	2.4	1260	35	4.5	25.5	908	500	24	4
Ex. 4	A	1.1	55	2.6	1280	30	5.8	28.6	925	570	26	4
Ex. 5	B	1.2	58	3.0	1230	39	4.8	22.7	930	530	30	5
Ex. 6	B	1.3	58	3.2	1290	25	5.7	28.6	922	567	32	5
Ex. 7	B	1.4	58	3.4	1210	37	3.8	21.7	917	550	34	5
Ex. 8	B	1.5	58	3.6	1250	27	4.3	23.3	920	562	36	5
Ex. 9	C	1.6	56	4.0	1220	34	3.2	23.6	860	555	40	6
Ex. 10	C	1.7	56	4.2	1245	32	3.3	25.2	920	500	25	6
Ex. 11	C	1.8	56	4.4	1215	31	3.5	21.3	924	525	28	6
Ex. 12	C	1.9	56	4.6	1295	26	5.8	29.9	919	560	34	6
Ex. 13	D	2.0	60	5.0	1265	33	4.2	24.4	875	580	29	7
Ex. 14	D	1.8	60	4.3	1225	36	3.6	25.8	886	525	30	7
Ex. 15	D	1.6	60	4.5	1205	40	3.1	22.9	885	595	31	7
Ex. 16	D	1.4	60	4.7	1300	28	5.9	30.0	913	600	33	7
Ex. 17	E	1.3	57	2.5	1248	29	4.6	23.7	930	530	35	5
Ex. 18	E	1.2	57	2.7	1285	25	5.8	28.6	922	597	21	5
Ex. 19	E	1.1	57	3.5	1226	40	3.8	23.7	880	570	23	5
Ex. 20	E	1.0	57	4.9	1270	30	4.1	26.3	920	562	27	5
Comp. Ex. 1	a	1.6	60	<u>6.0</u>	<u>1190</u>	40	5.2	23.4	<u>850</u>	550	20	4
Comp. Ex. 2	b	1.6	60	4.0	<u>1350</u>	40	<u>7.5</u>	<u>35.2</u>	880	580	<u>50</u>	5

(continued)

	Steel type	Product thickness (mm)	Slab thickness (mm)	Continuous casting withdrawl speed (m/min)	Slab heating temperature (°C)	Furnace time (min)	Oxide scale thickness (μm)	$(FeO+Fe_3O_4)$ content (wt%)	Rolling-end temperature (°C)	Average coiling temperature (°C)	Laminar cooling rate (°C/s)	Insulation cover treatment time (h)
Comp. Ex. 3	c	1.0	55	3.0	1240	<u>45</u>	<u>6.2</u>	28.9	900	<u>650</u>	30	3

Table 3

	Pickling speed (m/min)	Annealing temperature (°C)	Slow cooling rate (°C/s)	Rapid cooling start temperature (°C)	Rapid cooling end temperature (°C)	Rapid cooling rate (°C/s)	Reheating temperature (°C)	Reheating holding time (s)
Ex. 1	60	850	9	700	190	90	410	200
Ex. 2	65	845	7	715	180	70	420	160
Ex. 3	70	830	4	690	150	91	360	320
Ex. 4	75	860	8	700	230	51	405	220
Ex. 5	80	870	4	710	170	80	415	150
Ex. 6	85	840	9	730	200	94	460	110
Ex. 7	90	845	5	705	210	95	412	280
Ex. 8	95	825	4	696	220	78	425	220
Ex. 9	100	900	8	760	250	85	430	200
Ex. 10	105	890	9	730	160	62	422	240
Ex. 11	110	855	6	706	175	66	414	280
Ex. 12	115	843	8	725	185	86	435	150
Ex. 13	120	832	6	735	215	55	390	250
Ex. 14	125	820	5	713	199	76	399	220
Ex. 15	130	847	10	698	174	100	435	140
Ex. 16	135	880	10	720	225	70	419	200
Ex. 17	140	877	4	702	195	80	440	350
Ex. 18	145	842	9	740	170	90	450	110
Ex. 19	150	858	5	750	230	95	432	400
Ex. 20	112	860	4	695	220	65	400	240
Comp. Ex. 1	70	840	8	700	440	50	440	300
Comp. Ex. 2	160	920	4	730	200	20	390	90
Comp. Ex. 3	80	870	6	740	250	60	480	450

