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(54) ELECTRO-GALVANIZED SUPER-STRENGTH DUAL-PHASE STEEL RESISTANT TO DELAYED CRACKING, AND MANUFACTURING METHOD THEREFOR

(57) Disclosed is an electro-galvanized super-strength dual-phase steel resistant to delayed cracking. A matrix structure thereof is ferrite + tempered martensite and the steel contains the following chemical elements in the following mass percentages: C: 0.07-0.1%, Si: 0.05-0.3%, Mn: 2.0-2.6%, Cr: 0.2-0.6%, Mo: 0.1-0.25%, Al: 0.02-0.05%, Nb: 0.02-0.04%, and V: 0.06-0.2%. Also disclosed is a method for manufacturing the electro-galvanized super-strength dual-phase steel resistant to delayed cracking, the method comprising the steps of: smelting and continuous casting, hot rolling, cold rolling, annealing, tempering, leveling and electroplating. The electro-galvanized super-strength dual-phase steel resistant to delayed cracking according to the present invention not only has better mechanical properties, but also has excellent delayed cracking resistance and low initial hydrogen content.

EP 4 159 887 A1

Description

Technical Field

[0001] The present disclosure relates to a metallic material and a method of manufacturing the same, particularly to an electro-galvanized ultra-high-strength dual-phase steel and a method of manufacturing the same.

Background Art

[0002] As weight reduction and safety of vehicles 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, it is widely used in the production of automotive parts. At present, strength grades of 80 kg and 100 kg are mainly demanded in the market. To meet the requirement of anti-corrosion, galvanized steel plates are generally used in the automotive industry at present, but such steel plates have a general problem of delayed cracking.

[0003] Delayed fracture refers to a phenomenon that a material under static stress suffers a sudden brittle failure after a certain period of time. This phenomenon is a kind of embrittlement that occurs when the material interacts with the environmental stress, and it is a form of material deterioration caused by hydrogen. The phenomenon of delayed fracture is a major factor that hinders the application of ultra-high-strength steel, and it may be roughly classified into the following two categories:

(1) delayed fracture mainly caused by hydrogen intruding from the external environment (external hydrogen), such as bolts used in bridges and the like, which suffer delayed fracture due to long-term exposure to humid air, rain and other surroundings;

(2) delayed fracture caused by hydrogen intruding into the steel during manufacturing processes such as pickling and electroplating (internal hydrogen), such as electroplated bolts and the like which suffer delayed fracture after a short period of several hours or days after loading.

[0004] The former is generally caused by the intrusion of hydrogen generated by the corrosion reaction at a corrosion pit where corrosion occurs during long-term exposure; while the latter is caused by the concentration of hydrogen in the region of stress concentration under the action of stress wherein the hydrogen intrudes into the steel during manufacturing processes such as pickling and electroplating.

[0005] Chinese Patent No. CN107148486B, published on January 8, 2019 and entitled "High-strength Steel Plate, High-strength Hot-dip Galvanized Steel Plate, High-strength Hot-dip Aluminized Steel Plate, High-strength Electro-galvanized Steel Plate, And Manufacturing Methods Therefor", discloses a method for manufacturing an electro-galvanized high-strength steel comprising chemical ingredients of: C: 0.030% or more and 0.250% or less, Si: 0.01% or more and 3.00% or less, Mn: 2.60% or more and 4.20% or less, P: 0.001% or more and 0.100% or less, S: 0.0001% or more and 0.0200% or less, N: 0.0005% or more and 0.0100% or less, Ti: 0.005% or more and 0.200% or less, and a balance of Fe and unavoidable impurities. The slab is heated to 1100 °C or higher and 1300°C or lower, hot-rolled at a finish rolling exit-side temperature of 750 °C or higher and 1000°C or lower, coiled at 300°C or higher and 750°C or lower, and then descaled by pickling. The steel plate was held at a temperature ranging from the Ac1 transformation point + 20 °C to the Ac1 transformation point + 120 °C for 600 seconds or more and 21600 seconds or less, and cold rolled at a reduction rate of 30% or more. Then, the steel plate is held at a temperature ranging from the Ac1 transformation point to the Ac1 transformation point + 100 °C for 20 seconds or more and 900 seconds or less, cooled, and then subjected to electro-galvanization.

