Structure and Protective Properties of Ti-containing Organic-inorganic Hybrid Film on Stainless Steel Surface

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Abstract. In this paper, a dense structure of Ti-containing organic-inorganic hybrid transparent film was prepared on the surface of 304 stainless steel by sol-gel method combined with organic-inorganic hybridization theory. The basic properties and corrosion resistance of the hybrid film showed a unimodal change with the increase of the precursor content. When the molar ratio of the precursor to tetrabutyl titanate was about 0.75, the hybrid film obtained had the best performance. The microstructure of the film was analyzed by SEM and AFM technology. The Ti-containing organic–inorganic hybrid film was denser than the Si-containing hybrid film and epoxy film, which resulted in better salt spray resistance and EIS performance.

1. Introduction
Stainless steel generally has good corrosion resistance due to the spontaneous formation of a very thin passivation film on its surface. However, in the marine atmosphere, stainless steel is very prone to pitting, which may cause perforation of the equipment and shorten the service life of the stainless steel.

At present, the films for stainless steel anticorrosion mainly include: meta films [1-2] such as zinc, aluminum, rare earth aluminum and so on, metal oxide films such as Al2O3, inorganic films [3-4] and organic films [5] such as epoxy, olefin, polyurethane, silane and so on. There are other environmentally friendly surface treatment technologies such as self-assembled films [6]. The existing protective films have a certain protective effect on stainless steel, but the observation of pitting corrosion is not favorable, resulting in greater safety risks. Thus, the field of corrosion science is still seeking environmentally friendly, environmentally friendly, simple operation, and good surface treatment technology.

The organic-inorganic hybrid film has the advantages of good film-forming property, good adhesion, good shielding effect, and the advantages of inorganic film weathering, pollution resistance, high hardness, scrub resistance, non-combustion, and no pollution to the environment. It also greatly compensated for the lack of both. At present, there are many researches on Si-containing hybrid film [7]. The system of the organic-inorganic hybrid silicon film is relatively simple, and the obtained film is not highly resistant to corrosion and needs further modification. Titanium has the advantage of good chemical bonding, and its introduction into the organic-inorganic hybrid coating is beneficial to enhance the hardness [8] and corrosion resistance of the coating.

Based on the research of organic-inorganic hybrid films in this group, Ti-containing organic-inorganic hybrid films were prepared on the surface of 304 stainless steel. Compared with the properties of Si-containing hybrid film and epoxy film, the corrosion resistance, microstructure and interface bonding were studied to investigate the effect of structure on the performance of hybrid film.
2. Experimental

2.1. Preparation of Ti-containing Organic-inorganic Hybrid Film
Dissolve the epoxy-containing silane precursor into ethanol, slowly add a small amount of water and glacial acetic acid, and thoroughly hydrolyze the precursor, stir for 10 min. Then add a small amount of hydrolysis stabilizer. Tetrabutyl titanate was added and stirred for 20 min. Adding the above epoxy resin (bisphenol A type) with a mass fraction of 10wt.%, adding an appropriate amount of curing agent (the phenolic hydroxyl-containing cashew nut-shell curing agent YGF/amino curing agent TETA) in a ratio of epoxy groups to obtain stable Organic-inorganic composite sol. The composite sol was coated on a surface of 304 stainless steel(50mm×70mm×2mm)scrubbed with acetone in 5 min and cured at 20°C for 12 h.

2.2. Characterization
Hardness test refers to GB/T 6739-2006 "Color paint and varnish pencil method to determine the hardness of paint film", adhesion test refers to GB/T 5210-2006 "paint and varnish pull-off method adhesion test". The electrochemical impedance spectroscopy (EIS) was performed on a PARSTAT2273 workstation. Neutral salt spray test refers to GB/T 1771-2007 "Determination of neutral salt spray performance of paints and varnishes". The microscopic morphology of the film was characterized by a SEM model number QUANTA250 and an atomic force microscope (AFM) model Brucker Multimode VIII.

3. Results and Discussion

3.1. Effect of Precursor Contents on Basic Properties of Ti-containing Hybrid Film
The precursor has a great influence on the performance of the hybrid film. Therefore, in order to study the effect of precursor contents on the properties of the film, preparing Ti-containing organic-inorganic hybrid film with different molar ratio of precursors to tetrabutyl titanate (1.25:1, 1:1, 0.75:1, 0.5:1, 0.25:1), then testing basic performance of the obtained film. The effect of precursors contents on the gloss and mechanical properties of hybrid film are presented in Fig. 1 and Fig. 2. The hybrid film showed a unimodal change with the increase of the precursor contents. When the molar ratio of the current precursor to tetrabutyl titanate is about 0.75, the film formation performance of the obtained hybrid film is optimal.

![Figure 1. Effect of Precursor Content on the Gloss of Hybrid Film](image.png)
3.2. **EIS Analysis of Hybrid Film**

3.2.1 **Different Contents of Precursor Hybrid Film EIS Analysis.** In order to study the influence of the proportion of precursors on the protective performance of hybrid film, EIS analysis was performed on hybrid film with different contents of precursor film. The Nyquist and Bode curves are shown in Fig. 3. It can be seen that as the content of the precursor increases, the diameter of the capacitive anti-arc in the Nyquist curve first becomes larger and then smaller, and the amplitude of the impedance in the low-frequency region of the Bode curve increases first and then decreases. The Nyquist curve has the largest diameter of the arc resistance when the molar ratio of precursor to tetrabutyl titanate is around 0.75, and the Bode curve impedance amplitude reaches the maximum. That means hybrid film has the best corrosion resistance.

