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(54) **ULTRAHIGH-STRENGTH DUAL-PHASE STEEL AND MANUFACTURING METHOD THEREFOR**

(57) Disclosed in the present disclosure is an ultrahigh-strength dual-phase steel. The matrix structure of the ultrahigh-strength dual-phase steel is ferrite and martensite, wherein the ferrite and the martensite are evenly distributed in an island shape. The ultrahigh-strength dual-phase steel contains the following chemical elements in percentage by mass: 0.12-0.2% of C, 0.5-1.0% of Si, 2.5-3.0% of Mn, 0.02-0.05% of Al, 0.02-0.05% of Nb, 0.02-0.05% of Ti, and 0.001-0.003% of B. Further disclosed in the present disclosure is a manufacturing method for the ultrahigh-strength dual-phase steel, comprising the steps of smelting and continuous casting, hot rolling, cold rolling, annealing, tempering, and leveling. The ultrahigh-strength dual-phase steel in the present disclosure has not only good mechanical properties but also excellent delayed cracking resistance and low initial hydrogen content, and can be suitable for manufacturing of vehicle safety structural parts.



Figure 1

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Description

Technical Field

5 **[0001]** The present disclosure relates to a metallic material and a method of manufacturing the same, particularly to a dual-phase steel and a method of manufacturing the same.

Background Art

10 **[0002]** As weight reduction and safety are required in the automotive industry, the market has an increasing demand for higher-strength steel plates. Because dual-phase steel has excellent properties such as low yield strength, high tensile strength and high initial work hardening rate in addition to its low production cost and high manufacturability, it is widely used in the production of automotive parts.

15 **[0003]** At present, strength levels of 80 kg and 100 kg are mainly demanded in the market. The current highest strength level is 1180DP grade characterized by a tensile strength of greater than or equal to 1200 MPa, a yield strength of about 850 MPa, and a total elongation of about 10%. A critical continuous annealing process is used for the production of cold-rolled dual-phase steel whose tensile strength depends on the fraction of martensite in the annealed structure. The higher the martensite fraction, the higher the tensile strength. Thus, a higher annealing temperature is needed in the production to form a higher martensite fraction. The highest strength level of dual-phase steel that can be produced commercially is 1180 MPa, namely DP 1180 steel.

20 **[0004]** Chinese Patent Publication No. CN109504930A published on March 22, 2019 and entitled "Hot-dip Galvanized Steel Plate with Tensile Strength Greater Than 1300Mpa And Production Method Thereof" discloses a hot-dip galvanized steel plate having a tensile strength of greater than 1300 MPa and its production method. The chemical ingredients of the hot-dip galvanized steel plate substrate and their mass percentage contents are: C: 0.1-0.2%, Mn: 1.3-2.0%, S $\leq$ 0.005%, P $\leq$ 0.02%, Si: 0.2-0.3%, Al: 0.4-1.0%, Nb: 0.01-0.03%, Ti: 0.04-0.08%, B: 0.001-0.004%, Mo: 0.2-0.3%, Cr: 0.05-0.10%, V: 0.01-0.02%, and a balance of Fe and unavoidable impurities. In the slab heating step, the heating temperature is 1200-1320 °C, and the heating time is 120-200 min. In the hot-rolling step, rough rolling is performed for 3-7 passes; the temperature at the finishing mill entry is 1020-1080 °C; and the finishing rolling temperature is 820-880 °C. The coiling temperature is 550-650 °C. The production method includes steps of slab heating, hot rolling, pickling-rolling, continuous hot-dip galvanization, skin pass and passivation. In the step of continuous hot-dip galvanization, the soaking temperature is 760-840 °C; the holding time is 100-200 s; the slow cooling temperature is 680-740 °C; the slow cooling rate is 10-20 °C/s; the rapid cooling temperature is 420-450 °C; the rapid cooling rate is 35-65 °C/s; the galvanizing temperature is 458-462 °C; and the galvanizing time is 5-15 s.

30 **[0005]** Chinese Patent Publication No. CN108486494A published on September 4, 2018 and entitled "Method for Producing Vanadium Microalloying 1300 Mpa Grade High-strength Hot-Rolled Steel Plate and Cold-Rolled Dual-Phase Steel Plate" discloses a method for producing vanadium microalloying 1300 MPa grade high-strength hot-rolled steel plate and cold-rolled dual-phase steel plate. The chemical composition is: 0.10-0.30 wt% C, 1.50-4.50 wt% Mn, 0.00-0.120 wt% Al, 0.00-0.90 wt% Si, 0.05-0.50% V, P $\leq$ 0.020 wt%, S $\leq$ 0.02wt%, Fe: the balance. The high-strength steel combines the precipitation strengthening of nano-sized vanadium carbide particles with the martensitic transformation strengthening. The strength of the existing dual-phase steel is increased significantly, and the high production efficiency is also guaranteed.

35 **[0006]** Chinese Patent Publication No. CN109628846A published on April 16, 2019 and entitled "1300 MPa Grade Ultra-high-strength Cold-rolled Steel Plate for Automobiles and Its Production Method" discloses a hot-formed steel plate and a method for manufacturing the same. The chemical composition is: C: 0.1-0.2%, Mn: 1.3-2.0%, S $\leq$ 0.005%, P $\leq$ 0.02%, Si: 0.2-0.3%, Al: 0.4-1.0%, Nb: 0.01-0.03%, Ti: 0.04-0.08%, B: 0.001-0.004%, Mo: 0.2-0.3%, Cr: 0.05-0.10%, V: 0.01-0.02%, Fe: the balance. The production method includes steps of steelmaking, continuous casting, hot rolling, pickling-rolling, continuous annealing, temper rolling and tension leveling. In the hot rolling step, the temperature for heating the slab is $\geq$ 1200 °C; rough rolling is performed for 3-7 passes; the thickness of the intermediate slab after the rough rolling is 28-40 mm; the temperature at the finishing mill entry is 1020-1100 °C; the finishing rolling temperature is 820-900 °C; and the coiling temperature is 550-650 °C. In the pickling-rolling step, cold rolling is performed after pickling, wherein the cold rolling reduction is $\geq$ 45%. In the continuous annealing step, the holding temperature in the soaking stage is 760-840 °C, while the holding time is 60-225 s; and the holding temperature in the over-aging stage is 250-320 °C, while the holding time in the over-aging stage is 300-1225 s.