[0006] Chinese Patent No. CN106282790B, published on April 3, 2018 and entitled "Ultra-deep-drawing Cold-rolled Steel Plate For Electro-galvanization And Method For Producing Same", discloses a method for manufacturing an ultra-deep-drawing cold-rolled steel plate for electro-galvanization, wherein the steel plate comprises the following chemical ingredients: C≤0.002%, Si≤0.030%, Mn: 0.06%-0.15%, P≤0.015%, S≤0.010%, Als: 0.030%-0.050%, Ti: 0.040-0.070%, N≤0.0040%, and a balance of Fe and unavoidable impurities. The method for producing the cold-rolled steel plate includes the following steps: (1) molten steel pretreatment; (2) converter smelting; (3) alloy fine-tuning station; (4) RH furnace refining; (5) continuous casting; (6) hot rolling; (7) cold rolling; (8) continuous annealing; (9) temper rolling. The invention can improve the surface quality of the electro-galvanized steel plate and ensure that the electro-galvanized steel plate has a good shape. The mechanical properties of the cold-rolled steel plate are as follows: the yield strength is 120-180 MPa, and the tensile strength is higher than 260 MPa.

[0007] Chinese Patent Application No. CN1419607A, published on May 21, 2003 and entitled "High-strength Dual-phase Thin Steel Plate And High-strength Dual-phase Electroplated Thin Steel Plate And Method For Manufacturing Same" discloses a dual-phase steel plate having a tensile strength of 600-650MPa grade and a method for manufacturing

the same, wherein the steel plate comprises the following chemical ingredients: 0.01-0.08% C, not more than 2% Si, not more than 3.0% Mn, 0.01-0.5% V, V and C satisfying $0.5\times C/12\leq V/51\leq 3\times C/12$, and a balance of Fe and unavoidable impurities. The steel plate is heated to 1250 °C and soaked, and then subjected to three-pass rolling on a finishing mill at a conveying temperature of 900 °C, followed by a heat preservation treatment of 650 °C × 1 hour. Next, the thin steel plate is cold-rolled at a reduction rate of 70 °C/s to obtain a cold-rolled thin steel plate having a thickness of 1.2 mm. This is followed by recrystallization annealing at 850 °C for 60 seconds, cooling at a cooling rate of 30 °C/s, and then electroplating.

[0008] As it can be seen, the tensile strength grades of the products involved in the above-mentioned prior art patent documents are all less than 980 MPa, or the matrix is hot stamping steel. In view of the above, it's desirable to provide an electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking in order to meet the requirements in the industry.

Summary

[0009] One of the objects of the present disclosure is to provide an electro-galvanized ultra-high-strength dual-phase steel that is resistant to delayed cracking. In view of the attribute of ultra-high-strength steel that it is prone to delayed cracking, the composition of the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure is designed reasonably. That is, by reasonably designing carbon, silicon, manganese and micro-alloy elements such as niobium, vanadium, chromium, molybdenum and the like in coordination with the process, the resulting steel has both excellent resistance to delayed cracking and ultra-high strength. The electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking has a yield strength of ≥550 MPa, a tensile strength of ≥980 MPa, an elongation after fracture of ≥12%, an initial hydrogen content of ≤3 ppm, preferably ≤2 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. In a preferred embodiment, the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking does not experience delayed cracking when it is soaked in 1 mol/L hydrochloric acid for 300 hours under a pre-stress of 1.2 times the tensile strength. The excellent performances of the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking can meet the industrial requirements, and be used 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 electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking, having a matrix structure of ferrite+tempered martensite, wherein the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking comprises the following chemical elements in mass percentages, in addition to Fe:

C: 0.07-0.1%, Si: 0.05-0.3%, Mn: 2.0-2.6%, Cr: 0.2-0.6%, Mo: 0.1-0.25%, Al: 0.02-0.05%, Nb: 0.02-0.04%, V: 0.06-0.2%.

[0011] Further, in the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure, the mass percentages of the chemical elements are:

C: 0.07-0.1%, Si: 0.05-0.3%, Mn: 2.0-2.6%, Cr: 0.2-0.6%, Mo: 0.1-0.25%, Al: 0.02-0.05%, Nb: 0.02-0.04%, V: 0.06-0.2%, and a balance of Fe and other unavoidable impurities.

[0012] In the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking of the present disclosure, the chemical elements are designed according to the following principles:

C: In the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking 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 electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure, the mass percentage of C is controlled at 0.07-0.1%.

