Anti-Corrosion Methods and Materials

Emerald Article: Study of an environment-friendly insulating coating with high corrosion resistance on electrical steel

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Study of an environment-friendly insulating coating with high corrosion resistance on electrical steel

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Abstract

Purpose – The purpose of this paper is to study the corrosion resistance and the insulating characteristics of an environment-friendly chromium-free coating on electrical steel.

Design/methodology/approach – A water-based semi-inorganic environment-friendly insulating coating on electrical steel was developed. The coating system of silane coupling agent and rare earth salt were used first in this coating to replace the chromate containing coating. In this study, it provided a successful combination of coating and passivation.

Findings – Several test results, such as insulating ability, corrosion resistance, adhesion strength and hardness, showed that the performance of the film complied fully with the industry standards, particularly excellent in its corrosion resistance and the maximum corrosion resistance (neutral salt-spray test) time up to 20 h.

Originality/value – There have been few reports on the chromium-free insulating coating on electrical steel, and described in the paper, this environment-friendly insulating coating on electrical steel was found to be highly effective.

Keywords Corrosion resistance, Passivation, Salts, Steels, Coatings technology

Paper type Research paper

Introduction

Electrical steel has excellent electromagnetic performance and is applied mainly to various motors, transformers, for the iron core of barreters, electrical elements and so on. Therefore, a thin (0.5-5 μm) insulating film is required on the surface of the electrical steel to make a higher interface resistance for the silicon steel sheets, thereby minimizing inter-layer power loss of the silicon steel sheets, preventing short circuits between laminations to avoid vortex loss increase, and thus to improve its electromagnetic performance (Marder and Stephenson, 1990). On the other hand, the use of insulating thin film on electrical steel demands high corrosion resistance to avoid corrosion and rust caused by various corrosive media during storage, transport and use of electrical steel sheets (Han and Zhang, 2008). The recent increase in the environmental consciousness has highlighted that hexavalent chromium (Cr^{6+}) is extremely harmful or even deadly to human beings and would cause severe environmental pollution. The European Union has stopped using electrical steels with hexavalent chromium (Cr^{6+}) coatings since July 1, 2006. As a result, the study of chromium-free environmentally friendly insulating coatings is always encouraged and emphasized by the governments of countries around the world and, consequently, some progress has been made.

Japanese patent JP 7268641 (Kobayashi *et al.*, 1995) involved a phosphate-organic resin insulating coating with good corrosion resistance. Japanese patent JP 2005240125 (Takeda *et al.*, 2005) reported an aqueous insulating coating with excellent corrosion resistance, adhesion strength and insulating ability, which was free of chromium and friendly to the environment. Many researchers have reported research of similar semi-inorganic insulating coatings in Japanese patents like JP 2008127664 and JP 2008127674 (Sashi *et al.*, 2008a, b), which had better corrosion resistance, picking resistance and scratching resistance than do traditional chromate coatings. Pohang Iron and Steel Co., Ltd (POSCO) in South Korea reported two kinds of non-oriented electrical steel sheet insulating coating in its patents WO 2009082088 (Han *et al.*, 2009) and WO 2009084777 (Kim *et al.*, 2009). One of the semi-inorganic coatings had superior compatibility and surface gloss, and the other system, containing $BaSO_4$-TiO_2, had good insulation and heat resistance. Chinese patent CN 101486866 A (Zhang *et al.*, 2009) proposed a single-component chromium-free water-based insulating silicon

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steel coating, which maintained good insulating properties after exposure to high-temperature stress annealing.

The patent of "silicon steel sheet inorganic/organic coating" of the European and Chinese branches of the American Armocol Company involved a semi-inorganic chromium-free insulating coating, from a water-based suspension liquid, which could be used on non-oriented silicon steel sheets. Furthermore, it could be used to create an insulating film with high inter-layer resistivity.

