

Passivation Process of Carbon Steel Cerium Salt and Silane Composite Membrane

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Abstract. In this paper, the acid quick passivation process we adopted, put carbon steel after pretreatment, immerse in cerium salt solution and then form passivating film. Via orthogonal experiment, the optimum passivation process conditions are as follows: $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 30 g/L; H_2O_2 , 30 ml/L; pH value of 2; passivation time, 60s. Under the condition of the above, membrane resistance under the condition of 3% acidic copper sulfate intravenous drip experiment time can reach 1309s. Electrochemical impedance spectroscopy (EIS) measurements were assessed the corrosion resistance of passivation films; metallographic microscope and scanning electron microscopy (SEM) were used to characterize the composition structure and morphologies of sample surfaces; X-ray energy dispersive spectrometry (EDS) and X-ray photon spectroscopy (XPS) were used to identify the component of sample surfaces. The silane coupling agent was treated on the sample as two step passivation, in order to improve the anti-corrosion of cerium passivation film. Silane coupling agent secondary passivation process was that the sample was passivated for 1 minute in the KH-560 for 4% of silane coupling agent solution that the pH value is 2.5%, and cured for 1 hour under the condition of 120°C . Neutral salt spray and EIS test results of cerium-silane composite passivation film show that the anti-corrosion performance of passivation film has been greatly improved. SEM and EDS analysis results showed that the silane coupling agent very well covered cracks and filled the pores on surface of the cerium salt passivation film.

1. Introduction

More than 90% of the metal used by people is steel. However, about 10% of the existing steel and metal equipments were corroded every year, leading to serious economic losses [1]. Q235, which is one of the largest amount of basic materials in industry, has a good overall performance. Unlike carbon, Cu, Al, stainless steel and other metals who can be self-passivation in the environment, Q235 is prone to corrosion among humid atmospheric environment or in solution. Therefore, the study of corrosion and protection of carbon steel is significant.

Coating is an effective and commonly used technique for protecting steel materials. A complete metal protective coating system, mainly includes the surface pretreatment layer and the protective coating layer. Traditional surface pretreatment technology is the chromate and phosphate conversion treatment [2]. Moreover, there are some new surface pretreatment technologies such as molybdate, titanate, phytic acid, tannic acid, organic silane, rare earth passivation [3]. Rare earth passivation and silane passivation have attracted attention and have good prospects in recent years due to their non-



toxic, low cost, and good adhesion. More research was focus on organic silane, and the research for the composite passivation film from organic silane and inorganic passivating reagent was rare. In this paper the corrosion resistance of the composite passivation film of cerium salt silane was further studied [4].

2. Experimental materials, equipments and method

2.1. Experimental materials reagents

carbon steel(Q235) were in size of 50 mm×20 mm×0.8 mm, and the reagents used included $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, H_2O_2 (30% wt%), HNO_3 (65% wt%), HCl , NaOH , HBO_3 , NaCl , Na_2SiO_3 , Na_3PO_4 , Na_2CO_3 , emulsifier (OP-10), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, ethanol, carbinol, acetic acid, silane coupling agent (KH-560), paraffinwax, cellulose tape and deionized water.

2.2. Experimental instruments

The main instruments used in the experiment are shown in Table 1. In addition, the Pt electrode used in the experiment is self-made, the working area is about 2 cm^2 , and the reference electrode is the saturated calomel electrode purchased.

Table 1. Main experimental instruments

Equipments	Instrument model	Company
Electrochemical work station	CHI660b, CHI660d	Chenhua, Shanghai
Electrochemical work station	Autolab (PGSTAT302N)	-
Polishing machine	MP-2A	Guangxiang Zhiyang, Shanghai
Analytical balance	BS124S	Sartorius, Beijing
Constant-temperature air dry oven	DHG 90A series	Suopu, Shanghai
Thermostatic water bath	DK-600B	Senxin, Shanghai
Magnetic force heating mixer	DF-101S	Keer, Shanghai
pH meter	-	METTLER TOLEDO
Scanning electron microscope	S-550	Hitachi, Japan
X - ray photoelectron spectroscopy	ESCALAB 250Xi	Thermo Fisher, America
Electrochemical integrated test system	Parstat2273 (Amstel Inc.)	PRINSTON, America

2.3. Method Experimental

The Q235 carbon steel samples were polished by W40, W20 and W5 respectively, the black dirt wiped producing by rubbing with alcohol, welded to a copper wire about 10 cm, degreased by alkaline degreasing liquid and immersed in an acid solution for activation, passivated by a chemical immersion method[5] and aged for 24 h. at room temperature.

