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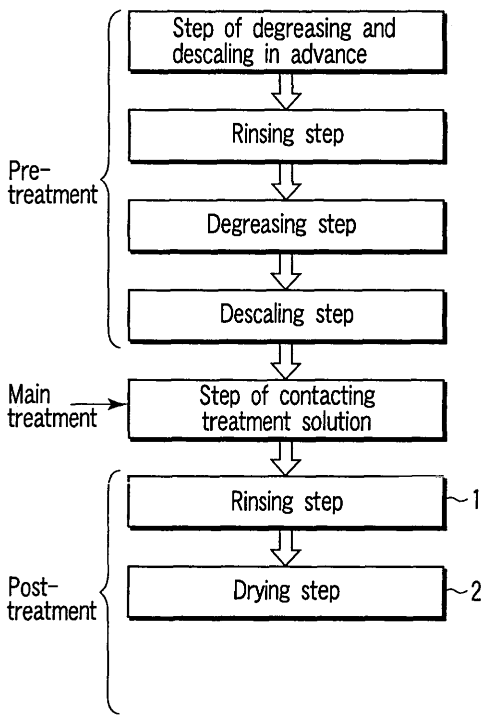
(54) Steel product excellent in corrosion resistance and corrosion fatigue resistance, and surface treatment method therefor

(57) The invention provides a steel product excellent in corrosion resistance and corrosion fatigue resistance, comprising a coating film on the surface of the steel product, wherein a ratio of the number of Al atoms to the total number of Fe, C, Al, P and O atoms and optionally added Si, Mn and Cr atoms is 0.5% or more in an average composition of the coating film, and the number of Al atoms in the average composition of the coating film is higher than the number of Al atoms in an average composition of the steel product before surface treatment.



(First example of surface treatment)

FIG. 1A

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Description

[0001] The present invention relates to a steel product excellent in corrosion resistance and corrosion fatigue resistance, and a surface treatment method therefor.

[0002] As is commonly known, in many cases, compositions of steel products are adjusted or coating films are formed by a surface treatment or the like in steel products used under corrosive environments. The purpose thereof is to prevent deterioration of static strength and fatigue strength characteristics due to corrosive thinning and occurrence of corrosion pits of the steel product from decreasing, and to prevent the appearance from worsening due to generation of rusts.

[0003] However, it has been a problem that the product cost and production cost are increased by adding or increasing the amount of corrosion resistant elements such as Cr, Ni and Mo for controlling the composition. Another method is to form a zinc film for the purpose of protection by so-called sacrificial corrosion by which a sacrificial corrosion layer is provided on a steel product as a surface treatment film to thereby retard corrosion of a base metal. However, management of processing conditions for preventing pine holes and irregular plating from occurring is necessary in a zinc electroplating method, for example. In addition, in the electroplating method, there is a need for a different treatment for preventing hydrogen embrittlement ascribed to invasion of hydrogen, that is generated by the surface of the steel product to be treated at a cathode, into steel. Accordingly, it has been a problem in the electroplating method that the production process becomes complicated and the production cost increases.

[0004] A coating film treatment with a zinc-containing phosphate system (chemical conversion treatment with zinc phosphate) may be applied relatively easily. However, corrosion resistance of the coating film is insufficient. In contrast, steel products plated with a Zn-Al-Si base molten alloy (trade name Galvanium Steel, manufactured by Nittetsu Steel Sheet Corporation) have been known as backside-treated steel products having both a sacrificial corrosion protective action of Zn and a self-repair action of Al. However, this molten alloy plating requires a plating bath temperature of 400°C or more. For this reason, the method cannot be employed when a decrease of the mechanical strength caused by heating the steel product during immersion in a molten alloy is of problem.

[0005] Examples of known patent publications related to the steel sheet proposed herein include Japanese Patent No. 3381647 (patent document 1) and Jpn. Pat. Appln. KOKAI Publication No. 9-272982 (patent document 2). Patent document 1 discloses an organic-coated steel sheet excellent in corrosion resistance. The organic-coated steel sheet is produced by forming a chemical conversion coating film on a zinc-plated steel sheet followed by forming an organic coating film containing aluminum phosphate. However, the process of the steel sheet disclosed in patent document 1 is complex with high processing cost since the chemical conversion treatment should be applied before forming the organic coating film containing aluminum phosphate.

[0006] Patent document 2 discloses a low iron loss unidirectional electromagnetic steel sheet and a method of producing the same. The electromagnetic steel sheet has a coating film comprising a first layer having a Young's modulus of 100 GPa or more and a difference of a linear coefficient of expansion of 2×10^{-6} or more from that of the steel sheet, and a second layer containing aluminum phosphate. In the producing method, the steel sheet is baked at a temperature in the range of 400 to 1000°C after applying a coating liquid and drying the coating film for forming the second layer. However, it has been a problem in patent document 2 that the mechanical strength of the steel product decreases when the steel product is baked at a temperature in the range of 400 to 1000°C.

