

EVALUATION OF THE ANTICORROSION OF WATERBORNE EPOXY COATINGS CONTAINING CERIUM SALT-ACTIVATED CERIA NANOPARTICLES DEPOSITED ONTO CARBON STEEL SUBSTRATE

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Received: 14 July 2018; Accepted for publication: 9 September 2018

ABSTRACT

The present work investigates the corrosion protection of waterborne epoxy coatings loading CeO₂ nanoparticles activated with cerium salt for the carbon steel substrates. First, the dispersion of activated nanoparticles in the epoxy matrix was observed by field emission scanning electron microscopy (FESEM). The electrochemical impedance spectroscopy (EIS) was carried out to evaluate the role of the activated-CeO₂ nanoparticles in the organic coatings immersed in a 0.5 M NaCl solution. Thus, the effect of the cerium ion activated ceria nanoparticles on the coatings presented the artificial defect in an aggressive environment was examined via salt spray test. Complementary studies were performed using cross-cut and pull-off test to assess the adherence properties of the samples. Results revealed that the presence of activated-CeO₂ nanoparticles enhanced corrosion protection properties of waterborne epoxy coating without losing adherence properties.

Keywords: ceria nanoparticles, cerium salt-activated, waterborne epoxy coatings, anticorrosion.

1. INTRODUCTION

Corrosion is the common problem in aeronautic, automobile industry that contributes to the degradation of materials. Many technologies were applied to delay this phenomenon such as using well-designed alloys [1, 2] or protective coatings [3-5]. The use of organic coatings is more popular because they provide a good protection against corrosion for different types of materials and a cost-effective method. Due to a high cross-linking density, epoxy coatings introduce a physical barrier between the metal surface and the corrosive species (oxygen, water and ions) in the environment. For improving anticorrosion properties of the epoxy coatings, inhibiting compounds have been incorporated into them. Recently, hexavalent chromium (Cr⁶⁺) is a well-known inhibiting compound that yields an excellent corrosion protection for metals [6-8]. However, Cr⁶⁺ compounds are recognized as a human carcinogen and cause hazardous consequences for the environment. Therefore, their application as anticorrosion pigment has been restricted in Europe since 2007 [9].

In recent years, numerous researches have been investigated focused on development of new effective and environment-friendly corrosion inhibitors [10-12]. However, when inhibitors are directly added into coating systems, it can conduce to undesired leaching of these compounds and the coating will be degraded [13, 14]. To solve this problem, the corrosion inhibitors are encapsulated into micro and nano containers such as layered double hydroxides, porous inorganic nanoparticle or halloysite nanotubes [15-18]. These results showed that the coatings containing the containers loaded corrosion inhibitors enhanced both active and passive anticorrosion performance compared to as-prepared coatings. On the other hand, depending on matrix system and types of solvent, inhibitor could provide positive or negative effect of anti-corrosion of the coatings. In our previous work [19], the corrosion properties of the cerium salt-activated cerium (IV) oxides for the carbon steel were studied. The obtained results demonstrated that the inhibition efficiency of $\text{Ce}(\text{NO}_3)_3$ in a NaCl solution is higher than that of activated- CeO_2 . However, when the latter inhibitor was inserted into poly-vinyl-butyrac coatings (organic solvent system), the sample containing the activated nanoparticles showed a better barrier and anti-corrosion properties.

The present work will report and discuss the effects of cerium (III) salt-activated ceria nanoparticles on corrosion protection properties of waterborne epoxy coatings. Electrochemical impedance spectroscopy (EIS) and salt spray tests were carried out to study the corrosion behavior of the waterborne epoxy coating with the presence of defects on the surface. Thus, the adherence properties of the samples were evaluated by using cross-cut and pull-off tests.

2. MATERIALS AND METHODS

2.1. Materials and sample preparation

The coating is a two-component water-based paint using an aliphatic polyamine (Epikure 8537-WY-60, Momentive) as hardener and a bisphenol A epoxy polymer (Epikote 828, Hexion) as base (3:2 ratio). Cerium (III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and ammonia solution were purchased from Merck and used to synthesize CeO_2 nanoparticles. XC35 carbon steel plates with thickness of 2 mm were used as metallic substrates. The plates were cut up into 150 mm x 100 mm pieces. Before coating deposition, the sheets were polished with SiC paper (grade 400) then were cleaned with distilled water and ethanol.