Additionally, there is an urgent need to solve the increasing safety and pollution problems caused by organic solvent volatilization, generated by traditional solvent-based silicon steel sheet coatings. At the present time, investigations carried out on water-soluble semi-inorganic/inorganic silicon steel sheets have become topical worldwide (Zhao *et al.*, 2008). Although researchers around the world have made great progress in this area, as yet the performances of the coatings cannot meet industrial requirements. However, the electrical steel insulating coating that is the subject of the present report is friendly to the environment, safe, effective and low cost. The test results show that the performance of the coating appeared to be in full compliance with industrial standards, especially in respect of its excellent corrosion resistance.

Experimental

Materials

In all experiments, electrical steel sheet (1.5-mm thickness), provided by Shanghai Bao Steel Group, was prepared by dividing into 80×60 mm sample plates. Every steel sheet sample was degreased at about 325 K for 5 min in an aqueous alkaline degreaser, after which its surface was polished with emery paper and rinsed with distilled water. Following these steps, the sample was rinsed with distilled water before use.

In order to meet industrial demands, all chemicals were chosen as being suitable for the iron and steel industry. Industrial chemicals including aluminum dihydrogen phosphate, polyvinyl alcohol, tetrabutyl titanate, acrylic resin, cerium salt, hydrogen peroxide, triethanolamine and so on were used in the experiments. A high-grade reagent of silane coupling agent (SCA) used in this experiment was a commercial product of Wuhan University Silicone New Material Co., Ltd, Hubei, PR China.

Coating preparation

An example of the insulating coating preparation on electrical steel sheets is described as follows: aluminum dihydrogen phosphate, cerium salt, molybdenum salt, hydrogen peroxide, triethanolamine and polyvinyl alcohol were first fed into a small grinder in a certain sequence and proportion. After this step, an aqueous solution containing SCA and methanol (hydrolyzed for several hours, 298 K, with agitation) were added into the mixture after the pH value of the aqueous solution had been adjusted to about 2.8. Finally, a 200-mesh filter was used to sieve the mixed coating solution.

The steel sample sheets then were rinsed thoroughly with distilled water and were treated in the foregoing solution immediately after they were acid activated in 3 mass percent HNO_3 at 298 K for about 10 s. Immediately after the roller coating process, the specimens with wet films were placed into a convection oven at 523-623 K for 5 min. The specimens were removed from the oven for natural aging for at least 2 h.

Test method

An LND-1 coating-4 coating viscosity meter was used for testing the viscosity of the coating solutions, and a TT220 digital coating thickness gauge was used for measuring the thickness of the films on the electrical steel sample sheets. The insulating ability, corrosion resistance, adhesion strength, film formation, hardness, blanking property and weldability of the films were tested according to corresponding Chinese national standards.

Results

Optimization of inorganic additives

According to some studies on relevant coating systems or chromate passivation replacement technologies in related references (Socha *et al.*, 2007), the combination between organic silane and inorganic systems was put forward and was used as an important film-forming method (Socha and Fransaer, 2005). Based on the traditional excellent insulating material, an inorganic chemical of aluminum dihydrogen phosphate was chosen at first as the main film-forming material, and SCA was used as an auxiliary material. In the present study, three kinds of inorganic passivators, i.e. a cerium salt, a molybdenum salt and a titanium salt were used as additives in the coating solution for comparison with a single factor. The test results are shown in Table I.

Table I shows that the corrosion resistance of the cerium salt system was the best of the three kinds of inorganic passivators. The coating solution of the cerium salt was colorless and transparent, whereas the other two salts were colored and opaque after being mixed with aluminum dihydrogen phosphate and acrylic resin, and therefore affected the appearance of coating to some extent. Corrosion pits appeared in the film of cerium salt coating after immersion in 5 percent NaCl solution for 24 h, and appeared in the other two salts after immersion for no more than 12 h, showing that the film based on cerium salt on the electrical steel could improve its corrosion resistance significantly. As for paintability, which could ensure the stability of the coating during industrial production, the coating solution based on the cerium salt was slightly better than those based on the molybdenum and titanium salts. Therefore, the rare earth salt was selected as the inorganic additive in electrical steel insulating coating system for the present study.

