

Anticorrosive Ability and Mechanism of Hydroxyapatite Pigment

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Hydroxyapatite(HAp) was synthesized using the waste sludge from semiconductor process and used as an anticorrosive pigment. The water absorption of coating pigmented with anticorrosive pigment and the corrosion at interface between coating and substrate were monitored using AC impedance techniques. The anticorrosive performance of HAp was compared with those of red lead(RL) and zinc potassium chromate(ZPC), which have been known as representative anticorrosive pigments. The amount of absorbed water in ZPC- and HAp- pigmented coatings was much higher compared to that in RL-pigmented and unpigmented film. However, it seems that the water absorbed into HAp- or ZPC-pigmented film is beneficial to anticorrosive function. The anticorrosive performance of HAp is superior or at least comparable to those of ZPC and RL. The excellent anticorrosive properties of HAp can be explained by its passivating ability, caused by the reaction of the soluble component of HAp with Fe to form iron phosphate in the presence of water.

Keywords : hydroxyapatite, anticorrosive pigment, passivation.

1. Introduction

Organic coatings are the most widely used method of protection against corrosion of metals. The protective organic coatings show several advantages. These coating can be applied over any size and structure of substrates, and protect any steel structure for a long time by repainting. Organic coatings containing compounds of lead or chromium as anticorrosive pigments have been extensively used to inhibit corrosion. The problems of environment protection set strict limits for the use of these toxic. Accordingly, there is a need to develop higher efficient and more environment friendly pigment.

The aim of the present study was to determine the protective ability and mechanism of hydroxyapatite(HAp). HAp was synthesized using the waste sludge from semiconductor process from the point of view of waste recycling. The water absorption of anticorrosive coating pigmented with HAp and the corrosion at interface between coating and substrate were monitored using AC impedance techniques. The anticorrosive properties of red lead(RL) and zinc potassium chromate(ZPC), which were historically introduced as corrosion inhibitors in anti-

corrosive coatings, were also investigated and compared with those of HAp.

2. Experimental

2.1 Synthesis of hydroxyapatite pigment

The sludge, obtained by neutralizing the waste acid from semiconductor process with calcium hydroxide, was dried at 120°C and then sintered at 700°C for 30 minutes. The sludge was reacted with aqueous solution of 1%-H₃PO₄ at 70°C to synthesize stoichiometric compound. After that, the sludge was dried again at 120°C and crystallized at 1000°C for 2 hours. The crystallized sludge was ground into the particles of 3~4 μm using a wet ball mill and used as pigment. The red lead and zinc potassium chromate were used as reference anticorrosive pigments.

Table 1. Physical and chemical properties of anticorrosive pigment used in the experiment

Pigment	Composition	Color	Specific gravity	Water soluble content(wt%)
Hydroxyapatite(HAp)	Ca ₁₀ (PO ₄) ₆ · (OH) ₂	Ivory	3.16	1.8
Zinc potassium chromate(ZPC)	K ₂ O · 4CrO ₃ · 4ZnO · 3H ₂ O	Yellow	3.80	7.0
Red lead(RL)	Pb ₃ O ₄	Red	8.90	<0.2

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The physical and chemical properties of the pigments used in the experiment are shown in Table 1.

2.2 Preparation of specimens

A cold press steel plate(150×75×7 mm) was polished with sand paper #400 and degreased with acetone and methyl alcohol. The air drying alkyd, the white enamel No. 2 was used as the coating material. To evaluate the anticorrosive effect of pigment, HAp, ZPC, and RL was added by 10 wt% to the coating material. Then the pigment was dispersed using the high speed dispersing machine (Dispermat, BYK) for 1 hour. The coating material was applied on the substrate to have dry film thickness of about 40 μm using a film applicator(Sheen, England). The coated substrates were dried at 20°C and 60% RH for 7 days in the temperature-humidity chamber(Tenney Engineering Inc., USA).

2.3 Measurement of AC impedance

The measurements of AC impedance were carried out by means of the two electrode method using the standard resistance under ambient conditions. The electrolyte was 0.5M-NaCl solution, and the electrode area was 7 cm². The frequency range was 10 kHz to 1 mHz.