CeO_2 nanoparticles were synthesized by the method reported in our previous work [19] and briefly recalled here. 4.34 g of $\text{Ce}(\text{NO}_3)_3$ was dissolved in a mixture of ethanol and distilled water (50:50 ratio). A 25% ammonia solution (10 mL) was added slowly drop-wise to this solution under stirring. The reaction was occurred at 60 °C for 2 h. Finally, the mixture showed a yellowish-hue color, the formed nanoparticles were extracted by centrifugation. Then, they were washed with distilled water several times until neutral pH and dried at 70 °C for 24 h. The average particle size of as prepared CeO_2 was about 11 nm [19].

For obtaining activated ceria nanoparticles ($\text{Ce}^{3+}/\text{CeO}_2$), as-prepared cerium (IV) oxide nanoparticles were dispersed into an aqueous solution of cerium (III) nitrate ($\text{Ce}^{3+}:\text{CeO}_2$ mole ratio = 1:1) by using ultrasonic waves for 1 h. This mixture was used for the preparation of epoxy waterborne coatings. Dispersion of the synthesized CeO_2 nanoparticles was also ultrasonically prepared for the same time and cerium salt was dissolved in an aqueous solution for incorporation into epoxy coating. The amount of distilled water used as a solvent for each sample was similar. The prepared dispersion was mechanically mixed with hardener for 30 mins, then epoxy resin was added to this mixture for 15 mins. All the epoxy coatings samples

contained 0.1 wt.% of filled compound (cerium salt, CeO_2 or cerium (III) activated ceria nanoparticles). The coatings were deposited onto carbon steel plates by spin coating at 600 rpm for 10 s and dried at room temperature for a week. The film thickness is about $70 \pm 5 \mu\text{m}$ (measured by a Minitest 600 Erichen digital meter).

2.2. Analytical methods

The morphology of the inhibitors in the epoxy coating matrix was observed by using Field emission scanning electron microscope (FESEM Hitachi S-4800). The samples were broken in liquid nitrogen. Microphotographs were recorded at the cross-section.

The anticorrosion property of the epoxy coatings containing $\text{Ce}(\text{NO}_3)_3$, CeO_2 or $\text{Ce}^{3+}/\text{CeO}_2$ was examined by electrochemical impedance spectroscopy technique with Biologic Potentiostat VSP-300. A cylindrical tube was fixed on top of the coated sample (20 cm^2) and filled with a 0.5 M NaCl solution. Measurements were realized under potentiostatic conditions with a 30 mV peak-to-peak sinusoidal perturbation at the open circuit potential in a frequency range of 100 kHz-10 mHz with 6 steps per decade. The repeatability of EIS measurements was checked at least three times.

In order to shorten the exposure time and accelerate the corrosion phenomenon, the salt spray method was carried out by using Q-FOGCCT-600 chamber (ASTM B117). A scratch of 3 cm length was manually created on the surface of the coating using a cutting knife according to ISO 17872 standard. All the samples were exposed in the chamber in which a 5 % NaCl solution was sprayed. The temperature was kept at 35°C during the test.

The adhesion of the epoxy coating deposited on the carbon steel plate was evaluated by crosscut test (ASTM D 3359). A crosshatch cutter six blades with 2 mm spaces between cutting edges was used. The pull-off test was also carried out using Positest model ATA20 to quantitatively measure the adherence properties of the samples.