Si and Al: In the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure, the Si and Al elements can improve the tempering resistance of martensite, and can inhibit precipitation and growth of Fe_3C, so that the dominated precipitates formed during tempering are ε carbides. In addition, it should be noted that Al is also a deoxygenating element, and it has the function of deoxygenation in the steel. Therefore, in the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure, the mass percentage of Si is controlled at 0.05-0.3%, and the mass percentage of Al is controlled at 0.02-0.05%.

Mn: In the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking 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 electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure, the mass percentage of Mn is

controlled at 2.0-2.6%.

Cr: In the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure, Cr can improve the tempering resistance of martensite effectively, which is very conducive to improvement of delayed cracking. The mass percentage of Cr in the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure is controlled at 0.2-0.6%.

Mo: In the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure, addition of an appropriate amount of the Mo element can help to form dispersively distributed fine precipitates, which is conducive to gathering of dispersed hydrogen. The Mo element can form a large quantity of MoC precipitates in the steel, which is conducive to gathering of dispersed hydrogen in local areas, and thus very helpful to reduce delayed cracking of the steel. Therefore, in the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure, the mass percentage of Mo is controlled at 0.1-0.25%.

Nb: In the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure, the Nb element is an element for precipitation of carbonitrides. It can refine grains, precipitate carbonitrides, and increase material strength. At the same time, the coherent micro-alloy precipitates are conducive to gathering of dispersed hydrogen, which helps to reduce delayed cracking. Therefore, in the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure, the mass percentage of Nb is controlled at 0.02-0.04%.

V: In the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure, V may play a role in refining grains. At the same time, the coherent micro-alloy precipitates are conducive to gathering of dispersed hydrogen. Therefore, in the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure, the mass percentage of V is controlled at 0.06-0.2%.

[0013] Further, the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure further comprises 0.0015-0.003% of element B.

[0014] In the technical solution according to the present disclosure, the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure may also comprise a small amount of element B. 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.

[0015] Further, in the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking 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 ≤0.012%, S≤0.003%, N≤0.005%.

[0016] In the above technical solution, in the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure, P, S and N 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 electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure, the mass percentage of P is controlled at P≤0.012%; the mass percentage of S is controlled at S≤0.003%; and the mass percentage of N is controlled at N≤0.005%.

[0017] Further, in the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure, the phase proportion (by volume) of the tempered martensite is >50%.

[0018] Further, in the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure, a large quantity of fine carbide particles are precipitated dispersively in the matrix structure. The carbide particles include MoC, VC, Nb (C, N), and the carbide particles are all distributed in the matrix structure in a coherent form.

[0019] Further, in the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure, the carbide particles have a size of ≤60 nm.

[0020] Further, in the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure, the tempered martensite further comprises coherently distributed ε carbides.

[0021] Further, the performances of the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure meet at least one of the following: yield strength ≥550 MPa, tensile strength ≥980 MPa, elongation after fracture ≥12%, initial hydrogen content ≤3 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.

[0022] Further, the performances of the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure meet the following: yield strength ≥550 MPa, tensile strength ≥980 MPa,

elongation after fracture ≥12%, initial hydrogen content ≤3 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.

[0023] Further, the yield ratio of the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure is in the range of 0.55-0.70.

[0024] Accordingly, another object of the present disclosure is to provide a method for manufacturing an electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking. The electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking manufactured by this method has a yield strength of ≥550 MPa, a tensile strength of ≥980MPa, an elongation after fracture of ≥12%, an initial hydrogen content of ≤3ppm, preferably ≤2ppm, 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.

[0025] In order to achieve the above object, the present disclosure provides a method for manufacturing the above electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking, comprising steps:

(1) Smelting and continuous casting;
(2) Hot rolling;
(3) Cold rolling;
(4) Annealing: heating to an annealing soaking temperature of 780-820 °C, preferably 790-810 °C at a heating rate of 3-10 °C/s, the annealing time being 40-200 s, preferably 40-160 s; and then rapidly cooling at a rate of 30-80 °C/s, preferably 35-80 °C/s, a starting temperature of the rapid cooling being 650-730 °C;
(5) Tempering: tempering temperature: 200-280 °C, preferably 210-270 °C; tempering time: 100-400 s, preferably 120-300 s;
(6) Temper rolling;
(7) Electroplating.