Selection of SCA

A comparison experiment was carried out for various kinds of SCA with different properties, and the orthogonal experiment method was used to observe the form and layering behavior of the coatings from a macroscopic standpoint. Subsequently, the

Table I Performance of inorganic additives

Inorganic passivator	Appearance of solutions	5% NaCl immersion testing	Coating solution features
Cerium salt	Colorless and transparent	Corrosion resistance for 24 h	Not demit easily
Molybdenum salt	Light blue	Corrosion resistance for 12 h	Demit easily
Titanium salt	Orange red	Corrosion resistance for 12 h	Demit easily

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SCA with the best performance was selected, based on the film testing results, which included insulating ability, corrosion resistance, adhesion strength, pencil and micro hardness determinations. In this study, four kinds of organic SCAs were chosen: γ-(2, 3-epoxy propoxy)glycidoxypropyltrimethoxysilane (molecular formula $C_9H_{20}O_5Si$, commercial name WD60), vinyltriethoxysilane (molecular formula CH_2-$CHSi(OC_2H_5)_3$, commercial name WD20), 1,2-double-vinyltrimethoxysilane (molecular formula $C_5H_{12}O_3Si$, commercial name 26M) and γ-aminopropyltriethoxysilane (molecular formula $C_9H_{23}NO_3Si$, commercial name WD50). Their molecular structures are shown in Figure 1. The four kinds of SCA were chosen for the reason that they contain the functional groups of epoxy, olefin, methoxy and ammonia, respectively. They were considered as being representative of numerous organic silane types.

Formulation of SCA

In order to better understand the mechanism of the compositions of these four kinds of SCA, it was necessary to avoid the crosslinking reaction that happens on the surface of electrical steel before the process of high-temperature treatment. If this is not avoided, such composite effects would seriously reduce the degree of crosslinking between the coating and the surface of the steel during the high-temperature treatment. The orthogonal experimental method was used to composite these four kinds of SCA with each of the two variants and the experimental results are shown in Table II.

Based on the experimental results shown in Table II, it was determined that no crosslinking reactions took place, and only in the compositive results of WD60-WD50 and WD20-26M did it occur, and thus could be used in the present coating solutions. Therefore, in the following experiments, organic SCA WD60, WD20, 26M, WD50, WD60-WD50 and WD20-26M were selected and applied to the coating for screening of the optimal SCA after carrying out serial performance tests.

Optimization of SCA

In the performance tests of the coatings on the steel sheets, five essential factors were chosen, including paintability, insulating ability, corrosion resistance, adhesion strength and the hardness of the films. Stamping ability implies a wear condition of coating toward the cutting edge, and weldability affects the welding performance of the silicon steel. Finally, the pencil hardness and micro hardness testing techniques were used to investigate the hardness of the coating. In comparison to traditional organic coatings, the shortcoming of the semi-organic coatings was reflected in their low toughness and high brittleness, which severely affects the sheet-punching properties and weldability of silicon steel sheet.

In the present study, the pencil hardness directly measured the thickness of the film from a macroscopic point of view, and the micro hardness assessed the performance of the film from a microscopic standpoint, using a micro thickness gauge (model HXS-1000 A), which was used for testing the film and observing the microscopic property of films after the application of 10 g pressure at 400 times magnification. If a film is over-brittle, it will show a cracked appearance under the microscope. The experimental results are shown in Figure 2.

There was no direct relationship between pencil hardness and micro hardness. Films with high pencil hardness might be brittle, and on the contrary, films with low pencil hardness might be more flexible. Take into consideration all of these factors, the SCA with the best performance was determined. The experimental results are shown in Table III.

As is shown in Figure 2, some cracks could be observed alongside the pressing print, indicating that the WD60 and WD20 films were brittle and therefore, were crushed during the

