

COLD-ROLLED HIGH-STRENGTH STEEL PLATE WITH EXCELLENT PHOSPHATING PERFORMANCE, AND MANUFACTURING METHOD THEREFOR

Technical Field

5 The present invention relates to a steel plate and a manufacturing method therefor, and particularly relates to a cold-rolled steel plate and a manufacturing method therefor.

Background Art

High-strength steel is a material that is being used more and more widely at present.
10 Cold-rolled high-strength steel usually requires an addition of relatively high contents of alloying elements such as C, Si, Mn, Cr, and Al, combined with the continuous annealing process and phase transformation strengthening to achieve certain strength and formability.

Phosphating is a pretreatment process before automotive electrophoretic coating. By immersing a steel plate or a part made of a steel plate in phosphating solution, a layer of
15 insoluble phosphating film is formed on the surface of the steel plate or the part, thereby improving the adhesion of the paint film.

However, when using continuous annealing to produce cold-rolled high-strength steel, alloying elements such as Si and Mn in the steel can form external oxidation on a surface of a strip steel after annealing. The external oxidation of Si and Mn on the surface of a steel plate can
20 affect the nucleation and growth of the phosphating film, thereby affecting the coating quality of automotive parts. Therefore, in recent years, the phosphating performance of high-strength steel has gradually attracted attention.

For example, the Chinese patent application with publication number CN107419185A, publication date December 1, 2017, and titled "A Cold-rolled Steel Plate with Good
25 Phosphating Performance and Production Method Therefor" mainly produces a cold-rolled plate with good phosphating performance by precisely controlling the composition, and simultaneously through hot rolling, pickling, five-stand full six-roller cold rolling, continuous annealing, and leveling process.

For another example, the Chinese patent application with publication number
30 CN111910123A, publication date November 10, 2020, and titled "Cold-Rolled Continuous Annealing Ultra-High Strength Steel with Good Phosphating Performance and Preparation Method Therefor" discloses an annealing process for obtaining good phosphating performance of cold-rolled continuously annealing ultra-high strength steel. It specifies that a H₂ content of an annealing atmosphere is 6% to 15%, a dew point is -45 °C to -41 °C, and an oxygen content

is 2 ppm to 5 ppm, whose purpose is to inhibit the selective oxidation of alloying elements through the above parameters, thereby achieving good phosphating performance.

It can be seen from this that in the prior art, controlling the content of alloying elements is a method for obtaining excellent phosphating performance, but limiting the content of alloy elements will affect the properties of the material.

In addition, controlling the annealing atmosphere is another method for improving the phosphating performance of a cold-rolled steel plate with high alloy content. However, a method of controlling both dew point and oxygen content at a relatively low level is rather difficult and costly; while a method of controlling a dew point at a relatively high level will cause decarburization on the surface of a steel plate, therefore this method also has certain limitations.

Based on this, it is desired to provide a novel cold-rolled high-strength steel plate that achieves excellent phosphating performance.

Summary

One object of the present invention is to provide a cold-rolled high-strength steel plate with excellent phosphating performance, which achieves excellent phosphating performance by controlling Mn and Si elements not enriching on the surface of the steel plate.

Based on the above-mentioned object, the present invention provides a cold-rolled high-strength steel plate with excellent phosphating performance, wherein, on an element mass percentage content-depth distribution curve with a depth in the range of 0-1000 nm from the surface of the steel plate, a mass percentage peak value of Mn element Mn_p is $\leq 10.0\%$, and a mass percentage peak value of Si Si_p is $\leq 4.0\%$, and both the mass percentage peak value of Mn element Mn_p and the mass percentage peak value of Si element Si_p are located at a depth of ≥ 50 nm from the surface of the steel plate. Herein, a mass percentage peak value of Mn element Mn_p and a mass percentage peak value of Si element Si_p are detected by glow discharge optical emission spectroscopy (GDOES).

In the present invention, the key to achieving excellent phosphating performance of a cold-rolled high-strength steel is that on an element mass percentage content-depth distribution curve with a depth in the range of 0-1000 nm from a surface layer of a steel plate detected by glow discharge optical emission spectroscopy (GDOES), a mass percentage peak value of Mn Mn_p is $\leq 10.0\%$, and a mass percentage peak value of Si Si_p is $\leq 4.0\%$. This is because in a cold-rolled high-strength steel produced through continuous annealing, alloying elements, such as Mn and Si, form external oxidation on the annealed steel plate, and the Si and Mn elements will be significantly enriched on the surface. The mass percentage peak values of Mn or Si on

the surface of the steel plate can reach several to dozens of times that of the matrix Mn or Si. These oxides will hinder the reaction between the phosphating solution and the steel plate, thereby affecting the phosphating performance of the high-strength steel.

Through research, the inventors have found that when a mass percentage peak value of Mn Mn_p exceeds 10% or a mass percentage peak value of Si Si_p exceeds 4%, on an element mass percentage content-depth distribution curve with a depth in the range of 0-1000 nm from a surface layer of a steel plate, the phosphating performance of a steel plate is poor. Therefore, the present invention controls $Mn_p \leq 10\%$ and $Si_p \leq 4\%$. In some embodiments, the present invention controls $Mn_p \leq 8.5\%$ and $Si_p \leq 3.0\%$. In some embodiments, Mn_p is between 5.0 and 10.0%, and Si_p is between 0.1 and 3.0%.

To achieve excellent phosphating performance, the present invention controls a depth of Mn_p t_{pMn} to ≥ 50 nm and a depth of Si_p t_{pSi} to ≥ 50 nm. This is because through research the inventors have found that when a depth of Mn_p and a depth of Si_p are less than 50 nm, even if Mn_p is $\leq 10\%$ or Si_p is $\leq 4\%$, external oxidation of Si and Mn at local positions cannot be avoided, and the local phosphating performance is poor.

Further, in the cold-rolled high-strength steel plate with excellent phosphating performance of the present invention, the mass percentage peak value of Mn element Mn_p and the mass percentage peak value of Si element Si_p are located at a depth of 50-500 nm from the surface of the steel plate.

Although the phosphating performance of a cold-rolled high-strength steel is also excellent when t_{pMn} is > 500 nm and t_{pSi} is > 500 nm, achieving these values requires a higher pre-oxidation temperature and a longer pre-oxidation time. Therefore, a preferred t_{pMn} of the present invention is ≤ 500 nm, and t_{pSi} is ≤ 500 nm. In some embodiments, the present invention controls t_{pMn} between 100 nm and 450 nm, and t_{pSi} between 100 nm and 450 nm.