[0026] In the method for manufacturing the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure, during heating in the continuous annealing, a medium to low temperature tempering treatment is utilized to control the relevant process parameters. This not only helps to reduce the hardness of martensite, but can also effectively avoid precipitation of coarse-grained martensite, which is very beneficial to the delayed cracking performance of the steel.

[0027] 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.

[0028] 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.

[0029] 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 1200-1260 °C, preferably 1210-1245 °C; then rolled with a finishing rolling temperature being controlled at 840-900 °C; then cooled at a rate of 20-70 °C/s after rolling; then coiled at a coiling temperature of 580-630 °C; and then subjected to heat preservation treatment or slow cooling treatment after coiling. Preferably, the heat preservation treatment is performed for 1-5 hours, or the slow cooling treatment is performed at a cooling rate of 3-5 °C/s.

[0030] In the method for manufacturing the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure, in step (2), in order to ensure the stability of the rolling load, the heating temperature is controlled at 1200 °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 1200-1260 °C.

[0031] In addition, it should be noted that, in step (2), the heat preservation after hot-rolling and coiling or the slow cooling after coiling is conducive to full precipitation of dispersive precipitates. Various types of dispersively distributed precipitates are conducive to adsorption of a small amount of hydrogen and dispersive distribution of hydrogen, thereby avoiding gathering of hydrogen. This helps to resist delayed cracking.

[0032] Further, in the manufacturing method according to the present disclosure, in step (3), the cold rolling reduction rate is controlled at 45-65%.

[0033] In the above technical solution, in step (3), the cold rolling reduction rate is controlled at 45-65%. Before the cold rolling, the iron oxide scale on the surface of the steel plate can be removed by pickling.

[0034] Further, in the manufacturing method according to the present disclosure, in step (6), the temper rolling reduction rate is controlled at ≤0.3%.

[0035] 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 <0.3%.

[0036] 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/m^2.

[0037] Compared with the prior art, the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking and the method of manufacturing the same according to the present disclosure have the following advantages and beneficial effects:

The composition of the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure is designed reasonably. That is, by reasonably designing carbon, silicon, manganese and micro-alloy elements such as niobium, vanadium, chromium, molybdenum and the like in coordination with the process, the resulting steel has both excellent resistance to delayed cracking and ultra-high strength. The electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking has a yield strength of ≥550 MPa, a tensile strength of ≥980 MPa, an elongation after fracture of ≥12%, an initial hydrogen content of ≤3 ppm, and delayed cracking does not occur 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. The excellent performances of the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking can meet the industrial requirements, suitable for manufacture of automotive safety structural parts. It is highly valuable and promising for popularization and application.

[0038] Due to the reasonable composition design and the continuous casting process utilized for the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure, the interior of the steel plate, especially the surface layer, is free of TiN, which is conducive to reducing gathering of hydrogen in the interior of the steel plate and improving the delayed cracking performance of the steel.

[0039] In the manufacturing method according to the present disclosure, a combination of high temperature soaking and medium temperature tempering is adopted. During the continuous annealing heating, 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. By adopting medium to low temperature tempering treatment and controlling relevant process parameters, not only reduction of the hardness of martensite is favored, but precipitation of coarse-grained martensite is also avoided effectively, so that the yield ratio of the material is moderate, and on the other hand, the delayed cracking performance of the steel is greatly favored. During tempering, if the tempering temperature used is too low, it is not conducive to reducing the hardness of martensite; if the tempering temperature is too high, martensite will decompose, and the final strength will be lower than 980 MPa. The use of high temperature soaking and medium temperature tempering in combination according to the present disclosure effectively ensures that the prepared electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking has the characteristics of excellent delayed-cracking resistance and low initial hydrogen content.

Detailed Description

[0040] The electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking and the method for manufacturing the same according to the present 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 present disclosure.