40 **[0007]** As it can be seen, the products whose tensile strength grade is greater than or equal to 1300 MPa as disclosed by the existing patent documents are generally galvanized, and contain high Si and high Al according to some patents, which is not conducive to surface quality and production. In some patent technologies, the products contain relatively high amounts of precious alloy elements such as Cr and Mo, and thus the production cost is high.

Summary

[0008] One of the objects of the present disclosure is to provide an ultra-high-strength dual-phase steel. By a reasonable design of the chemical elements in the ultra-high-strength dual-phase steel, i.e. a design of medium Si and low Al to reduce the use of alloy elements such as Si and Al, the problems with the surface quality caused by high Si and the slab defects caused by high Al are avoided.

[0009] In addition, precious alloy elements such as Cr and Mo are not used in the ultra-high-strength dual-phase steel according to the present disclosure, and thus the alloy cost is controlled effectively. At the same time, the contents of impurity elements P and S are reduced, which is beneficial to promotion of performances and improvement of delayed cracking. The ultra-high-strength dual-phase steel has a yield strength of ≥ 900 MPa, preferably ≥ 930 MPa, a tensile strength of ≥ 1300 MPa, preferably ≥ 1320 MPa, an elongation after fracture of $\geq 5\%$, preferably $\geq 5.5\%$, an initial hydrogen content of ≤ 10 ppm, preferably ≤ 7 ppm; and it does not experience delayed cracking when it is soaked in 1 mol/L hydrochloric acid for 300 hours under a pre-stress of greater than or equal to the tensile strength, and preferably does not experience delayed cracking when it is soaked in 1 mol/L hydrochloric acid for 300 hours under a pre-stress of greater than or equal to 1.2 times of the tensile strength. It can be used effectively for manufacture of automotive safety structural parts. It is highly valuable and promising for popularization and application.

[0010] In order to achieve the above object, the present disclosure provides an ultra-high-strength dual-phase steel having a matrix structure of ferrite + martensite, wherein ferrite and martensite are distributed evenly like islands, and wherein the ultra-high-strength dual-phase steel comprises the following chemical elements in mass percentages, in addition to Fe:

C: 0.12-0.2%, Si: 0.5-1.0%, Mn: 2.5-3.0%, Al: 0.02-0.05%, Nb: 0.02-0.05%, Ti: 0.02-0.05%, B: 0.001%-0.003%.

[0011] Further, the ultra-high-strength dual-phase steel comprises the following chemical elements in mass percentages:

C: 0.12-0.2%, Si: 0.5-1.0%, Mn: 2.5-3.0%, Al: 0.02-0.05%, Nb: 0.02-0.05%, Ti: 0.02-0.05%, B: 0.001%-0.003%, and a balance of Fe and other unavoidable impurities.

[0012] In the ultra-high-strength dual-phase steel, the various chemical elements are designed according to the following principles:

C: In the ultra-high-strength dual-phase steel according to the present disclosure, C is a solid solution strengthening element, and it is a guarantee for the material to obtain high strength. However, it should be noted that the higher the C content in the steel, the harder the martensite and the greater the tendency for delayed cracking to occur. Therefore, when a product is designed, it's better to choose a low-carbon design. In the ultra-high-strength dual-phase steel according to the present disclosure, the mass percentage of C is controlled at 0.12-0.2%.

[0013] In some preferred embodiments, the mass percentage of C may be controlled at 0.14-0.18%.

[0014] Si: In the ultra-high-strength dual-phase steel according to the present disclosure, Si has an effect of increasing the elongation of the steel. Si also has a great influence on the structure of the steel. Particularly, it promotes purification of ferrite and formation of retained austenite. At the same time, it can improve the tempering resistance of martensite, and inhibit precipitation and growth of Fe_3C , so that the dominated precipitates formed during tempering are ϵ carbides. However, it should be noted that when the mass percentage of Si in the steel is less than 0.5%, the elongation and tempering resistance of the steel will be affected; if the mass percentage of Si is higher than 1.0%, other metallurgical quality defects will be caused. Therefore, in the ultra-high-strength dual-phase steel according to the present disclosure, the mass percentage of Si is controlled at 0.5-1.0%.

[0015] Mn: In the ultra-high-strength dual-phase steel according to the present disclosure, Mn is an element that strongly improves the hardenability of austenite, and it can improve the strength of the steel effectively by forming more martensite. Therefore, in the ultra-high-strength dual-phase steel according to the present disclosure, the mass percentage of Mn is controlled at 2.5-3.0%.

[0016] In some preferred embodiments, the mass percentage of Mn may be controlled at 2.5-2.8%.

[0017] Al: In the ultra-high strength dual-phase steel according to the present disclosure, Al is a deoxygenating element. It can remove oxygen and refine grains in the steel. Therefore, in the ultra-high-strength dual-phase steel according to the present disclosure, the mass percentage of Al is controlled at 0.02-0.05%.