Further, in the cold-rolled high-strength steel plate with excellent phosphating performance of the present invention, on an element mass percentage content-depth distribution curve with a depth in the range of 0-1000 nm from the surface of the steel plate, a mass percentage peak value of Fe element Fe_p is $\geq 85\%$, and a mass percentage peak value of Fe element Fe_p is located within a depth range of 0- t_{pSi} from the surface of the steel plate, wherein t_{pSi} represents a depth position where a mass percentage peak value of Si element Si_p appears. In the present invention, Fe_p refers to a mass percentage peak value of Fe element with a depth in the range of 0- t_{pSi} from the surface of the steel plate.

When Fe_p is $\geq 85\%$, it can be ensured that during the phosphating process of a cold-rolled high-strength steel, there is sufficient Fe on the surface to react with the phosphating solution,

thereby achieving excellent phosphating performance.

Further preferably, when Fe_p is $\geq 90\%$, the phosphating performance is even better.

Further, a cold-rolled high-strength steel plate with excellent phosphating performance of the present invention comprises a base layer, a surface layer and a transition layer between the
5 base layer and the surface layer in the thickness direction; wherein a microstructure of the surface layer is ferrite.

Further, in a cold-rolled high-strength steel plate with excellent phosphating performance of the present invention, a thickness of the surface layer is 50-500 nm.

When the thickness of the surface layer, i.e., the ferrite layer, is 50-500 nm, it can be
10 ensured that a mass percentage peak value of Mn Mn_p and a mass percentage peak value of Si element Si_p are located at a depth t_p of 50-500 nm, on the element mass percentage content-depth distribution curve detected by glow discharge optical emission spectroscopy (GDOES).

In a high-strength steel with excellent phosphating performance of the present invention,
15 when a thickness of a surface layer is 50-500 nm, the Mn and Si elements that diffuse outward from the matrix during annealing are primarily enriched in a transition layer. The ferrite surface layer can effectively prevent alloying elements such as Mn and Si from diffusing to the surface of the ferrite, thereby ensuring that a mass percentage peak value of Mn Mn_p and a mass percentage peak value of Si Si_p are located at a depth t_p of 50-500 nm, on the element mass
20 percentage content-depth distribution curve detected by glow discharge optical emission spectroscopy (GDOES).

Further, in a cold-rolled high-strength steel plate with excellent phosphating performance of the present invention, a microstructure of the base layer is martensite + ferrite, or martensite + ferrite + residual austenite.

Further, in a cold-rolled high-strength steel plate with excellent phosphating performance
25 of the present invention, the transition layer comprises oxides of Mn, Si, and Fe and/or composite oxides of Mn, Si, and Fe. Oxides of Mn, Si, and Fe refer to oxides of Mn, oxides of Si, or oxides of Fe. Composite oxides of Mn, Si, and Fe refer to oxides of two or three elements of Mn, Si, and Fe.

Furthermore, the oxides of Mn, Si and Fe are at least one of the following: MnO , MnO_2 , SiO_2 , FeO , Fe_2O_3 and Fe_3O_4 ; the composite oxides of Mn, Si and Fe are at least one of the
30 following: $MnSiO_3$, Mn_2SiO_4 , Mn_2FeO_3 , Mn_2FeO_4 , $FeSiO_3$, Fe_2SiO_3 and Fe_2SiO_4 .

Further, a cold-rolled high-strength steel plate with excellent phosphating performance of the present invention has a tensile strength of ≥ 780 MPa. Further, a cold-rolled

high-strength steel plate with excellent phosphating performance of the present invention has a tensile strength of ≥ 980 MPa. Further, a cold-rolled high-strength steel plate with excellent phosphating performance of the present invention has a tensile strength of ≥ 1180 MPa.

5 There are no special restrictions on the type and elemental composition of a cold-rolled high-strength steel in this application. Various cold-rolled high-strength steels known in the art are prepared by the method of the present invention, thereby having the structure (such as the element distribution described herein) and phosphating performance described herein.

10 In some embodiments, a cold-rolled high-strength steel sheet with excellent phosphating performance of the present invention comprises the following elements with mass percentages as follows:

C: 0.07-0.30%, Si: 0.07-3.0%, Mn: 1.5-5.0%.

15 Furthermore, the mass percentages of each chemical elements of a cold-rolled high-strength steel sheet with excellent phosphating performance of the present invention are as follows:

C: 0.07-0.30%, Si: 0.07-3.0%, Mn: 1.5-5.0%, and one or more of Nb, Ti, Al, B, Cr, Mo, Ni, and V, with a total mass percentage of Nb, Ti, Al, B, Cr, Mo, Ni, and V being less than or equal to 2.0%; and a balance of Fe and inevitable impurities.

20 The inevitable impurities are mainly S and P, and their contents are expected to be as low as possible. In some embodiments, P can be controlled to be $\leq 0.05\%$ and S can be controlled to be $\leq 0.02\%$.

The design principles of the above elements are as follows:

25 C: Carbon is a solid solution strengthening element necessary for ensuring strength in steel. When the C content is too low, the strength of the steel is relatively low, while when the C content is too high, the weldability of the steel is poor. Therefore, the C content of the present invention is controlled at 0.07-0.30%.

Si: Silicon has an effect of improving both the strength and formability of the steel, but when the Si content is too high, the difficulty of production and manufacturing increases.

30 Therefore, the Si content of the present invention is controlled at 0.07-3.0%.

Mn: Manganese is an element that increases the stability of austenite, has the effect of reducing the critical cooling rate during quenching of steel and improving the hardenability of steel. Mn can also improve the work hardening performance of steel, thereby increasing the strength of steel. Therefore, the Mn content of the present invention is controlled at 1.5-5.0%.

Nb, Ti, Al, B, Cr, Mo, Ni, and V elements have the effects of solid solution strengthening, refining microstructure, and improving hardenability. Adding a small amount helps to further improve the strength and toughness of steel. Therefore, the present invention may also comprise one or more of Nb, Ti, Al, B, Cr, Mo, Ni, and V elements, and their total amount by mass percentage is controlled to be less than or equal to 2.0%. In some embodiments, when present, the content of Nb may be 0.01-0.1%, the content of Ti may be 0.01-0.05%, the content of Al may be 0.01-1.5%, the content of B may be 0.0002-0.0008%, the content of Cr may be 0.01-0.5%, the content of Mo may be 0.1-0.3%, the content of Ni may be 0.0001-0.03%, and the content of Ni may be 0.01-0.1%.

Another object of the present invention is to provide a manufacturing method for the cold-rolled high-strength steel plate with excellent phosphating performance. The manufacturing method adopts a unique continuous annealing process to control the enrichment position and enrichment amount of the Mn and Si elements in the steel plate, thereby achieving excellent phosphating performance.

Based on the above object, the present invention provides a manufacturing method for the above cold-rolled high-strength steel sheet with excellent phosphating performance, comprising the following steps of: smelting, casting, hot rolling, pickling, cold rolling, and continuous annealing; wherein, in the continuous annealing step, a first-stage heating is performed to the cold-rolled sheet in an oxidizing atmosphere, then a second-stage heating and soaking are performed in a reducing atmosphere, followed by cooling and coiling.