Examples 1-6 and Comparative Examples 1-14

[0041] Table 1 lists the mass percentages of various chemical elements in the steel grades corresponding to the electro-galvanized ultra-high-strength dual-phase steels resistant to delayed cracking in Examples 1-6 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	Cr	Mo	Al	N	V	B
Ex. 1	A	0.07	0.05	2.07	0.011	0.001	0.022	0.34	0.21	0.021	0.0035	0.11	0.0015
Ex. 2	B	0.073	0.08	2.14	0.008	0.0008	0.024	0.38	0.23	0.033	0.0044	0.15	0.0020
Ex. 3	C	0.078	0.13	2.48	0.009	0.003	0.032	0.45	0.25	0.028	0.0037	0.09	0.0018
Ex. 4	D	0.088	0.24	2.02	0.012	0.002	0.039	0.36	0.12	0.049	0.0028	0.17	-
Ex. 5	E	0.096	0.17	2.28	0.01	0.001	0.027	0.22	0.18	0.038	0.0032	0.14	0.0024
Ex. 6	F	0.1	0.28	2.33	0.005	0.0005	0.034	0.57	0.17	0.037	0.0047	0.08	0.0029
Comp. Ex. 1	G	**0.044**	0.27	2.25	0.011	0.002	0.024	0.43	0.24	0.034	0.0028	0.12	0.0016
Comp. Ex. 2	H	**0.123**	0.09	2.19	0.009	0.0008	0.038	0.45	0.22	0.027	0.0044	0.16	0.0024
Comp. Ex. 3	I	0.085	0.17	**1.92**	0.012	0.001	0.033	0.35	0.12	0.032	0.0037	0.15	0.0019
Comp. Ex. 4	J	0.092	0.25	**2.65**	0.01	0.002	0.037	0.43	0.23	0.023	0.0028	0.13	0.0026
Comp. Ex. 5	K	0.075	0.14	2.08	0.011	0.002	0.025	**0.18**	**0.02**	0.025	0.0042	0.11	0.0015
Comp. Ex. 6	L	0.072	0.18	2.15	0.011	0.002	**0.01**	0.56	0.13	0.029	0.0042	**0.02**	0.0022
Comp. Ex. 7-14	M	0.084	0.25	2.28	0.012	0.002	0.033	0.26	0.16	0.026	0.0028	0.17	0.0017

[0042] The electro-galvanized ultra-high-strength dual-phase steels resistant to delayed cracking in Examples 1-6 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 1200-1260 °C, and then rolled, wherein the finishing rolling temperature was controlled at 840-900 °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 580-630°C. After coiling, an insulation cover was used to hold the temperature for 1-5 hours;
(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 780-820 °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 650-730 °C;
(5) Tempering: The tempering temperature was 200-280 °C, and the tempering time was 100-400 s;
(6) Temper rolling: The temper rolling reduction rate was controlled at ≤0.3%;
(7) Double-side electro-galvanization: The weight of the plating layer on each side was 10-100 g/m^2.

[0043] It should be noted that the chemical compositions of the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking in Examples 1-6 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 M 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.

[0044] Tables 2-1 and 2-2 list the specific process parameters for the electro-galvanized ultra-high-strength dual-phase steels resistant to delayed cracking in Examples 1-6 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	0.9	1230	885	35	585	50
Ex. 2	B	1.1	1240	860	30	595	60
Ex. 3	C	1.5	1220	890	65	605	65
Ex. 4	D	1.3	1215	875	40	625	55
Ex. 5	E	1.1	1224	880	35	615	48
Ex. 6	F	1.5	1230	890	60	600	58
Comp. Ex. 1	G	1.4	1235	895	60	595	50
Comp. Ex. 2	H	1.2	1200	875	65	620	64
Comp. Ex. 3	I	1.5	1210	855	70	625	49
Comp. Ex. 4	J	0.9	1255	845	55	590	52
Comp. Ex. 5	K	1.4	1250	880	45	615	62

(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. 6	L	1.0	1225	870	65	620	55
Comp. Ex. 7	M	0.9	**1185**	905	30	590	62
Comp. Ex. 8	M	1.1	**1265**	900	35	610	50
Comp. Ex. 9	M	0.9	1245	855	60	**550**	55
Comp. Ex. 10	M	1.5	1220	865	40	**660**	65
Comp. Ex. 11	M	1.0	1225	895	55	600	56
Comp. Ex. 12	M	1.5	1230	875	45	610	61
Comp. Ex. 13	M	1.3	1245	855	60	625	52
Comp. Ex. 14	M	1.2	1230	890	45	595	60

