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Effects of ammonium tungstate on the properties of insulating coating for grain-oriented silicon steel

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ABSTRACT

The effects of $(NH_4)_2WO_4$ on the properties of phosphate insulating coating for grain-oriented silicon steel were studied. It is shown that, with gradually replacing CrO_3 by $(NH_4)_2WO_4$ in the coating solution, the wettability of coating solution first enhances and then degrades. The interlamination resistance, lamination factor and magnetism induction intensity of silicon steel first increase and then decrease, the core loss first decreases and then increases. When the $(NH_4)_2WO_4$ content is 1.0 wt%, the coating solution shows the best wettability on the silicon steel substrate. The formed insulating coating is compact and smooth with improved corrosion resistance, there is a transition layer 0.6–0.8 μm between the insulating coating and the forsterite sub-coating. Furthermore, the humidity resistance of the insulating coating is not significantly changed. The optimal interlamination resistance, lamination factor, magnetism induction intensity and core loss of grain-oriented silicon steel can be obtained, which are 18,021 $\Omega \cdot mm^2$, 97.1%, 1.872 T and 1.113 $W \cdot kg^{-1}$, respectively.

1. Introduction

Grain-oriented silicon steel is a kind of soft magnetic Fe-Si alloy with (1 1 0) [0 0 1] Goss texture. It is mainly used to make the core for generators, motors and transformers [1,2]. In order to prevent the bonding between the silicon steel sheets in the process of high temperature annealing, an MgO layer should be coated on the surface of silicon steel. During the high temperature annealing, the MgO will react with the SiO_2 film which is formed on the surface of silicon steel in the decarburization annealing process. The reaction between MgO and SiO_2 leads to the formation of forsterite (Mg_2SiO_4) sub-coating. To further improve the insulating property and corrosion resistance of silicon steel, an insulating coating needs to be coated on the forsterite sub-coating [3]. Before actual use, the silicon steel should undergo the stress relief annealing ~780 °C to further reduce the core loss. Thus, the insulating coating should be inorganic for the oriented silicon steel [4]. There are several types of inorganic insulating coatings, such as TiN, CrN, TiC, chromate, and phosphate coatings [5,6]. The TiN, CrN and TiC ceramic coatings prepared by magnetron sputtering equipment have not been extensively applied in industrial production. The inorganic phosphate coating for silicon steel is the most widely used in industry. The phosphate coating solution is mainly composed of aluminum dihydrogen phosphate, colloidal silica and deionized water. The chromic anhydride is often used as an additive in the phosphate coating solution, which not only improves the wettability of the coating solution but also improves the adhesivity, humidity resistance and other properties of the coating [6]. Due to the high toxicity and carcinogenicity of hexavalent chromium in chromic anhydride, it is harmful to human and environment. With the growth of people's consciousness on environmental protection, it is urgent to decrease the chromic anhydride content in the coating solution and maintain the properties of the insulating coating [7]. At present, the works dealing with the environmental friendly phosphate insulating coatings for oriented silicon steel are limited and most of them are appeared as patents [8–10].

Fuji et al. reported that the chromium anhydride can be replaced by the oxide colloidal substances [11,12] or the boron compounds [13], such as alumina, zirconia and calcium borate, to make the chromium-free insulating coating. Haselkorn et al. [14] reported that a chromium-free insulating coating could be formed for oriented silicon steel by using aluminum silicate, silicon dioxide, alumina and metal dihydrogen phosphate salt as coating solution. However, the addition of insoluble solid particles mentioned above could lead to the agglomeration and precipitation in the coating solution, thus deteriorates the stability of coating solution. Cakici and other researchers [15–24] reported some

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Table 1
The contents of ammonium tungstate and chromic anhydride in the insulating coating solution (the total amount of ammonium tungstate and chromium anhydride in the coating solution is 2.5 wt%).

Insulating coating solution	Content of ammonium Tungstate/wt%	Content of Chromium Anhydride/wt%
Sample No. 1	0	2.5
Sample No. 2	0.5	2.0
Sample No. 3	1.0	1.5
Sample No. 4	1.5	1.0
Sample No. 5	2.0	0.5
Sample No. 6	2.5	0

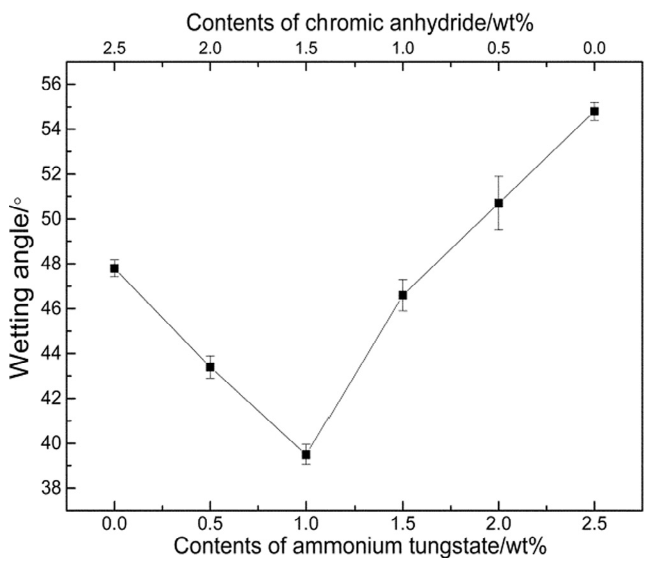

Fig. 1. The wetting angles between the grain-oriented silicon steel substrate and the insulating coating solutions with different contents of ammonium tungstate and chromic anhydride.