[0007] Accordingly, an object of the present invention is to provide a steel product excellent in corrosion resistance and corrosion fatigue resistance and a surface treatment method therefor, wherein problems of high production cost, complex production process, hydrogen embrittlement and reduced strength of materials can be solved as a surface treatment method capable of substituting conventional surface treatment methods such as electroplating, chemical conversion coating and molten alloy plating.

[0008] According to a first aspect of the present invention, there is provided a steel product excellent in corrosion resistance and corrosion fatigue resistance, comprising a coating film on the surface of the steel product, wherein a ratio of the number of Al atoms to the total number of Fe, C, A1, P and O atoms and optionally added Si, Mn and Cr atoms is 0.5% or more in an average composition of the coating film, and the number of Al atoms in the average composition of the coating film is higher than the number of Al atoms in an average composition of the steel product before surface treatment.

[0009] According to a second aspect of the present invention, there is provided a steel product excellent in corrosion resistance and corrosion fatigue resistance, comprising a coating film on the surface of the steel product, wherein a ratio of the number of Al atoms to the total number of Fe, C, Al, P and O atoms and optionally added Si, Mn and Cr atoms is 0.5% or more in an average composition in a region from the surface to a depth of 5 μm of the steel product, and the number of Al atoms in an average composition of the coating film is higher than the number of Al atoms in an average composition of the steel product before surface treatment.

[0010] According to a third aspect of the present invention, there is provided a surface treatment method for a steel product: comprising rinsing the steel product after allowing an aqueous solution at room temperature having an acidity ratio in the range of 3.3 to 5.7 and containing Al ions to contact the surface of the steel product; and drying the steel product.

[0011] According to a fourth aspect of the present invention, there is provided a surface treatment method for a steel product, comprising: drying the steel product after allowing an aqueous solution at room temperature having an acidity ratio in the range of 3.3 to 5.7 and containing Al ions to contact the surface of the steel product; and drying again the steel product after rinsing.
[0012] This summary of the invention does not necessarily describe all necessary features so that the invention may also be a sub-combination of these described features.
[0013] The invention can be more fully understood from the following detailed description when taken in conjunction with the accompanying drawings, in which:

FIG. 1A is a flowchart illustrating a first example of surface treatment according to the invention; and
FIG. 1B is a flowchart illustrating a second example of surface treatment according to the invention.

[0014] The present invention will be described in more detail hereinafter.
[0015] The present inventors have completed the following invention through intensive studies on a mechanism of corrosion of a steel product and a chemical conversion treatment method.

1. A steel product excellent in corrosion resistance and corrosion fatigue resistance according to a first embodiment of the invention has a coating film on the surface of the steel product, wherein a ratio of the number of Al atoms to the total number of Fe, C, Al, P and O atoms and optionally added Si, Mn and Cr atoms is 0.5% or more in an average composition of the coating film, and the number of Al atoms in the average composition of the coating film is higher than the number of Al atoms in an average composition of the steel product before surface treatment.
2. A steel product excellent in corrosion resistance and corrosion fatigue resistance according to a second embodiment of the invention has a coating film on the surface of the steel product, wherein a ratio of the number of Al atoms to the total number of Fe, C, Al, P and O atoms and optionally added Si, Mn and Cr atoms is 0.5% or more in an average composition in a region from the surface to a depth of 5 μm of the steel product, and the number of Al atoms in an average composition of the coating film is higher than the number of Al atoms in an average composition of the steel product before surface treatment.
In the items 1 and 2 of the invention, the measurement of "a ratio of the number of Al atoms to the total number of Fe, C, Al, P and O atoms, and selectively added Si, Mn and Cr atoms" is based on elementary analysis, and the analysis is sufficient by measuring a region from the surface of the steel product to a depth of 5 μm from the surface. This region may be only the coating film or both the coating film and base material. The phrase "selectively added Si, Mn and Cr" means that these atoms are not added at all or at least one atom of them is added.
The ratio of the number of Al atoms to the total number of atoms of Fe, C, Al, P and O, and selectively added Si, Mn and Cr in the invention 2 is preferably 0.5% or more, particularly preferably 3% or more. When the proportion of the number of Al atoms is less than 0.5%, both sacrificial corrosion protective action and passive state forming action to be described below are weak to fail in obtaining sufficient corrosion resistance and corrosion fatigue resistance.
3. A surface treatment method for a steel product according to a third embodiment of the invention, comprises rinsing the steel product after allowing an aqueous solution at room temperature having an acidity ratio in the range of 3.3 to 5.7 and containing Al ions to contact the surface of the steel product followed by drying the steel product.
4. A surface treatment method for a steel product according to a fourth embodiment of the invention, comprises: drying the steel product after allowing an aqueous solution at room temperature having an acidity ratio in the range of 3.3 to 5.7 and containing Al ions to contact the surface of the steel product; and drying again after rinsing.