[0018] Nb and Ti: In the ultra-high-strength dual-phase steel according to the present disclosure, Nb and Ti are elements for precipitation of carbonitrides. They can refine grains, precipitate carbonitrides, and improve the strength of the material. They can be added separately or in combination. However, it should be noted that if the mass percentage of Nb or Ti in the steel is higher than 0.05%, the strengthening effect is not obvious. Therefore, in the ultra-high-strength dual-phase steel of the present disclosure, the mass percentage of Nb is controlled at 0.02-0.05%, and the mass percentage of Ti is controlled at 0.02-0.05%.

[0019] B: In the ultra-high-strength dual-phase steel according to the present disclosure, B is used as a strong element for hardenability. An appropriate amount of B can increase the hardenability of the steel, and promote formation of martensite. Therefore, in the ultra-high-strength dual-phase steel according to the present disclosure, the mass percent-

age of B is controlled at 0.001%-0.003%.

[0020] Further, in the ultra-high-strength dual-phase steel according to the present disclosure, the unavoidable impurities include the P, S and N elements, and the contents thereof are controlled to be at least one of the following: $P \leq 0.01\%$, $S \leq 0.002\%$, $N \leq 0.004\%$.

[0021] In the above technical solution, in the ultra-high-strength dual-phase steel according to the present disclosure, the P, S and N elements are all unavoidable impurity elements in the steel. It's better to lower the contents of the P, S and N elements in the steel as far as possible. S tends to form MnS inclusions which will seriously affect the hole expansion rate. The P element may reduce the toughness of the steel, which is not conducive to the delayed cracking performance. An unduly high content of the N element in the steel is prone to causing cracks on the surface of the slab, which will greatly affect the performances of the steel. Therefore, in the ultra-high-strength dual-phase steel according to the present disclosure, the mass percentage of P is controlled at $P \leq 0.01\%$; the mass percentage of S is controlled at $S \leq 0.002\%$; and the mass percentage of N is controlled at $N \leq 0.004\%$.

[0022] Further, in the ultra-high-strength dual-phase steel according to the present disclosure, the mass percentage contents of the chemical elements satisfy at least one of the following:

C: 0.14-0.18%,
Mn: 2.5-2.8%.

[0023] Further, in the ultra-high-strength dual-phase steel according to the present disclosure, the phase proportion (by volume) of martensite is $>90\%$.

[0024] Further, in the ultra-high-strength dual-phase steel according to the present disclosure, martensite further comprises coherently distributed ϵ carbides.

[0025] Further, the performances of the ultra-high-strength dual-phase steel according to the present disclosure meet at least one of the following: yield strength ≥ 900 MPa, tensile strength ≥ 1300 MPa, elongation after fracture $\geq 5\%$, initial hydrogen content ≤ 10 ppm; no delayed cracking when soaked in 1 mol/L hydrochloric acid for 300 hours under a pre-stress of greater than or equal to the tensile strength.

[0026] Further, the performances of the ultra-high-strength dual-phase steel according to the present disclosure meet at least one of the following: yield strength ≥ 930 MPa, tensile strength ≥ 1320 MPa, elongation after fracture $\geq 5.5\%$, initial hydrogen content ≤ 7 ppm; no delayed cracking when soaked in 1 mol/L hydrochloric acid for 300 hours under a pre-stress of greater than or equal to 1.2 times of the tensile strength.

[0027] Further, the ultra-high-strength dual-phase steel according to the present disclosure has a yield strength of ≥ 930 MPa, a tensile strength of ≥ 1320 MPa, an elongation after fracture of $\geq 5.5\%$, an initial hydrogen content of ≤ 7 ppm; and it does not experience delayed cracking when it is soaked in 1 mol/L hydrochloric acid for 300 hours under a pre-stress of greater than or equal to 1.2 times of the tensile strength.

[0028] Accordingly, another object of the present disclosure is to provide a method for manufacturing an ultra-high-strength dual-phase steel. The ultra-high-strength dual-phase steel manufactured by this method has a yield strength of ≥ 900 MPa, a tensile strength of ≥ 1300 MPa, an elongation after fracture of $\geq 5\%$, an initial hydrogen content of ≤ 10 ppm, and it does not experience delayed cracking when it is soaked in 1 mol/L hydrochloric acid for 300 hours under a pre-stress of greater than or equal to the tensile strength. It can be used effectively for manufacture of automotive safety structural parts. It is highly valuable and promising for popularization and application.

[0029] To fulfil the above object, the present disclosure proposes a method for manufacturing the above ultra-high-strength dual-phase steel, comprising steps of:

- (1) Smelting and continuous casting;
- (2) Hot rolling;
- (3) Cold rolling;
- (4) Annealing: heating to an annealing soaking temperature of 800-850 °C, preferably 805-845 °C at a heating rate of 3-10 °C/s, the annealing time being 40-200 s; and then rapidly cooling at a rate of 30-80 °C/s, a starting temperature of the rapid cooling being 670-730 °C;
- (5) Tempering: tempering temperature: 260-320 °C, preferably 260-310 °C; tempering time: 100-400 s, preferably 100-300 s;
- (6) Temper rolling;
- (7) Electro-galvanizing.

[0030] A combination of high temperature soaking and medium temperature tempering is employed for the annealing. The high temperature soaking gives rise to more austenite transformation, and thus more martensite is obtained during the subsequent rapid cooling, which finally guarantees higher strength before tempering. The medium temperature tempering provides the material with a moderate yield ratio on the one hand, and on the other hand, it has a better effect

in improving the delayed cracking performance. In a preferred embodiment, the ultra-high-strength dual-phase steel according to the present disclosure has a yield ratio of 0.70-0.75.