3. RESULTS AND DISCUSSION

3.1. Morphological investigation

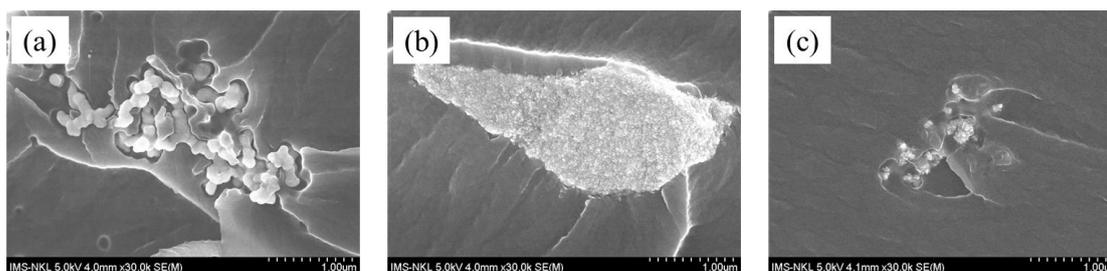


Figure 1. FESEM micrographs observed at cross-section of the epoxy coatings containing: (a) $\text{Ce}(\text{NO}_3)_3$, (b) CeO_2 , and (c) $\text{Ce}^{3+}/\text{CeO}_2$.

FESEM images in Fig. 1 show the micrographs of fracture surface for the epoxy coatings containing different pigments. It can be seen that the cerium salts were crystallized and agglomerated in the epoxy matrix (Fig. 1a). Moreover, the space between the cerium crystals and epoxy matrix was observed, that can affect to the barrier and adherence of the coating. For

the sample containing cerium (IV) oxide, a phenomenon of agglomeration is clearly noticed (around 2 μm) (Fig. 1b). On the other hand, Fig. 1c presents the salt-activated ceria particles with the size of about 50-100 nm. There is no space detected at interface inhibitors/epoxy matrix. This result reveals that the cerium (III) activated CeO_2 has better distribution and compatibility with the epoxy-polyamide matrix than cerium (III) nitrate and cerium (IV) oxide nanoparticles.

3.2. Corrosion behavior of epoxy coatings

Figure 2 shows the impedance diagrams (Nyquist plots) obtained with the blank coating and the coatings containing $\text{Ce}(\text{NO}_3)_3$, CeO_2 nanoparticles and $\text{Ce}^{3+}/\text{CeO}_2$ after 24 h exposure time in the 0.5 M NaCl solution. Only one-time constant is observed for all coatings. Two systems containing nanoparticles (CeO_2 and $\text{Ce}^{3+}/\text{CeO}_2$) present higher resistance values of film ($2.2 \cdot 10^6 \Omega \text{ cm}^2$ and $2.6 \cdot 10^6 \Omega \text{ cm}^2$, respectively) than that of blank epoxy ($1.5 \cdot 10^6 \Omega \text{ cm}^2$), meaning a better barrier protection. For the film incorporated with cerium (III) salt, the capacitive loop is smaller compared to epoxy coating without additives. It can be due to $\text{Ce}(\text{NO}_3)_3$ leaching when the coating was in contact with the aqueous solution.

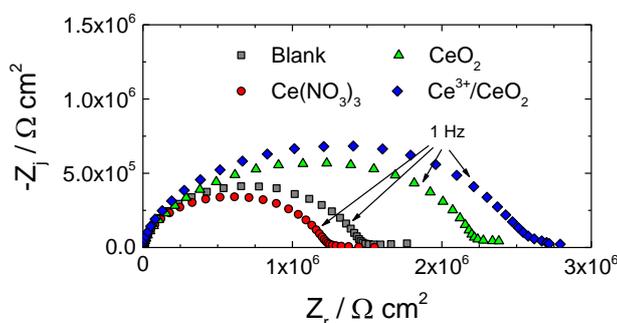


Figure 2. Nyquist representation of the impedance obtained after 24 h immersion in a 0.5 M NaCl solution for the epoxy coatings with or without pigments (as indicated on the figure)..