In the manufacturing method of the present invention, smelting, casting, hot rolling, pickling and cold rolling all adopt existing conventional processes. In an exemplary method, in the hot rolling step, a heating temperature is controlled to be 1150-1260 °C, a start temperature of the finishing rolling is 1100-1220 °C, and a final temperature of the finishing rolling is 900-950 °C. In the cold rolling step, a cold rolling reduction ratio is controlled to be $\geq 50\%$. In some embodiments, commercially available cold-rolled steel can be used to implement the annealing process of the present application.

In the continuous annealing step, the purpose of adopting an oxidizing atmosphere in the first-stage heating is to form iron oxide on the surface of the steel plate during the first-stage heating process, and the purpose of adopting a reducing atmosphere in the second-stage heating and soaking is to reduce the iron oxide formed during the first-stage heating process to form ferrite, thereby forming a surface layer composed entirely of ferrite, so that Mn and Si elements cannot be enriched on the surface of the steel plate.

Further, in some embodiments of the manufacturing method of the present invention,

the oxidizing atmosphere of the first-stage heating is obtained by controlling the air-fuel ratio of the direct-fired furnace to be 0.95-1.05.

In some embodiments, when the first-stage heating is performed using a direct-fired furnace, an oxidizing atmosphere can be achieved by adjusting the air-fuel ratio. When the air-fuel ratio is less than 0.95, oxidation is insufficient; when the air-fuel ratio is greater than 1.05, excessive oxidation occurs. Therefore, the air-fuel ratio is controlled to be 0.95-1.05.

Further, in other embodiments of the manufacturing method of the present invention, the oxidizing atmosphere of the first-stage heating is a mixture gas of N_2 and O_2 , wherein the volume percentage of O_2 is 0.01-1%.

In other embodiments, when the first-stage heating is performed using an infrared radiation furnace, an oxidizing atmosphere is achieved by using a mixed gas of N_2 and O_2 . When the volume percentage of O_2 is less than 0.01%, oxidation is insufficient; when the volume percentage of O_2 is greater than 1%, further increasing O_2 will lead to excessive oxidation. Therefore, the volume percentage of O_2 is controlled to be 0.01-1%.

Further, in the manufacturing method of the present invention, the heating rate of the first-stage heating is 1-50 °C/s, the first-stage heating is heating from room temperature to T_1 , and T_1 and the mass percentage of Si satisfy: $570 + 4000 \times Si \leq T_1 \leq 600 + 9000 \times Si$.

The thickness of the oxide layer on the surface of the steel plate will increase as the end temperature T_1 of the first-stage heating increases. Therefore, in order to obtain an appropriate thickness of an oxide layer, the upper and lower limits of the T_1 temperature need to be controlled. Through research, the inventors found that, when the T_1 temperature is the same, the thickness of the iron oxide on the surface of the steel plate is also affected by a composition of a steel plate, with the Si content having the most significant influence. When the Si content in a steel plate is relatively high, a higher T_1 temperature is required to obtain the iron oxide with same thickness during the first-stage heating. An appropriate thickness of an oxide layer can be obtained when the T_1 temperature and the Si content of a steel plate satisfy the following relationship: $570 + 4000 \times Si \leq T_1 \leq 600 + 9000 \times Si$. In some embodiments, T_1 is 580 °C - 800 °C. Preferably, the thickness of an oxide layer formed during the first-stage heating is 50-500 nm.

Further, in the manufacturing method of the present invention, a dew point of the oxidizing atmosphere of the first-stage heating is ≥ -50 °C, preferably ≥ -40 °C. In some embodiments, a dew point of the oxidizing atmosphere of the first-stage heating is between -50°C and 50°C. In some embodiments, a dew point of the oxidizing atmosphere of the first-stage heating is between -50 °C and 0 °C.

Further, in the manufacturing method of the present invention, a dew point of the reducing atmosphere of the second-stage heating and soaking is $\leq 10\text{ }^{\circ}\text{C}$, such as $\leq 0\text{ }^{\circ}\text{C}$, $\leq -10\text{ }^{\circ}\text{C}$ or $\leq -20\text{ }^{\circ}\text{C}$. In some embodiments, a dew point of the reducing atmosphere of the second-stage heating and soaking is $10\text{ }^{\circ}\text{C}$ to $-50\text{ }^{\circ}\text{C}$, such as $0\text{ }^{\circ}\text{C}$ to $-50\text{ }^{\circ}\text{C}$ or $-20\text{ }^{\circ}\text{C}$ to $-50\text{ }^{\circ}\text{C}$.

It should be particularly noted here that, in the present invention, a dew point of the atmosphere of the first-stage heating, the second-stage heating and soaking is not a necessary technical feature of this case. In other words, even without special control over the dew point of the atmosphere of the first-stage heating, the second-stage heating and soaking, a product characteristic of a mass percentage peak value of Mn $Mn_p \leq 10.0\%$ and a mass percentage peak value of Si $Si_p \leq 4.0\%$ on an element mass percentage content-depth distribution curve with a depth in the range of 0-1000 nm from the surface of the steel plate can be obtained. This is because, during the first-stage heating, when iron oxide is formed, some Mn in the matrix oxidizes along with Fe, but the oxides formed by Si are primarily located in the transition layer. During the second-stage heating and soaking, when the reduced iron is reduced, regardless of the atmosphere's dew point, the selective oxidation of alloying elements such as Mn and Si in the matrix is primarily concentrated below the ferrite formed after the iron oxide is reduced, i.e., in the transition layer, and does not enrich on the surface of ferrite. Therefore, the present invention differs from existing techniques, which promote the internal oxidation of alloy elements and reduce external oxidation by increasing the dew point of reducing atmosphere.

However, the inventors have found that increasing the dew point of the oxidizing atmosphere of the first-stage heating is beneficial for lowering the T_1 temperature. This is because, increasing the dew point of the atmosphere during the first-stage heating will increase the internal oxidation of alloying elements, thereby reducing oxidation of alloying elements at the interface of iron oxide/substrate, especially the oxidation of Si element. Therefore, preferably, a dew point of the oxidizing atmosphere of the first-stage heating is controlled to be $\geq -40\text{ }^{\circ}\text{C}$. Since an excessively high dew point of the second-stage heating and soaking can lead to decarburization, preferably, a dew point of the atmosphere of the second-stage heating and soaking is controlled to be $\leq -20\text{ }^{\circ}\text{C}$.

Further, in the manufacturing method of the present invention, the reducing atmosphere of the second-stage heating and soaking is a mixture gas of N_2 and H_2 , wherein the volume percentage of H_2 is 0.5-20%.