[0031] In the method for manufacturing the ultra-high strength dual-phase steel according to the present disclosure, by adopting the medium to low temperature tempering treatment after the continuous annealing and controlling the relevant process parameters, uniform, fine and dispersive coherent ϵ carbides can be easily precipitated during tempering of martensite on the one hand, and on the other hand, the manner of long-term tempering at medium to low temperature enables removal of superfluous hydrogen from the steel plate to the greatest extent, i.e. diffusion of it out of the steel plate, so that the amount of hydrogen in its original state in the steel plate can be reduced. This is not only beneficial to reduce the hardness of martensite and the diffusion of hydrogen inside the steel plate, but also very beneficial to the mechanical properties and delayed cracking performance of the steel.

[0032] Further, in the manufacturing method according to the present disclosure, in step (1), a drawing speed in the continuous casting is controlled at 0.9-1.5 m/min.

[0033] In the above technical solution, in the manufacturing method according to the present disclosure, in step (1), the continuous casting may be performed in a secondary cooling mode with a large amount of water to minimize segregation.

[0034] Further, in the manufacturing method according to the present disclosure, in step (2), the cast slab is controlled to be soaked at a temperature of 1220-1260 °C, preferably 1220-1250 °C; then rolled with a finishing rolling temperature being controlled at 880-920 °C; then cooled at a rate of 20-70 °C/s after rolling; then coiled at a coiling temperature of 600-650 °C, preferably 605-645 °C; and then subjected to heat preservation treatment after coiling. Preferably, the heat preservation treatment is performed for 1-5 hours after coiling.

[0035] In the method for manufacturing the ultra-high-strength dual-phase steel according to the present disclosure, in step (2), in order to guarantee the stability of the rolling load, the heating temperature is controlled at 1220 °C or higher. Meanwhile, the upper limit of the heating temperature is controlled to be 1260 °C in order to prevent increase of oxidative burning loss. Therefore, the cast slab is finally controlled to be soaked at a temperature of 1220-1260 °C.

[0036] Further, in the manufacturing method according to the present disclosure, in step (3), the cold rolling reduction rate is controlled at 45-65%.

[0037] In the above technical solution, in the step (3), before cold rolling at a cold rolling reduction rate controlled at 45-65%, iron oxide scale on the surface of the steel plate can be removed by pickling.

[0038] Further, in the manufacturing method according to the present disclosure, in step (6), the temper rolling reduction rate is controlled at $\leq 0.3\%$.

[0039] In the above technical solution according to the present disclosure, in step (6), in order to guarantee the flatness of the steel plate, a certain amount of temper rolling needs to be performed, but an excessively large amount of temper rolling will increase the yield strength of the steel too much. Therefore, in the manufacturing method according to the present disclosure, the temper rolling reduction rate is controlled at $\leq 0.3\%$.

[0040] In the above technical solution according to the present disclosure, step (7) may be performed by a conventional electro-galvanizing method. Preferably, double-side plating is performed, and the weight of the plating layer on one side is in the range of 10-100 g/m².

[0041] Compared with the prior art, the ultra-high-strength dual-phase steel and the manufacturing method thereof have the following advantages and beneficial effects:

The composition of the ultra-high-strength dual-phase steel according to the present disclosure is designed reasonably. That is, a design of medium Si and low Al is employed to reduce the use of alloy elements such as Si and Al, so that the problems with the surface quality caused by high Si and the slab defects caused by high Al are avoided. In addition, the steel is free of precious alloy elements such as Cr and Mo, and the alloy content is low. The manufacturability and economic efficiency of the steel are very good. The alloy cost is controlled effectively. The ultra-high-strength dual-phase steel has a yield strength of ≥ 900 MPa, a tensile strength of ≥ 1300 MPa, an elongation after fracture of $\geq 5\%$, an initial hydrogen content of ≤ 10 ppm; and it does not experience delayed cracking when it is soaked in 1 mol/L hydrochloric acid for 300 hours under a pre-stress of greater than or equal to the tensile strength. It can be used effectively for manufacture of automotive safety structural parts. It is highly valuable and promising for popularization and application.

[0042] In addition, in the manufacturing method according to the present disclosure, by adopting the medium to low temperature tempering treatment after the continuous annealing and controlling the relevant process parameters, uniform, fine and dispersive coherent ϵ carbides can be easily precipitated during tempering of martensite on the one hand, and on the other hand, the manner of long-term tempering at medium to low temperature enables removal of superfluous hydrogen from the steel plate to the greatest extent, i.e. diffusion of it out of the steel plate, so that the amount of hydrogen in its original state in the steel plate can be reduced. This is not only beneficial to reduce the hardness of martensite and the diffusion of hydrogen inside the steel plate, but also very beneficial to the mechanical properties and delayed cracking performance of the steel, thereby effectively ensuring that the produced ultra-high strength dual-phase steel has excellent mechanical properties, excellent resistance to delayed cracking, and a lower initial hydrogen content.

Description of the Drawing

[0043] Figure 1 shows the structure of the cold-rolled and annealed dual-phase steel of Example 1.

Detailed Description

[0044] The ultra-high-strength dual-phase steel and the method for manufacturing the same according to the disclosure will be further explained and illustrated with reference to the specific Examples. Nonetheless, the explanation and illustration are not intended to unduly limit the technical solution of the disclosure.

Examples 1-7 and Comparative Examples 1-14

[0045] Table 1 lists the mass percentages of various chemical elements in the steel grades corresponding to the ultra-high-strength dual-phase steels in Examples 1-7 and the steels in Comparative Examples 1-14.