[0016] The acidity ratio is determined to be in the range of 3.3 to 5.7 in the methods cited in the items 3 and 4 of the invention for the following reasons. That is, the coating film is suppressed from being formed due to too severe corrosion of the steel product when the acidity ratio is less than 3.3. On the other hand, the formation of the coating film takes a long period of time since the corroding action of the steel product is too weak when the acidity ratio exceeds 5.7. The acidity ratio is more preferably in the range of 3.8 to 5.4.
[0017] It is preferable in the methods cited in the items 3 and 4 of the invention to allow the aqueous solution containing Al ions to contact the surface of the steel product for 30 seconds or more at a temperature in the range of 40 to 50°C. When the contact period is less than 30 seconds, the corroding action of the steel product is insufficient to fail in obtaining a coating film excellent in corrosion resistance and corrosion fatigue resistance.
[0018] It is also preferable in the methods cited in the items 3 and 4 of the invention to allow the aqueous solution containing Al ions to contact the surface of the steel product for 180 seconds or more at 30°C. When the contact period is less than 180 seconds, the corroding action of the steel product is insufficient to fail in obtaining a coating film excellent in corrosion resistance and corrosion fatigue resistance.
[0019] It is preferable in the method in the item 4 of the invention to dry the steel product at 50°C or less after allowing

the surface of the steel product to contact the aqueous solution at room temperature containing Al ions before washing with water. The drying temperature is prescribed to be 50°C or less because, when the temperature exceeds 50°C, denseness of the coating film decreases due to too rapid evaporation of water to result in a decrease of the strength of the coating film.

[0020] The treatment work is easy with a low processing cost in the steel product subjected to surface treatment in the invention, and excellent corrosion resistance and corrosion fatigue resistance are manifested without causing hydrogen embrittlement and decreased strength of the material.

[0021] The invention will be described in detail hereinafter.

[0022] FIG. 1A shows an example of the surface treatment according to the invention, which is a first example of the surface treatment in which a drying step 2 as a post treatment is carried out after a rinsing step 1. FIG. 1B shows another example of the surface treatment according to the invention, which is a second example of the surface treatment in which the rinsing step 1 and a second drying step 2b as post treatments are sequentially carried out after a first drying step 2a.

[0023] The surface of the steel product is preferably washed with an aqueous cleaning solution containing an organic solvent or a surfactant in advance for degreasing as in the pre-treatments in FIGS. 1A and 1B, or subjected to descaling with an acid solution. This allows the effect of the invention to be further manifested. Water to be used for rinsing in FIGS. 1A and 1B desirably contains C1 as small as possible. The solution for use in the treatment in FIGS. 1A and 1B (referred to the treatment solution hereinafter) is obtained by adding aluminum phosphate ($AlPO_4$) in water, and further adding phosphoric acid (H_3PO_4) for dissolving $AlPO_4$. The concentration by weight of $AlPO_4$ is favorably in the range of 1 to 10%.

[0024] When the concentration of $AlPO_4$ exceeds 10%, the steel product may be eroded with the acid because the concentration of H_3PO_4 added for dissolving $AlPO_4$ increases. On the other hand, when the concentration of $AlPO_4$ is below 1%, processability decreases since $AlPO_4$ is frequently replenished. For example, industrial water, city water and distilled water may be used as water used for the solvent. However, if any Cl that may accelerate erosion is contained in water, Cl is preferably removed as much as possible.

[0025] Any methods such as immersion, air spray and brush coating may be used for allowing the treatment solution to contact the steel product. While the mechanism for forming the coating film has not been fully elucidated, it is conjectured as follows.

[0026] Aluminum primary phosphate ($Al(H_2PO_4)_3$), H_3PO_4 and $AlPO_4$ are in an equilibrium state represented by the following formula (1) in the treatment solution. When the steel product contacts the treatment solution, H_3PO_4 interacts with Fe as shown in the following formula (2), and the concentration of H_3PO_4 decreases in the solution near the surface of the steel product as shown in the formula (1). Accordingly, the equilibrium shown in the formula (1) shifts to the right side, and hardly soluble $AlPO_4$ seems to precipitate on the surface of the steel product to form a coating film.

$$Al(H_2PO_4)_3 \text{ (soluble)} \Leftrightarrow 2H_3PO_4 \text{ (liquid)} + AlPO_4 \text{ (hardly soluble)} \qquad (1)$$

$$Fe + 2H_3PO_4 \rightarrow Fe(H_2PO_4)_2 + H_2 \uparrow \qquad (2)$$

[0027] The coating film is considered to be formed based on the steel product corroding action of H_3PO_4 and deposition of hardly soluble $AlPO_4$ formed by decomposition of $Al(H_2PO_4)_3$. It may be also considered that dissolved Fe is contained in $AlPO_4$ formed as described above, and a film comprising Al, Fe, P and O is formed. Accordingly, the molar ratio between H_3PO_4 and $Al(H_2PO_4)_3$ is important in the treatment condition by the treatment solution of the invention, and specifically, control of the acidity ratio is important.

