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(54) ENVIRONMENT-FRIENDLY WATER-BASED TREATMENT AGENT FOR IMPROVING PHOSPHATABILITY OF HIGH-STRENGTH STEEL

(57) The present invention belongs to the technical field of surface treatment for metal materials, and particularly relates to an environment-friendly water-based treatment agent for improving the phosphatability of high-strength steel. The water-based treatment agent is prepared by dissolving or dispersing a composition in an aqueous medium. The water-based treatment agent specifically consists of: A. a fluoride ion-containing compound; B. a compound selected from metal ion compounds containing Cu, Zn, Mn, Ni or Fe; C. a compound selected from organic acids; and D. a compound selected from surfactant. The water-based treatment agent can be diluted in water at a ratio of 1:0-20 for subsequent use. The treatment agent can enable the surface of a high-strength steel plate to have excellent phosphatability and is mainly applied to high-strength steel surface modification treatment.

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Description

Technical Field

[0001] The present disclosure pertains to the technical field of surface treatment of metal materials, and in particular relates to an environmentally friendly water-based treatment agent for high-strength coiled steel surface. The treatment agent can impart excellent phosphatability to the surface of a high-strength steel sheet, and is mainly used for surface modification treatment of high-strength steel.

Background Art

[0002] The phosphating process may be dated back to the early 20th century, and is currently used widely in the process for treating automobiles/home appliances prior to painting. After a century of technological development, a very mature technical system has been formed in terms of the phosphating solution formula, film-forming mechanism and action mechanism. Phosphating treatment mainly involves contact between a phosphating solution and a steel sheet surface. Due to the action of acid corrosion and the oxidation of a promoter, the hydrogen ion content in the interface area decreases rapidly, and the phosphate radical dissociates gradually and combines with metal ions to form a phosphate salt which deposits. A uniform and fine phosphating layer that completely covers the metal surface can effectively improve coating adhesion and under-film corrosion resistance. Ordinary cold rolling is used for conventional vehicle bodies, phosphating treatment is compatible with galvanizing materials, and the effect is good and stable. At present, the application of phosphating to automotive materials with new surface characteristics is a challenge, and it is also a research hotspot in the industry.

[0003] In recent years, along with the advancement of the steel material technology, ultra-high-strength steel has been used more and more widely, especially automotive high-strength steel. Given its outstanding role in improving safety, environmental protection and lightweight, the ultra-high-strength steel material technology has entered a stage of rapid development, promotion and application. However, ultra-high-strength steel requires incorporation of more alloying elements, which directly changes the surface properties of the material. Studies have shown that the composition formed by selective oxidation of elements such as Mn, Si, and Cr is enriched on the surface of the steel sheet. During the phosphating process, problems such as coarse grains and poor coverage often occur, and the phosphatability is reduced significantly, which cannot meet the requirements of painting applications. In this regard, major domestic and foreign steel suppliers have conducted a lot of technical research work to optimize the phosphatability of high-strength steel surfaces. Most of them focus on the control of the selective oxidation of elements such as Mn, Si, Cr, and the like on steel sheet polar surfaces (e.g., CN102834531, CN102482728, CN102534359, CN108368590). This type of patent technology needs to effectively balance the degree of internal oxidation and the oxidation state of the polar surface while controlling the selective oxidation precipitates on the surface. The process window is narrow, the difficulty is high, and it is incompatible with materials of different composition systems. Hence, customized process designs are needed.

[0004] The patents on the technology for modifying high-strength steel surface to obtain good phosphatability mainly include two processes: surface electrolytic pickling for removing an oxide-rich layer and surface flash plating for covering an oxide-rich layer. In Publication Nos. CN104136644, CN103124799, CN104508155 and CN103305749, methods are proposed for removing an oxide-rich layer, which affects the phosphatability, from the surface of high-strength steel by electrolytic pickling of a cold-rolled sheet surface. This type of technology is highly implementable, compatible with materials of different composition systems. However, it also has the problems of high energy consumption and environmental pollution. It requires an additional pickling process, unsuitable for a conventional high-strength steel production line.