Table 4

No.	Yield strength YS (MPa)	Tensile strength TS (MPa)	Elongation at break TEL (%)	Steel leakage rate during continuous casting (%)	Substandard rate due to cracks (%)
Ex. 1	1086	1511	18.88	0	0
Ex. 2	1192	1501	20.21	0	0
Ex. 3	1212	1589	18.12	0	0
Ex. 4	1190	1532	19.79	0.5	0.8
Ex. 5	1092	1542	18.24	0	0
Ex. 6	1165	1512	19.21	0	0
Ex. 7	1158	1593	18.12	0	0
Ex. 8	1221	1597	18.91	0	0

(continued)

No.	Yield strength YS (MPa)	Tensile strength TS (MPa)	Elongation at break TEL (%)	Steel leakage rate during continuous casting (%)	Substandard rate due to cracks (%)
Ex. 9	1300	1530	18.01	0.6	1.0
Ex. 10	1290	1576	18.22	0	0
Ex. 11	1216	1521	18.22	0	0
Ex. 12	1192	1503	21.96	0	0
Ex. 13	1095	1505	20.21	0	0
Ex. 14	1102	1508	23.21	0	0
Ex. 15	1006	1510	18.01	0	0
Ex. 16	1143	1566	18.23	0	0
Ex. 17	1242	1558	18.64	0.5	0
Ex. 18	1187	1503	19.41	0	0
Ex. 19	1201	1543	19.89	0	0
Ex. 20	1123	1502	20.76	0	0
Comp. Ex. 1	970	1410	11.33	50	30
Comp. Ex. 2	1210	1605	9.51	60	40
Comp. Ex. 3	920	1370	13.32	1.0	1.0

Table 5

	Ferrite (vol.%)	Martensite (vol.%)	Retained austenite (vol.%)	Fraction of ≤5μm ferrite grains (%)	Fraction of ≤3μm ferrite grains (%)	Average size of retained austenite (μm)	C content in retained austenite (wt%)
Ex. 1	10.25	77.56	12.19	91.77	72.35	0.6	1.27
Ex. 2	10.98	77.55	11.47	95.64	64.53	0.7	1.23
Ex. 3	12.76	76.12	11.12	90.97	74.24	0.8	1.55
Ex. 4	11.32	76.34	12.34	95.98	69.62	1.1	1.25
Ex. 5	12.08	75.15	12.77	96.06	64.35	1.0	1.37
Ex. 6	10.81	75.78	13.41	92.19	77.60	1.3	1.74
Ex. 7	11.78	76.33	11.89	93.24	62.88	0.9	1.38
Ex. 8	12.70	74.45	12.85	94.26	64.45	1.4	1.21
Ex. 9	10.54	79.34	10.12	97.24	73.50	0.7	1.31
Ex. 10	11.55	76.67	11.78	98.66	72.49	1.2	1.24
Ex. 11	13.70	74.34	11.96	93.84	73.96	0.9	1.63
Ex. 12	11.11	76.12	12.77	90.29	76.51	0.6	1.27
Ex. 13	12.89	76.23	10.88	97.12	79.01	1.6	1.36
Ex. 14	13.34	74.96	11.70	93.22	75.06	1.1	1.34
Ex. 15	11.67	76.45	11.88	93.67	74.51	1.4	1.25
Ex. 16	12.07	76.56	11.37	95.74	70.73	1.2	1.32
Ex. 17	15.00	70.23	14.77	95.06	64.35	1.0	1.34
Ex. 18	12.81	75.78	11.41	93.19	75.60	1.2	1.26

(continued)

	Ferrite (vol.%)	Martensite (vol.%)	Retained austenite (vol.%)	Fraction of ≤5μm ferrite grains (%)	Fraction of ≤3μm ferrite grains (%)	Average size of retained austenite (μm)	C content in retained austenite (wt%)
Ex. 19	11.78	76.33	11.89	93.54	65.88	0.9	1.21
Ex. 20	10.70	76.45	12.85	95.44	64.65	1.9	1.43

Claims

1. A high-plasticity ultra-high strength steel having a tensile strength of ≥1500MPa, comprising the following components in weight percentage:

   C: 0.35-0.40%;
   Si: 1.0-1.8%;
   Mn: 1.5-2.0%;
   Cr: 0.3-0.6%;
   Al: 0.02-0.05%;
   Ti: 0.02-0.05%;
   B: 0.002-0.02%;
   a balance comprising Fe and other unavoidable impurities, wherein the following is satisfied:

   carbon equivalent in peritectic reaction zone C_{eq1}>0.17%, C_{eq1}=C-0.03Mn-0.06Si-0.222S-0.04P; and welding carbon equivalent C_{eq2}≤0.56%, C_{eq2}=C+Mn/20+Si/30+2P+4S.