Passivation film adhesion test was according to GB9791-88 "zinc and chromium chromate conversion film test method." The initial test of the film anti-corrosion was used copper sulfate drip test, further testing was used salt water immersion test, EIS and polarization curvilinear test. The morphology of the film was observed by SEM, and the composition was analyzed by EDS and XPS.

3. Experimental results and analysis

3.1. The best passivation conditions

According to the literature reports and the properties of various cerium salt solutions, $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were used as the main salt species in this study. Orthogonal experiments were set up to study the optimum technological conditions of rare earth passivation. Five factors level selection of orthogonal experiment conditions are as shown in Table 2. $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ orthogonal experiment design are as shown in Table 3, Table 4 below. Taking into account the time of copper sulfate drip experiment, cerium chloride passivation film titration was used 3% neutral copper sulfate,

cerium nitrate passivation film was adjusted[6], changed to acidic copper sulfate, the specific formula is 3% CuSO₄:0.1molHCl=10 ml:0.2 ml.

Table 2. Factors of the orthogonal experiment

Level	Factors				
	A	B	C	D	E
	Temperature (°C)	CeCl ₃ ·6H ₂ O g/L or Ce(NO ₃) ₃ ·6H ₂ O	H ₂ O ₂ (30%) (ml/L)	pH	Passivation time (s)
	25	10	10	1.5	15
	35	20	20	2	30
	45	30	30	2.5	45
	55	40	40	3	60

Table 3. CeCl₃·7H₂O orthogonal experiment design

Order number	Temperature (°C)	CeCl ₃ ·6H ₂ O (g/L)	H ₂ O ₂ (30%) (ml/L)	pH	Passivation time (s)	3% Neutral copper sulfate titration(s)
1	25	10	10	1.5	15	34
2	25	20	20	2	30	40
3	25	30	30	2.5	45	41
4	25	40	40	3	60	47
5	35	10	20	2.5	60	34
6	35	20	10	3	45	40
7	35	30	40	1.5	30	41
8	35	40	30	2	15	47
9	45	10	30	3	30	31
10	45	20	40	2.5	15	29
11	45	30	10	2	60	189
12	45	40	20	1.5	45	88
13	55	10	40	2	45	38
14	55	20	30	1.5	60	35
15	55	30	20	3	15	45
16	55	40	10	2.5	30	48

Orthogonal experiments show that, the optimum passivation process conditions are as follows: Ce (NO₃)₃·6H₂O, 30 g/L; H₂O₂, 30 ml/L; pH value of 2; passivation time, 60s. Under the condition of the above, membrane resistance under the condition of 3% acidic copper sulfate intravenous drip experiment time can reach 1309s.

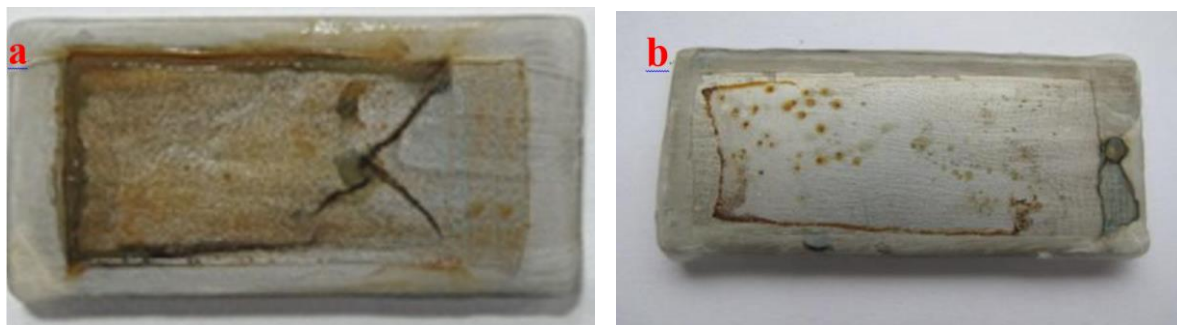
3.2. Passivation film characteristics

Adhesion, anti-corrosion, topography, and EDS testing of passivation films under optimal passivation conditions are demonstrated in Section 3.4. After rubbing with non-sand rubber, there is no obvious wear and no peeling off on the surface of passivation film, indicating that cerium nitrate conversion film has good adhesion to the matrix. The results of the anti-corrosion test are as follows.