[0005] In Publication No. CN104471115, there is proposed a method for galvanizing a steel sheet surface with a coverage rate of at least 60% by flash plating to optimize the surface phosphatability and galling resistance. At the same time, this public literature also reports the technology for manufacturing high-strength steel with good phosphatability by flash nickel plating and flash iron plating. This type of technology can provide the surface of a high-strength steel material with new and stable properties by the coating treatment. However, it consumes too much energy, is not environmentally friendly, and requires an additional electroplating process, unsuitable for a conventional high-strength steel production line.

[0006] The development of an environmentally friendly water-based treatment agent that can achieve optimized control of the phosphatability of the surface of high-strength steel is of great significance to the efficient application and promotion of the automotive high-strength steel technology.

Summary

[0007] One object of the present disclosure is to provide an environmentally friendly water-based treatment agent useful for optimized modification of the phosphatability of the surface of high-strength steel.

[0008] By means of theoretical analysis, extensive laboratory research and practical verification, the inventors have finally determined the technical route of the environmentally friendly water-based treatment agent for surface nano-modification to obtain good phosphatability. In view of the typical characteristics of a high-strength steel surface, a water-based treatment agent comprising one or more components of a fluorine compound, a metal ion compound, an organic acid compound, and a surfactant is formed. The treatment agent can meet the requirements for use in a high-speed continuous process for producing high-strength steel coils and a process for manufacturing processed parts. The specific treatment process may involve formation of a wet film on the surface of a steel sheet by immersion, spraying, roller coating, etc., and the treatment agent may be allowed to quickly form a surface modification layer of several nanometers thick on the surface of the steel sheet by blow drying or heat drying. This modification layer enables epitaxial growth of active crystal nuclei on the surface of the steel sheet with the same orientation as phosphating crystallization, thereby significantly improving the phosphatability of the surface of the high-strength steel sheet containing high contents of alloying elements (such as Mn, Si, Cr, Mo, etc.) without affecting the processing performances such as forming and connecting performances.

[0009] The technical solution of the present disclosure:
An environmentally friendly water-based treatment agent for modification of the surface of a high-strength steel product to obtain good phosphatability, wherein the surface treatment agent (water-based treatment agent) is prepared by dissolving or dispersing a composition in an aqueous medium, wherein the surface treatment agent specifically comprises:

A. a compound selected from compounds containing fluoride ions;
B. a metal ion compound selected from compounds containing Cu, Zn, Mn, Ni, and Fe;
C. a compound selected from organic acids; and
D. a compound selected from surfactants.

[0010] The present disclosure relates to use of the surface treatment agent, wherein the surface treatment agent may be diluted by adding 0 to 20 parts of water per part of the treatment agent prior to use. The surface treatment agent may be used directly without adding water.

[0011] The metal ions involved in the present disclosure are not limited to specific valence states.

[0012] The compound containing fluoride ions in the water-based treatment agent of the present disclosure comprises one or more of ammonium fluorotitanate, ammonium fluorozirconate, potassium fluorotitanate, potassium fluorozirconate and the like. The molar concentration of the F element in the solution is 0.3-1.8 mol/L, preferably 0.3-1.7 mol/L, and more preferably 0.6-1.1 mol/L. On the one hand, this additive acts to enable uniform surface etching, and on the other hand, titanium or zirconium allows for dotted deposition on the surface of the material to form active nucleation sites that are conducive to phosphating. If the F content is lower than 0.3 mol/L, the film-forming performance of the surface treatment agent will deteriorate, affecting the modification effect; if the F content is higher than 1.8 mol/L, the stability of the surface treatment agent tends to decrease notably.

