Hybrid organo-ceramic corrosion protection coatings with encapsulated organic corrosion inhibitors

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Abstract

To improve corrosion protection properties of sol–gel derived hybrid coatings; two organic corrosion inhibitors (mercaptobenzothiazole and mercaptobenzimidazole) have been encapsulated within the coating matrix in either the presence or absence of β-cyclodextrin. Corrosion protection performance of the developed coatings on AA 2024-T3 has been examined by potentiodynamic scan method and scanning vibrating electrode technique. Superior corrosion protection properties have been found for formulations that contain β-cyclodextrin and can be explained by the act of slow release of the inhibitor from the cyclodextrin/inhibitor inclusion complexes and by the self-healing of corrosion defects. The effectiveness of the approach for long-term protection of the high strength aluminum alloys against atmospheric corrosion is discussed.

Keywords: Coating; Corrosion; Inhibitor; Cyclodextrin; Sol–gel

1. Introduction

Recently developed nanostructured inorganic/organic hybrid conversion coatings for long-term protection of aluminum alloys against atmospheric corrosion are based on a unique combination of a sol–gel processing of organo-functional silanes and a conventional coating formation process [1]. This hybrid approach has been termed self-assembled nanophase particle (SNAP) coating process and is considered as an environmentally benign alternative to existing chromate-based conversion surface treatments. In this coating process, organo-silicate nano-particles with peripheral epoxy functional groups are pre-formed in an aqueous sol–gel process by hydrolysis and condensation of appropriate organo-silanes and then assembled and crosslinked upon application to the substrate surface. Chemical structure and organic functionality of silanes and crosslinking agents can be varied and optimized to achieve the maximum effect on hydrolytic stability of the metal/coating interface and desirable barrier and adhesion properties of the coating, making the SNAP process a very versatile coating approach.

Although SNAP coatings exhibit excellent adhesion and barrier properties on high strength aluminum alloys, their corrosion protection performance is only maintained if the coating is undamaged. To improve corrosion protection properties of the coating when it is mechanically damaged, the incorporation of potent corrosion inhibitors into the coating is needed. Among various types of corrosion inhibitors, organic corrosion inhibitors appear to be the most suitable for physical entrapment within SNAP coating material by adding the inhibitor in the reaction mixture with subsequent crosslinking and formation of a host network structure. Once trapped within the coating material, the organic corrosion inhibitor becomes active in the corrosive environment, when the entrapped inhibitor can slowly diffuse out of the host material. Despite the simplicity of this doping method, it is difficult to control leaching of the entrapped inhibitors out of the coating film. Solubility of the
organic inhibitor in the coating solution can also be a concern especially for poorly soluble organic reagents.

To alleviate these problems, organic corrosion inhibitors can be incorporated into the coating material as inclusion complexes with cyclodextrin. Schematic representation of this concept is shown in Fig. 1. Cyclodextrins are cyclic oligosaccharides consisting of several glucopyranose units and are often described as truncated cone-shaped structures with a hydrophilic exterior surface and a hydrophobic interior cavity [2,3]. Cyclodextrins are known as effective complexation agents, which have an ability to form inclusion complexes with various organic guest molecules that fit the size of the cyclodextrin cavity. Organic aromatic and heterocyclic compounds are usually predominant candidates for the inclusion complexation reaction [3]. β-Cyclodextrin was selected as a complexation reagent in this work since it is the most studied cyclodextrin compound.

The encapsulation of organic corrosion inhibitors in the form of their inclusion complexes with cyclodextrin has several advantages over the encapsulation of these inhibitors in their free molecular forms. First, the inclusion complexes are more bulky and expected to be more easily trapped within the crosslinked nanoporous coating material making the inhibitor more difficult to leach out and thus prolonging the inhibition effect of the doping agent. Also, it has been shown for many organic compounds with poor solubility that their solubility can be significantly enhanced by inclusion complexation with cyclodextrins [4]. Therefore, we consider the encapsulation of organic corrosion inhibitors into the coating host material as inclusion complexes with cyclodextrin as effective delivery systems of organic inhibitors in active corrosion protection applications. The slow release of organic corrosion inhibitor from the molecular cavity of cyclodextrin ensures the long-term delivery of corrosion inhibitor and thus the healing of a damaged coating.

