Anticorrosion Property of Chemically Bonded Phosphate Ceramic Coatings with Silica Sol

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Abstract. To protect steel from corrosion in the service environments, a chemically bonded phosphate coating was successfully prepared in this study. The coating consists of aluminium dihydrogen phosphate, silica sol, aluminium hydroxide, silica, magnesium. Then, the microstructure and anticorrosion property of the coating were studied. By using XRD and SEM characterization, it is found that a crystalline Newberyite (MgHPO4·3H2O) and amorphous species formed in microstructure of coating matrix. The anticorrosion property was investigated by salt spray test, in which the coating was brushed on the surface of steel substrate in advance. Then, the anticorrosion property was carried out by an electrochemical test. Results indicated that the coating has an excellent effect in protecting steel substrate from corrosion. Because the compositions of the coating are water based, and it does not need any organic solvent, therefore the coating is both green and environmentally friendly.

1. Introduction
Metal corrosion is the process of changing from active metal materials to inactive oxides in the service environment [1]. Metal corrosion also brings many safety issues. Corrosion leakage of oil pipelines, toxic and hazardous medium storage equipment, production equipment, etc., will cause environmental pollution, and in serious cases will endanger human life [2-3]. Coating anti-corrosion is one of the effective means of coating protection. The direct contact between the protected substrate and the corrosive medium in the service environment of the coating is isolated to avoid contact between the metal surface and the external environment, so as to play a role of anticorrosion.

Recently, coatings of anti-corrosive covered on metal has been extensive researched, especially the phosphate coatings. Chen et al [4] reported that monoaluminium phosphate is the most effective binding phase in the synthesized aluminum phosphate binder, and the wear durability of ceramic coating of Al2O3-SiC prepared by Al(H2PO4)3 is about two times that of the control group. Wang et al [5] also reported that titanium hybrid silica sol coating showed better salt spray resistance compared to ordinary one. However, the microstructure of the coating is one of the important factors to keep durability of substrate protection. In silica sols, the surface of SiO2 contains a large number of active groups such as water and hydroxyl groups, which can be cross-linked with phosphate via reactive hydroxyl groups and promote the formation of coating network structures [6].

Silica sol is colloidal solution of silica colloidal particles dispersed in water, also known as silicic acid sol, or silica hydrosol. In view of the specific property such as good dispersion, excellent adhesion and favourable reactivity, silica sol is widely used in the industries of fabric, fiber, rubber, paint ceramics etc [7]. Also as environmentally-friendly material, silica sol was investigated with coatings of thermal
reflective insulation [8], high temperature absorber [9], water repellent [10-11], antireflective [12-14] and anti-corrosive [5, 15].

In this work, the chemically bonded phosphate coating was synthesized by aluminum dihydrogen phosphate, silica sol, aluminum hydroxide, and magnesium oxide. This coating was tested by salt spray, acid and alkali immersion, XRD, and SEM methods were used to study the composition and structure of the phosphate coating, which laid the foundation for the research of similar materials in the future.

2. Experimental procedures

2.1. Preparation of anticorrosive coating
A3 steel with a size of 30mm×30mm×2mm and 80mm×20mm×2mm was used as the substrate. The A3 substrates with size of 30mm×30mm×2mm is used for potentiodynamic polarization curve measurements. Salt spray test were conducted using samples with the size of 80mm×20mm×2mm. The substrates were immersed for 3min in an aqueous solution containing 5wt.% H2SO4(analytical pure, Chengdu Kelong chemical reagent factory) and then immersed for 3min in an aqueous solution containing 5% NaOH(Analytical pure, Chengdu Kelong chemical reagent factory), and then rinsed by deionized water and dried in air.

The coating was prepared by aluminium dihydrogen phosphate mixed with silica sol (Jinan Yinfeng Silicon products Co., Ltd., silica contain is 15.94%, sodium oxide 0.17%, density is 1.098, pH is 9.49, and particle diameter is 9.5nm), aluminium hydroxide(Analytical pure, Chengdu Kelong chemical reagent factory), silica(Analytical pure, Chengdu Kelong chemical reagent factory), and magnesium(Douao Technology Co. Ltd) for 10 minutes and then brushed on treated substrates. In addition, the main flow is shown in figure 1.

![Fig. 1 Phosphate inorganic coating preparation process](image)

2.2. Coating characterization
The crystalline phase of the samples was examined by X-ray diffraction (XRD, D8ADVANCE, Bruker-AXS, Germany) with graphite monochromatized Cu Ka radiation operating at 40 kV and 40 mA at room
temperature. The surface morphologies of anticorrosive coating were observed with a scanning electron microscope (SEM, Quanta TM 250 FEG, FEI) at an accelerating voltage within the range of 10–15 kV.