[0013] The one or more metal ion compounds containing Cu, Zn, Mn, Ni, and Fe in the water-based treatment agent of the present disclosure include: sulfates, carbonates, and nitrates that contain copper ions; sulfates, phosphates, formates, and acetates that contain Zn ions; phosphates, carbonates, and nitrates that contain Mn ions; nitrates and oxalates that contain Fe ions; and sulfates, nitrates, and carbonates that contain Ni ions. The molar concentration of the metal ion compound in the solution is 0.05-0.6 mol/L, preferably 0.07-0.6 molk/L, and more preferably 0.1-0.25 mol/L. This additive mainly acts to further supplement the isomorphous nucleation sites for phosphating crystallization. If the content is lower than 0.05 mol/L, the effect of supplementing the nucleation sites for phosphating cannot be achieved; if the content is higher than 0.6 mol/L, the thickness of the modification film layer will be too large, so that a uniform passivation effect will be resulted, which will directly affect the paintability of the treated surface.

[0014] The organic acid compound in the water-based treatment agent of the present disclosure includes an organic acid compound with a complexing or chelating function such as citric acid, oxalic acid, tannic acid, lactic acid, tartaric acid, salicylic acid, etc. In some embodiments, the organic acid compound is citric acid, oxalic acid, tartaric acid, or tannic acid. The molar concentration of the organic acid compound in the solution is 0.03-0.4 mol/L, preferably 0.05-0.2 mol/L. This compound has a certain cleaning effect on the surface of the steel sheet. At the same time, the resulting reaction products partially adhere to the surface of the steel sheet, and can promote rapid nucleation and growth of the phosphating film. If the content is lower than 0.03 mol/L, the surface cleaning effect will be reduced notably; if the content is higher than 0.4 mol/L, the stability of the treatment agent system will be affected significantly.

[0015] The compound selected from surfactants in the surface treatment agent of the present disclosure mainly includes: sodium dodecyl sulfate, sodium dodecyl sulfonate, calcium dodecyl sulfonate, octadecylamine, triethanolamine, etc. The molar concentration of the surfactant compound in the solution is 0.002-0.015 mol/L, preferably 0.003-0.01 mol/L. The main function of this additive is to enhance the film-forming performance of the treatment agent, while reducing the surface tension after the film is formed, and optimizing the effect of the phosphating agent in rapidly wetting the steel sheet surface during the pre-painting treatment process, thereby achieving the purpose of improving the phosphatability. If the content is lower than 0.002 mol/L, the film-forming performance of the treatment agent cannot be optimized significantly; if the content is higher than 0.015 mol/L, the film-forming quality of the treatment agent will be affected notably, and the effect of optimizing the phosphatability after film formation decreases.

[0016] The environmentally friendly water-based treatment agent for improving the phosphatability of high-strength steel described in the present disclosure can be used on a continuous production line of pickled high-strength steel or cold-rolled high-strength steel, wherein a wet film is formed on the surface of the steel sheet by immersion, spraying, roller coating, etc. The treatment agent can form a nano-scale surface modification layer quickly on the surface of the steel sheet by blow drying or heat drying, thereby achieving the effect of significant optimization of the phosphatability of the high-strength steel surface.

[0017] In some embodiments, the present disclosure provides a method for improving the phosphatability of high-strength steel, wherein the method comprises: treating the high-strength steel with the environmentally friendly water-based treatment agent described herein by immersion, spraying or roller coating. In some embodiments, the method further comprises: treating the high-strength steel with a degreasing agent to remove dirt and oil adhering to its surface, then washing it with pure water to remove alkaline matter remaining on the surface, and then using the environmentally friendly water-based treatment agent to perform surface treatment on the high-strength steel after blow drying. In some embodiments, the high-strength steel is pickled high-strength steel or cold-rolled high-strength steel.

[0018] In some embodiments, the present disclosure provides a method for phosphating high-strength steel, comprising: treating the surface of the high-strength steel using the method described herein, and subjecting the high-strength steel obtained by the surface treatment to degreasing, water washing, surface conditioning, phosphating, water washing and drying in sequence, so that the high-strength steel is phosphated.