methods to prepare the surface modified oxide nanoparticles in the researches of supercapacitance, photocatalytic and adsorbent. These methods may be adopted to improve the dispersity of solid particles and the stability of coating solution for grain-oriented silicon steel. Xu et al. [25] reported a method of forming a chromium-free insulating film for non-oriented silicon steel using metal dihydrogen phosphate salt, epoxy resin, naphthenate drier or isooctanoate metal salt drier. But the coating solution is not suitable for oriented silicon steel, the organic additions will be decomposed during the stress relief annealing ~780 °C. Furthermore, the literatures about the humidity resistance property of insulating coating for oriented silicon steel are also limited.

In this paper, the water-soluble ammonium tungstate was used to gradually replace the highly toxic chromic anhydride in the phosphate coating solution. The effects of ammonium tungstate addition on the microstructure, insulating and humidity resistance properties of insulating coating were investigated. The properties of oriented silicon steel, such as core loss, were also reported.

2. Material and methods

The substrates for experiments in this paper were the grain-oriented silicon steel sheets (0.285 mm thickness) with a forsterite coating on surface, which were produced by New Wanxin (Fujian) Precision Sheet Co., Ltd (Xianyou, China). The insulating coating solution is comprised of aluminum dihydrogen phosphate, colloidal silica, ammonium tungstate, chromic anhydride and deionized water. Except for the deionized water, the chemicals in this paper were obtained from Sinopharm Chemical Reagent Co.,Ltd (Shanghai, China). The contents of ammonium tungstate and chromic anhydride are different for the coating solution, as shown in Table 1.

The substrates were rinsed with deionized water and dried in flowing argon. The insulating coating solutions were uniformly coated on the substrates by a rubber roller. Then, the coated samples were dried at 450 °C for 35 s and then heated at 820 °C for 45 s in flowing argon. Finally, the coated samples were stress relief annealed at 780 °C for 2 h in flowing argon.

The wetting angle is used to indicate wettability between solution and substrate. It refers to the angle between the liquid solid interface and the tangent of the liquid surface at the contact point of the liquid phase and the solid phase. The wetting angle between the insulating coating solution and the substrate was measured by SL200B contact angle measurement instrument. The volume of the insulating coating solution dropped onto the substrate was 1 μL. The surface morphology, cross-sectional microstructure and the elemental composition of the insulating coating were examined by scanning electron microscopy (SEM, ZEISS SUPRA 55) equipped with energy-dispersive X-ray spectroscopy (EDS). The Fourier transform infrared spectrum (FTIR, Nicolet 360) was used to study the chemical structure of insulating coating. The phase compositions of insulating coatings were examined by X-ray diffraction (XRD, Cu K_α, Rigaku Ultima III). The dehydration weight loss experiment was performed in flowing argon using thermogravimetric analysis (TGA, SDT Q600) from 30 to 500 °C. The data of FTIR and TGA were used to estimate the humidity resistance of the insulating coating. The core loss $P_{17/50}$ and the magnetic induction intensity B_8 were obtained by an Epstein square (Chinese National Standard, GB/T 3655–2008 Methods of measurement of the magnetic properties of electrical steel sheet and strip by means of an Epstein square). The interlamination resistance was measured by insulating resistance tester (HT-2007) (Chinese National Standard, GB/T 2522–2007 Methods of test for the determination of surface insulation resistance and coating adhesion of electric sheet and strip). The lamination factor of grain-oriented silicon steel was measured by lamination factor tester (DZ-2007) (Chinese National Standard, GB/T 19289-2003 Methods of measurement of density, resistivity and lamination factor of electrical steel sheet and strip). The lamination factor refers to the ratio of the net metal volume (not include the volume of coating) to the core volume (include the volume of net metal and coating). The adhesion of the coating was measured by the bend method (Chinese National Standard, GB/T 2522–2007 Methods of test for the determination of surface insulation resistance and coating adhesion of electric sheet and strip). The adhesion degree has four levels (A, B, C, D), A means the best adhesion and D means the worst adhesion. The corrosion resistance of the samples was investigated via electrochemical testing using an electrochemical workstation (CHI660D) at 25 °C. The electrochemical measurements were conducted in 3.5 wt% NaCl solution by standard three-electrode cells. An SCE electrode was used as reference electrode, a platinum electrode (20 mm × 20 mm) was used as counter electrode and the samples with the area of 1 cm^2 were used as the working electrode.

3. Results and discussion

The wetting angles between the grain-oriented silicon steel substrate and the different insulating coating solutions are shown in Fig. 1. With gradually increasing the content of ammonium tungstate in the composite additive, the wetting angle first decreases and then increases. It indicates that the wettability of the insulating coating solution first improves and then degrades. While the combined addition of 1.0 wt% ammonium tungstate and 1.5 wt% chromic anhydride in the coating solution, the wetting angle is the smallest 39.5°, which means the best wettability of the coating solution. It indicates that the appropriate substitution of chromic anhydride by ammonium tungstate can improve the wettability of the coating solution.

Generally, wettability can be improved by three methods: 1)