Figure 1 Molecular structures of four kinds of organic SCAs

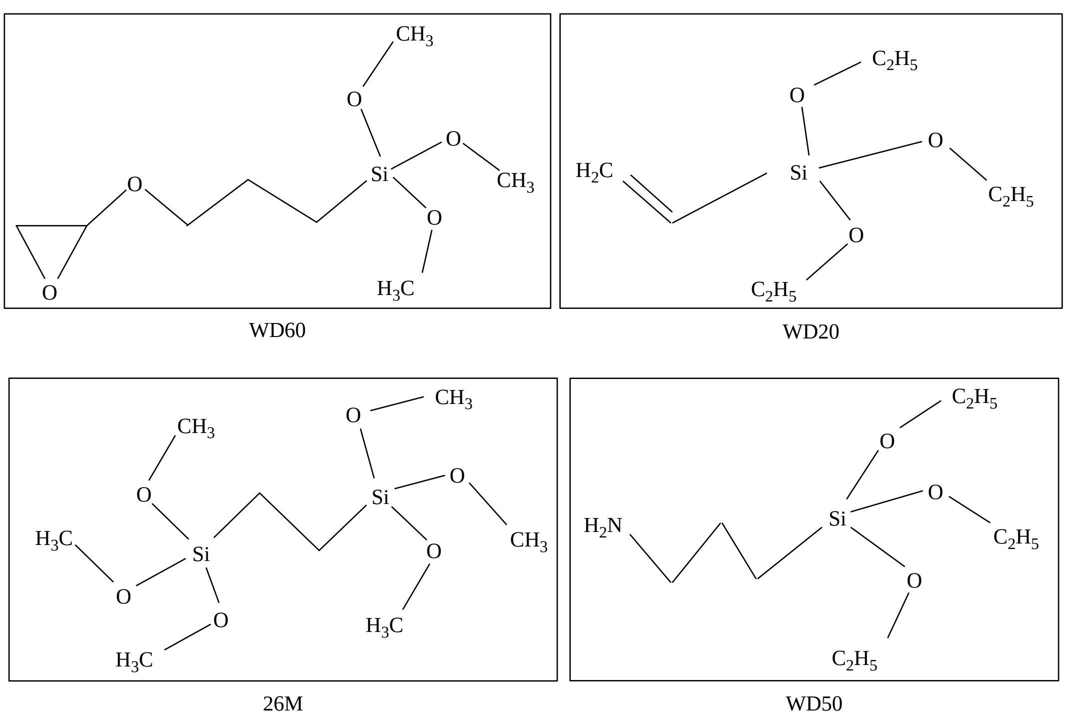
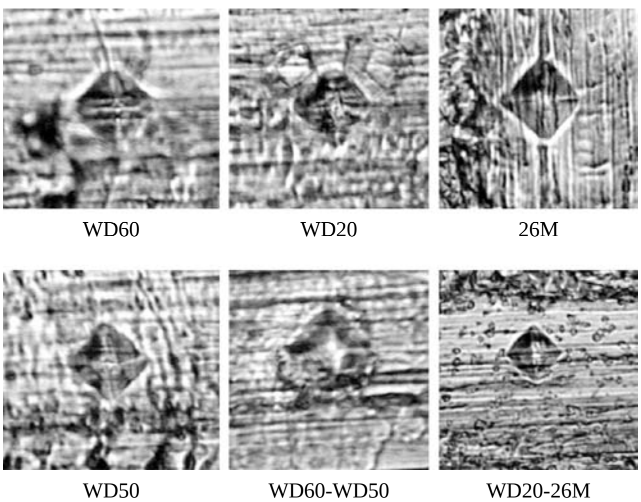


Table II Compositive results of SCAs

	WD60	WD20	26M	WD50
WD60	–	Uniform colloid precipitation	Floccus precipitation codensity	Clear and transparent without precipitation
WD20	–	–	Clear and transparent without precipitation	Uniform colloid precipitation
26M	–	–	–	Floccus precipitation codensity
WD50	–	–	–	–

Figure 2 Micro hardness of films of different SCAs



Note: 10g pressure, 400x

pressing test. As is known, materials with high brittleness might impair the sheet-punching and weldability properties of electrical steels. As for the pencil hardness of the WD60 and WD20 films, they were very high, thus complying with the industrial standard. However, the corrosion resistance of the WD20 film proved to be very poor and did not meet the industrial standard (6 h).

From Table III it can be determined that the inter-layer resistance and breakdown voltage of all of the SCA coatings exceeded the requirements of the industrial standards and their adhesion strength were all of the highest grade (O), thereby demonstrating very good insulating ability and adhesion strength. Based on the other two important factors (corrosion resistance and solution appearance), it was found that, as for other performances, different SCA had quite different results.