[0019] In some embodiments, there is further provided a high-strength steel herein, wherein the surface of the high-strength steel has a nano-scale surface modification layer, wherein the nano-scale surface modification layer is formed from the surface treatment agent described herein after drying. After the high-strength steel is phosphated, the phosphating crystal coverage rate is ≥80%, preferably 100%; the phosphating crystal size is ≤6μm, preferably ≤4μm; and the phosphating film weight is ≥2g/m^2, preferably ≥2.3g/m^2. Therefore, in some embodiments, there is further provided a phosphated steel sheet obtained by phosphating the high-strength steel described herein, characterized by: a phosphating crystal coverage rate is ≥ 80%, preferably 100%; a phosphating crystal size is ≤ 6μm; a phosphating film weight is ≥ 2g/m^2. In the present disclosure, a conventional treatment agent (such as PB-L3065 phosphating solution) may be used to implement the phosphating treatment herein.

[0020] Beneficial technical effects of the present disclosure: the environmentally friendly water-based treatment agent provided by the present disclosure for improving the phosphatability of high-strength steel enables the surface of the high-strength steel sheet to have excellent phosphatability. The water-based treatment agent of the present disclosure can meet the requirements for use in a high-speed continuous process for producing high-strength steel coils and a process for manufacturing processed parts; at the same time, it does not affect the processing performances such as forming and connection performances. It is also an environmentally friendly water-based treatment agent.

Detailed Description

[0021] In order to provide better understanding of the present disclosure, the present disclosure is illustrated specifically by listing examples and comparative examples, but the scope of the present disclosure is not limited by these examples. The compositions of the surface treatment agents used and the type of the steel sheet to be treated are described as follows:

(1) Test sample sheet:

[0022] The material used in the examples was a typical 80 kg grade ultra-high strength steel with a specification of 1.2 mm and a composition as shown in Table 1.

Table 1: Composition information of the common cold-rolled steel sheet used in the examples

Chemical composition % (mass percentage)							
C	Mn	Si	Al	Cr	Mo	Nb	Ti
0.12	1.550	1.100	0.020	0.650	0.000	0.030	0.070

(2) Process for processing and cleaning the sample sheet:

[0023] The above material was processed into 30*70mm sample pieces by shearing, spray-cleaned with an alkaline degreasing agent (pH=11-12) to remove dirt and oil adhering to the surface, then cleaned with pure water to remove residual alkaline matter on the surface, and dried with cold air for later use.

(3) Compositions of the water-based surface treatment agents

[0024] The compositions and treatment methods of the environmentally friendly water-based surface treatment agents used in the examples are shown in Table 2. Comparative Example 4 means a material with a virgin surface that had not been surface treated with the treatment agent.

Table 2: Examples and compositions of the surface treatment agents used

Designation	F-containing compound (A) F element content "mol/L"		Metal salt (B) molar content "mol/L"		Organic acid compound (C) molar content "mol/L"		Surfactant (D) molar content "mol/L"		Coating method
	Type	Content	Type	Content	Type	Content	Type	Content	Method
Ex. 1	Ammonium fluorotitanate	1.7	Zn-containing phosphate	0.07	Citric acid	0.03	Triethanolamine	0.002	Immersion
Ex. 2	Potassium fluorozirconate	1.7	Cu-containing sulfate	0.25	Oxalic acid	0.1	Sodium dodecyl sulfonate	0.015	Spraying
Ex. 3	Potassium fluorotitanate	0.3	Fe-containing nitrate	0.6	Tartaric acid	0.4	Sodium dodecyl sulfate	0.002	Immersion
Ex. 4	Ammonium fluorozirconate	0.9	Mn-containing phosphate	0.25	Oxalic acid	0.1	Calcium dodecyl sulfonate	0.009	Spraying
Ex. 5	Potassium fluorozirconate	0.3	Ni-containing carbonate	0.07	Tannic acid	0.4	Octadecylamine	0.002	Roller coating
Ex. 6	Potassium fluorotitanate	0.9	Zn-containing phosphate	0.6	Citric acid	0.03	Calcium dodecyl sulfonate	0.009	Roller coating
Comp. Ex. 1	Potassium fluorozirconate	0.02	Cu-containing nitrate	0.03	Tartaric acid	0.01	Calcium dodecyl sulfonate	0.001	Spraying
Comp. Ex. 2	Potassium fluorotitanate	2	Mn-containing phosphate	0.7	Citric acid	0.1	Octadecylamine	0.015	Immersion
Comp. Ex. 3	Ammonium fluorozirconate	0.9	Mqn-containing phosphate	0.25	Oxalic acid	0.1	Calcium dodecyl sulfonate	0.02	Spraying
Comp. Ex. 4	--	--	--	--	--	--	--	--	--

