Surface Properties of the Silicon Steel Coated with Metal Phosphate Solution

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The surface properties of the silicon steel coated with the mixture of aluminum and zinc phosphate solution were investigated as an alternative treatment to chromate conversion coating. The solution used for the silicon steel coating is consisted of the mixture of aluminum and zinc phosphate, colloidal silica, emulsion polymer, titanium chelate and metal hydroxide. The surface properties of silicon steel were compared with those of chromate type coating solution. From the experimental results, it was found that adding titanium chelate and metal hydroxide to the mixture of aluminum and zinc phosphate solution enhanced the adhesion and corrosion properties of the silicon steel surface.

Introduction

Generally, non-oriented electrical steel sheets are used for iron cores of motors or generators. These non-oriented electrical steel sheets are classified into electrical steel sheets that require that stress relief annealing (SRA) be performed to improve magnetic properties after punching and electrical steel sheets that do not require SRA to be performed when the costs of heat treatment are excessive in consideration of the increase in magnetic properties due to SRA. In a process of manufacturing this non-oriented electrical steel sheet, a coating step of forming an insulation film for the interlayer insulation between iron plates is performed in a finishing step.
Generally, an insulation film for a non-oriented electrical steel sheet contains chromium. The chromium is helpful in improving the material properties of the insulation film after SRA. However, in a chromium-free coating agent, phosphate is used as an alternative material for chromium. In this case, the problem with hygroscopicity caused by a very small amount of free phosphoric acid remaining in the film and the problem with adhesivity in annealing due to the hygroscopicity may occur[1~2]. Paradoxically, these problems can be solved by the introduction of chromium (refer to Equation 1).

$$CrO_3 + 2H_3PO_4 \rightarrow Cr(PO_4)_2 + 6H_2O \quad \text{--------} \ (1)$$

Therefore, in this study the surface properties of the silicon steel coated with the mixture of

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aluminum and zinc phosphate solution were investigated as an alternative treatment to chromate conversion coating.

Experimental

A non-oriented electrical steel sheet including 0.1% by weight of silicon and having a thickness of 0.50 mm and an area of 120×60 mm was used as a sample, and various treatment liquids were applied on the sample in the range of 0.5 ~ 6.0 g/m^2 using a coating bar.
Subsequently, the sample treated in this way was dried at a temperature of 650℃ for several seconds and was then air-cooled.
The insulation properties of the sample was evaluated by measuring the current value when a voltage of 0.5 V and a current of 1.0 A were applied under a pressure of 300 PSI, the adhesivity there of was evaluated by measuring the minimum diameter of the arc on which there was no peeled film when the sample was formed into respective arcs having diameters of 10, 20, and 30 to 100 mm and was then bent at an angle of 180°, and the appearance of film was evaluated by observing striping, gloss, and the like with the naked eye.

Results and discussion

Table 1 shows the corrosion resistance of the coating composition depending on the kind of metal phosphate and metal oxide. In order to prepare a chromium-free coating composition, the corrosion resistance and adhesion thereof must be secured through the effective combination of the metal phosphates, and the metal oxides, added in place of chromium, must be able to prevent the sticking of phosphate and the formation of powder of phosphate. Therefore, Table 1 shows the test results for finding the component composition suitable for this chromium-free coating composition. In this case, the weight ratio of the phosphate solution and the emulsified polyester resin was adjusted to a ratio of 1:2, in which the stability there between is best[3-8].
As given in Table 1, as the result of evaluating the corrosion resistance of test samples by mixing monoaluminum phosphate ($Al(H_2PO_4)_3$) and monozinc phosphate ($Zn(H_2PO_4)_2$), it could be seen that the test example 11, in which about 2g of a solid, in which cobalt hydroxide and strontium hydroxide were mixed at a ratio of 50:50, is added to a 100g phosphate solution having a solid content of 60% by weight and a viscosity of 30 ~ 70 cp, particularly 50 cp, in which the monoaluminum phosphate ($Al(H_2PO_4)_3$) and the monozinc phosphate ($Zn(H_2PO_4)_2$) are mixed at a ratio of 50:50, is suitable for preventing the surface stickiness caused by phosphate and the precipitation of powder and for improving the corrosion resistance.
Further, from the above Table 1, in order to evaluate the degree of improvement of film adhesion and film strength after SRA using a material, in which about 2g of a solid, in which cobalt hydroxide and strontium hydroxide are mixed at a ratio of 50:50, is added to a 100g phosphate solution in which monoaluminum phosphate ($Al(H_2PO_4)_3$) and monozinc phosphate ($Zn(H_2PO_4)_2$) are mixed, the material was prepared by changing the amount of a titanium chelator that is added. Moreover, in order to prevent the stickiness caused by phosphate, the amount of colloidal silica was also changed.
Table 2 shows the coating compositions prepared by changing the amount of the titanium chelator and colloidal silica. Also, Table 2 shows the characteristics of the film formed by applying the prepared coating compositions such that the application amount thereof is 2.5 g/m^2 and then drying them.