The paint solution of some SCAs will separate after resting for several days. In order to solve the problem of demixing, a thickener was added to the paint solution, and finally, the composition of SCA WD60-WD50 was decided as the SCA for the electrical steel insulating coating to be investigated further in the present study.

Tafel studies

Figure 3 shows the polarization curves of steel electrodes coated with films in aerated 0.5M NaCl solution at about 298 K. Both the cathodic and the anodic processes of steel corrosion were suppressed to some extent by covering the surface with four kinds of films: A, A + C, A + B and A + B + C, where A stands for aluminum dihydrogen phosphate, B for cerium salt and C for WD60-WD50. The E_{corr} values of these films on the electrodes were changed toward a more positive potential from the value of uncoated electrode, and comparing with the blank steel electrode, the steel electrode coated with A + B + C film was relatively better than the other films. The small shift in corrosion potential might be attributed to inhibition of both anodic and cathodic processes by these films.

Performance of coatings

The performance of the electrical steel insulating environment-friendly coatings using the compositive SCA (WD60-WD50) and rare earth were tested and measured according to Chinese national standard test methods. Finally, as is shown in Table IV, the test results were estimated and compared with the relevant industrial standards.

Neutral salt-spray tests

Figure 4 shows the images of six kinds of specimens based on different SCAs (WD60, WD20, 26M, WD50, WD60-WD50 and WD20-26M) in a salt-spray atmosphere of NaCl solution for 12 h. It was observed that the time for red rust to form on samples coated with silica-based polymer films increased significantly, compared to untreated samples, as is shown in Figure 4.

Table III Performances test table of SCAs

	Industrial standards	WD60	WD20	26M	WD50	WD60-WD50	WD20-26M
Solutions appearances	Homogeneous and stable	Easy demixing	Easy demixing	Not easy demixing	Rather easy demixing	Easy demixing	Not easy demixing
Inter-layer resistance ($\Omega^*mm^2/0.5\,\mu m$)	700	936	705	852	1,100	1,488	784
Breakdown voltage (V)	300	350	365	325	350	350	345
Salty-spray corrosion resistance (h)	6	10	5	10	20	20	10
Adhesion strength	Grade O or grade A	Grade O	Grade O	Grade O	Grade O	Grade O	Grade O
Pencil hardness	6H	6H	6H	3H	6H	6H	5H
Micro hardness	Good sheet punching and weldability	With cracking lines	Without crack lines	Without crack lines	Without crack lines	Without crack lines	Without crack lines

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Figure 3 Polarization curves (the potential, *E* and the current density, *i*) of steel electrodes in an aerated 0.5M NaCl solution and the electrodes covered with A, A + C, A + B and A + B + C film, respectively