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

	Steel grade	C	Si	Mn	P	S	Nb	Ti	Al	N	B
Ex. 1	A	0.122	0.54	2.52	0.01	0.001	0.036	0.033	0.034	0.0030	0.0011
Ex. 2	B	0.147	0.72	2.64	0.008	0.0008	0.044	0.038	0.043	0.0027	0.0024
Ex. 3	C	0.131	0.63	2.98	0.009	0.002	0.022	0.045	0.028	0.0033	0.0029
Ex. 4	D	0.158	0.84	2.56	0.007	0.0007	0.043	0.037	0.022	0.0028	0.0015
Ex. 5	E	0.164	0.55	2.82	0.01	0.001	0.027	0.025	0.038	0.0032	0.0018
Ex. 6	F	0.173	0.95	2.73	0.005	0.0015	0.033	0.038	0.034	0.0029	0.0016
Ex. 7	G	0.194	0.66	2.65	0.009	0.0009	0.048	0.04	0.049	0.0026	0.0021
Comp. Ex. 1	H	0.118	0.67	2.65	0.006	0.002	0.025	0.043	0.034	0.0028	0.0013
Comp. Ex. 2	I	<u>0.205</u>	0.58	2.53	0.009	0.0008	0.038	0.025	0.027	0.0034	0.0025
Comp. Ex. 3	J	0.144	0.47	<u>2.42</u>	0.01	0.0016	0.043	0.035	0.022	0.0037	0.0016
Comp. Ex. 4	K	0.153	0.65	<u>3.05</u>	0.0007	0.0013	0.037	0.043	0.037	0.0028	0.0022
Comp. Ex. 5	L	0.149	0.72	2.75	0.01	0.0008	0.025	<u>0.013</u>	0.025	0.0022	0.0017
Comp. Ex. 6	M	0.162	0.64	2.58	0.0005	0.0012	<u>0.01</u>	0.035	0.039	0.0032	0.0024
Comp. Ex. 7-14	N	0.175	0.77	2.55	0.008	0.0009	0.033	0.026	0.046	0.0028	0.0018

[0046] The ultra-high-strength dual-phase steels in Examples 1-7 according to the present disclosure and the steels in Comparative Examples 1-14 were all prepared by the following steps:

- (1) Smelting and continuous casting: The drawing speed in the continuous casting was controlled to be 0.9-1.5 m/min during the continuous casting process, and the continuous casting was carried out in a secondary cooling mode with a large amount of water;
- (2) Hot rolling: The cast slab was soaked at a temperature controlled at 1220-1260 °C, and then rolled, wherein the finishing rolling temperature was controlled at 880-920 °C. After rolling, the steel was cooled at a rate of 20-70 °C/s. Then, the steel was coiled at a coiling temperature of 600-650°C. After coiling, an insulation cover was used to perform heat preservation treatment;
- (3) Cold rolling: The cold rolling reduction rate was controlled at 45-65%;
- (4) Annealing: The temperature was raised to the annealing soaking temperature of 800-850 °C at a heating rate of 3-10 °C/s, wherein the annealing time was 40-200 s. Then, rapid cooling was performed at a rate of 30-80 °C/s, wherein the starting temperature of the rapid cooling was 670-730 °C;
- (5) Tempering: The tempering temperature was 260-320 °C, and the tempering time was 100-400 s;
- (6) Temper rolling: The temper rolling reduction rate was controlled at $\leq 0.3\%$;
- (7) Double-side electro-galvanization: The weight of the plating layer on each side was 10-100 g/m².

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[0047] It should be noted that the chemical compositions of the ultra-high-strength dual-phase steel in Examples 1-7 and the related process parameters all met the control requirements of the design specification according to the present disclosure. The chemical compositions of the steels in Comparative Examples 1-6 all included parameters that failed to meet the requirements of the design according to the present disclosure. Although the chemical composition of steel grade N in Comparative Examples 7-14 met the requirements of the design according to the present disclosure, the related process parameters all included parameters that failed to meet the requirements of the design according to the present disclosure.

[0048] Tables 2-1 and 2-2 list the specific process parameters for the ultra-high-strength dual-phase steels in Examples 1-7 and the steels in Comparative Examples 1-14.

Table 2-1

No.	Steel grade	Step (1)	Step (2)				Step (3)
		Drawing speed in continuous casting (m/min)	Soaking temperature (°C)	Finishing rolling temperature (°C)	Cooling rate (°C/s)	Coiling temperature (°C)	Cold rolling reduction rate (%)
Ex. 1	A	1.0	1250	895	25	605	55
Ex. 2	B	1.2	1245	880	30	625	60
Ex. 3	C	1.5	1220	890	45	645	45
Ex. 4	D	0.9	1234	905	50	625	50
Ex. 5	E	1.1	1224	910	35	615	52
Ex. 6	F	1.3	1240	890	60	600	48
Ex. 7	G	1.0	1250	885	65	630	62
Comp. Ex. 1	H	1.2	1230	895	40	615	50
Comp. Ex. 2	I	0.9	1228	915	55	620	56
Comp. Ex. 3	J	1.4	1250	890	70	625	49
Comp. Ex. 4	K	1.3	1255	900	45	615	52
Comp. Ex. 5	L	0.6	1230	905	35	615	62
Comp. Ex. 6	M	1.0	1225	890	65	620	58
Comp. Ex. 7	N	1.2	<u>1199</u>	905	30	625	50
Comp. Ex. 8	N	1.1	<u>1273</u>	900	35	610	55
Comp. Ex. 9	N	1.3	1255	885	60	<u>580</u>	55
Comp. Ex. 10	N	1.4	1230	895	50	<u>665</u>	52
Comp. Ex. 11	N	1.1	1225	905	55	600	56
Comp. Ex. 12	N	1.2	1240	910	45	610	60