The modulus value at low frequency ($Z_{10\text{mHz}}$) of the coatings was extracted from impedance data to evaluate the barrier properties of the systems as a function of immersion time in the 0.5 M NaCl solution (Fig. 3). It reports that, after the first exposure day, impedance value obtained at 10 mHz of the coating filled with $\text{Ce}(\text{NO}_3)_3$ increase slightly until the end of the test. This phenomenon can be attributed to the protective film formed by released Ce^{3+} ions at the interface substrate/coating. For the sample containing CeO_2 nanoparticles, the value of $Z_{10\text{mHz}}$ is high at the beginning but it decreases during immersion time and the corrosion appears after 7 days of exposure in the aggressive solution. This trend can be explained by the presence of only nanoparticles that are likely agglomerates and generated large defects in the system (as observed in Fig. 1b). Thus, they promoted electrolyte uptake and corrosion activity. It can be seen that the coatings containing salt-activated CeO_2 nanoparticles had a high value of $Z_{10\text{mHz}}$ along the exposure of time and the outstanding features of both cerium (III) salt and ceria nanoparticles. The film filled with activated nanoparticles shows no agglomeration and a better protection compared to the others.

To obtain more information about the effects of activated nanoparticles in the epoxy matrix, the salt spray test was carried out. Fig. 4 shows the qualitative results of scratched samples after 48 h exposure time. The delamination zones were observed around the artificial scratch of all samples. For the blank epoxy and coatings filled with CeO_2 nanoparticles, the detached area is

larger than that in the films containing cerium (III) salt and activated nanoparticles. It can be attributed to the leaching of the inhibitors incorporated into the two latter coatings that prevents the penetration of aggressive agents from the defect on the surface of the samples. However, due to an uncontrolled release of $\text{Ce}(\text{NO}_3)_3$ during the test, many black points were detected around the edge of the scratch [20]. This phenomenon is not observed in the case of epoxy- $\text{Ce}^{3+}/\text{CeO}_2$ nanoparticles coatings. These results demonstrate that the cerium (III) salt-activated ceria nanoparticles can enhance both passive and active anticorrosion properties of epoxy coatings.

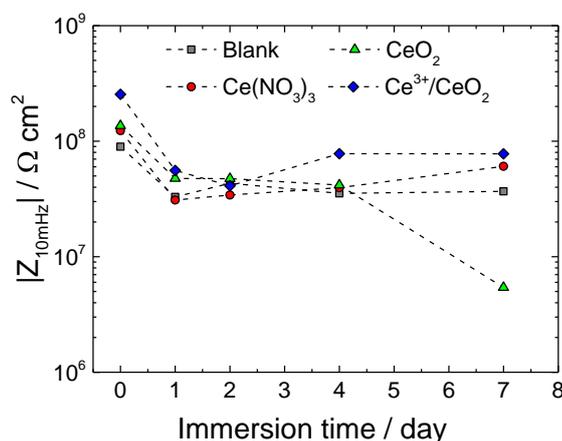


Figure 3. Impedance modulus value measured at low frequency ($f = 10$ mHz) as function of immersion time for different coating systems (indicated on the figure) in a 0.5 M NaCl solution.

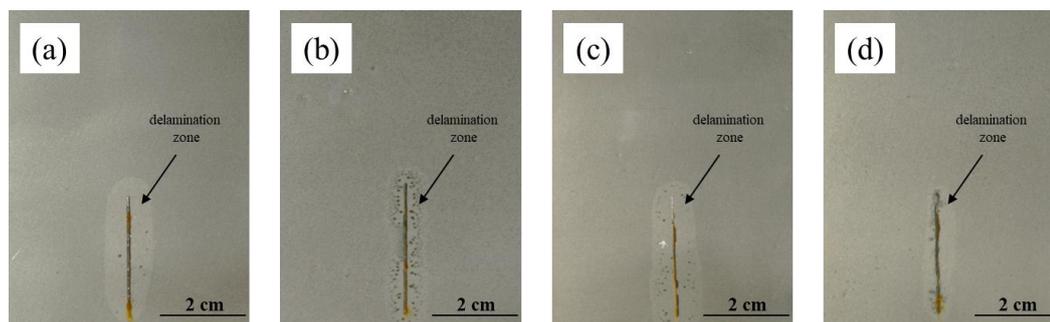


Figure 4. Photographs of epoxy coating without inhibitors (a) and with $\text{Ce}(\text{NO}_3)_3$ (b), CeO_2 (c) and $\text{Ce}^{3+}/\text{CeO}_2$ (d) after 48 h of salt spray exposure.