3.2.1. Brine immersion experiment. The passivated steel plate was sealed with paraffin and scotch tape on the back and sides, then immersed in 3.5% saline for 24h. The surface corrosion status is shown in Fig.1. The area of unpassivated steel (a) is more than 80%, and the steel sheet(b) under optimum passivation shows only non-uniform pitting corrosion and does not develop as massive corrosion zone, indicating the first corrosion occurred where the passive film growth is poor.

Table 4. Ce (NO₃)₃·6H₂O orthogonal experiment design

Order number	Temperature (°C)	CeCl ₃ ·6H ₂ O (g/L)	H ₂ O ₂ (30%) (ml/L)	pH	Passivation time(s)	3% Acidic copper sulfate titration(s)
1	25	10	10	1.5	15	145
2	25	20	20	2	30	206
3	25	30	30	2.5	45	189
4	25	40	40	3	60	730
5	35	10	20	2.5	60	515
6	35	20	10	3	45	447
7	35	30	40	1.5	30	115
8	35	40	30	2	15	362
9	45	10	30	3	30	123
10	45	20	40	2.5	15	117
11	45	30	10	2	60	88
12	45	40	20	1.5	45	1309
13	55	10	40	2	45	82
14	55	20	30	1.5	60	76
15	55	30	20	3	15	110
16	55	40	10	2.5	30	547

**Figure 1.** Corrosion condition under brine immersion for blank and optimal passivation

3.2.2. EIS test and polarization curve test. EIS of the best passivation of cerium nitrate film is shown in Fig.2. Comparing the results of EIS with the blank samples and the best passivation conditions, it is concluded that the best passivation process conditions are better than the passivated steel plate samples only after the surface pretreatment, the resistance value of the treated carbon steel plate has been greatly improved, indicating the anti-corrosion of the sample has been greatly improved.

Polarization curves in the etching solution of blank sample and optimal conditions passivation film are shown in Fig.3, the anodic polarization curve is relatively steep, and the cathodic polarization curve is relatively gentle, indicating that the anodic polarizability is larger than the cathodic, that is, Corrosion Polarization is controlled by the anode. Compared with the blank sample, the self-corrosion current densities of passivated samples decreased (Table 5), and both the anode branch and the cathode branch current densities present some extent reduce, indicating carbon steel plate anode and cathode reaction are inhibited by cerium passivation film.

3.2.3. XPS test. Fig.4 (a) shows the XPS spectra under the optimal passivation conditions. By comparing the characteristic peaks of the elements, the presence of elements such as Ce, O and Fe in the film can be sure. In order to understand the structure and composition of passivation film, narrow scan of Ce, Fe, O in the passivation layer were carried out. Ce3d spectra (b) show Ce3d5/2, Ce3d3/2 spin orbitals for Ce⁴⁺ and the same as Ce³⁺ [7, 8]. Table 6 shows the positions of the main peaks and

satellite peaks of Ce^{4+} and Ce^{3+} . According to the peak area, Ce^{4+} content is more than Ce^{3+} . The Fe2p spectrum(c) shows that Fe and its oxides are present on the passive film surface. O1s spectrum(d), 531.6ev corresponds OH^- characteristic peak, 529.3ev corresponds O^{2-} characteristic peak, indicating the passivation film may contain oxides and hydroxides of cerium or iron, and O^{2-} fitting peak has a larger area, indicating that main composition of the passive film surface is hydroxides.