3.3. **Salt Spray Resistance Test**

3.3.1 **Comparative Analysis of Salt Spray Resistance of Ti-containing Hybrid Film and Si-containing Hybrid Film.** A neutral salt spray comparison test was carried out on the Si-containing hybrid film and the Ti-containing hybrid film sample and the microscopic changes of the two films were periodically recorded. Fig. 4 is a confocal micrograph of a salt spray resistant sample. It can be seen that the Si-containing hybrid film has been exposed to a large pitting corrosion in the neutral salt spray box for
30 days, however the Ti-containing hybrid film remained intact after 56 days. Obviously, the corrosion resistance of the Ti-containing hybrid film is superior to that of the Si-containing hybrid film.

![Figure 4. Confocal micrograph of hybrid films tested with salt spray](image)

3.4. Micro Structure

3.4.1 SEM. SEM images of a Ti-containing hybrid film, a Si-containing hybrid film, and an epoxy film are presented in Fig. 5. On the whole, the organic-inorganic hybrid film has a smooth surface, good compactness, no obvious surface defects, no gaps and slag inclusions. The surface of the epoxy film is distributed with tiny pits and peaks. The surface of the silicon-containing hybrid film has a small amount of microscopic defects, and its structure is not dense with a titanium-containing hybrid film.

3.4.2 AFM. AFM of a Si-containing hybrid film, a Si-containing hybrid film are presented in Fig. 6. It can be seen that the hybrid film has peaks and pits in the microscopic morphology, and the peak is caused by the precipitation of the silicon phase. The surface roughness of the Si-containing film is slightly higher than the surface roughness of the Ti-containing film. The contour arithmetic mean deviation $S_a$ represents the arithmetic mean of the absolute values of the points on the contour to the midline ordinate value within the length of the sample [8], reflecting the microscopic geometric properties of the material, related to the height of the valley and the shape of the contour, as opposed to Roughness is more able to express the magnitude of the contour error. As can be seen from the analysis in Tab. 1, the $S_a$ value of the Ti-containing film sample was 12.5 nm, and the $S_a$ value of the Si-containing film sample was 41.5 nm, which was about 3.3 times that of the Ti-containing film sample.

In the study of the three-dimensional microscopic morphology of the material, the root mean square deviation $S_q$ represents the root mean square value of the surface roughness deviating from the reference datum in the sampling region. The $S_q$ value of the Ti-containing film was 17.5 nm, and the $S_q$ value of the Si-containing film was 52.7 nm, which indicates that the surface morphology of the Si-containing film fluctuated greatly, which was due to an increase in the $S_q$ value due to a large number of peaks.
Figure 5. SEM image of Ti-containing hybrid film, Si-containing hybrid film and epoxy film.

Figure 6. AFM of hybrid films.
Table. 1. Surface roughness of organic-inorganic hybrid films

| surface              | average deviation of roughness Sa/nm | root mean square deviation of surface morphology Sq/nm |
|----------------------|--------------------------------------|--------------------------------------------------------|
| Si-containing hybrid film | 41.5                                 | 52.7                                                   |
| Ti-containing hybrid film  | 12.5                                 | 17.5                                                   |

3.4.3 Discuss the Relationship Between Structure and Protective Performance. Si is the main group IV element in the third cycle, C is also the main element of the IV main group in the second cycle, Ti is the fourth sub-group element in the fourth cycle. According to the law of electronegativity of the periodic table, the electronegativity of C is the largest and the electronegativity of Ti is the smallest. It combines with the electron-positive O to form a bond, the Ti-O bond is the largest, and the C-O bond is the smallest, the steric hindrance of the Ti-containing group is the smallest. The Ti-containing organic-inorganic hybrid film contains a large amount of Ti-O network, and the Si-containing hybrid film contains a large amount of Si-O network. A large amount of titanium hydroxy or silanol groups in the hybrid film, so that the hydroxyl groups in the hybrid film can condense with the hydroxyl groups on the metal surface to form Ti/Si-O-Fe bonds, enhance the adhesion of the hybrid film. The bond energy of the Ti-O bond is larger than that of the Si-O bond, and the atomic radius of Ti is larger than that of Si. Therefore, the Ti-containing hybrid film has higher compactness, and the Ti-containing hybrid film has better corrosion resistance than the Si-containing hybrid film. The epoxy film contains a large amount of carbon hydroxyl groups, condenses with the hydroxyl groups on the metal surface to form a CO-Fe bond, which has a small bond energy and poor adhesion, so the epoxy film has the worst compactness and resistance. The corrosion performance is also the weakest.

4. Conclusion
(1) The basic properties and EIS properties of Ti-containing organic-inorganic hybrid film showed a unimodal change with the increase of precursor content. When the molar ratio of the precursor to tetrabutyl titanate was about 0.75, the hybrid film obtained had the best performance.
(2) The microstructure of the film was analyzed by SEM and AFM technology. The Ti-containing organic-inorganic hybrid film was denser than the Si-containing organic-inorganic hybrid film and epoxy film, which resulted in better salt spray resistance. The Si-containing hybrid film showed large pitting corrosion for 30 days, while the transparent Ti-containing hybrid film (10-20 μm) could be placed in a neutral salt spray box for 56 days (greater than 1344 h) intact.

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6. References
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