Further, in the manufacturing method of the present invention, the heating rate of the

second-stage heating is 1-20 °C/s, the second-stage heating is heated from T_1 to a soaking temperature of 720-920 °C, and a soaking time is 30-200 s.

The soaking temperature T_2 is controlled to be 720-920 °C, and the soaking time is controlled to be 30-200 s, mainly to obtain an appropriate mechanical property of a cold-rolled high-strength steel, which has little correlation with the phosphating performance.

The cold-rolled high-strength steel plate with excellent phosphating performance of the present invention has the following beneficial effects:

The present invention solves the problem of poor phosphating performance of cold-rolled high-strength steel by controlling the mass percentage peak values of Mn and Si and their depth positions on an element mass percentage content-depth distribution curve of a steel plate, thereby improving the coating performance of a cold-rolled high-strength steel.

In some more preferred embodiments, a steel plate with excellent phosphating performance also has a tensile strength of ≥ 780 MPa.

Description of the Drawing

Fig. 1 is a comparison of mass percentage content-depth distribution curves of Mn element with a depth in the range of 0-1000 nm from the surface of the steel plate of Example A1 and Comparative Example A1 of the present invention.

Fig. 2 is a comparison of mass percentage content-depth distribution curves of Si element with a depth in the range of 0-1000 nm from the surface of the steel plate of Example A1 and Comparative Example A1 of the present invention.

Fig. 3 is a comparison of mass percentage content-depth distribution curves of Fe element with a depth in the range of 0-1000 nm from the surface of the steel plate of Example A1 and Comparative Example A1 of the present invention.

Fig. 4 is a comparison of mass percentage content-depth distribution curves of Mn element with a depth in the range of 0-1000 nm from the surface of the steel plate of Example B1 and Comparative Example B1 of the present invention.

Fig. 5 is a comparison of mass percentage content-depth distribution curves of Si element with a depth in the range of 0-1000 nm from the surface of the steel plate of Example B1 and Comparative Example B1 of the present invention.

Fig. 6 is a comparison of mass percentage content-depth distribution curves of Fe element with a depth in the range of 0-1000 nm from the surface of the steel plate of Example B1 and Comparative Example B1 of the present invention.

Detailed Description

The cold-rolled high-strength steel plate with excellent phosphating performance and the manufacturing method therefor of the present invention will be further explained and illustrated below with reference to specific embodiments and drawings. However, such explanations and descriptions do not constitute an improper limitation on the technical solution of the present invention.

Table 1 lists the composition ratios of the steel grades adopted in each example and comparative example of the present invention.

Table 1 (wt%, with a balance of Fe)

Steel plate code	C	Si	Mn	P	S	Al	Nb	Ti	B	Cr	Mo	V	Ni
A	0.08	0.4	2.2	0.012	0.002	-	0.04	0.03	-	-	-	-	-
B	0.2	1.8	2.3	0.007	0.001	0.03	-	0.02	-	-	-	-	-
C	0.07	0.07	2.1	0.010	0.0008	0.6	-	0.01	0.0006	-	0.2	-	-
D	0.13	0.26	2.4	0.011	0.0017	-	-	-	-	0.4	-	-	-
E	0.22	1.8	2.8	0.014	0.0014	0.03	-	0.02	-	-	-	-	-
F	0.11	1.2	1.5	0.006	0.0007	-	-	-	-	-	-	-	-
G	0.3	3	3	0.022	0.005	1.5	-	-	-	0.5	-	-	-
H	0.09	0.8	1.8	0.0091	0.02	0.03	-	-	0.0004	0.03	-	0.0003	0.07
I	0.2	0.5	5	0.05	0.0017	1.5	-	-	-	-	-	0.02	-

Based on the composition of a steel plate in Table 1, the steel plates of each example and comparative example of the present invention are prepared according to the following steps, and the specific process parameters of the continuous annealing steps of each example and comparative example are listed in Table 2:

(1) conventional smelting;

(2) conventional casting;

(3) conventional hot rolling;

(4) conventional pickling and cold rolling;

(5) continuous annealing: heating the cold-rolled sheet in an oxidizing atmosphere for

the first-stage heating; wherein the heating rate of the first-stage heating is 1-50 °C/s, the first-stage heating is heated from room temperature to T_1 , and T_1 and the mass percentage of Si satisfy: $570 + 4000 \times \text{Si} \leq T_1 \leq 600 + 9000 \times \text{Si}$; then performing the second-stage heating and soaking in a reducing atmosphere, the reducing atmosphere in the

second-stage heating is a mixture gas of N_2 and H_2 , wherein the volume percentage of H_2 is 0.5-20%; followed by cooling and coiling.

In some embodiments, the oxidizing atmosphere of the first-stage heating is a mixture gas of N_2 and O_2 , wherein the volume percentage of O_2 is 0.01-1%.

- 5 In other embodiments, the oxidizing atmosphere of the first-stage heating is obtained by controlling the air-fuel ratio of the direct-fired furnace to be 0.95-1.05.

In some embodiments, the dew point of the oxidizing atmosphere of the first-stage heating is $\geq -40\text{ }^{\circ}\text{C}$, the dew point of the reducing atmosphere of the second-stage heating is $\leq -20\text{ }^{\circ}\text{C}$.

- 10 In some embodiments, the heating rate of the second-stage heating is 1-20 $^{\circ}\text{C/s}$, the second-stage heating is heated from T_1 to a soaking temperature of 720-920 $^{\circ}\text{C}$, and a soaking time is 30-200 s.

Table 2

No.	Steel plate composition code	First-stage heating					Second-stage heating				Soaking			
		Air-fuel ratio	O ₂ content Volume %	H ₂ content Volume %	Dew point °C	Heating rate °C/s	Temperature T ₁ °C	H ₂ content Volume %	Dew point °C	Heating rate °C/s	Temperature T ₂ °C	H ₂ content Volume %	Dew point °C	Time s
Ex. A1	A	/	0.2	/	-50	10	580	2	-50	4	820	2	-50	100
Ex. A2	A	/	0.01	/	-20	5	600	5	-40	4	820	5	-40	100
Ex. A3	A	/	0.5	/	-10	20	580	5	-10	4	800	5	-10	150
Ex. A4	A	/	1	/	-40	1	600	5	-40	5	780	5	-40	120
Ex. A5	A	/	1	/	-40	10	600	5	-20	1	780	5	-20	120
Ex. A6	A	/	1	/	-40	10	600	0.5	0	5	780	0.5	0	120
Comp. Ex. A1	A	/	/	2	-50	10	580	2	-50	4	820	2	-50	100
Comp. Ex. A2	A	/	/	5	-40	10	600	5	-40	5	780	5	-40	120
Comp. Ex. A3	A	/	/	5	-20	1	600	5	-20	5	780	5	-20	120
Comp. Ex. A4	A	/	/	5	0	10	600	5	0	5	780	5	0	120
Ex. B1	B	0.95	/	/	50	50	650	2	-40	5	870	2	-40	180
Ex. B2	B	1	/	/	50	50	680	2	-40	5	870	2	-40	180
Ex. B3	B	1.05	/	/	50	50	700	20	-40	20	870	20	-40	180
Ex. B4	B	/	0.5	/	-10	10	730	5	-10	4	920	5	-10	180
Comp. Ex. B1	B	/	/	2	-20	10	700	2	-20	4	870	2	-20	200
Comp. Ex. B2	B	<u>0.9</u>	/	5	-40	35	570	5	-40	10	870	5	-40	180
Comp. Ex. B3	B	1	/	5	10	50	<u>550</u>	5	10	20	870	5	10	180
Ex. C1	C	/	0.5	/	-35	15	580	10	-20	5	720	10	-20	30
Ex. C2	C	0.95	/	/	40	25	580	5	-20	5	780	5	-20	120