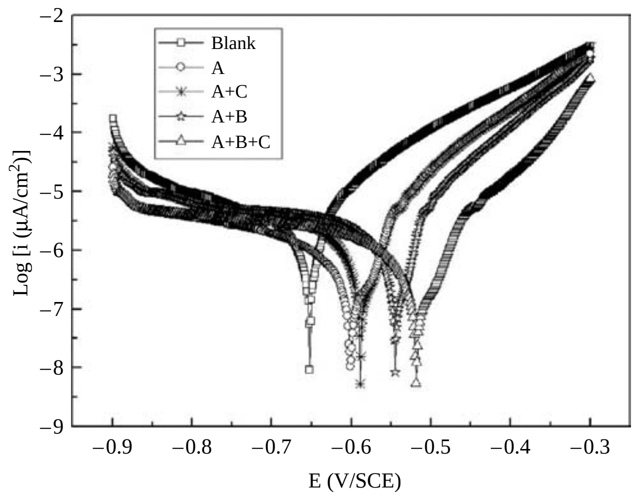
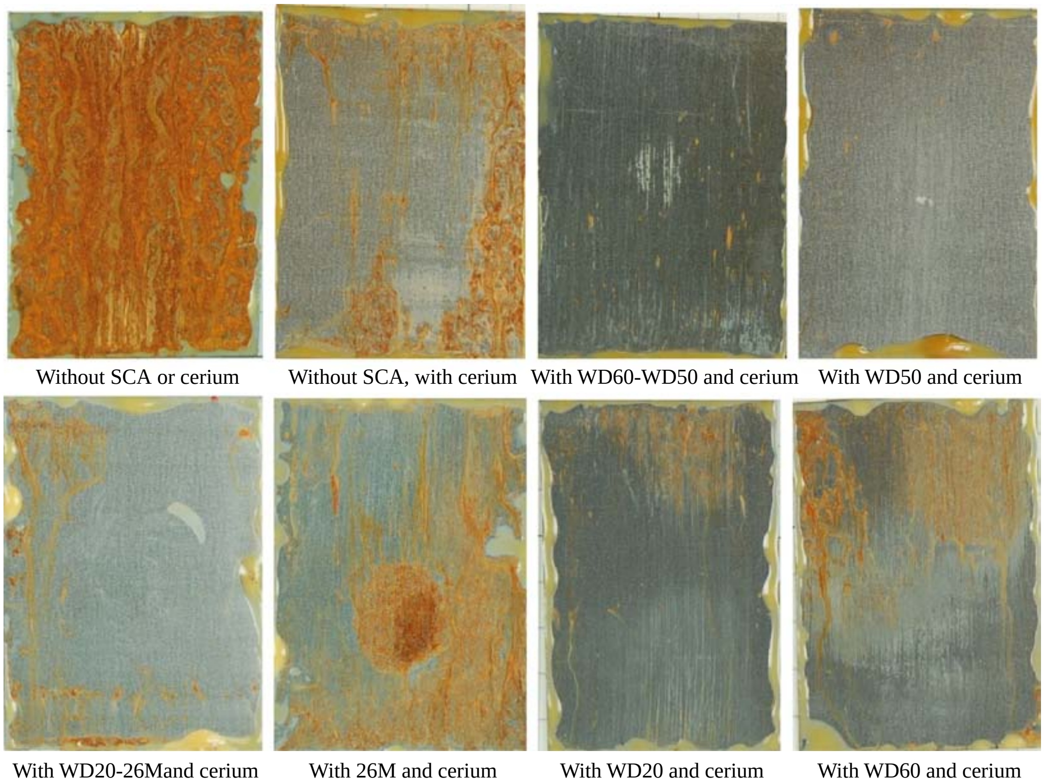


Table IV Comparison table of performance test results

	Chinese experimental standard	Chinese evaluation standard	Electrical steels environment-friendly insulating coating	Industrial standard
Coating thickness (μm)	GB/T 1764 Painting film thickness testing method	TT220 digital coating thickness gauge	0.5-3	0.5-3
Viscosity (s)	GB/T 1723-93 Coatings viscosity testing method	GB/T 1723-93 GB/T 2522-2007	18 1,488	30 ± 15 700
Inter-layer resistance (dry film) (Ω*mm²/0.5 μm)	GB/T 2522-2007 Electrical steel sheets (with) surface insulating resistance and coating adhesion testing method			
Breakdown voltage (V)	GB/T 1408.1-2006 Solid insulating material electrical strength test method under the frequency	GB/T 1408.1-2006 (φ20-mm spheroid gauge)	350	300
Corrosion resistance (salty-spray) (h)	GB/T 10125-1997 Artificial-atmosphere corrosion test and salt-spray test	GB/T 6461-2002 Metallic and other organic coatings on metal matrix, evaluation for samples and test pieces after corrosion test	20	6
Adhesion strength	GB/T 2522-2007 Electrical steel sheets (with) surface insulating resistance and coating adhesion testing method	GB 2522-2007 (φ20- , φ10- and φ5-mm rod gauges)	Grade O	Grades O and A
Pencil hardness (H)	GB/T 6739-2006 Paints and varnishes, painting film hardness testing with pencil method	GB/T 6739-2006 (6B-9H pencil)	6	6
Stamping ability (times)	The maximum stamping frequency of lamination under certain conditions	Stamping frequency	1,200,000	1,200,000
Weldability (cm/min)	The maximum welding speed of lamination face welding under specified air bubbles generated	Welding speed	80	80
Annealing performance	750°C, 2 h, 10% H_2 + 90% N_2	Even surface with shedding	Even surface without shedding	Even surface without shedding

Figure 4 The images of steel sheets coated by solutions containing different SCAs in the neutral salt-spray test for 12 h



Furthermore, steel sheets coated with solutions containing different SCAs could have differing corrosion resistances, and films based on WD50 had the highest corrosion resistance of the six types of SCA tested, as illustrated by the images shown in Figure 4.