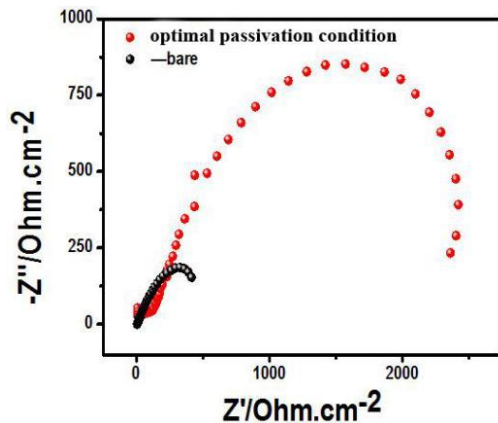


Figure 2. EIS of blank and optimal passivation condition film

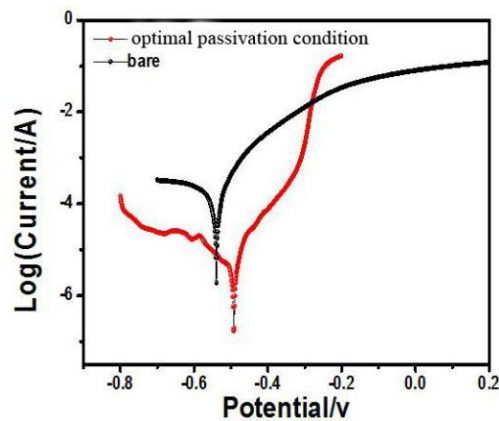


Figure 3. Polarization curves of blank sample and optimal conditions passivation film

Table 5. The self-corrosion current density of blank and optimal passivation condition film

Sample type	Self-corrosion current density
Blank sample	2.865e-04
optimal conditions passivation film	1.237e-05

Table 6. The positions of the main peaks and satellite peaks of Ce

Valence	Peak position(ev)					
Ce^{4+}	882.1	889.9	897.9	990.8	906.6	916.2
Ce^{3+}	884.8	880.2	903.4	898.2		

3.3. Composite membrane research

The anti-corrosion of the single cerium passivation film on the surface of carbon steel shows not enough ideal anti-corrosion via the above findings, and its anti-corrosion is lower than the conventional chromate passivation film. In this paper, silane coupling agent secondary passivation was used to improve the rare earth cerium salt passivation treatment process to improve its anti-corrosion [9, 10].

3.3.1. Silane best dip conditions. The volume ratio of KH-560, absolute ethanol, deionized water 2: 2: 96; 4: 4: 92; 6: 6: 88; were mixed, with glacial acetic acid to adjust the pH of the solution = 4.0, at 35°C constant temperature water bath, stirring, hydrolyzed about 4 h, then dip coated blank steel plate. EIS was shown in Fig.5 (a), with the increase of the amount silane increases, the silane coating resistance generally increases first and then decreases, the reason may be due to this phenomenon when the proportion of silane added is too high, the binding force decreases of the coating to the substrate. When the proportion of silane is 4%, the dip-coated steel sheet has the best anti-corrosion.