2.3. Testing methods
Polarization curve test using CHI 660D electrochemical workstation at 25°C measured the potentiodynamic polarization curve of coating in 3.5% NaCl (mass fraction). A three-electrode system was used. The reference and auxiliary electrodes were saturated calomel (SCE) and platinum electrodes, respectively. The working electrode was a coated metal. For the difference in open circuit potential between the substrate and the coating, the polarization curve of the substrate has a potential sweep range of -1.0 to 1.0 V (vs SCE) and a coating scan range of -1.5 to 0.5 V (vs SCE), the scan rate is 0.005 V/s. In the AC impedance test, the working potential of the sample is kept at the self-corrosion potential, the sine wave excitation signal is 5 mV, and the scanning frequency range is 1×(10⁻² to 10⁵) Hz.

Salt spray test refers to the use of salt spray test equipment to create artificial simulated salt spray environmental conditions, in order to assess the environmental testing of steel and other metal materials, corrosion resistance. The salt spray corrosion resistance of the coating was tested with a neutral salt spray test (GB/T 1771-2007). The corrosive medium was a 3.5 g/L NaCl solution, and the temperature in the salt spray chamber was set at 25°C.

3. Results and discussion
3.1. Characterization of XRD and SEM
The prepared samples were subjected to X-ray diffraction analysis and difference between samples was the content of silica sol. All samples were identified as one-phase system of newberyite[16], as shown in Fig.2. The diffraction peaks of MgHPO₄·3H₂O appear at 2θ=14.8, 16.6, 25.7, 29.2, etc. However, there are some peaks of SiO₂ and Al(OH)₃ which can be assigned as strengthening the mechanical property of the coating.

Fig.3 shows the SEM image of newberyite coating surface. The coating surface composed of rhombic and flocculent structures that are a few micrometers in size. The formation of these structures during the synthesis of the newberyite coating shown as follows:

\[
\text{Al(OH)}_3 \rightleftharpoons \text{Al}^{3+} + 3\text{OH}^- \tag{1}
\]

\[
\text{Al}^{3+} (aq) + \text{H}_2\text{PO}_4^- + \text{HPO}_4^{2-} + 3\text{H}_2\text{O} \rightarrow \text{AlH}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O} \tag{2}
\]

\[
\text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg}^{2+} (aq) + 2\text{OH}^- \tag{3}
\]

\[
\text{Mg(OH)}_2 + \text{HPO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{MgHPO}_4 \cdot 3\text{H}_2\text{O} \tag{4}
\]

This reaction is an exothermic reaction. The heat released from the curing reaction promotes water evaporation of the matrix and accelerates the solidification process of the coating. When the inside temperature rises, the aluminum and magnesium phosphate gradually lose water and polymerize, eventually forming a network of aluminum-magnesium spinel, so that the coating exhibits good high temperature performance [17]. It can be clearly observed from Fig.3 that the coating is dense and no obvious defects. Besides, with the increase of silica sol from 2.8% to 8.4%, the addition of excess silica sol will cause weak aggregation of particles in the sol, forming flocculate crystal-filled microscopic pores, adding a layer of shielding to the coating, as shown in Figure 3(a)-(h). In addition, the fine particles have strong penetrability to the base layer and can penetrate into the interior of the base material through capillary action, so that the coating has a strong adhesive force [18], maintains a very high bonding strength at room temperature.
3.2. Anticorrosion Property

Polarization curves of the A3 steel and the phosphate coating coated on the A3 steel in a 3.5wt.% NaCl aqueous solution are shown in Fig. 4. The current density and self-corrosion potential obtained from the Tafel curve extrapolation method are shown in Table 1. The corrosion potential ($E_{corr}$) of the A3 steel was -910mV, which is considerably negative and is indicative of the reactivity of A3 steel in the aqueous solution. The evolution of hydrogen might result in an increase in the cathodic currents when the potential is smaller than $E_{corr}$. At more positive potential than $E_{corr}$, the metal dissolves continuously because of the absence of a passivation layer. The high chloride concentration caused the absence of the passivation layer. On the other hand, the $E_{corr}$ of phosphate coating is much smaller than that of the A3 steel. The $E_{corr}$ of sample with 5.6wt.% silica sol exhibit the most positive value was -682mV. The corresponding current density was 0.089μA, almost decreased by more than 4times as compared to the control sample A3 steel, as observed from its polarization curve. Besides, it can be seen from the Table 1 that other samples also have a significant difference in corrosion potential and current density.
compared to A3 steel. Since the phosphate coating contains unreacted MgO and soluble phosphate, it can change the pH value of the solution and release Mg$^{2+}$ and PO$_4^{3-}$, which can change the corrosive environment [19]. Within a certain pH range of the solution, when OH$^-$ and Fe$^{2+}$ released from the anode region form insoluble phosphate as passivation layer covering the anode region, the anode current is reduced to protect the substrate.