2. The high-plasticity ultra-high strength steel having a tensile strength of ≥1500MPa according to claim 1, wherein the balance is Fe and other unavoidable impurities.

3. The high-plasticity ultra-high strength steel having a tensile strength of ≥1500MPa according to claim 1 or 2, wherein the content of C is 0.36-0.38 wt%.

4. The high-plasticity ultra-high strength steel having a tensile strength of ≥1500MPa according to claim 1 or 2, wherein the content of Si is 1.4-1.7 wt%.

5. The high-plasticity ultra-high strength steel having a tensile strength of ≥1500MPa according to claim 1 or 2, wherein the content of Mn is 1.7-2.0 wt%.

6. The high-plasticity ultra-high strength steel having a tensile strength of ≥1500MPa according to claim 1 or 2, wherein the content of Cr is 0.4-0.6 wt%.

7. The high-plasticity ultra-high strength steel having a tensile strength of ≥1500MPa according to claim 1 or 2, wherein among the other unavoidable impurities: P is ≤0.015wt%, S is ≤0.002wt%, O is ≤0.002wt%, N is ≤0.004wt%.

8. The high-plasticity ultra-high strength steel having a tensile strength of ≥1500MPa according to any one of claims 1-7, wherein the ultra-high strength steel has a microstructure of 10%-15% by volume of ferrite + 70%-80% by volume of martensite + retained austenite.

9. The high-plasticity ultra-high strength steel having a tensile strength of ≥1500MPa according to claim 8, wherein in the ferrite in the microstructure of the ultra-high strength steel, the number of grains with a grain size of ≤5 μm accounts for 90% or more, and the number of grains with a grain size of ≤3 μm accounts for 60% or more.

10. The high-plasticity ultra-high strength steel having a tensile strength of ≥1500MPa according to claim 8, wherein an average grain size of the retained austenite in the microstructure of the ultra-high strength steel is ≤2 μm; and/or an average C content C(ra) in the retained austenite satisfies: 1.2wt%≤C(ra)≤2.0wt%.

11. The high-plasticity ultra-high strength steel having a tensile strength of ≥1500MPa according to any one of claims 1-10, wherein the ultra-high strength steel has a yield strength of 1000-1300 MPa, a tensile strength of ≥1500 MPa, and an elongation at break of ≥18%.

12. A method for manufacturing the high-plasticity ultra-high strength steel having a tensile strength of ≥1500MPa according to any one of claims 1-11, comprising the following steps:

1) Smelting and casting
Smelting and casting the components according to claims 1-7 into a slab, preferably by thin slab continuous casting, wherein a slab thickness at a continuous casting outlet is controlled to be 55-60 mm, and a continuous casting withdrawl speed is controlled to be 2-5 m/min;
2) Slab heating
Heating temperature: 1200-1300°C, furnace time: 25-40min;
3) Hot rolling and cooling
Performing high-pressure descaling first, controlling a rolling-end temperature at 860-930°C, and then performing laminar cooling to 500-600°C with a cooling rate controlled at 20-40°C/s, followed by coiling;
4) Slow cooling treatment
After coiling of a hot-rolled coil, laying down the coil and sealing it in-situ with an insulation cover, or transferring it into a sealed insulation cover for slow cooling; and after treatment in the insulation cover for ≥4h, opening the cover and taking out the hot-rolled coil; preferably, after the coiling of the hot-rolled coil, allowing it to stay on a reel for ≥3min, and then sealing it in-situ with an insulation cover, or transferring it into a sealed insulation cover for slow cooling;
5) Pickling
Controlling a pickling speed at 60-150m/min;
6) Annealing
Performing continuous annealing at an annealing temperature of 820-900°C; slow cooling to 690-760°C at a cooling rate of 3-10°C/s; then rapid cooling to 150-250°C at a cooling rate of 50-100°C/s; then reheating to 360-460°C, holding for 100-400s, and finally cooling to room temperature.