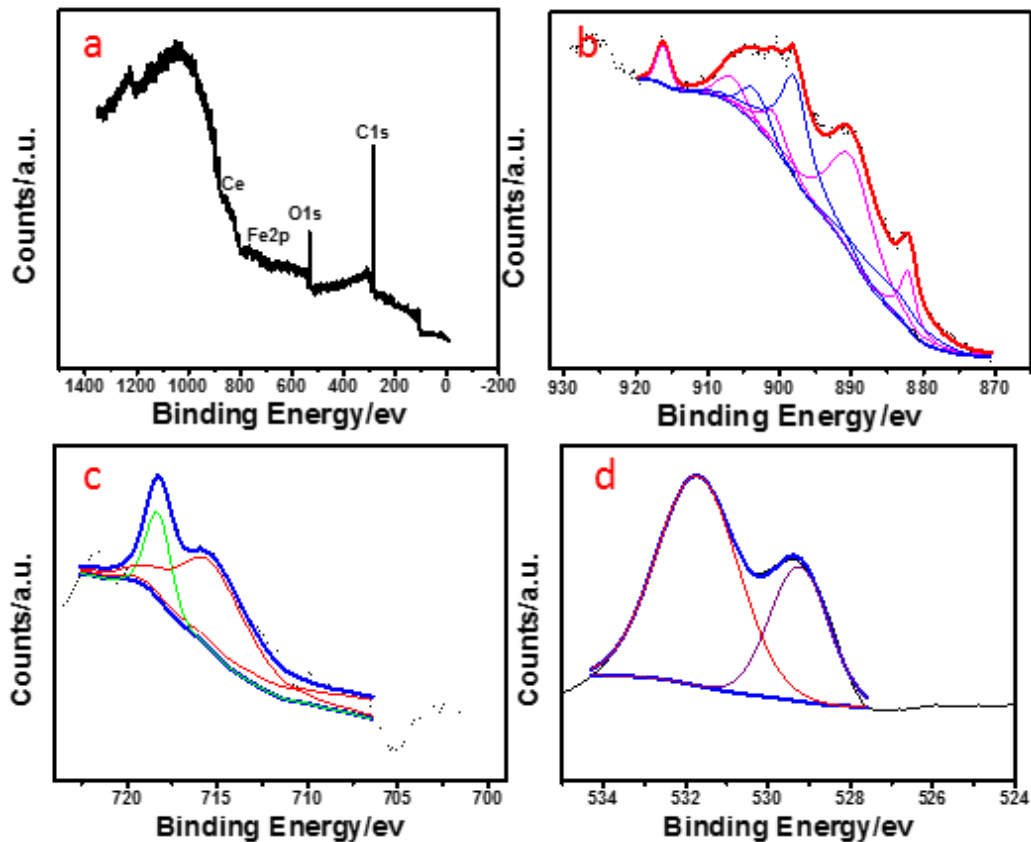


Figure 4. XPS pattern of optimum passivation conditions passivation film

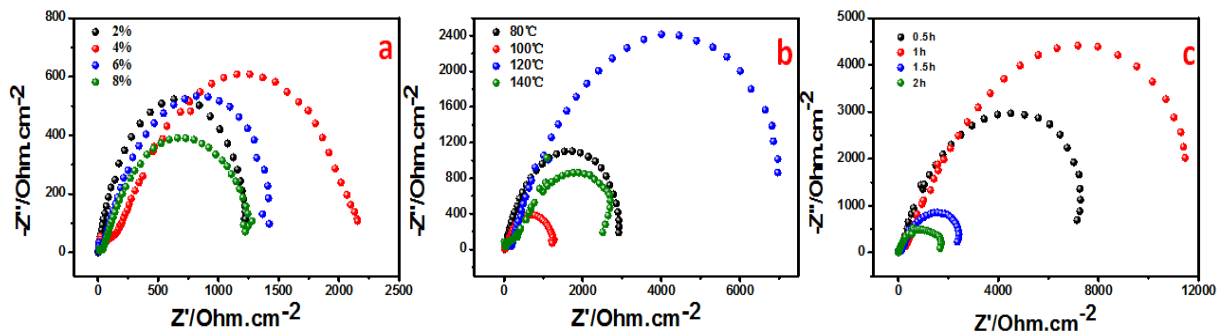


Figure 5. Silane best dip conditions

Fig.5 (b) shows the EIS test pattern of the silane coating after one hour of curing at the same silane loading (4%), 80°C, 100°C, 120°C, and 140°C cure temperatures. With the increase of the curing temperature, the impedance of the membrane shows a trend of first increasing and then decreasing. At 120°C, the anti-corrosion of the membrane is the best.

Fig.5 (c) shows the EIS test spectra of silane films prepared at different cure times over a range of 0.5h, 1h, 1.5h, and 2h. With the extension of curing time, the resistance of coating increases first and then decreases. After 1h, impedance value will instead decline, because at a certain temperature, the extended curing time will damage the densification of membrane densification, thereby reducing the anti-corrosion. When the passivation time achieved 1 h, the membrane displays best anti-corrosion.

3.4. Composite film anti-corrosion

The composite membrane samples were treated according to the previous sample treatment and the 24 h brine immersion experiments were performed in the same manner. Fig.6 is the picture of a composite film after 24 h salt water immersion experiment. The surface of the composite film almost has no pitting or massive corrosion phenomenon, the anti-corrosion of the composite film has been greatly improved for a single cerium nitrate passivation. Fig.7 is impedance test results of composite passivation film. It can be seen from the figure that the anti-corrosion of the composite film is greatly improved compared with the single cerium nitrate passivation film.