Comp. Ex. C1	C	/	/	5	-20	15	<u>570</u>	10	-20	5	780	10	-20	30
Ex. D1	D	/	0.5	/	0	10	590	5	0	5	780	5	0	120
Ex. D2	D	/	0.5	/	0	10	620	5	0	5	780	5	0	120
Comp. Ex. D1	D	/	/	5	0	10	590	5	0	5	780	5	0	120
Comp. Ex. D2	D	/	/	5	-10	10	620	5	-10	5	780	5	-10	120
Ex. E1	E	/	0.2	/	-40	10	750	5	-40	5	840	5	-40	120
Ex. E2	E	/	0.2	/	-40	10	750	5	-20	5	840	5	-20	120
Ex. E3	E	/	0.2	/	-40	10	750	5	0	5	840	5	0	120
Comp. Ex. E1	E	/	/	5	-40	10	750	5	-40	5	840	5	-40	120
Comp. Ex. E2	E	/	/	5	-40	10	750	5	-20	5	840	5	-20	120
Comp. Ex. E3	E	/	/	5	-40	10	750	5	0	5	840	5	0	120
Ex. F1	F	0.95	/	/	42	50	618	5	0	5	800	5	-30	200
Comp. Ex. F1	F	/	/	5	-30	20	630	5	-30	5	845	5	-30	150
Ex. G1	G	/	0.05	/	10	10	800	2	-40	10	850	2	-40	120
Ex. G2	G	/	0.05	/	10	10	800	2	-10	10	850	2	-10	120
Ex. G3	G	/	0.05	/	10	10	800	2	10	10	850	2	10	120
Comp. Ex. G1	G	/	/	2	10	10	700	2	-40	10	850	2	-40	120
Comp. Ex. G2	G	/	/	2	10	10	700	2	-10	10	850	2	-10	120
Ex. H	H	/	0.5	/	-50	25	602	5	10	5	780	5	10	120
Ex. I	I	/	0.5	/	-50	25	590	5	-30	5	845	5	-30	240

In Table 2 above, examples with an air-fuel ratio indicated by "/" indicate that the oxidizing atmosphere adopted in these examples is a mixed gas of N₂ and O₂. The air-fuel ratio and oxygen content of Comparative Examples A1-A4, D1-D2, E1-E3, F1, and G1-G2 are all indicated by "/", indicating that no oxidizing atmosphere is used in the first-stage heating in these comparative examples. The codes "A," "B," ..., "H," and "I" of each example and comparative example in Table 2 indicate that the composition of the steel plate corresponding to the code in Table 1 is used.

Table 3 lists the characteristics of the steel plates of each example and comparative example produced using the compositions of the steel plates of A-I and the process parameters listed in Table 2, as well as the phosphating performance corresponding to each steel plate, wherein Mn_p, Si_p, t_{pSi}, t_{pMn}, and Fe_p are detected by GDOES.

Table 3

No.	Mn _p	Si _p	t _{pMn}	t _{pSi}	Fe _p	phosphating performance
	mass%	mass%	nm	nm	mass%	
Ex. A1	6.4	1.2	224	228	87.5	○
Ex. A2	8.2	0.8	272	275	92.0	○
Ex. A3	7.2	1	420	427	85.0	○
Ex. A4	6.2	1.2	181	188	90.1	○
Ex. A5	7.2	1	188	298	89.1	○
Ex. A6	6	1	213	222	88.7	○
Comp. Ex. A1	<u>25.3</u>	3.2	<u>6.0</u>	<u>7.5</u>	<u>23.0</u>	×
Comp. Ex. A2	<u>30.7</u>	3.6	<u>11.8</u>	<u>13.2</u>	<u>15.6</u>	×
Comp. Ex. A3	<u>29.8</u>	3.8	<u>12.7</u>	<u>13.8</u>	<u>26.0</u>	×
Comp. Ex. A4	<u>25.5</u>	2.7	<u>9.3</u>	<u>10.2</u>	<u>37.0</u>	×
Ex. B1	9.1	2.1	316	323	91.4	○
Ex. B2	5.2	3.5	380	390	88.8	○
Ex. B3	6.5	2.8	450	455	93.2	○
Ex. B4	8.3	2.3	280	283	89.1	○
Comp. Ex. B1	<u>30.3</u>	<u>12.2</u>	<u>15.9</u>	<u>16.4</u>	<u>5.4</u>	×
Comp. Ex. B2	<u>33.1</u>	<u>12.9</u>	<u>9.7</u>	<u>11.2</u>	<u>4.2</u>	×
Comp. Ex. B3	<u>17.9</u>	<u>4.9</u>	<u>5.4</u>	<u>6.8</u>	<u>34.9</u>	×
Ex. C1	7.4	0.2	170	174	92.1	○
Ex. C2	5.9	0.1	120	123	91.2	○
Comp. Ex. C1	<u>59.3</u>	2.9	<u>12.5</u>	<u>13.0</u>	<u>20.2</u>	×