13. The method for manufacturing the high-plasticity ultra-high strength steel having a tensile strength of ≥1500MPa according to claim 12, wherein in step 1), a steel leakage rate during the thin slab continuous casting is controlled to be ≤1%, and a substandard rate due to cracks is controlled to be ≤1.2%.

14. The method for manufacturing the high-plasticity ultra-high strength steel having a tensile strength of ≥1500MPa according to claim 12, wherein in step 3), during the high-pressure descaling, water pressure of a first descaling pass is controlled to be not less than 260 bar, and water pressure of a second descaling pass is controlled to be not less than 340 bar; and/or a U-shape coiling mode is used for the coiling in step 3), wherein a coiling temperature is controlled at 550-650°C within a distance of ≤30 m from a head to a tail of a steel strip.

15. The method for manufacturing the high-plasticity ultra-high strength steel having a tensile strength of ≥1500MPa according to claim 12, wherein in the annealing process in step 6), the annealing temperature is 840-870°C, followed by slow cooling to 700-730°C at a cooling rate of 3-10°C/s; rapid cooling to 170-230°C; and then reheating to 400-430°C after the rapid cooling, and holding for 150-300s; and/or a volume content of hydrogen in a reducing atmosphere in a continuous annealing furnace is controlled to be 10-15%.