[0028] The term "acidity ratio" as used herein refers to a ratio of a point of acidity of total phosphoric acid (H_3PO_4 and $Al(H_2PO_4)_3$) to a point of acidity of free phosphoric acid (H_3PO_4) in the treatment solution. The "point" is as described below. A treatment solution (10 cc) is neutralized with 0.1 N sodium hydroxide (NaOH) by adding 2 to 3 drops of methyl orange solution as an indicator at room temperature. The point of acidity of free phosphoric acid is the volume of the aqueous NaOH solution represented by a cc unit when the color of the solution changes to orange. Likewise, the point of total acidity is the volume of the aqueous NaOH solution represented by the cc unit when the same solution is neutralized as described above by adding 2 to 3 drops of phenolphthalein solution and the color of the solution changes to pale pink. The acidity ratio of the treatment solution can be controlled by adding a basic aqueous solution such as an aqueous NaOH solution.

[0029] For example, a treatment solution ready for forming the coating film may be obtained for maintaining the equilibrium in formula (1) by increasing the acidity ratio, or by decreasing the amount of H_3PO_4. In a specific treatment condition, the acidity ratio is desirably in the range of 3.3 to 5.7, particularly of 3.8 to 5.4. When the acidity ratio is less than 3.3 (too much H_3PO_4), the coating film is suppressed from being formed due to too vigorous corrosion of the steel product. When the acidity ratio exceeds 5.7 (to little H_3PO_4), on the other hand, a long period of time is necessary for forming the coating film since the corrosion action for the steel product is weak.

[0030] When the steel product is made to contact the treatment solution, using the heated treatment solution is preferable since the reaction rate of the formula (2) increases and formation of the coating film is accelerated. The required contact periods of the steel product with the treatment solution are 1000 seconds or more, 180 seconds or more and 30 seconds or more when the temperatures of the treatment solution are room temperature, 30°C and in the range of 40 to 50°C, respectively. However, the action for eroding the steel product is insufficient at the contact period shorter than the above-mentioned period, and a coating film excellent in corrosion resistance and corrosion fatigue resistance cannot be obtained. The upper limit temperature of the treatment solution is desirably 50°C or less since temperature control is difficult at a higher temperature while the cost for maintaining the temperature is high.

[0031] The steel product may be immediately rinsed (first example of surface treatment: A) after the above-mentioned treatment as shown in FIG. 1A, or may be rinsed after drying (second example of surface treatment: B) after the above-mentioned treatment as shown in FIG. 1B. Since drying is applied for removing adhered water, the steel product may be left at room temperature or in a heated atmosphere. Otherwise, a conventional drying furnace may be used. The temperature of the first drying step in the second example of the surface treatment is desirably 50°C or less. A temperature exceeding 50°C is not preferable since water is so rapidly evaporated that denseness of the coating film decreases to reduce the strength of the coating film.

[0032] The steel product treated as described above is expected to have a sacrificial corrosion protective action by the Al component in the coating film formed on the surface and an action for forming a passive film by oxidation of the Al component. The concentration of Al atoms in the coating film at the surface of the steel product is quantitatively analyzed by elementary analysis in the region from the surface to a depth of 5 μm using an EDX (Energy Dispersive X-ray spectroscopy) device, and is corrected by ZAF correction (Z: difference of emitted X-ray intensity depending on difference of sample compositions; A: absorption X-ray in sample; F: fluorescence excitation by emitted X-rays in sample). When the number of Al atoms is represented by A and the total number of atoms of the elements constituting the steel product and of the elements constituting the treatment solution is represented by B based on the quantitative analysis above, the ratio of A (the ratio of the number of Al atoms) to B should be 0.5% or more, particularly desirably 3% or more. When the ratio of the number of Al atoms is less than 0.5%, both the above-mentioned sacrificial corrosion protective action and action for forming a passive film are so weak that sufficient corrosion resistance and corrosion fatigue resistance cannot be obtained.

[0033] According to the invention, a surface treatment with a low cost is possible since aluminum phosphate, phosphoric acid and distilled water are cheaply and readily available and the treatment is simple. Since the treatment solution is weakly acidic and the amount of hydrogen generated from the steel product is very small, the steel product is substantially free from hydrogen embrittlement. Further, all the treatments are performed at 50°C or less, so that the strength of the materials is hardly reduced.

(Example)

[0034] While examples will be shown below, the invention is not restricted to these examples.