[0025] The surface-treated sample pieces obtained in the above Examples and Comparative Examples were coated with anti-rust oil in an amount of 1000 mg/m^2, allowed to stand for one week, and then subjected to pre-painting treatment for evaluation of phosphatability. Laboratory simulation was performed with reference to the pre-painting treatment process flow in an automobile factory, mainly including steps of degreasing, surface conditioning and phosphating. The relevant treatment agents selected were commercial products available from Parkerizing. The specific process parameters are shown in Table 3.

Table 3: Phosphating process parameters

Step	Degreasing	Water washing	Surface conditioning	Phosphating	Water washing	Pure water was hing	Drying
Treatment agent	FC-L4460	--	PL-Z	PB-L3065	--	--	--
Treatment method	Immersion	Spraying	Immersion	Immersion	Spraying	Spraying	Heat drying
Treatment temperature	40°C	Room temperature	Room temperature	35°C	Room temperature	Room temperature	90°C
Treatment time	90s	20s	30s	120s	20s	20s	--

[0026] After the sample pieces were treated in the above manner, the phosphating crystal coverage rate and crystal size were observed microscopically using a scanning electron microscope, and the phosphating film weight was measured using a chemical dissolution method. The specific methods are as follows:

(1) Evaluation of phosphating crystal coverage rate

[0027] The phosphated surfaces of the sample pieces were observed using a scanning electron microscope (equipment: Zeiss SEM SIGMA500) at a magnification of 1000 times, and the evaluation was done in terms of the fraction of the area covered by the phosphating film.

◎: Phosphating film coverage rate = 100%
◦: 80%≤ Phosphating film coverage rate<100%
Δ: 60%≤ Phosphating film coverage rate<80%
×: Phosphating film coverage rate < 60%

(2) Determination of phosphating crystal size

[0028] The phosphated surfaces of the sample pieces were observed using a scanning electron microscope (equipment: Zeiss SEM SIGMA500) at a magnification of 2000 times. The length dimensions of 5 random phosphating crystals were measured using the scale, and the average value was taken.

(3) Determination of phosphating film weight

[0029] First, a 30*70mm phosphated sample piece was weighed (Mettler MS-TS analytical balance) and recorded as W_0. Then, the sample piece was immersed in a phosphating film stripping solution (solution: 50g/L anhydrous chromic acid, temperature: 75°C) for 15min. After taking the sample piece out, it was rinsed with deionized water for 40s, dried with cold air, and weighed for the second time to obtain a weight recorded as W_1. The weight of the phosphating film W was obtained by calculation:

$$W=(W_0-W_1)/S_{\text{surface area of sample piece}}.$$

[0030] As it can be seen from the implementation effect (as shown in Table 4), Examples 1-6 exhibited good phosphatability with regard to all of the various evaluation items, especially Examples 1, 2, 3, 4 and 6 which showed excellent overall performances. A comparison between the Examples and Comparative Example 4 shows that the phosphatability of each of the materials that were surface treated with the treatment agent was improved significantly. A comparison between Example 6 and Comparative Example 1 shows that when the contents of the components in the treatment agent were insufficient, it was unlikely to improve the phosphatability of the sample surface effectively by the treatment. As it can be seen from Examples 1, 2 and Comparative Example 2, the addition of appropriate amounts of the F-containing compound and metal salt could optimize the phosphatability of the sample surface, but excessive addition was not conducive to rapid growth of the phosphating film due to the increase in film thickness, resulting in a decrease in phosphatability. As it can be seen from Example 4 and Comparative Example 3, excessive addition of the surfactant affected the film-forming effect of the treatment agent, and thus notably reduced the effect of the treatment on the optimization of the phosphatability of the sample surface. As it can be seen from Examples 3, 4 and 5, the treatment agent was compatible with typical coating methods such as spraying, immersion and roller coating, and had a wider range of process adaptability.