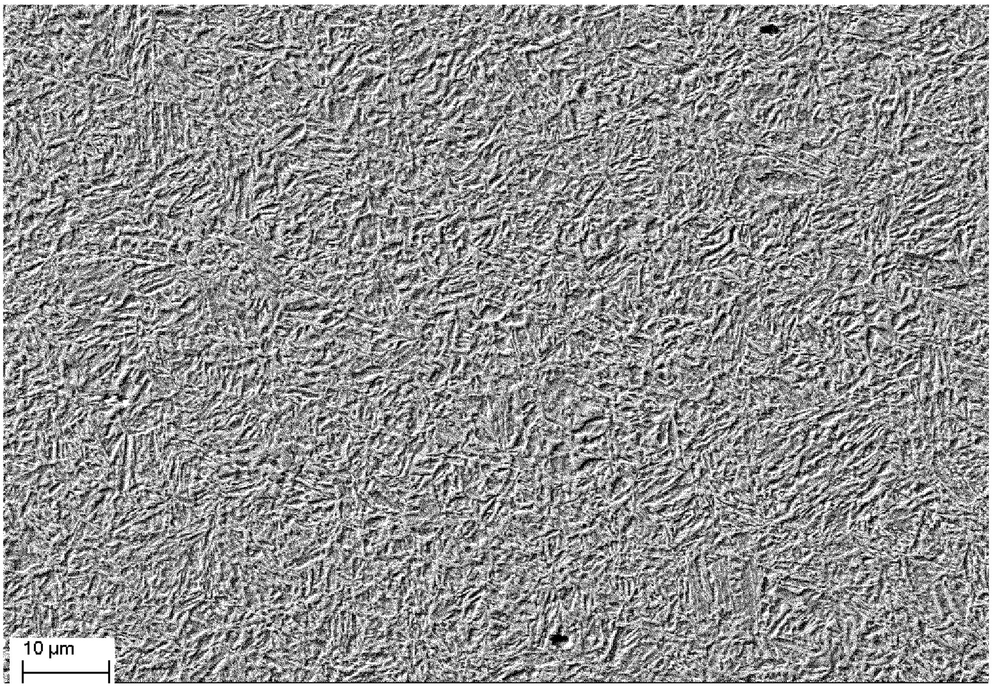

FIG. 1

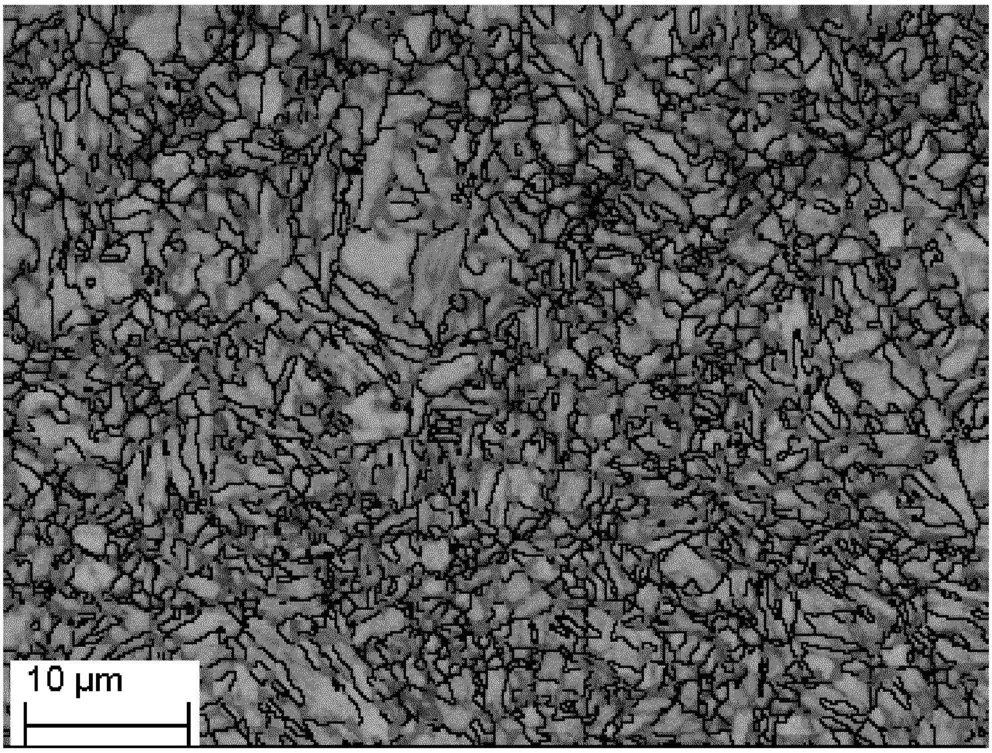

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2023/102330

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/02(2006.01)i; C22C38/34(2006.01)i; C22C38/06(2006.01)i; C22C38/28(2006.01)i; C22C38/32(2006.01)i; C22C33/04(2006.01)i; C21D8/02(2006.01)i; C21D1/26(2006.01)i; C21D1/74(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: 宝钢, 宝山钢铁, 陈濛潇, 钟勇, 王利, 高强, 抗拉强度, 1500MPa, 1.5GPa, 高塑性, 延伸率, 碳当量, 包晶, 焊接, 马氏体, 薄板坯, 铬, 硅, 铝, 锰, 硼, 钛, Cr, Si, Al, Mn, B, Ti, Carbon, Silicon, manganese, high strength, tension set, extensibility, high plastic+, high ductil+, carbon equivalent, peritectic, martensite

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CN 101270449 A (CENTRAL IRON & STEEL RESEARCH INSTITUTE) 24 September 2008 (2008-09-24) description, page 2, paragraph 2 to page 5, paragraph 3, and tables 1-2	1-15
Y	CN 108018484 A (BAOSHAN IRON & STEEL CO., LTD.) 11 May 2018 (2018-05-11) description, paragraphs 6-52	1-15
Y	CN 106086684 A (WUHAN IRON AND STEEL CO., LTD.) 09 November 2016 (2016-11-09) description, paragraphs 6-23	12-15
A	CN 113388779 A (ANGANG STEEL COMPANY LIMITED) 14 September 2021 (2021-09-14) entire document	1-15
A	JP H0525583 A (NIPPON KOKAN K. K.) 02 February 1993 (1993-02-02) entire document	1-15

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

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

Date of the actual completion of the international search	Date of mailing of the international search report
22 August 2023	**12 September 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.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2023/102330

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
CN	101270449	A	24 September 2008	None			
CN	108018484	A	11 May 2018	WO	2018076965	A1	03 May 2018
				EP	3533894	A1	04 September 2019
				US	2019256945	A1	22 August 2019
				US	11279986	B2	22 March 2022
				KR	20190071755	A	24 June 2019
				JP	2019534941	A	05 December 2019
				JP	6770640	B2	14 October 2020
				CN	108018484	B	31 January 2020
CN	106086684	A	09 November 2016	US	2019185953	A1	20 June 2019
				US	11124851	B2	21 September 2021
				WO	2018036346	A1	01 March 2018
				KR	20190021451	A	05 March 2019
				CN	106086684	B	12 January 2018
CN	113388779	A	14 September 2021	CN	113388779	B	22 July 2022
JP	H0525583	A	02 February 1993	None			

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

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- CN 103667884 B **[0004]**
- CN 106244918 B **[0005]**
- CN 106917055 B **[0006]**
- CN 108018484 A **[0007]**
- CN 111455282 B **[0009]**
- CN 114012056 A **[0010]**