[0035] The surface of a steel product SAE9254 (Fe-0.56%C-1.42%Si-0.75%Mn-0.68% Cr) with a diameter of 4 mm and a length of 20 to 80 mm was treated under the conditions shown in Table 1. The steel product was a material obtained by removing in advance solid and thick oxidized scales by blast treatment. The pre-treatment procedure comprises washing the steel product with distilled water, degreasing with acetone, and then removing the scale again by immersing the steel product in dilute aqueous hydrochloric acid. Then, the steel product to be treated was immersed in the treatment solution under the conditions shown in Table 1, washed with distilled water, and allowed to spontaneously dry (the condition in which the column of drying at 50°C in Table 1 is represented by "none (-)"). The acidity ratio was controlled by adding an aqueous sodium hydroxide solution in the treatment solution. The steel product was dried after immersion, if necessary, by leaving it in an oven maintained at 50°C in air (the condition in which the column of drying at 50°C in Table 1 is represented by "yes").

[0036] The ratio of the number of Al atoms on the surface of the steel product, corrosion resistance and corrosion fatigue resistance were evaluated by using the surface-treated product as a test material.

[0037] The ratio of the number of Al atoms in the region from the surface to a depth of 5 μm was quantitatively analyzed through elementary analysis by using the EXD device, and the measured value was corrected by ZAF. The ratio of A to B was calculated and evaluated based on the result of the quantitative analysis, where A denotes the number of Al atoms and B denotes the total number of Fe, C, Al, P and O atoms, and of Si, Mn, Cr atoms that are optionally added. The material with a ratio of 3% or more was represented by "3 or more", the product with a ratio in the range of 0.5% or more and less than 3% was represented by "0.5 to 3", and the product with a ratio of less than 0.5% was represented by "less than 0.5".

[0038] The corrosion resistance was evaluated by leaving the test material in a constant temperature-constant humidity chamber (26°C, 95% RH) for 200 hours. The proportion of the rusted area to the total area after leaving for 200 hours was visually evaluated. The products with a surface ratio of the rusted surface of less than 80%, in the range of 80% or more and less than 90%, and 90% or more were evaluated as "best (a level having quite excellent corrosion resistance)", "good (a level having excellent corrosion resistance)" and "poor (a level having poor corrosion resistance)", respectively, by using the proportion of the rusted area C in Comparative Example 1 as a standard.

[0039] The corrosion fatigue resistance was evaluated by repeating the steps of vibrating a test material left under salt water spray (35°C, 5% NaCl) for 30 minutes at a shear stress τ of 733 $\pm$ 441 MPa for 3,000 times (1.5 Hz, for about 33 minutes), and leaving the test material in a constant temperature-constant humidity chamber (26°C, 95% RH) until the test material was broken. The corrosion fatigue resistance was evaluated as "best (a level quite excellent in corrosion fatigue resistance)" when the duration count was 120% or more, as "good (a level excellent in corrosion fatigue resistance)" when the duration count was in the range of 10% or more and less than 120%, and as "poor (a level poor in corrosion fatigue resistance" when the duration count was less than 110% on the basis of the duration count D in Comparative Example 1 as a standard.

[0040] The results are shown in Table 1. The steel product in Comparative Example 1 is a non-treated product, and serves as a standard for evaluating corrosion resistance and corrosion fatigue resistance.

Table 1

	Surface treatment condition					Evaluation of ratio of Al atoms	Evaluation of corrosion resistance	Evaluation of corrosion fatigue resistance
	Surface treatment example	Acidity ratio	Bath temperature (°C)	Immersion period (seconds)	Temperature of drying step (°C)			
Comparative example 1	-	-	-	-	-	Less than 0.5	Poor	Poor
Comparative example 2	B	2.0	Room temperature	180	50	Less than 0.5	Poor	Poor
Comparative example 3	B	2.5	Room temperature	180	50	Less than 0.5	Poor	Poor
Example 1	B	3.3	Room temperature	180	50	0.5 to 3	Good	Good
Example 2	B	3.8	Room temperature	180	50	3 or more	Best	Best
Example 3	B	4.7	Room temperature	180	50	3 or more	Best	Best
Example 4	B	5.0	Room temperature	180	50	3 or more	Best	Best
Example 5	B	5.4	Room temperature	180	50	3 or more	Best	Best
Example 6	B	5.7	Room temperature	180	50	0.5 to 3	Good	Good
Example 7	B	4.7	Room temperature	5	50	0.5 to 3	Good	Good
Example 8	B	4.7	Room temperature	30	50	3 or more	Best	Good
Example 9	B	4.7	Room temperature	360	50	3 or more	Best	Best
Example 10	B	4.7	Room temperature	1000	50	3 or more	Best	Best

(continued)

	Surface treatment condition					Evaluation of ratio of Al atoms	Evaluation of corrosion resistance	Evaluation of corrosion fatigue resistance
	Surface treatment example	Acidity ratio	Bath temperature (°C)	Immersion period (seconds)	Temperature of drying step (°C)			
Comparative example 4	A	4.7	Room temperature	5	-	Less than 0.5	Poor	Poor