【Table 1】

No.	Class.	Kind of phosphate	Viscosity of phosphate (cp)	Polyester resin (solid weight)	Oxides		Corro-sion	Sticki-ness
					Kind	Weight		
1	Test	Al+Zn (7/3)	100	200	Co. Hydro.	2	□	x
2	Test	Al+Zn (5/5)	50	200	Co. Hydro.	2	Δ	Δ
3	Test	Al+Zn (3/7)	40	200	Co. Hydro.	2	x	□
4	Test	Al+Zn (7/3)	100	200	St. Hydro	2	x	x
5	Test	Al+Zn (5/5)	50	200	St. Hydro	2	□	Δ
6	Test	Al+Zn (3/7)	40	200	St. Hydro	2	x	□
7	Test	Al+Zn (7/3)	100	200	Co.hy+St.hy(7/3)	2	□	x
8	Test	Al+Zn (5/5)	50	200	Co.hy+St.hy(7/3)	2	□	○
9	Test	Al+Zn (3/7)	40	200	Co.hy+St.hy(7/3)	2	□	Δ
10	Test	Al+Zn (7/3)	100	200	Co.hy+St.hy(5/5)	2	□	Δ
11	Test	Al+Zn (5/5)	50	200	Co.hy+St.hy(5/5)	2	○	○
12	Cr type		-	-	-	2	●	●

[Evaluation of material properties / excellent: ●, good: ○, ordinary: Δ, poor: □, bad: x]

As given in the Table 2, it was found that the test examples 11-8 and 11-9, in which 1.0 ~ 3.0g of aluminum silicate and 0.1 ~ 0.5g of a titanium chelator are added to a 100g phosphate solution having a solid content of 60% by weight, in which the monoaluminum phosphate ($Al(H_2PO_4)_3$) and the monozinc phosphate ($Zn(H_2PO_4)_2$) are mixed and the cobalt hydroxide and strontium hydroxide are added thereto, have improved corrosion resistance and film adhesion. Further, it was found that the test examples 11-8 and 11-9 have equal or better corrosion resistance and film adhesion than conventional chromium-containing coating compositions.

Conclusions

There is provided a chromium-free coating composition for forming an insulation film, the composition having excellent corrosion resistance and excellent film adhesion and film strength after stress relief annealing (SRA), including, based on a 100g phosphate solution having a solid content of 60% by weight, in which monoaluminum phosphate and monozinc phosphate are mixed at a 1:1 ratio: 0.5 ~ 5g of a solid in which cobalt hydroxide and strontium hydroxide are mixed at a 1:1 ratioc; 100 ~ 300g of an emulsified polyester resin or an emulsified epoxy resin having a solid content of 20% by weight; 3 ~ 10g of aluminum silicate having a solid content of 20% by weight; and 0.1 ~ 6g of a titanium chelator. According to the present research, an insulation film having excellent corrosion resistance and excellent film adhesion and film strength after stress relief annealing (SRA) can be formed on a non-oriented electrical steel sheet using a coating composition including a phosphate solution in which monoaluminum phosphate and monozinc phosphate are mixed, a solid in which cobalt hydroxide and strontium hydroxide are mixed, an emulsified polyester resin, aluminum silicate and a titanium chelator.

【Table 2】

No.	Class.	Kind of phosphate	Viscosity phosphate	Polyester resin	Oxides (Weight)		Ti	Corro-sion	Adhesivity (mmφ)
11-3	Test	Al+Zn (5/5)	50	200	Co.hy+St.hy	0.5	2	○	30
11-4	Test	Al+Zn (5/5)	50	200	Co.hy+St.hy	1	2	○	30
11-5	Test	Al+Zn (5/5)	50	200	Co.hy+St.hy	5	2	○	30
11-6	Test	Al+Zn (5/5)	50	200	Co.hy+St.hy	8	2	○	30
11-7	Test	Al+Zn (5/5)	50	200	Co.hy+St.hy	0.05	2	○	30
11-8	Test	Al+Zn (5/5)	50	200	Co.hy+St.hy	0.1	2	●	20
11-9	Test	Al+Zn (5/5)	50	200	Co.hy+St.hy	0.5	2	●	20
11-10	Test	Al+Zn (5/5)	50	200	Co.hy+St.hy	1	2	○	40
Cr-type								○	

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