The impedance was obtained by combining the potentiostat/galvanostat (HA-303, The HOKUTO Denko Co., Japan) connected with GP-IB and the response analyzer (S-5720C, NF Circuit Design Block Co., Japan). The applied voltage was 10 mV. Platinum was used as a counter electrode. The measured impedance data were fitted in the Bode plots.

2.4 Analysis by XRD and EPMA

To investigate anticorrosive mechanism of HAp, the reaction products of Fe with the soluble component of the pigment were analyzed using XRD(X'Pert-MPD, Philips, Nethland) and electron probe microanalyzer (EPMA ;1600, Shimadzu Co., Japan). To prepare the extract solution of HAp, 25 g of HAp was added into 500 ml of distilled water, stirred in the shaker for 24 hours and filtered through the membrane filter. Then 10 g of Fe powder was added to 100 ml of the extract solution of pigment and stirred for 24 hours. The reaction product was filtered and washed with distilled water. The dried reaction product was analyzed using XRD and EPMA.

3. Results and discussion

3.1 The water absorption into coating

The corrosion prevention properties of pigments can be achieved by either one or several mechanisms ; reducing

the permeation of corrosive such as water and oxygen, passivating the substrate, and preventing the saponification of the binder. However, the relative importance of the barrier function of organic coatings in corrosion prevention has been debated for a long time. A number of different theories concerning the role of the barrier function of organic coatings in corrosion prevention have been proposed.¹⁾

When coated metals are exposed to wet corrosive environments, the first process causing the onset of corrosion could be uptake of water by the coatings and permeation of water to the coating-metal interface.

In this study, the influence of addition of anticorrosive pigment on the water absorption by coating film was studied. The water absorbed into film can be estimated from the change of impedance, because the capacitance of film changes by permeation of water(dielectric constant of water ; about 80).

Table 2. presents the amount of water absorbed into coatings at various exposure time for the films pigmented with HAp, ZPC and RL.

Table 2. Amount of water adsorbed into coating films

Water uptake, Xv/vol%	Time	Time, t / hrs									
	1	2	3	4	5	6	10	15	20	24	
HAp	17.18	24.36	25.88	26.25	26.33	26.35	26.14	25.80	25.85	26.01	
RL	9.67	12.35	13.58	14.14	14.56	14.92	15.98	16.61	16.82	17.00	
ZPC	23.02	24.88	26.06	26.67	27.38	27.90	28.56	28.59	28.67	28.77	

As can be seen in Table 2, all films absorbed water rapidly at initial stage of absorption, and then the rate of water absorption showed only a small increase with time. All films seemed to be saturated with water after 24 hours of exposure time and these results are well agree with the fact that the coating film of thickness of below 100 μm can be saturated within 24 hours in electrolyte solution.²⁾

The amount of water absorbed into coating film is virtually dependent on the pigment used. The amount of absorbed water decreased in the order of ZPC- > HAp- > RL-pigmented film.

It was reported that if water can accumulate at the pigment-binder interface water absorption tends to increase with pigment volume concentration(PVC).¹⁾ All pigmented films absorbed much more water than the unpigmented film, indicating that the major part of water is absorbed at the pigment-binder interface. The film pigmented with RL showed smaller water absorption,

compared to the other pigmented films. It may be attributed to the fact that RL has higher specific gravity and consequently lower PVC than ZPC and HAp. Accordingly, RL-pigmented film has much smaller pigment-binder interface, resulting in lower water absorption of the film.

Besides PVC, the water soluble content of pigment (Table 1) also seems to influence the water uptake of coating film. The film pigmented with ZPC, which has lower PVC (higher specific gravity) than HAp, revealed higher uptake of water compared to that pigmented with HAp. The water soluble component of pigment may enhance the accumulation of water at pigment-binder interface.

From the above results, it can be shown that the absorption of water into the coating film pigmented with anticorrosive pigment may depend on PVC and the water soluble content of pigment as well.

3.2 Evaluation of the anticorrosive performance of the coatings by electrochemical impedance method

The electrochemical impedance spectroscopy(EIS) has been widely employed as a method for the interpretation the electrode reaction, the estimation of the corrosion-resisting properties of metals, and monitoring of corrosion.³⁾⁻⁵⁾ Recently it gained widespread use in the development of new coatings or in the study of corrosion phenomena involving coated metals.