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(continued)

No.	Steel grade	Step (1)	Step (2)				Step (3)
		Drawing speed in continuous casting (m/min)	Soaking temperature (°C)	Finishing rolling temperature (°C)	Cooling rate (°C/s)	Coiling temperature (°C)	Cold rolling reduction rate (%)
Comp. Ex. 13	N	0.9	1245	895	40	625	52
Comp. Ex. 14	N	1.5	1238	885	60	612	50

Table 2-2

No.	Step (4)					Step (5)		Step (6)
	Heating rate (°C/s)	Annealing soaking temperature (°C)	Annealing time (s)	Rapid cooling rate (°C/s)	Starting temperature of rapid cooling (°C)	Tempering temperature (°C)	Tempering time (s)	
Ex. 1	5	825	120	45	705	280	200	0.2
Ex. 2	8	820	75	35	670	290	300	0.1
Ex. 3	10	845	180	80	690	265	210	0.1
Ex. 4	9	805	100	55	700	305	250	0.3
Ex. 5	4	810	45	48	670	285	120	0.2
Ex. 6	3	828	55	56	680	290	300	0.3
Ex. 7	6	824	85	55	725	266	125	0.2
Comp. Ex. 1	6	832	150	48	695	286	330	0.1
Comp. Ex. 2	5	840	90	65	675	315	205	0.3
Comp. Ex. 3	8	800	105	70	705	307	190	0.1
Comp. Ex. 4	9	818	180	62	720	274	180	0.3
Comp. Ex. 5	5	835	60	58	715	264	240	0.2
Comp. Ex. 6	4	812	75	80	670	292	225	0.1
Comp. Ex. 7	8	834	120	55	720	305	325	0.2
Comp. Ex. 8	7	826	135	38	700	269	290	0.1
Comp. Ex. 9	6	819	95	80	680	296	175	0.2

(continued)

No.	Step (4)					Step (5)		Step (6)
	Heating rate (°C/s)	Annealing soaking temperature (°C)	Annealing time (s)	Rapid cooling rate (°C/s)	Starting temperature of rapid cooling (°C)	Tempering temperature (°C)	Tempering time (s)	
Comp. Ex. 10	10	830	105	55	685	288	205	0.1
Comp. Ex. 11	3	<u>794</u>	145	62	695	308	380	0.1
Comp. Ex. 12	8	<u>865</u>	65	56	705	275	280	0.3
Comp. Ex. 13	5	807	175	48	710	<u>340</u>	300	0.2
Comp. Ex. 14	6	814	125	54	690	<u>230</u>	290	0.1

[0049] A variety of performance tests were performed on the ultra-high-strength dual-phase steels in Examples 1-7 and the steels in Comparative Examples 1-14. The test results obtained are listed in Table 3.

[0050] As to the performance test method, GB/T 13239-2006 Metallic Materials - Tensile Testing at Low Temperature was referred to. A standard sample was prepared, and subjected to static stretching on a tensile testing machine to obtain a corresponding stress-strain curve. After data processing, the parameters of yield strength, tensile strength and elongation after fracture were obtained finally.

[0051] Method for measurement of hydrogen content: The sample was heated to a certain temperature, and a hydrogen analyzer was used to measure the concentration of hydrogen released along with the change (rise) of the temperature, thereby judging the initial hydrogen content in the steel.

[0052] Table 3 lists the performance test results for the ultra-high-strength dual-phase steels in Examples 1-7 and the steels in Comparative Examples 1-14.

Table 3

No.	Yield strength (MPa)	Tensile strength (MPa)	Elongation after fracture (%)	Initial hydrogen content (ppm)	Stresslevel 0.6*TS	Stresslevel 0.8*TS	Stresslevel 1.2*TS
Ex. 1	932	1329	9.7	5	○	○	○
Ex. 2	955	1338	9.2	7	○	○	○
Ex. 3	961	1340	8.5	3	○	○	○
Ex. 4	987	1364	7.6	6	○	○	○
Ex. 5	1004	1385	6.8	4	○	○	○
Ex. 6	1046	1407	6.2	1	○	○	○
Ex. 7	1065	1421	5.7	2	○	○	○
Comp. Ex. 1	877	1285	11.3	3	○	○	○
Comp. Ex. 2	1126	1469	4.3	9	○	X	X
Comp. Ex. 3	854	1276	11.5	2	○	○	○
Comp. Ex. 4	1134	1480	3.9	8	○	X	X
Comp. Ex. 5	865	1291	11.8	3	○	○	○
Comp. Ex. 6	839	1274	12.2	7	○	○	○
Comp. Ex. 7	852	1258	12.8	4	○	○	○
Comp. Ex. 8	1100	1446	4.7	8	○	○	X
Comp. Ex. 9	1098	1439	4.4	2	○	○	X
Comp. Ex. 10	870	1268	12.6	6	○	○	○
Comp. Ex. 11	886	1275	11.3	5	○	○	○
Comp. Ex. 12	1133	1485	3.9	8	○	○	X

(continued)

No.	Yield strength (MPa)	Tensile strength (MPa)	Elongation after fracture (%)	Initial hydrogen content (ppm)	Stress level 0.6*TS	Stress level 0.8*TS	Stress level 1.2*TS
Comp. Ex. 13	865	1286	11.6	6	○	○	○
Comp. Ex. 14	1108	1455	5.1	3	○	○	X
Note: The results of soaking the steel plates in 1 mol/L hydrochloric acid for 300 hours under a certain internal stress level: O represents no cracking, X represents cracking.							