Ex. D1	6.1	1.2	165	171	87.9	○
Ex. D2	7.2	1.3	248	261	91.2	○
Comp. Ex. D1	<u>46.3</u>	1.9	<u>4.6</u>	<u>5.5</u>	<u>27.7</u>	×
Comp. Ex. D2	<u>53.9</u>	3.1	<u>2.1</u>	<u>3.2</u>	<u>14.3</u>	×
Ex. E1	9.2	2.1	298	305	90.8	○
Ex. E2	7.4	1.9	306	324	90.6	○
Ex. E3	6.6	2.1	305	320	88.1	○
Comp. Ex. E1	<u>29.5</u>	<u>11.8</u>	<u>24.1</u>	<u>25.3</u>	<u>12.5</u>	×
Comp. Ex. E2	<u>23</u>	<u>9.3</u>	<u>11.2</u>	<u>13.4</u>	<u>26.5</u>	×
Comp. Ex. E3	<u>17.7</u>	<u>5.6</u>	<u>6.5</u>	<u>8.0</u>	<u>37.7</u>	×
Ex. F1	7.8	2.1	230	237	93.2	○
Comp. Ex. F1	<u>51.2</u>	<u>6.8</u>	<u>9.5</u>	<u>11.0</u>	<u>5.9</u>	×
Ex. G1	9.3	3.5	198	212	89.7	○
Ex. G2	8	2.9	192	200	90.5	○
Ex. G3	6.1	2.9	211	220	91.0	○
Comp. Ex. G1	<u>51.9</u>	<u>5.3</u>	<u>4.5</u>	<u>6.2</u>	<u>19.9</u>	×
Comp. Ex. G2	<u>52.5</u>	3.3	<u>4.7</u>	<u>6.2</u>	<u>23.1</u>	×
Ex. H1	6.4	2.9	50	53	86.8	○
Ex. I1	9.8	1.4	120	128	85.2	○

Figures 1, 2, and 3 respectively show the element mass percentage content-depth distribution curves of Mn, Si, and Fe with a depth in the range of 0-1000 nm from the surface of the steel plate of Example A1 and Comparative Example A1. The characteristic values Mn_p , Si_p , Fe_p , and t_p are marked on the curves. t_p in Figure 1 represents t_{pMn} , t_p in Figure 2 represents t_{pSi} , and t_p in Figure 3 represents t_{pFe} .

As shown in Table 2, Example A1 undergoes the first-stage heating in an oxidizing atmosphere, while it is heated to 580 °C at a heating rate of 10 °C/s. The oxidizing atmosphere is a mixture gas of N₂ and O₂, wherein a volume percentage of O₂ is 0.2%, and a dew point is -50 °C. Then the second-stage heating and soaking are carried out in a reducing atmosphere, wherein a heating rate is 4 °C/s, a soaking temperature is 820 °C, and a soaking time is 100 s. The reducing atmosphere in the second-stage heating and soaking is a mixture gas of N₂ and H₂, wherein a volume percentage of H₂ is 2%, and a dew point of the atmosphere is -50 °C.

GDOES is used to detect the element depth distribution on a surface of an annealed steel plate, and the element mass percentage content-depth distribution curves of Mn, Si, and Fe with

a depth in the range of 0-1000 nm as shown in Figures 1 to 3 are obtained.

Comparative Example A1 undergoes the first-stage heating, the second-stage heating and soaking in a reducing atmosphere, with a heating rate, a temperature and a time all being the same as those of Example A1. The element mass percentage content-depth distribution curves of Mn, Si, and Fe with a depth in the range of 0-1000 nm from a surface of Comparative Example A1 after annealing are shown in Figures 1 to 3.

Example A1 and Comparative Example A1 are subjected to phosphating treatment under the same conditions. The phosphating film on the surface of Example A1 is uniform and dense, and the phosphating performance meets the requirements (in Table 2-2 indicated by "o").

However, the phosphating film on the surface of Comparative Example A1 is sparse, with a large area not covered by the phosphating film, and the phosphating performance does not meet the requirements (in Table 2-2 indicated by "x"). Herein, phosphating performance is judged by observing the phosphating film on the surface of the steel plate after phosphating treatment. A coverage rate of the phosphating film is 100%, a size of phosphating crystals is less than 12 microns, and a weight of the phosphating film is more than 2 g/m², indicating that the phosphate performance meets the requirements. Phosphating treatment is carried out using commercially available treatment agents. The specific steps and processes are as follows: (1) pre-degreasing spray: 45–55 °C, 1 min; (2) degreasing spray: 45–55 °C, 2.0 min; (3) second water cleaning spray: room temperature, 1 min; (4) surface conditioning spray: room temperature, 1 min; (5) phosphating spray: 50–60 °C, 2.0 min; (6) water cleaning spray: room temperature, 1 min; (7) Drying.

Figures 4, 5, and 6 respectively show the mass percentage content-depth distribution curves of Mn, Si, and Fe elements with a depth in the range of 0-1000 nm from the surface of the steel plate of Example B1 and Comparative Example B1. The characteristic values Mn_p, Si_p, Fe_p, and t_p are marked on the curves. t_p in Figure 4 represents t_{pMn}, t_p in Figure 5 represents t_{pSi}, and t_p in Figure 6 represents t_{pFe}.

Example B1 undergoes the first-stage heating in an oxidizing atmosphere, while it is heated to 650°C at a heating rate of 50 °C/s. The oxidizing atmosphere is achieved by a direct-fired heating furnace, with an air-fuel ratio of 0.95 and a dew point of 50 °C. Then, the second-stage heating and soaking are carried out in a reducing atmosphere, wherein a heating rate is 5 °C/s, a soaking temperature is 870 °C, and a soaking time is 180 s. The atmosphere of the second-stage heating and soaking is a mixed gas of N₂ and H₂, wherein a volume percentage of H₂ is 2%, and a dew point of the atmosphere is -40 °C.

GDOES is used to detect the element depth distribution on a surface of an annealed steel plate, and the element mass percentage content-depth distribution curves of Mn, Si, and Fe with

a depth in the range of 0-1000 nm as shown in Figures 4 to 6 are obtained. The sample of Example B1 is subjected to phosphating treatment, the phosphating film is uniform and dense, and the phosphating performance meets the requirements.

Comparative Example B1 undergoes the first-stage heating, the second-stage heating and soaking in a reducing atmosphere. The reducing atmosphere is a mixed gas of N₂ and H₂, wherein a volume percentage of H₂ is 2% and a dew point of the atmosphere is -20 °C. The soaking temperature and soaking time are the same as those of Example B1. The element mass percentage content-depth distribution curves of Mn, Si, and Fe with a depth in the range of 0-1000 nm from the surface of the steel plate after annealing of Comparative Example B1 are shown in Figures 4-6. The sample of Comparative Example B1 is subjected to phosphating treatment, and the phosphating film is uneven and non-dense, with some local positions not covered by the phosphating film, thus the phosphating performance did not meet the requirements.

The inventors also adapt the method of using scanning electron microscopy to observe the cross-sectional metallography after erosion by nitric acid alcohol solution to detect the microstructures of each example and comparative example. Cross-sectional transmission electron microscopy samples of the surface layer and transition layer are prepared using a focused ion beam microscope. The thickness of the surface layer is measured and the types of oxides in the transition layer are analyzed under a transmission electron microscope, and the test results are listed in Table 4.