In this study, anticorrosive behaviors of HAp, ZPC and RL pigment were investigated by means of AC impedance method. To evaluate the anticorrosive performance of pigment, the pigmented film was exposed to 0.5 M NaCl solution and its aging process was monitored.

It is generally known that the coating films showing the resistance of higher than $10^8 \Omega/\text{cm}^2$ reveals good anticorrosive performance, while that showing the resistance of lower than $10^6 \Omega/\text{cm}^2$ has poor anticorrosive properties.⁶⁾

Fig. 1. shows the impedance of coating films at 1 day and around 140 days of exposure. In the case of $40 \mu\text{m}$ RL-pigmented film, the resistance at 10 mHz was higher than $10^8 \Omega/\text{cm}^2$ at the beginning of exposure. After 142 days of exposure, however, a few blisters were found on the specimen and the resistance was $7 \times 10^6 \Omega/\text{cm}^2$. The $42 \mu\text{m}$ ZPC-pigmented film showed the resistance of $4 \times 10^7 \Omega/\text{cm}^2$ at the beginning of exposure and the resistance increased to $5 \times 10^8 \Omega/\text{cm}^2$ after 146 days of exposure. In the case of $40 \mu\text{m}$ HAp-pigmented film, the resistance was around $10^8 \Omega/\text{cm}^2$ at the beginning of exposure and decreased to $8 \times 10^7 \Omega/\text{cm}^2$ after 139 days.

Fig. 2. shows the change of impedance(at 10 mHz) of coatings with exposure time. The RL-pigmented film

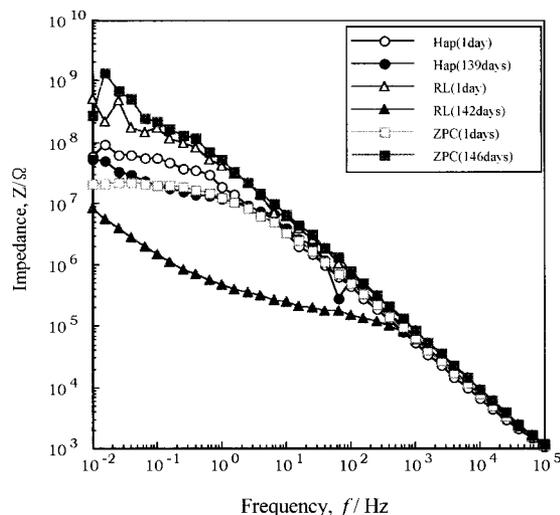


Fig. 1. Impedance spectra of coating films.

showed relatively high resistance at the initial stage of exposure. The resistance was higher than $10^8 \Omega/\text{cm}^2$ up to the first 107 days of exposure. And then, however, it decreased quickly. It is well known that basic pigment, like red lead, easily reacts with oil based resin to form metal soap.⁷⁾ Consequently, mechanical strength of film is improved by the formation of metal soap. However RL does not possess the ability to passivate substrate. These facts seems to affect the result for RL-pigmented film, that is, the resistance is high at the initial stage of exposure and then it decreases quickly after some period of exposure. In the case of ZPC- and HAp-pigmented film, the impedance at 100 mHz increased continuously with time. It is well known that ZPC prevents corrosion by passivation of metal surface, which is caused by the oxidizing function of chromate. Accordingly the impedance of ZPC-pigmented film increased continuously with time. HAp showed similar trend of change in impedance to ZPC. Therefore HAp is also expected to form passive film during exposure. As will be seen later, the reaction of water soluble component of HAp with Fe substrate may be responsible for the passivation of substrate.

3.3 Nature of passive film

As can be seen in Fig. 2, the impedance of HAp-pigmented film increased continuously with time. Thus it is expected that the anticorrosive property of HAp is probably due to efficient passivation of steel substrate as mentioned above.