[0053] As it can be seen from Table 3, high-strength steels having a strength of at least 1300 MPa can be manufactured according to the present disclosure. Each Example according to the present disclosure has a yield strength of ≥ 900 MPa, a tensile strength of ≥ 1300 MPa, an elongation after fracture of $\geq 5\%$, and an initial hydrogen content of ≤ 10 ppm. The ultra-high-strength dual-phase steel in each Example has an ultra-high strength and a delayed cracking performance that is significantly better than that of a comparative steel grade of the same level. No delayed cracking occurs when the steel plate is soaked in 1 mol/L hydrochloric acid for 300 hours under a pre-stress of greater than or equal to the tensile strength. The ultra-high-strength dual-phase steel in each Example has excellent performances. It is suitable for manufacture of automotive safety structural parts, and it is highly valuable and promising for popularization and application.

[0054] It's to be noted that the prior art portions in the protection scope of the present disclosure are not limited to the examples set forth in the present application file. All the prior art contents not contradictory to the technical solution of the present disclosure, including but not limited to prior patent literature, prior publications, prior public uses and the like, may all be incorporated into the protection scope of the present disclosure. In addition, the ways in which the various technical features of the present disclosure are combined are not limited to the ways recited in the claims of the present disclosure or the ways described in the specific examples. All the technical features recited in the present disclosure may be combined or integrated freely in any manner, unless contradictions are resulted.

[0055] It should also be noted that the Examples set forth above are only specific examples according to the present disclosure. Obviously, the present disclosure is not limited to the above Examples. Similar variations or modifications made thereto can be directly derived or easily contemplated from the present disclosure by those skilled in the art. They all fall in the protection scope of the present disclosure.

Claims

1. An ultra-high-strength dual-phase steel, wherein the ultra-high-strength dual-phase steel has a matrix structure of ferrite + martensite, wherein the ferrite and the martensite are distributed evenly like islands, and wherein the ultra-high-strength dual-phase steel comprises the following chemical elements in mass percentages, in addition to Fe: C: 0.12-0.2%, Si: 0.5-1.0%, Mn: 2.5-3.0%, Al: 0.02-0.05%, Nb: 0.02-0.05%, Ti: 0.02-0.05%, B: 0.001%-0.003%.
2. The ultra-high-strength dual-phase steel according to claim 1, wherein the chemical elements have the following mass percentages: C: 0.12-0.2%, Si: 0.5-1.0%, Mn: 2.5-3.0%, Al: 0.02-0.05%, Nb: 0.02-0.05%, Ti: 0.02-0.05%, B: 0.001%-0.003%, and a balance of Fe and other unavoidable impurities.
3. The ultra-high-strength dual-phase steel according to claim 2, wherein the unavoidable impurities include elements P, S and N, and contents thereof are controlled to be at least one of the following: $P \leq 0.01\%$, $S \leq 0.002\%$, $N \leq 0.004\%$.
4. The ultra-high-strength dual-phase steel according to any one of claims 1-3, wherein the mass percentages of the chemical elements satisfy at least one of:

C: 0.14-0.18%,
Mn: 2.5-2.8%.

5. The ultra-high-strength dual-phase steel according to any one of claims 1-3, wherein the martensite has a phase proportion of >90%.
6. The ultra-high-strength dual-phase steel according to any one of claims 1-3, wherein the martensite comprises coherently distributed ϵ carbides.
7. The ultra-high-strength dual-phase steel according to any one of claims 1-3, wherein the ultra-high-strength dual-phase steel has performances that meet at least one of the following: yield strength ≥ 900 MPa, tensile strength ≥ 1300 MPa, elongation after fracture $\geq 5\%$, initial hydrogen content ≤ 10 ppm; no delayed cracking when soaked in 1 mol/L hydrochloric acid for 300 hours under a pre-stress of greater than or equal to the tensile strength.
8. The ultra-high-strength dual-phase steel according to any one of claims 1-3, wherein the ultra-high-strength dual-phase steel has performances that meet at least one of the following: yield strength ≥ 930 MPa, tensile strength ≥ 1320 MPa, elongation after fracture $\geq 5.5\%$, initial hydrogen content ≤ 7 ppm; no delayed cracking when soaked in 1 mol/L hydrochloric acid for 300 hours under a pre-stress of greater than or equal to 1.2 times of the tensile strength.
9. The ultra-high-strength dual-phase steel according to any one of claims 1-3, wherein the ultra-high-strength dual-phase steel has a yield ratio of 0.70-0.75.
10. A manufacturing method for the ultra-high-strength dual-phase steel according to any one of claims 1-9, wherein the method comprises steps of:
 - (1) Smelting and continuous casting;
 - (2) Hot rolling;
 - (3) Cold rolling;
 - (4) Annealing: heating to an annealing soaking temperature of 800-850 °C at a heating rate of 3-10 °C/s, the annealing time being 40-200 s; and then rapidly cooling at a rate of 30-80 °C/s, a starting temperature of the rapid cooling being 670-730 °C;
 - (5) Tempering: tempering temperature: 260-320 °C; tempering time: 100-400 s;
 - (6) Temper rolling;
 - (7) Electrogalvanizing.
11. The manufacturing method according to claim 10, wherein in step (1), a drawing speed in the continuous casting is controlled at 0.9-1.5 m/min during the continuous casting process.
12. The manufacturing method according to claim 10, wherein in step (2), a cast slab is controlled to be soaked at a temperature of 1220-1260 °C; then rolled with a finishing rolling temperature being controlled at 880-920 °C; then cooled at a rate of 20-70 °C/s after the rolling; then coiled at a coiling temperature of 600-650 °C; and then subjected to heat preservation treatment after the coiling.
13. The manufacturing method according to claim 10, wherein in step (3), a cold rolling reduction rate is controlled at 45-65%.
14. The manufacturing method according to claim 10, wherein in step (6), a temper rolling reduction rate is controlled at $\leq 0.3\%$; and/or in step (7), double-side electrogalvanizing is performed with a plating layer weight of 10-100 g/m² on each side.
15. The manufacturing method according to claim 10, wherein in step (2), a cast slab is controlled to be soaked at a temperature of 1220-1250 °C, and a coiling temperature is 605-645 °C; in step (4), the annealing soaking temperature is 805-845 °C; in step (5), the tempering temperature is 260-310 °C, and the tempering time is preferably 100-300 s.