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)	Temper rolling reduction rate (%)
Ex. 1	5	795	60	55	710	260	100	0.1
Ex. 2	8	790	80	35	680	240	300	0.1
Ex. 3	7	785	120	80	650	210	250	0.3
Ex. 4	4	794	160	45	730	270	200	0.1
Ex. 5	3	810	40	45	670	230	120	0.2
Ex. 6	10	806	160	72	660	265	300	0.1
Comp. Ex. 1	8	796	40	45	650	240	340	0.1
Comp. Ex. 2	4	785	80	50	670	200	400	0.3
Comp. Ex. 3	3	800	120	60	705	245	260	0.1
Comp. Ex. 4	10	795	160	55	650	235	170	0.3
Comp. Ex. 5	8	805	120	38	725	240	330	0.2
Comp. Ex. 6	8	786	160	80	670	225	280	0.1
Comp. Ex. 7	9	788	40	45	720	250	200	0.2
Comp. Ex. 8	6	785	80	70	700	235	160	0.1
Comp. Ex. 9	3	802	120	44	680	240	300	0.2
Comp. Ex. 10	4	814	160	50	660	240	240	0.1

(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)	Temper rolling reduction rate (%)
Comp. Ex. 11	8	**765**	40	62	695	200	190	0.1
Comp. Ex. 12	7	**845**	80	55	708	250	300	0.3
Comp. Ex. 13	9	795	100	48	710	**300**	210	0.2
Comp. Ex. 14	5	805	95	56	690	**160**	180	0.1

[0045] A variety of performance tests were performed on the electro-galvanized ultra-high-strength dual-phase steels resistant to delayed cracking in Examples 1-6 and the steels in Comparative Examples 1-14. The test results obtained are listed in Table 3.

[0046] Table 3 lists the performance test results for the electro-galvanized ultra-high-strength dual-phase steels resistant to delayed cracking in Examples 1-6 and the steels in Comparative Examples 1-14. 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.

[0047] 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.

Table 3

No.	Yield strength (MPa)	Tensile strength (MPa)	Elongation after fracture (%)	Stress level 0.6*TS	Stress level 0.8*TS	Stress level LOTS	Stress level 1.2*TS	Initial hydrogen content (ppm)
Ex. 1	575	988	16.4	○	○	○	○	0.7
Ex. 2	602	1001	15.8	○	○	○	○	1.0
Ex. 3	628	1015	15.1	○	○	○	○	0.6
Ex. 4	655	1028	13.9	○	○	○	○	2.0
Ex. 5	684	1032	13.1	○	○	○	○	2.0
Ex. 6	703	1044	12.6	○	○	○	○	1.5
Comp. Ex. 1	477	865	20.6	○	○	○	○	0.6
Comp. Ex. 2	745	1088	9.8	○	○	X	X	1.9
Comp. Ex. 3	465	884	21.2	○	○	○	○	0.5
Comp. Ex. 4	753	1091	10.2	○	○	X	X	1.8
Comp. Ex. 5	625	1008	13.9	○	○	X	X	1.5
Comp. Ex. 6	616	996	14.2	○	○	X	X	1.0
Comp. Ex. 7	594	965	16.6	○	○	○	○	0.9
Comp. Ex. 8	749	1079	10.8	○	○	○	X	1.8
Comp. Ex. 9	762	1085	10.4	○	○	○	X	2.0
Comp. Ex. 10	599	975	16.7	○	○	○	○	0.9
Comp. Ex. 11	518	924	19.6	○	○	○	○	0.6
Comp. Ex. 12	805	1127	7.8	○	○	○	X	3.5

(continued)

No.	Yield strength (MPa)	Tensile strength (MPa)	Elongation after fracture (%)	Stress level 0.6*TS	Stress level 0.8*TS	Stress level LOTS	Stress level 1.2*TS	Initial hydrogen content (ppm)
Comp. Ex. 13	623	969	16.5	○	○	○	○	0.8
Comp. Ex. 14	715	1065	12.8	○	○	○	X	1.7
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.								

[0048] As it can be seen from Table 3, each Example according to the present disclosure had a yield strength of ≥ 550 MPa, a tensile strength of ≥ 980 MPa, an elongation after fracture of ≥ 12%, and an initial hydrogen content of ≤3 ppm. The electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking in each Example had an ultra-high strength and a delayed cracking performance that was significantly better than that of a comparative steel grade of the same level. No delayed cracking occurred when the steel plate was soaked in 1 mol/L hydrochloric acid for 300 hours under a pre-stress of greater than or equal to the tensile strength. The excellent performances of the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to the present disclosure can meet the industrial requirements, suitable for manufacture of automotive safety structural parts. It is highly valuable and promising for popularization and application.

[0049] 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.