Table 1

	Surface treatment condition					Evaluation of ratio of Al atoms	Evaluation of corrosion resistance	Evaluation of corrosion fatigue resistance
	Surface treatment example	Acidity ratio	Bath temperature (°C) Room	Immersion period (seconds)	Temperature of drying step (°C)			
Comparative example 5	A	4.7	temperature	30	-	Less than 0.5	Poor	Poor
Comparative example 6	A	4.7	Room temperature	180	-	Less than 0.5	Poor	Poor
Comparative example 7	A	4.7	Room temperature	360	-	Less than 0.5	Poor	Poor
Example 11	A	4.7	Room temperature	1000	-	3 or more	Best	Best
Comparative example 8	A	4.7	30	5	-	Less than 0.5	Poor	Poor
Comparative example 9	A	4.7	30	30	-	Less than 0.5	Poor	Poor
Example 12	A	4.7	30	180	-	0.5 to 3	Good	Good
Example 13	A	4.7	30	360	-	0.5 to 3	Good	Good
Example 14	A	4.7	30	1000	-	3 or more	Best	Best
Comparative example 10	A	4.7	40	5	-	Less than 0.5	Poor	Poor
Example 15	A	4.7	40	30	-	3 or more	Best	Good
Example 16	A	4.7	40	180	-	3 or more	Best	Best
Example 17	A	4.7	40	360	-	3 or more	Best	Best
Example 18	A	4.7	40	1000	-	3 or more	Best	Best
Comparative example 11	A	4.7	50	5	-	Less than 0.5	Poor	Poor
Example 19	A	4.7	50	30	-	3 or more	Best	Good
Example 20	A	4.7	50	180	-	3 or more	Best	Best

(continued)

	Surface treatment condition							
	Surface treatment example	Acidity ratio	Bath temperature (°C) Room	Immersion period (seconds)	Temperature of drying step (°C)	Evaluation of ratio of Al atoms	Evaluation of corrosion resistance	Evaluation of corrosion fatigue resistance
Example 21	A	4.7	50	360	-	3 or more	Best	Best
Example 22	A	4.7	50	1000	-	3 or more	Best	Best

[0041] Steel products in Comparative Examples 2 and 3 and in Examples 1 to 6 are in accordance with the second examples of the surface treatment in FIG. 1B. That is, the products were dried in air by heating at 50°C (first drying step) after immersing in the treatment solution at room temperature for 180 seconds, and then spontaneously dried again (second drying step) after rinsing, where the acidity ratio of the treatment solution was changed in the range of 2.0 to 5.7. The ratio of the number of Al atoms is "0.5 to 3" or "3 or more" in the products in Examples 1 to 6 in which the acidity ratio is in the range of 3.3 to 5.7. In particular, all the ratios of Al atoms are "3 or more" in the products in Examples 2 to 5 in which the acidity ratio is in the range of 3.8 to 5.4. However, all the ratios of Al atoms are "less than 0.5" in the products in Comparative Examples 2 and 3 in which the acidity ratio is 2.5 or less.

[0042] Corrosion resistance and corrosion fatigue resistance are "good (excellent level)" or "best (quite excellent level)" in the products in Examples 1 to 6 in which the acidity ratio is in the range of 3.3 to 5.7. In particular, both the corrosion resistance and corrosion fatigue resistance are "best (quite excellent level)" in the products in Examples 2 to 5 in which the acidity ratio is in the range of 3.8 to 5.4. However, both the corrosion resistance and corrosion fatigue resistance are "poor (poor level)" in the products in Comparable Examples 2 and 3 in which the activity ratio is 2.5 or less.

[0043] The steel products in Examples 7 to 10 are in accordance with the second example of the surface treatment in FIG. 1B. That is, the products were dried by heating at 50°C in air after immersing in the treatment solution with an acidity ratio of 4.7 at room temperature, and then spontaneously dried after rinsing, where the immersion period was changed in the range form 5 to 1000 seconds. The atomic ratio of the number of Al atoms is "0.5 to 3" or "3 or more" in all these examples. In particular, the ratio of the number of Al atoms is "3 or more" in the products in all Examples 8 to 10 in which the immersion period is 30 seconds or more. Corrosion resistance and corrosion fatigue resistance are "good (excellent level)" or "best (quite excellent level)" in the products in all the examples. In particular, corrosion resistance and corrosion fatigue resistance are "best (quite excellent level)" in the products in Examples 9 and 10 in which the immersion period is 360 seconds or more.

[0044] The steel products in Comparative Examples 4 to 7 and Example 11 are in accordance with the first example of the surface treatment in FIG. 1A. That is, the products were rinsed and spontaneously dried after immersing in the treatment solution with an acidity ratio of 4.7 at room temperature, where the immersion period was changed in the range of 5 to 1000 seconds. The atomic ratio of the number of Al atoms is "3 or more" in the product in Example 11 with an immersion period of 1000 seconds. However, the ratio of the number of Al atoms is "less than 0.5" in the products in Comparative Examples 4 to 7 with an immersion period of 360 seconds or more. Corrosion resistance and corrosion fatigue resistance are "best (quite excellent level)" in the product in Example 11 with an immersion period of 1000 seconds. However, corrosion resistance and corrosion fatigue resistance are "poor" (poor level) in the products in Comparative Examples 4 to 7 with an immersion period of 360 seconds or less.