Table 4: Performances of the examples

Designation	Coverage rate (rating)	Crystal size (μm)	Film weight (g/m^2)
Ex. 1	◎	3.2	2.5
Ex. 2	◎	2.3	2.3
Ex. 3	◎	3.6	2.5
Ex. 4	◎	2.9	2.4
Ex. 5	○	5.7	2
Ex. 6	◎	3.8	2.3
Comp. Ex. 1	Δ	8.1	1.9
Comp. Ex. 2	×	7.9	1.6
Comp. Ex. 3	Δ	8.5	1.8
Comp. Ex. 4	×	10.1	1.4

[0031] Of course, those skilled in the art should appreciate that the above examples are only used to illustrate the present disclosure, rather than to limit the present disclosure. Any changes or modifications to the above examples will fall within the scope of the claims in the present disclosure, so long as they are within the spirit of the present disclosure.

Claims

1. An environmentally friendly water-based treatment agent for improving phosphatability of high-strength steel, wherein the water-based treatment agent is prepared by dissolving or dispersing a composition in an aqueous medium, wherein the water-based treatment agent specifically comprises:

A. a compound selected from compounds containing fluoride ions;
B. a metal ion compound selected from compounds containing Cu, Zn, Mn, Ni, and Fe;
C. a compound selected from organic acids;
D. a compound selected from surfactants.

2. The environmentally friendly water-based treatment agent for improving phosphatability of high-strength steel according to claim 1, wherein the compound containing fluoride ions is selected from one or more of ammonium fluorotitanate, ammonium fluorozirconate, potassium fluorotitanate, potassium fluorozirconate.

3. The environmentally friendly water-based treatment agent for improving phosphatability of high-strength steel according to claim 1 or 2, wherein a molar concentration of the F element in the water-based treatment agent solution is 0.3-1.8 mol/L, preferably 0.3-1.7 mol/L, and more preferably 0.6-1.1 mol/L.

4. The environmentally friendly water-based treatment agent for improving phosphatability of high-strength steel according to claim 1, wherein

the metal ion compound containing Cu is selected from sulfates, carbonates, and nitrates that contain copper ions;
the metal ion compound containing Zn is selected from sulfates, phosphates, formates, and acetates that contain

Zn ions;
the metal ion compound containing Mn is selected from phosphates, carbonates, and nitrates that contain Mn ions;
the metal ion compound containing Ni is selected from sulfates, nitrates, and carbonates that contain Ni ions;
the metal ion compound containing Fe is selected from nitrates and oxalates that contain Fe ions.

5. The environmentally friendly water-based treatment agent for improving phosphatability of high-strength steel according to claim 1 or 4, wherein a molar concentration of the metal ion compound in the water-based treatment agent solution is 0.05-0.6mol/L, preferably 0.07-0.6mol/L, and more preferably 0.1-0.25mol/L.

6. The environmentally friendly water-based treatment agent for improving phosphatability of high-strength steel according to claim 1, wherein the organic acid compound is an organic acid compound with a complexing or chelating function, preferably selected from one or more of citric acid, oxalic acid, tannic acid, lactic acid, tartaric acid, and salicylic acid.

7. The environmentally friendly water-based treatment agent for improving phosphatability of high-strength steel according to claim 1 or 6, wherein a molar concentration of the organic acid compound in the water-based treatment agent solution is 0.03-0.4mol/L, preferably 0.05-0.2mol/L.

8. The environmentally friendly water-based treatment agent for improving phosphatability of high-strength steel according to claim 1, wherein the compound selected from surfactants is selected from one or more of sodium dodecyl sulfate, sodium dodecyl sulfonate, calcium dodecyl sulfonate, octadecylamine and triethanolamine.