Scanning electron microscope (SEM) microanalysis

Microscopic observations of the samples shown in Figure 5 revealed that uniform films were formed on the electrodes. All the films coated on the electrodes, magnified 1,000 times, are shown in Figure 5.

It was verified that the morphology of all the films was light grayish and transparent and the microscopic structures of the surfaces of the films were similar to each other. Tiny bubbles can be found on the surface of films prepared without SCA or cerium, because the formulation of the coating lacks organic matter. Microgrooves were distributed on the film instead of cracks, which may affect adversely the anti-corrosion capability of the films. The addition of tetrabutyl titanate and acrylic resin to the solution in the present study was observed to enhance adhesion between steel sheet and the semi-inorganic insulating coatings.

Discussion

After due consideration, the following conclusions could be made for coating and passivation process applied on the surface of the steel sheets (Fang *et al.*, 2009). At the very beginning, the cerium ions exist in its trivalent form in the aqueous solution, and then a compound action takes place between the cerium ions and the SCA during the film formation process and the later dehydration process at high temperature. Meanwhile, the trivalent cerium ions exist during the coating and passivation process are oxidized to quadrivalent cerium ions by the oxygen ions generated by the hydrogen peroxide. After this step, the quadrivalent cerium ion will enter the polymer stereo crosslinking structure in the form of cerium oxide during the high-temperature drying process. The passive film of the cerium/metal mixture formed on the substrate of steel sheet is very compact and corrosion resistant and has high binding force, which provides its corrosion shielding and protecting abilities.

In the technology of electrical steel insulating coatings (Iler, 1979), the reaction of organic SCA is based on the hydrolyzation effect of its siloxy group, thus forming various kinds of silanol, which has proved to be the key chemical agent in the solution. On the other hand, it is relatively easy for the previously activated ferric ions to form a Fe—O—Si bond with silanol after the film is coated on the surface of steel sheet. The whole reaction processes happen in a short time, and during this process, the silane molecule gathers and forms a Fe—O—Si bond on the steel substrate, resulting in a very small chance for the iron to react with hydrogen or dissolved oxygen for depolarization. Therefore, a film with a network-type structure (Si—O—Si bond) was formed between the silane polymer molecule and the steel substrate which, to some extent, improved the degree of crosslinking to the film and increased film formation performance.

In terms of the stability of the various kinds of SCA, many paint solutions based on them will separate after resting for less than two days. In consequence, the stability of paint solutions based on SCAs may become an issue for industrial applications. Owing to the symmetric methoxy groups of the molecule structure of 26M, the paint solution 26M will not separate after resting for