[0045] The steel products in Comparative Examples 8 and 9 and Examples 12 to 14 are in accordance with the first example of the surface treatment in FIG. 1A. That is, the products were rinsed and spontaneously dried after immersing in the treatment solution with an acidity ratio of 4.7 at 30°C, where the immersion period was changed in the range form 5 to 1000 seconds. The atomic ratio of the number of A1 atoms is "0.5 to 3" or "3 or more" in the products in Examples 12 to 14 with an immersion period of 180 seconds or more. In particular, the ratio of the number of Al atoms in the product in Example 14 with an immersion period of 1000 seconds is "3 or more". However, the ratio of the number of Al atoms is "less than 0.5" in the products in Comparative examples 8 and 9 with an immersion period of 30 seconds or less. Corrosion resistance and corrosion fatigue resistance are "good (excellent level)" or "best (quite excellent level)" in the products in Examples 12 to 14 with an immersion period of 180 seconds or more. In particular, corrosion resistance and corrosion fatigue resistance are "best (quite excellent level)" in the product in Example 14 with an immersion period of 1000 seconds. However, Corrosion resistance and corrosion fatigue resistance are "poor (poor level)" in the products in Comparative Examples 8 and 9 with an immersion period of 30 seconds or less.

[0046] The steel products in Comparative Examples 10 and 11 and Examples 15 to 22 are in accordance with the first example of the surface treatment in FIG. 1A. That is the products were rinsed and spontaneously dried after immersing in the treatment solution with an acidity ratio of 4.7 at 40°C or 50°C, where the immersion period was changed in the range of 5 to 1000 seconds. The ratio of the number of Al atoms is "3 or more" in the products in Examples 15 to 22 with an immersion period of 30 seconds or more. However, the ratio of the number of Al atoms is "less than 0.5" in the products in Comparative Examples 10 and 11 with an immersion period of 5 seconds. Corrosion resistance and corrosion fatigue resistance are "good (excellent level)" or "best (quite excellent level)" in the products in Examples 15 to 22 with an immersion period of 30 or more. In particular, corrosion resistance and corrosion fatigue resistance are "best (quite excellent level)" in the products in Examples 16 to 18 and Examples 20 to 22 with an immersion period of 180 seconds. However, corrosion resistance and corrosion fatigue resistance are "poor (poor level)" in the products in Comparative Examples 10 and 11 with an immersion period of 5 seconds.

[0047] While spring steel products have described in above-mentioned examples, these examples may be conveniently applied to bolts and various iron-base constructions.

[0048] The invention is not restricted to a steel product SAE9254 having the above-mentioned diameter and length, instead the invention is applicable to other steel products at a practical stage in the range not departing from the spirit of the invention. Specifically, the invention is applicable to all the steel products containing at least Fe and C with optionally added at least one of Si, Mn and Cr. In addition, the surface treatment conditions (for example, bath temperature, immersion period and the like) are not restricted to those as set forth in the examples, but an appropriate combination is possible in the range not modifying the spirit of the invention.

Claims

1. A steel product excellent in corrosion resistance and corrosion fatigue resistance, **characterized by** comprising a coating film on the surface of the steel product, wherein a ratio of the number of Al atoms to the total number of Fe, C, Al, P and 0 atoms and optionally added Si, Mn and Cr atoms is 0.5% or more in an average composition of the coating film, and the number of Al atoms in the average composition of the coating film is higher than the number of Al atoms in an average composition of the steel product before surface treatment.

2. A steel product excellent in corrosion resistance and corrosion fatigue resistance, **characterized by** comprising a coating film on the surface of the steel product, wherein a ratio of the number of Al atoms to the total number of Fe, C, Al, P and 0 atoms and optionally added Si, Mn and Cr atoms is 0.5% or more in an average composition in a region from the surface to a depth of 5 μm of the steel product, and the number of Al atoms in an average composition of the coating film is higher than the number of Al atoms in an average composition of the steel product before surface treatment.

3. The steel product excellent in corrosion resistance and corrosion fatigue resistance according to claim 1 or 2, **characterized in that** the ratio of the number of Al atoms to the total number of Fe, C, Al, P and 0 atoms and optionally added Si, Mn and Cr atoms is 3% or more.

4. A surface treatment method for a steel product, in particular for a steel product according to claim 1 or 2, **characterized by** comprising:

   rinsing (1) the steel product after allowing an aqueous solution at room temperature having an acidity ratio in the range of 3.3 to 5.7 and containing Al ions to contact the surface of the steel product; and
   drying (2) the steel product.