9. The environmentally friendly water-based treatment agent for improving phosphatability of high-strength steel according to claim 1 or 8, wherein a molar concentration of the surfactant in the water-based treatment agent solution is 0.002-0.015mol/L, preferably 0.003-0.01mol/L.

10. The environmentally friendly water-based treatment agent for improving phosphatability of high-strength steel according to claim 1, wherein the water-based treatment agent further comprises 0-20 parts by weight of water.

11. Use of the environmentally friendly water-based treatment agent for improving phosphatability of high-strength steel according to any one of claims 1-10 on a continuous production line of pickled high-strength steel or cold-rolled high-strength steel.

12. A method for improving phosphatability of high-strength steel, wherein the method comprises: treating the high-strength steel with the environmentally friendly water-based treatment agent according to any one of claims 1-10 by immersion, spraying or roller coating; preferably, the high-strength steel is pickled high-strength steel or cold-rolled high-strength steel.

13. The method according to claim 12, wherein the method further comprises: treating the high-strength steel with a degreasing agent to remove dirt and oil adhering to its surface, then washing it with pure water to remove alkaline matter remaining on the surface, and then using the environmentally friendly water-based treatment agent to perform surface treatment on the high-strength steel after blow drying.

14. A high-strength steel or a phosphated steel sheet obtained by phosphating the high-strength steel, wherein the high-strength steel has a nano-scale surface modification layer on the surface, wherein the nano-scale surface modification layer is formed from the environmentally friendly water-based treatment agent according to any one of claims 1-10 after drying; preferably, the phosphated steel sheet has a phosphating crystal coverage rate of $\geq 80\%$, preferably 100%; a phosphating crystal size of $\leq 6\mu m$; and a phosphating film weight of $\geq 2g/m^2$.

15. A method for phosphating high-strength steel, comprising: treating the surface of the high-strength steel using the method according to claim 12 or 13, and subjecting the high-strength steel obtained by treating the surface to degreasing, water washing, surface conditioning,
phosphating, water washing and drying in sequence, so that the high-strength steel is phosphated.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2023/110360

A. CLASSIFICATION OF SUBJECT MATTER

C23C 22/36(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC:C23C 22

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, USTXT, DPI, VEN, USTXT, ISI WEB OF SCIENCE: 宝山钢铁股份有限公司, 磷化, 水基处理剂, 氟, 金属离子, 铜, 锌, 锰, 镍, 铁, 柠檬酸, 草酸, 酒石酸, 水杨酸, 表面活性剂; phosphating, Water-Based Treating Agents, Fluoride, metal, Cu, Zn, Mn, Ni, Fe, Citric acid, Oxalic acid, Tartaric acid, salicylic acid, surfactant

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CN 102719819 A (CHONGQING RONGSHI METAL SURFACE TREATMENT AGENT CO., LTD.) 10 October 2012 (2012-10-10) description, paragraphs 6-21	1-15
Y	CN 114075663 A (BAOSHAN IRON & STEEL CO., LTD.) 22 February 2022 (2022-02-22) description, paragraphs 34 and 40-50	1-15
Y	US 5268041 A (METALLGESELLSCHAFT AG) 07 December 1993 (1993-12-07) claim 1, and description, column 4, lines 3-25	1-15
Y	CN 107326353 A (HANGZHOU PENTATOMIC SCIENCE & TECHNOLOGY INDUSTRIAL CO., LTD.) 07 November 2017 (2017-11-07) description, paragraphs 6-23	1-15
A	CN 103060788 A (BAOSHAN IRON & STEEL CO., LTD.) 24 April 2013 (2013-04-24) entire document	1-15

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search **18 September 2023**	Date of mailing of the international search report **26 October 2023**
Name and mailing address of the ISA/CN **China National Intellectual Property Administration (ISA/CN)** **China No. 6, Xitucheng Road, Jimenqiao, Haidian District, Beijing 100088**	Authorized officer Telephone No.

INTERNATIONAL SEARCH REPORT
Information on patent family members

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