Table 4

No.	Thickness of surface layer (nm)	Microstructure of surface layer	Microstructure of base layer	Oxides of Mn, Si, Fe and/or composite oxides of Mn, Si, Fe in the transition layer
Ex. A1	217	F	F+M	MnO, SiO ₂ , FeO, Mn ₂ SiO ₄ , Mn ₂ FeO ₃ , Mn ₂ FeO ₄
Ex. A2	266	F	F+M	MnO, SiO ₂ , FeO, Mn ₂ SiO ₄ , Mn ₂ FeO ₃ , Mn ₂ FeO ₄
Ex. A3	410	F	F+M	MnO, SiO ₂ , FeO, Mn ₂ SiO ₄ , Mn ₂ FeO ₃ , Mn ₂ FeO ₄
Ex. A4	176	F	F+M	MnO, SiO ₂ , FeO, Mn ₂ SiO ₄ , Mn ₂ FeO ₃ , Mn ₂ FeO ₄
Ex. A5	180	F	F+M	MnO, SiO ₂ , FeO, Mn ₂ SiO ₄ , Mn ₂ FeO ₃ , Mn ₂ FeO ₄
Ex. A6	203	F	F+M	MnO, SiO ₂ , FeO, Mn ₂ SiO ₄ ,

				Mn ₂ FeO ₃ , Mn ₂ FeO ₄
Comp. Ex. A1	-	-	F+M	Without transition layer
Comp. Ex. A2	-	-	F+M	Without transition layer
Comp. Ex. A3	-	-	F+M	Without transition layer
Comp. Ex. A4	-	-	F+M	Without transition layer
Ex. B1	303	F	F+M+R	MnO, MnO ₂ , SiO ₂ , MnSiO ₃ FeSiO ₃ , Fe ₂ SiO ₃ , Fe ₂ SiO ₄
Ex. B2	370	F	F+M+R	MnO, MnO ₂ , SiO ₂ , MnSiO ₃ FeSiO ₃ , Fe ₂ SiO ₃ , Fe ₂ SiO ₄
Ex. B3	440	F	F+M+R	MnO, MnO ₂ , SiO ₂ , MnSiO ₃ FeSiO ₃ , Fe ₂ SiO ₃ , Fe ₂ SiO ₄
Ex. B4	265	F	F+M+R	MnO, MnO ₂ , SiO ₂ , MnSiO ₃ FeSiO ₃ , Fe ₂ SiO ₃ , Fe ₂ SiO ₄
Comp. Ex. B1	-	-	F+M+R	Without transition layer
Comp. Ex. B2	-	-	F+M+R	Without transition layer
Comp. Ex. B3	-	-	F+M+R	Without transition layer
Ex. C1	160	F	F+M	MnO, MnO ₂ , Mn ₂ FeO ₃ , Mn ₂ FeO ₄
Ex. C2	108	F	F+M	MnO, MnO ₂ , Mn ₂ FeO ₃ , Mn ₂ FeO ₄
Comp. Ex. C1	-	-	F+M	MnO, MnO ₂ , Mn ₂ FeO ₃ , Mn ₂ FeO ₄
Ex. D1	157	F	F+M	MnO, MnO ₂ , SiO ₂ , Mn ₂ FeO ₃ , Mn ₂ FeO ₄
Ex. D2	238	F	F+M	MnO, MnO ₂ , SiO ₂ , Mn ₂ FeO ₃ , Mn ₂ FeO ₄
Comp. Ex. D1	-	-	F+M	Without transition layer

Comp. Ex. D2	-	-	F+M	Without transition layer
Ex. E1	283	F	F+M+R	MnO, MnO ₂ , SiO ₂ , MnSiO ₃ FeSiO ₃ , Fe ₂ SiO ₃ , Fe ₂ SiO ₄
Ex. E2	290	F	F+M+R	MnO, MnO ₂ , SiO ₂ , MnSiO ₃ FeSiO ₃ , Fe ₂ SiO ₃ , Fe ₂ SiO ₄
Ex. E3	295	F	F+M+R	MnO, MnO ₂ , SiO ₂ , MnSiO ₃ FeSiO ₃ , Fe ₂ SiO ₃ , Fe ₂ SiO ₄
Comp. Ex. E1	-	-	F+M+R	Without transition layer
Comp. Ex. E2	-	-	F+M+R	Without transition layer
Comp. Ex. E3	-	-	F+M+R	Without transition layer
Ex. F1	220	F	F+M+R	MnO, MnO ₂ , SiO ₂ , MnSiO ₃ FeSiO ₃ , Fe ₂ SiO ₃ , Fe ₂ SiO ₄
Comp. Ex. F1	-	-	F+M+R	Without transition layer
Ex. G1	192	F	F+M+R	MnO, MnO ₂ , SiO ₂ , FeO, Fe ₂ O ₃ , Fe ₃ O ₄ , MnSiO ₃ , Mn ₂ SiO ₄ , Mn ₂ FeO ₃ , Mn ₂ FeO ₄ , FeSiO ₃ , Fe ₂ SiO ₃ , Fe ₂ SiO ₄
Ex. G2	184	F	F+M+R	MnO, MnO ₂ , SiO ₂ , FeO, Fe ₂ O ₃ , Fe ₃ O ₄ , MnSiO ₃ , Mn ₂ SiO ₄ , Mn ₂ FeO ₃ , Mn ₂ FeO ₄ , FeSiO ₃ , Fe ₂ SiO ₃ , Fe ₂ SiO ₄
Ex. G3	204	F	F+M+R	MnO, MnO ₂ , SiO ₂ , FeO, Fe ₂ O ₃ , Fe ₃ O ₄ , MnSiO ₃ , Mn ₂ SiO ₄ , Mn ₂ FeO ₃ , Mn ₂ FeO ₄ , FeSiO ₃ , Fe ₂ SiO ₃ , Fe ₂ SiO ₄
Comp. Ex. G1	-	-	F+M+R	Without transition layer
Comp. Ex. G2	-	-	F+M+R	Without transition layer
Ex. H1	50	F	F+M+R	MnO, MnO ₂ , SiO ₂ , FeO, Fe ₂ O ₃ ,

				Fe ₃ O ₄
Ex. I1	112	F	F+M+R	MnO, MnO ₂ , SiO ₂ , FeO, Fe ₂ O ₃ , Fe ₃ O ₄

Note: in Table 4, F represents ferrite, M represents martensite, and R represents residual austenite. The surface layer of each comparative example is denoted by "-", indicating that the comparative examples do not have a surface layer.

- 5 The inventors also test the tensile strength of each example and comparative example by the tensile test in accordance with the national standard GB/T 228.1, and the test results are listed in Table 5.