[0050] 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 electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking, wherein the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking has a matrix structure of ferrite+tempered martensite, and comprises the following chemical elements in mass percentages, in addition to Fe:
   C: 0.07-0.1%, Si: 0.05-0.3%, Mn: 2.0-2.6%, Cr: 0.2-0.6%, Mo: 0.1-0.25%, Al: 0.02-0.05%, Nb: 0.02-0.04%, V: 0.06-0.2%.

2. The electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to claim 1, wherein the chemical elements have the following mass percentages:
   C: 0.07-0.1%, Si: 0.05-0.3%, Mn: 2.0-2.6%, Cr: 0.2-0.6%, Mo: 0.1-0.25%, Al: 0.02-0.05%, Nb: 0.02-0.04%, V: 0.06-0.2%, and a balance of Fe and other unavoidable impurities.

3. The electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to claim 1 or 2, wherein it further comprises 0.0015-0.003% of element B.

4. The electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking 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 ≤0.012%, S≤0.003%, N<_0.005%.

5. The electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to claim 1 or 2,

wherein a phase proportion of the tempered martensite is >50%.

6. The electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to claim 1 or 2, wherein dispersive fine carbide particles are precipitated in the matrix structure, wherein the carbide particles include MoC, VC, Nb(C, N), and wherein the carbide particles are all distributed in the matrix structure in a coherent form.

7. The electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to claim 6, wherein the carbide particles have a size of ≤60 nm.

8. The electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to claim 1 or 2, wherein the tempered martensite further comprises coherently distributed ε carbide.

9. The electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to claim 1 or 2, wherein its properties meet at least one of the following: yield strength ≥550 MPa, tensile strength ≥980 MPa, elongation after fracture ≥12%, initial hydrogen content ≤3 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.

10. A manufacturing method for the electro-galvanized ultra-high-strength dual-phase steel resistant to delayed cracking according to any one of claims 1-9, wherein the method comprises the following steps:

(1) Smelting and continuous casting;
(2) Hot rolling;
(3) Cold rolling;
(4) Annealing: heating to an annealing soaking temperature of 780-820 °C at a heating rate of 3-10 °C/s, an 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 650-730 °C;
(5) Tempering: tempering temperature: 200-280 °C; tempering time: 100-400 s;
(6) Temper rolling;
(7) Electroplating.

11. The manufacturing method according to claim 10, wherein in the 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 1200-1260 °C; then rolled with a finishing rolling temperature being controlled at 840-900 °C; then cooled at a rate of 20-70 °C/s after rolling; then coiled at a coiling temperature of 580-630 °C; and then subjected to heat preservation treatment after 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 ≤0.3%.

15. The manufacturing method according to claim 10, wherein in step (2), a cast slab is controlled to be soaked at a temperature of 1210-1245 °C; in step (4), heating at a heating rate of 3-10 °C/s is performed to achieve an annealing soaking temperature of 790-810 °C, the annealing time being 40-160 s, and then rapid cooling is performed at a rate of 35-80 °C/s, a starting temperature of the rapid cooling being 650-730 °C; in step (5), the tempering temperature is 210-270 °C, and the tempering time is 120-300 s.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2021/095802

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/38(2006.01)i; C22C 38/26(2006.01)i; C22C 38/24(2006.01)i; C22C 38/22(2006.01)i; C22C 38/06(2006.01)i; C22C 38/02(2006.01)i; B22D 11/16(2006.01)i; C21D 1/26(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 B22D 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; ISI_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, 铬, 钼, 铝, 铌, 钒, 铁素体, 回火马氏体, 电镀, C, Si, Mn, Cr, Mo, Al, Nb, V, double phase, two phase, carbon, silicon, manganese, chromium, molybdenum, aluminium, niobium, vanadium, ferrite, temper+, martensite, electrogalvaniz+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 1930316 A (NIPPON STEEL CORPORATION) 14 March 2007 (2007-03-14) description page 2 line 17 - page 4 line 24	1-15
X	CN 107208205 A (JFE STEEL CORPORATION) 26 September 2017 (2017-09-26) description, paragraphs [0020]-[0034]	1-15
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A	JP 2008208406 A (JFE STEEL K. K.) 11 September 2008 (2008-09-11) entire document	1-15

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

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Date of the actual completion of the international search	Date of mailing of the international search report
20 July 2021	**12 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/CN2021/095802

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