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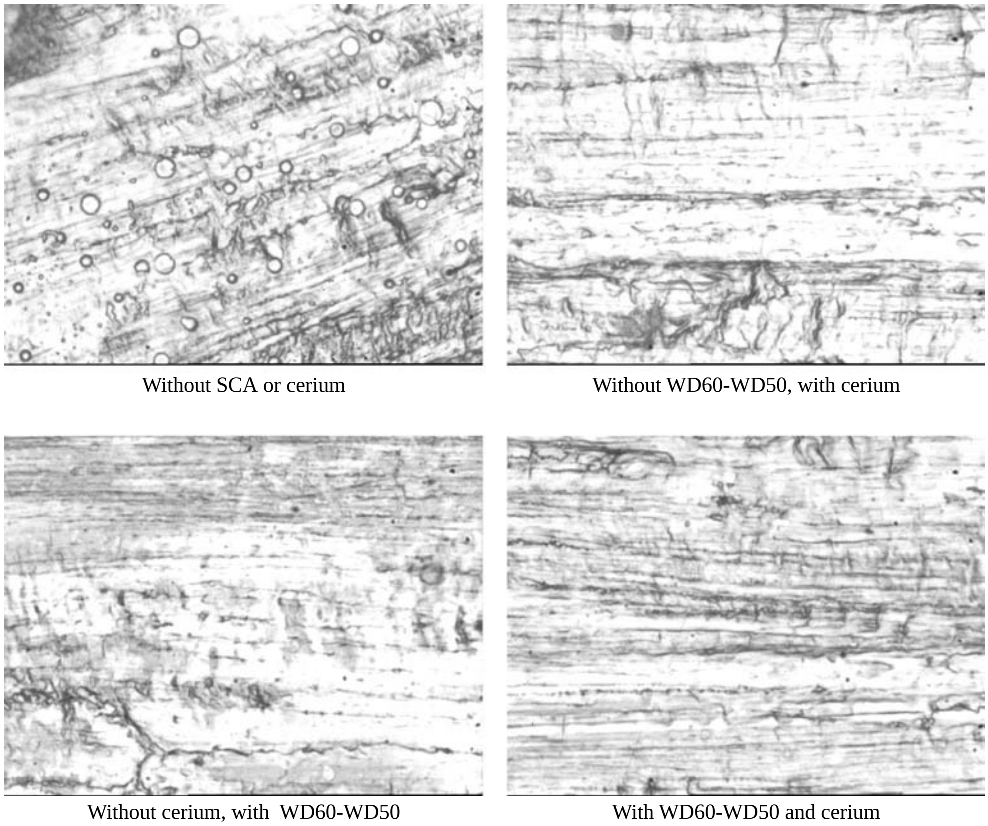
Figure 5 Surface morphology (SEM) of the electrodes coated with different films



several days. Moreover, the fact that the molecule structure of 26M does not contain other functional groups contributes to the stability of this paint solution. However, the pencil hardness of the 26M film was unsatisfactory and did not meet the requisite industrial standards (6H). On the other hand, its micro hardness showed the toughness of the 26M film was relatively high. Of all the coatings studied in this research, the corrosion resistance of the WD50 film was the highest, and the possible cause was the functional group of ammonia in the molecule structure of this coating, which had excellent corrosion resistance compared to inorganic system coatings and would combine more firmly with the surface of the steel during high-temperature treatment. However, the WD50 paint solution separated easily after resting for about two days, due to the asymmetric functional group.

Finally, in the present investigation, the corrosion resistance mechanism of the insulating environmental-friendly electrical steel coating can be inferred as follows: cerium oxide enters the polymer stereo crosslinking structure formed by the SCA during the high-temperature treatment process and the coating of cerium/metal mixture linked closely with passivation film on the substrate steel sheets. This played an important role in delivering its shielding effect and anti-corrosion capability.

Conclusion

It was shown from the analysis of the aforementioned data that of the three kinds of inorganic passivation systems, containing cerium, molybdenum and titanium salts, the performance (mainly the corrosion resistance) of the rare earth system was evidently better than the other two systems.

The optimal composition was determined for each of the four kinds of SCA coatings, WD60, WD20, 26M and WD50, and various performance criteria, including insulating ability, corrosion resistance, adhesion strength and hardness, were considered in order to estimate comprehensively the characteristics of the SCA, and the overall decision was that WD60-WD50 was the most effective, based on its high-performance results.

Materials such as aluminum dihydrogen phosphate were considered as the main film-forming materials. The compositive SCA WD60-WD50 and rare earth passivation system were used to replace the unpopular chromate compounds. Additionally, the passivation process was combined with the film-forming process, thus developing a special insulating coating system for electrical steels.

All the performance test results of the environmentally friendly insulative coatings for electrical steels showed excellent corrosion resistance with the highest salt-spray resistance time up to 20 h, ensuring acceptable and stable properties of silicon steel sheet during its service life. Accordingly, this should assure the improved operational reliability of electric motors, transformers, barreter cores and electrical elements.

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