| Table 1 Polarization curve fitting results of phosphate coating |
|---------------------------------------------------------------|
| Substrates | 2.8% | 3.8% | 5.6% | 8.4% |
| --- | --- | --- | --- | --- |
| Self corrosion potential /mV | -910 | -714 | -690 | -682 | -702 |
| Corrosion current density / (A/μm$^2$) | 0.448 | 0.116 | 0.101 | 0.089 | 0.107 |
| The cathode slope bc / (mV) | 217.97 | 352.40 | 490.36 | 560.13 | 433.93 |
| The anode slope ba / (mV) | 77.96 | 543.21 | 554.36 | 732.80 | 357.19 |
| Polarization resistance (Ω) | 3702600 | 7671058 | 11150363 | 15378125 | 7922829 |

Fig. 5 shows the polarization Resistance Rp of the different specimens calculated by the formula plotted as a bar graph. It can be seen from Fig.4 that the polarization resistance of the A3 steel was $3.76 \times 10^6$ Ω which is much smaller than the samples coated the phosphate coating. The polarization resistance of the samples with 2.8wt.% silica sol was $7.67 \times 10^6$ Ω. The polarization resistance of the sample with 3.8wt.% silica sol was $11.15 \times 10^6$ Ω, 5.6wt.%. The polarization resistance of the sample with 5.6wt.% silica sol was $15.37 \times 10^6$ Ω, and the polarization resistance of 8.4wt% silica sol sample was $7.92 \times 10^6$Ω. From the polarization resistance results, the optimal amount of silica sol was 5.6wt%. This also indicated that the incorporation of the silica sol significantly enhances the polarization resistance of the sample. According to the electron microscopy results, due to the denseness of the microstructure of the coating, the corrosion by external chemical medium infiltration can be prevented.
Fig. 6 Sample appearance after neutral salt spray test

(a) Initial salt spray test sample  
(b) The samples underwent 96h of neutral salt spray test
(c) The samples underwent 30d of neutral salt spray test  
(d) The morphology of the corrosion sample substrate

Fig. 6(a) shows the surface morphology of samples with different silica sol content at the beginning. Fig. 5(b) and Fig. 6(c) shows the corrosion morphology samples after 96h and 30 day undergoing a neutral salt spray test. The content from left to right is 2.8wt.%, 3.8wt.%, 5.6wt.% and 8.4 wt.% respectively. It can be seen from Fig.6(a) that in the initial stage, the surface of the sample without rupture or peel off. After 96 h neutral salt spray test, as shown in Fig.6(b), the surface of the coating was not corroded, no exfoliation, embrittlement and foaming, and some sodium chloride particles were precipitated on the surface of the samples. After 30 days of the test, the edges of the A3 steel developed yellow rust spots mainly because the particles deposited by salt spray adhered to the surface of the service material. Moisture absorption occurs quickly and then dissolves into an aqueous solution of chloride or a dissociated chloride ion, which seeps into the material system through tiny pores in the coating serving in that environment, lead to corrosion of metals and even aging of materials [20]. At the moment, the impermeability of the coating on the edge of samples decreases gradually, which almost can’t preventing the salt water permeating to uncoated substrate. As the test went on, the corrosion of samples become more and more serious. Fig 6(d) shows the samples substrates after 30d of the test. As can be seen from the figure, there are different degrees of pitting on the X-site of the sample center painting. In addition, the edges of the substrates have different degrees of rust. However, in general, the salt spray test results after 30 days, that is, 720 hours, indicate that the phosphate coating can effectively block the intrusion of external corrosive media on the steel plate substrate, and has good corrosion protection for steel substrates.

4. Conclusions
An chemically bonded phosphate ceramic coatings was successfully coated on an A3 steel and cured at room temperature. The coating was a single-phase system of newberyite with an orthorhombic crystal structure. The corrosion current density of the coating decreased by more than 4 times as compared to that of A3 steel. The sample with silica sol content of 5.6wt% has the largest value of corrosion potential. In addition, the coating exhibited good protection ability for salt spray erosion. The silica sol greatly improved the corrosion resistance of the coating compared to the A3 steel.

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