In this paper, we report results of electrochemical evaluation of the corrosion protection properties of SNAP coatings doped with organic corrosion inhibitors. Two organic corrosion inhibitors, mercaptobenzothiazole (MBT) and mercaptobenzimidazole (MBI), were selected. MBT and MBI were encapsulated within the hybrid organo-ceramic network both as their free molecular forms and as inclusion host/guest complexes with β-cyclodextrin. Corrosion protection performance of sol–gel derived coatings doped with the inclusion complexes of the corrosion inhibitors is discussed with the emphasis on the effectiveness of the coating performance in the long-term protection of aluminum alloys against atmospheric corrosion.

2. Experimental

2.1. Reagents and equipment

Tetramethoxysilane (TMOS) and 3-glycidoxypropyltrimethoxysilane (GPTMS) were purchased from Gelest (Tullytown, PA, USA). 2-Mercaptobenzothiazole (98% pure), β-cyclodextrin hydrate, and diethylenetriamine (DETA) were purchased from Aldrich. 2-Mercaptobenzothiazole (97% pure) was obtained from Avocado Research Chemicals. All chemicals were used as received. Water was purified to Type I using a Millipore Milli-Q water purification system. Coupons of AA 2024-T3 (2 × 3 inches) were cleaned in a standard four bath cleaning process including a degreasing Oakite® Aluminum Cleaner 164 solution and Turco Smut-Go NC-B deoxidizer, as mentioned elsewhere [1].
Potentiodynamic scan (PDS) measurements [5] were performed in dilute Harrison’s solution (0.35 wt.% (NH₄)₂SO₄ and 0.05 wt.% NaCl) using a Gamry PC3/300 potentiostat coupled with Gamry Corrosion Measurement System CMS100. This mixture of electrolytes is considered to closely emulate the atmospheric environment for aircraft [6]. A removable glass cylinder (1 inch ID) was attached to the surface of the panel using a metal clamp and a rubber o-ring. Electrochemical measurements were performed using a one-chamber, three-electrode cell. The working electrode consisted of an exposed area of 0.8 cm² on the surface of the film prepared by masking off part of the panel with Gamry electrochemical sample masks. The reference and auxiliary electrodes were a saturated calomel electrode (SCE) and a platinum mesh electrode, respectively. Potentiodynamic scan was acquired in the region from −100 mV vs. \( E_{oc} \) (open circuit potential) to +500 mV vs. \( E_{oc} \).

Coatings were made by a dip-coating procedure using a Model 201 dip-coater from Chemat Technology, Inc. Film thickness was measured with a Tencor KLA surface profilometer and found to be on the order of 1 µm. Scanning electron microscopy (SEM) was performed with a Leica Cambridge 360 FE microscope using a backscattered or a secondary electron image detector at 15 kV and 100 pA probe current.

Scanning vibrating electrode technique (SVET) measurements were performed with a SVET system of Applicable Electronics Inc. (Forestdale, MA, USA) connected to a Potentiostat/Galvanostat (Model 263A) and a Frequency Response Detector (Model 1025) manufactured by EG & G Princeton Applied Research. Automated scanning electrode technique (ASET) software, manufactured by Applicable Electronics Inc., was used to program the desired scan parameters. An artificial Al–Cu galvanic couple was made on the specimen surface by applying a small drop (1 µl) of 2% CuCl₂. The specimen was rinsed with excess of water, dried and then coated with a SNAP coating. The coupons were masked by electrochemical tape (3M Company) to leave only a small area of the surface (5×5 mm) exposed. The measurements were performed in an electrochemical cell consisting of an acrylic cylinder (1/8-inch height, 2-inches diameter) attached to the sample surface. The measurements were taken at open circuit potential in dilute Harrison’s solution using a platinum microelectrode (Micro Probe Inc, Potomac, MD) as the vibrating probe and a platinum wire as reference electrode. Scans consisted of 400 data points obtained on 20×20 grid of an approximately 4 mm² sample area. At least three specimens of each sample type were prepared and scanned to evaluate the reproducibility of the observed phenomena. For each case, representative scans were selected for presentation.