Figure 6. salt water immersion for membrane

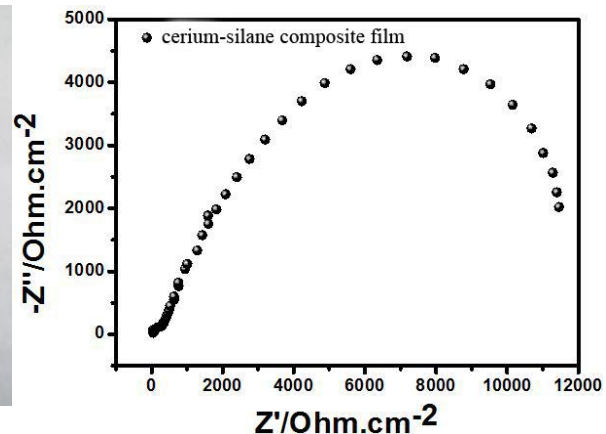


Figure 7. EIS of cerium-silane composite film

3.5. Microscopic comparison between cerium nitrate passivation and composite films

3.5.1. Topography changes. Figure 8 is the 400 times the metallographic microscope of blank (only pretreated steel), single and composite film, unpassivated sample(a) showed a flat structure, the scratch is due to pre-treatment metallographic sanding caused. Single optimal conditions passivation film (b) is very uneven, the size of the block varies, and there are many cracks and voids, which is also a major reason for the poor anti-corrosion of the single passivation film. The composite film after passivating with silane(c) has less cracks and voids than the single cerium nitrate passivation film, so its anti-corrosion is better than it.

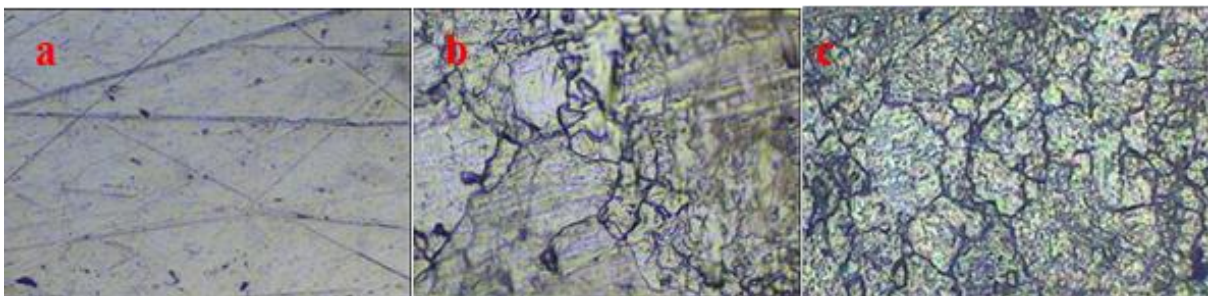


Figure 8. Metallographic microscope of blank, single, cerium-silane composite film

Fig.9 is a 50000 times SEM image of blank (pretreated steel plate only), single, and composite film. The surface of the unpassivated sample(a) has a flat structure, a single optimum film(b) passivation film can be clearly seen the particle morphology, the size of dozens of nanometers, in some places appear massive collapse, where the film is relatively weak place will take the lead in corrosion. After the second passivation with silane(c), the surface of the particles is smaller and distribution than the

previous single nitrate cerium oxide passivation film, uniform, dense, block size is also smaller, the anti-corrosion of the film will be better accordingly.

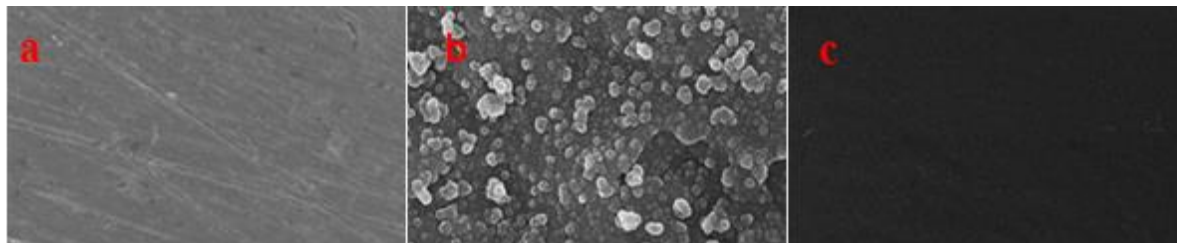


Figure 9. SEM image of blank, single, cerium-silane composite passivation film

3.5.2. Composition changes. Fig.10 shows EDS surface scan of single, compound passivation film. The deposition of cerium on the surface of single passivation film (a). The main elements on surface of.