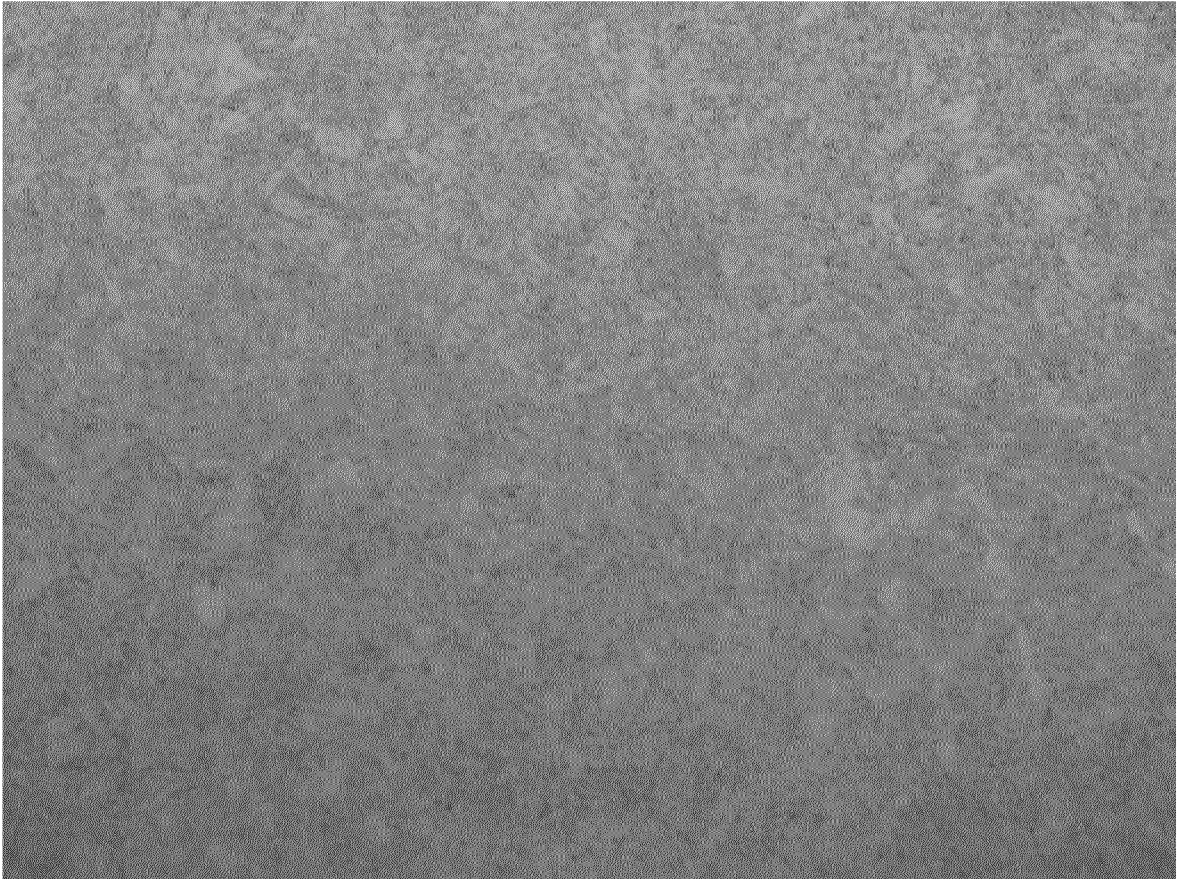


Figure 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2021/095807

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/02(2006.01)i; C22C 38/04(2006.01)i; C22C 38/06(2006.01)i; C22C 38/12(2006.01)i; C22C 38/14(2006.01)i; C21D 8/00(2006.01)i; C22C 33/04(2006.01)i; C21D 8/02(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C 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; CNKI; VEN; WOTXT; EPTXT; USTXT; ISL WEB OF SCIENCE: 宝山钢铁股份有限公司, 双相, 两相, 二相, DP钢, MD组织, 碳, 硅, 锰, 铝, 铌, 钛, 硼, 铁素体, 马氏体, C, Si, Mn, Al, Nb, Ti, B, double phase, two phase, carbon, silicon, manganese, aluminium, niobium, titanium, boron, ferrite, martensite

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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☐ Further documents are listed in the continuation of Box C.
 ☒ See patent family annex.

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
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"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)	"&" document member of the same patent family
"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	

Date of the actual completion of the international search 19 July 2021	Date of mailing of the international search report 11 August 2021
Name and mailing address of the ISA/CN China National Intellectual Property Administration (ISA/ CN) No. 6, Xitucheng Road, Jimenqiao, Haidian District, Beijing 100088 China	Authorized officer
Facsimile No. (86-10)62019451	Telephone No.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2021/095807

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