Table 5

No.	Tensile strength (MPa)
Ex. A1	1043
Ex. A2	1074
Ex. A3	1090
Ex. A4	986
Ex. A5	1025
Ex. A6	1048
Comp. Ex. A1	1050
Comp. Ex. A2	1078
Comp. Ex. A3	1100
Comp. Ex. A4	1002
Ex. B1	1210
Ex. B2	1123
Ex. B3	1024
Ex. B4	1030
Comp. Ex. B1	1190
Comp. Ex. B2	1110
Comp. Ex. B3	1030
Ex. C1	798
Ex. C2	810
Comp. Ex. C1	830
Ex. D1	817
Ex. D2	812

Comp. Ex. D1	806
Comp. Ex. D2	820
Ex. E1	1320
Ex. E2	1200
Ex. E3	1380
Comp. Ex. E1	1310
Comp. Ex. E2	1210
Comp. Ex. E3	1370
Ex. F1	857
Comp. Ex. F1	846
Ex. G1	1511
Ex. G2	1493
Ex. G3	1522
Comp. Ex. G1	1488
Comp. Ex. G2	1497
Ex. H1	1052
Ex. I1	1543

It can be seen from this that a cold-rolled steel plate manufactured by the present invention exhibits excellent phosphating performance while also having relatively high strength.

5 It should be noted that the combination of the various technical features in this case is not limited to the combination described in the claims of this case or the combination described in the specific embodiments. All technical features described in this case can be freely combined or combined in any way unless there is a contradiction between them.

10 It should also be noted that the embodiments listed above are only specific embodiments of the present invention. Obviously, the present invention is not limited to the above embodiments. Similar changes or modifications made therewith are directly derived from the contents disclosed in the present invention or can be easily associated with by those skilled in the art and should all fall within the scope of protection of the present invention.

Claims

What is claimed is:

1. A cold-rolled high-strength steel plate with excellent phosphating performance, wherein on an element mass percentage content-depth distribution curve with a depth in the range of 0-1000 nm from a surface of the steel plate, a mass percentage peak value of Mn element Mn_p is $\leq 10.0\%$, and a mass percentage peak value of Si element Si_p is $\leq 4.0\%$, and both the mass percentage peak value of Mn element Mn_p and the mass percentage peak value of Si element Si_p are located at a depth of ≥ 50 nm from the surface of the steel plate.

2. The cold-rolled high-strength steel plate with excellent phosphating performance according to claim 1, wherein the mass percentage peak value of Mn element Mn_p and the mass percentage peak value of Si element Si_p are located at a depth of 50-500 nm from the surface of the steel plate.

3. The cold-rolled high-strength steel plate with excellent phosphating performance according to claim 1, wherein on an element mass percentage content-depth distribution curve with a depth in the range of 0-1000 nm from the surface of the steel plate, a mass percentage peak value of Fe element Fe_p is $\geq 85\%$, and the mass percentage peak value of Fe element Fe_p is located within a depth range of 0- t_{pSi} from the surface of the steel plate, wherein t_{pSi} represents a depth position where the mass percentage peak value of Si element Si_p appears.

4. The cold-rolled high-strength steel plate with excellent phosphating performance according to any one of claims 1 to 3, wherein the steel plate comprises a base layer, a surface layer and a transition layer between the base layer and the surface layer in the thickness direction; wherein the microstructure of the surface layer is ferrite.

5. The cold-rolled high-strength steel plate with excellent phosphating performance according to claim 4, wherein a thickness of the surface layer is 50-500 nm.

6. The cold-rolled high-strength steel plate with excellent phosphating performance according to claim 4, wherein a microstructure of the base layer is martensite + ferrite, or martensite + ferrite + residual austenite.

7. The cold-rolled high-strength steel plate with excellent phosphating performance according to claim 4, wherein the transition layer comprises oxides of Mn, Si, and Fe and/or composite oxides of Mn, Si, and Fe.

8. The cold-rolled high-strength steel plate with excellent phosphating performance according to claim 7, wherein the oxides of Mn, Si and Fe are at least one of the following: MnO , MnO_2 , SiO_2 , FeO , Fe_2O_3 and Fe_3O_4 ; and the composite oxides of Mn, Si and Fe are at least one of the following: $MnSiO_3$, Mn_2SiO_4 , Mn_2FeO_3 , Mn_2FeO_4 , $FeSiO_3$, Fe_2SiO_3 and Fe_2SiO_4 .

9. The cold-rolled high-strength steel plate with excellent phosphating performance according to claim 1, wherein the cold-rolled high-strength steel plate has a tensile strength of $\geq 780\text{MPa}$.

10. The cold-rolled high-strength steel plate with excellent phosphating performance according to claim 1, wherein the cold-rolled high-strength steel plate comprises the following elements with mass percentages as follows: C: 0.07-0.30%, Si: 0.07-3.0%, Mn: 1.5-5.0%.

11. The cold-rolled high-strength steel plate with excellent phosphating performance according to claim 10, wherein the mass percentages of each chemical elements are:

C: 0.07-0.30%, Si: 0.07-3.0%, Mn: 1.5-5.0%, and one or more of Nb, Ti, Al, B, Cr, Mo, Ni, and V, with a total mass percentage of Nb, Ti, Al, B, Cr, Mo, Ni, and V being less than or equal to 2.0%; and a balance of Fe and inevitable impurities.

12. A manufacturing method for the cold-rolled high-strength steel plate with excellent phosphating performance according to any one of claims 1 to 11, comprising the following steps of: smelting, casting, hot rolling, pickling, cold rolling, and continuous annealing; wherein in the continuous annealing step, a first-stage heating is performed to a cold-rolled plate in an oxidizing atmosphere, then a second-stage heating and soaking are performed in a reducing atmosphere, followed by cooling and coiling.

13. The manufacturing method according to claim 12, wherein the oxidizing atmosphere of the first-stage heating is obtained by controlling an air-fuel ratio of a direct-fired furnace to be 0.95-1.05; alternatively, the oxidizing atmosphere of the first-stage heating is a mixture gas of N_2 and O_2 , wherein the volume percentage of O_2 is 0.01-1%.

14. The manufacturing method according to claim 12, wherein a heating rate of the first-stage heating is 1-50 $^{\circ}\text{C/s}$, the first-stage heating is heated from room temperature to T_1 , and T_1 and a mass percentage of Si satisfy: $570 + 4000 \times \text{Si} \leq T_1 \leq 600 + 9000 \times \text{Si}$; preferably, T_1 is 580-800 $^{\circ}\text{C}$.

15. The manufacturing method according to claim 12, wherein the manufacturing method has one or more of the following features:

a dew point of the oxidizing atmosphere in the first-stage heating is $\geq -50\text{ }^{\circ}\text{C}$;

the reducing atmosphere in the second-stage heating and soaking is a mixture gas of N_2 and H_2 , wherein a volume percentage of H_2 is 0.5-20%;

a dew point of the reducing atmosphere in the second-stage heating and soaking is $\leq 10\text{ }^{\circ}\text{C}$;

a heating rate in the second-stage heating is 1-20 $^{\circ}\text{C/s}$, the second-stage heating is heated from T_1 to a soaking temperature of 720-920 $^{\circ}\text{C}$, and a soaking time is 30-200 s.