3.3. Adherence properties

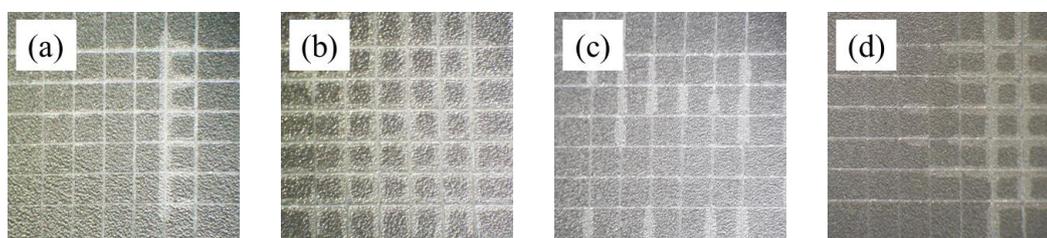


Figure 5. Images of the sample surfaces after the cross-cut test: as-prepared epoxy (a), epoxy- $\text{Ce}(\text{NO}_3)_3$ (b), epoxy- CeO_2 (c) and epoxy- $\text{Ce}^{3+}/\text{CeO}_2$ (d).

The effect of $\text{Ce}^{3+}/\text{CeO}_2$ nanoparticles on the behavior of the substrate/coating was characterized by two adherence test methods. Firstly, the crosscut test was performed to qualitatively evaluate the adherence property of the samples. Figure 5a shows that the crosscut area of blank epoxy coatings presents a little detached area at the edge of scratches. For the film filled with cerium (III) salt, the delamination is detected throughout the crosscut area (Fig. 5b), meaning a poor adherence property. This result can be attributed to the incompatibility of $\text{Ce}(\text{NO}_3)_3$ in the epoxy matrix (crystalline agglomeration and created holes). On the contrary, the coatings filled with nano-ceria and activated nanoparticles have much less detached area on the tested zone. These crosscut test results were confirmed by pull-off method. Table 1 reports a good adherence property for the blank epoxy film (4.23 MPa). When incorporated with the pigments such as nano CeO_2 and nano $\text{Ce}^{3+}/\text{CeO}_2$, the value measured decrease slightly to 4.09 and 4.02 MPa, respectively. The coating containing cerium salt presents the lowest value of pull-off force, meaning less adherence property compared to the other samples.

Table 1. Crosscut classification and pull-off test results for the epoxy coatings with or without inhibitors.

Sample	Crosscut classification	Pull-off force (MPa)
Blank	3B	4.23 ± 0.15
$\text{Ce}(\text{NO}_3)_3$	2B	3.77 ± 0.05
CeO_2	3B	4.09 ± 0.15
$\text{Ce}^{3+}/\text{CeO}_2$	3B	4.02 ± 0.12

4. CONCLUSIONS

In this study, the effect of cerium (III) ions activated CeO_2 nanoparticles on the corrosion protection properties of the epoxy waterborne coating was investigated. The comparison between the pigments (activated nanoparticles, $\text{Ce}(\text{NO}_3)_3$ and CeO_2) was also realized. The activated nanoparticles showed a better dispersion in the epoxy matrix than the other inhibitors. The epoxy coating incorporated with $\text{Ce}^{3+}/\text{CeO}_2$ had the best barrier property compared to the other samples. Due to a controlled inhibitor leaching phenomenon of the inhibitor, there was less detached zone around the scratch after exposure in the aggressive environment for the coating containing ion-activated ceria nanoparticles. With 0.1 wt.%, the adherence property of Epoxy- $\text{Ce}^{3+}/\text{CeO}_2$ coating was slightly decreased compared to the blank coating. It was shown that the presence of $\text{Ce}^{3+}/\text{CeO}_2$ in epoxy coatings exhibited better barrier and corrosion protection properties due to the outstanding features of both cerium (III) ions and CeO_2 nanoparticles.

Acknowledgements. The authors gratefully acknowledge the financial support of Vietnam Academy of Science and Technology.

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