5. A surface treatment method for a steel product, in particular for a steel product according to claim 1 or 2, **characterized by** comprising:

   drying (2a) the steel product after allowing an aqueous solution at room temperature having an acidity ratio in the range of 3.3 to 5.7 and containing Al ions to contact the surface of the steel product; and
   drying (2b) again the steel product after rinsing (1).

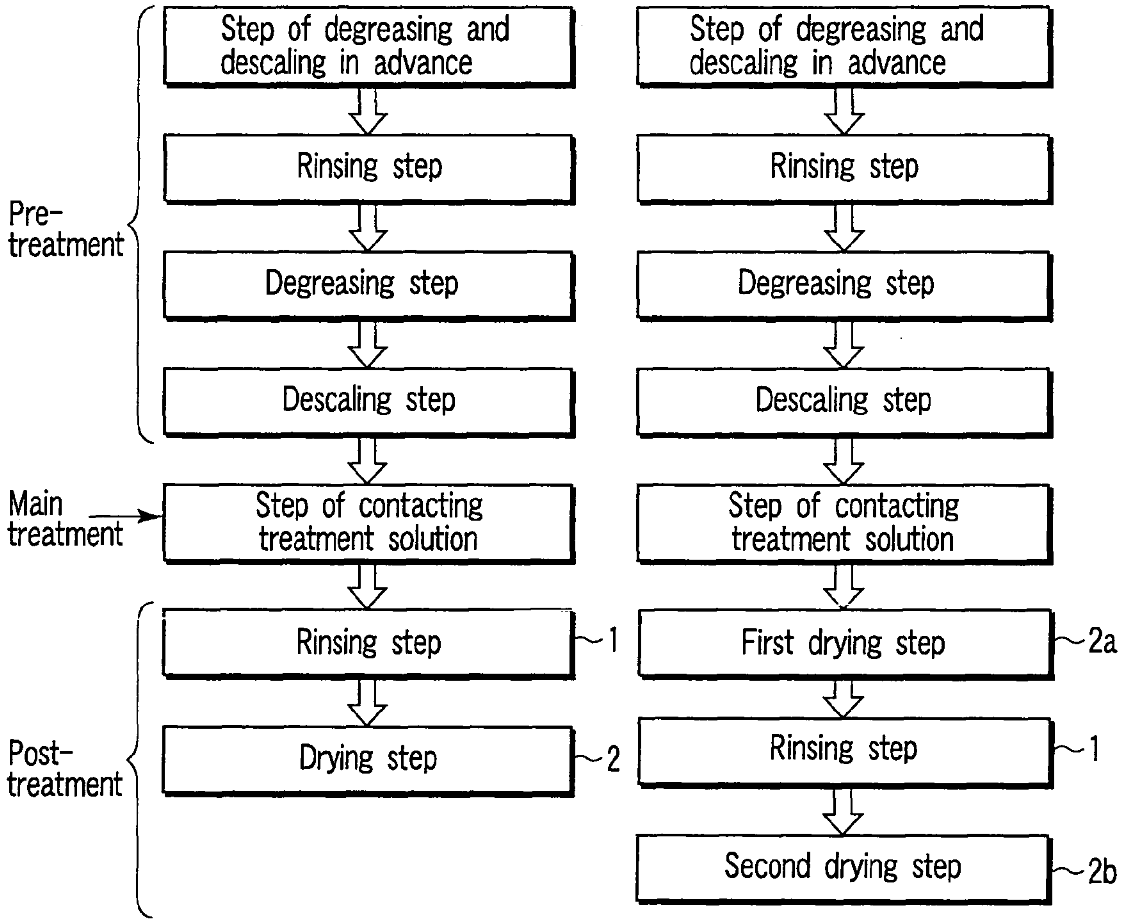
6. The surface treatment method for a steel product, according to claim 4 or 5, **characterized by** comprising allowing an aqueous solution containing Al ions to contact the surface of the steel product at a temperature from 40 to 50°C for 30 seconds or more.

7. The surface treatment method for a steel product, according to claim 4 or 5, **characterized by** comprising allowing an aqueous solution containing Al ions to contact the surface of the steel product at 30°C for 180 seconds or more.

8. The surface treatment method for a steel product, according to claim 5, **characterized by** comprising drying at 50°C or less after allowing the steel product to contact the aqueous solution containing Al ions and before rinsing.

9. The surface treatment method for a steel product, according to any one of claims 4 to 8, **characterized in that** the acidity ratio of the aqueous solution containing Al ions is in the range of 3.8 to 5.4.

10. The surface treatment method for a steel product, according to any one of claims 4 to 8, **characterized in that** an aqueous solution having a concentration by weight of aluminum phosphate in the range of 1 to 10%, and having an acidity ratio in the range of 3.8 to 5.4 is used as a surface treatment solution.



(First example of surface treatment)

FIG. 1A

(Second example of surface treatment)

FIG. 1B

REFERENCES CITED IN THE DESCRIPTION

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