Fig. 3. and 4 show the results of EPMA and XRD measurement, respectively, for the reaction products of Fe with the soluble component of HAp. Fig. 3 reveals that the reaction product contains P, and Fig. 4 indicates that

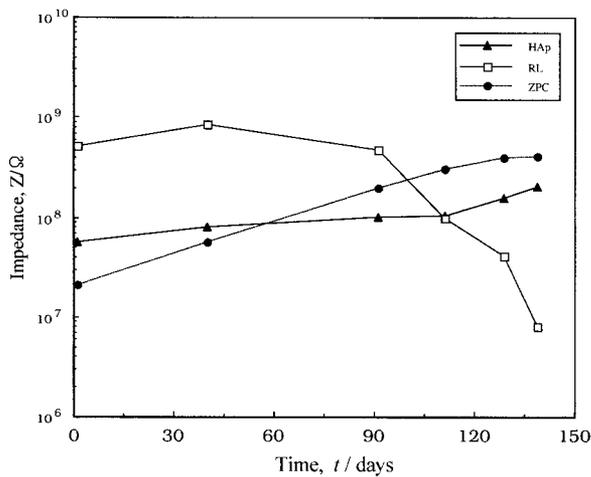


Fig. 2. Change of impedance at 10 mHz with time.

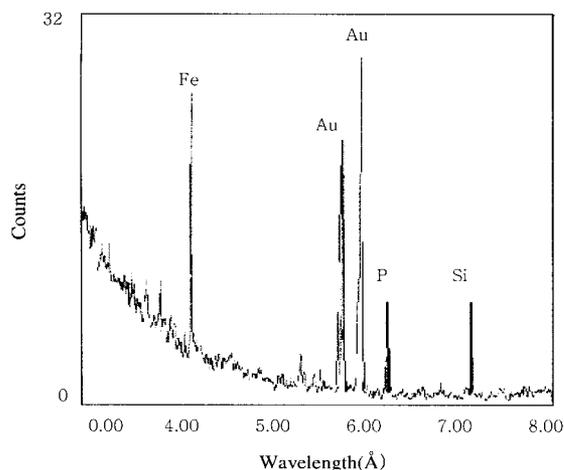


Fig. 3. Result of EPMA measurement for the reaction products of Fe with the extract solution of Hap.

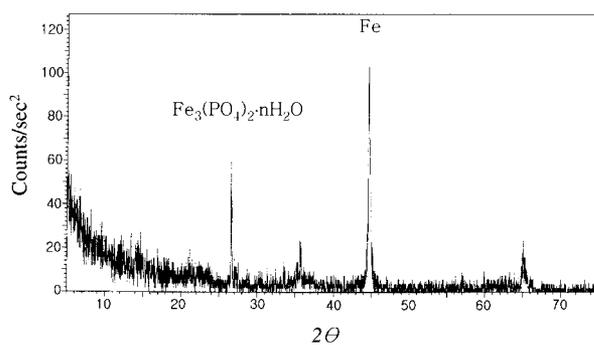


Fig. 4. Result of XRD measurement for the reaction products of Fe with the extract solution of Hap.

iron phosphate, $\text{Fe}_3(\text{PO})_4$, is formed of by the reaction of Fe with extract solution of HAp. From the above results, it can be expected that, in the presence of water, soluble component of HAp pigment dissolves and reacts with the substrate, Fe, to form stable compound, such as iron phosphate.

From the comparison of results for HAp-, ZPC-, and RL-pigmented coating film, it can be seen that the anticorrosive performance of HAp is superior or at least comparable to those of ZPC and RL, which have been known as representative anticorrosive pigments, even though HAp-pigmented film showed comparatively high absorption of water. Therefore it is expected that the water absorbed into HAp- or ZPC-pigmented film is beneficial to anticorrosive function, namely it allows diffusion of the dissolved anticorrosive component to coating-metal interface to passivate substrate.⁸⁾

4. Conclusions

The hydroxyapatite(HAp) synthesized using the waste sludge from semiconductor process functions as a good anticorrosive pigment, and its anticorrosive efficiency is even superior to that of red lead(RL) or zinc potassium chromate(ZPC). The anticorrosive property of HAp is probably due to efficient passivation of steel substrate. The passive film seems to be iron phosphate formed by the reaction of the soluble component of HAp with steel substrate. It seems that the water absorbed in HAp-pigmented coating film enhances the passivating function of HAp.

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