Cerium-silane composite passivation film are silicon, cerium, oxygen, carbon and iron, the silicon content has reached about 20 %.

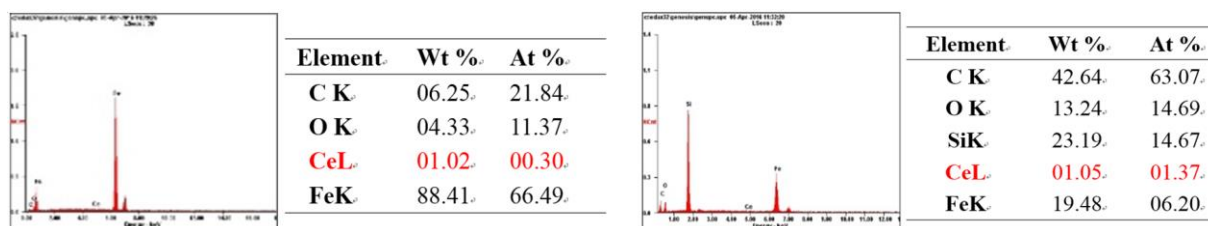


Figure 10. EDS surface scan of single, salt-silane composite passivation film

4. Conclusion

The anti-corrosion of the passivation film formed by cerium nitrate as the main salt is stronger than cerium chloride as the main salt. Compared with the blank steel plate, the passivation film has better resistance to salt soaking, larger resistance value, and smaller anode and cathode current densities of the polarization. The presence of Ce on the surface of cerium passivation film is composed of Ce^{3+} and Ce^{4+} , and the content of Ce^{4+} is higher than Ce^{3+} . The binding form of cerium is mainly composed of hydroxide and oxide, and mainly hydroxide.

The addition of KH-560, 4%, the curing temperature, 120°C , curing time, 1 h, the anti-corrosion of silane coating on steel plate is the best. The surface of the salt-silane composite passivation film is more smooth and dense than the single cerium nitrate passivation film. EDS showed the composite film containing Si elements, silane has been covered in the cerium passivation film surface.

References

- [1] Yunping Liu. Preparation of hybrid membrane on carbon steel and anti-corrosion properties research [D]. Qingdao: Ocean University of China, 2011.
- [2] Chu Nan Cao. The quiet destruction: metal corrosion [M]. Tsinghua University Press Co., Ltd., 2000.
- [3] Wei Chen. A dissertation presented to Zhejiang University in partial fulfillment of the requirements for the degree master science [D]. Zhejiang: Zhejiang University, 2014.
- [4] Dajing Fang. Study on environmental protection type chromium free passivation for zinc based materials [D]. Wuhan: Wuhan University, 2009.
- [5] BETHENCOURT M, BOTANA F, CALVINO J, et al. Lanthanide compounds as environmentally-friendly corrosion inhibitors of aluminium alloys: a review [J]. Corrosion

- Science, 1998, **40** (11): 1803-19.
- [6] Minghai Feng, xiao Ju Geng, Dirong Hu.. Comparison of the Testing Method of Anticorrosion Property of Phosphate Coatings [J]. Journal of Xinyang Teachers College: Natural Science Edition, 2011, **24** (3): 377-379.
 - [7] WAGNER C D, MUILENBERG G. Handbook of X-ray photoelectron spectroscopy [M]. Perkin-Elmer, 1979.
 - [8] Composition-and-behaviour-of-cerium-films-on-galvanised-steel 2001. Progress-in-Organic-Coatings [J]. Progress in Organic Coatings, 2001, **43** (4): 274-281.
 - [9] SiwuWU, Huanqing CAI, Honghong Lei, et al. anti-corrosion of cerium salt on carbon steel after passivation [J]. Material protection, 2015, **48** (9): 39-40.
 - [10] SiwuWU, Honghong Lei, Huanqing CAI, et al. anti-corrosion of cerium salt passivation film and cerium-silane compound passivation film on carbon steel [J]. Material protection, 2015, **48** (9): 4-6.