2.2. Procedures

The SNAP solution was prepared by a hydrolysis and condensation of a mixture of TMOS and GPTMS (1:3 mol ratio) in 0.05 M acetic acid at the conditions of high water/silane ratio, equal to 15. The application solutions were prepared by diluting the SNAP solution (20 ml) aged for 3 days with water by a factor of 1.75 followed by the addition of an organic corrosion inhibitor and optional β-cyclodextrin. The solution was vigorously stirred and sonicated for 1–3 min then a crosslinking agent (diethylenetriamine, DETA, 0.5 ml) and a surfactant solution (0.2 ml, 3M FC-430, 4 wt./v% and FC-171, 1 wt./v%) were added to the final mixture. The molar concentration of a corrosion inhibitor and β-cyclodextrin in the application solution was \( 2.6×10^{-3} \) M. The final mixture was vigorously stirred and applied to the cleaned aluminum alloy panels by dip-coating at a withdrawal speed of 10 cm/min. The coated panels were dried under ambient conditions for 24 h before testing was performed.

Formation constants for inclusion complexes of β-cyclodextrin and organic corrosion inhibitors (MBI and MBT) were determined by a spectrophotometric method based on a concurrent complexation with p-nitrophenol [7]. Spectrophotometric measurements were performed with a Perkin–Elmer Lambda 9 spectrophotometer with 1 cm cuvet at 22 °C and pH 6.8 (0.1 M phosphate buffer).

3. Results and discussion

The choice of organic corrosion inhibitors was performed based on a combination of different parameters

![Fig. 2. Potentiodynamic scans of bare AA 2024 in dilute Harrison’s solution: without additives (○), with 2.6×10^{-3} M MBT (•), and with both 2.6×10^{-3} M MBT and 2.6×10^{-3} M β-cyclodextrin (●). The inset is corrosion current densities and corrosion potentials estimated by Tafel analysis of the scans.](image)
such as inhibitor activity for corrosion protection of the high strength aluminum alloys, capability to form inclusion complexes with \(\beta\)-cyclodextrin and compatibility of the corrosion inhibitor with the coating material.

To the best of our knowledge, none of the selected organic corrosion inhibitors has been reported in complexation reaction with \(\beta\)-cyclodextrin, and no data on their stability constants are available in the literature. The capacity of MBT and MBI to form inclusion complexes with \(\beta\)-cyclodextrin has been assumed based on certain structural similarities with other reported aromatic and heterocyclic organic compounds [3]. The formation constants (log \(K\)) of the inclusion complexes of \(\beta\)-cyclodextrin with MBI and MBT determined by means of a spectrophotometric method were found to be 2.17 \(\pm\) 0.06 and 2.10 \(\pm\) 0.07, respectively. Since SNAP formulations are essentially water-based, similar complexation behavior is expected in SNAP application solution.

To investigate whether the complexation of the inhibitor with \(\beta\)-cyclodextrin could affect its inhibition activity, the PDS measurements have been performed on the samples of AA2024 in dilute Harrison’s solution containing a corrosion inhibitor with and without the addi-

Fig. 3. SEM images of the artificial copper deposits on aluminum substrate (a), copper deposits covered with the SNAP coating (b) and the SNAP film on AA 2024 (c).
Fig. 4. Current density distribution maps at different times of immersion in electrolyte for Al/Cu artificial defects on AA 2024 coated with SNAP without inhibitors.

Fig. 5. Optical microscopy images of SNAP films coated over artificial copper deposits on AA 2024 after immersion in electrolyte: SNAP coating without inhibitor after 3 h of immersion (a), SNAP coating with encapsulated MBI/β-cyclodextrin complexes after 8 days of immersion (b).

tion of β-cyclodextrin. As an example, potentiodynamic scans for mercaptobenzothiazole are shown in Fig. 2. Corrosion parameters, such as corrosion current density ($I_{corr}$) and corrosion potential ($E_{corr}$), are estimated by the Tafel method, [8] and shown as an inset. It is evident from the figure that the addition of β-cyclodextrin does not affect the inhibition activity of MBT, which in both cases (with and without β-cyclodextrin) has demonstrated strong corrosion protection activity with the reduction of corrosion current by a factor of 50 as compared with bare AA2024-T3.

The nanostructured organo-ceramic coatings produced by the SNAP process were developed as an aluminum substrate pretreatment to ensure the formation of a continuous, durable, and protective film on the metal surface (Fig. 3c), which serves simultaneously as a barrier-type corrosion protective coating and a well-adherent conversion boundary layer between a metal surface and a subsequent primer coating. The continuous three-dimensional nanostructured matrix of the coating with film thickness of 1–1.5 μm is able to store an encapsulated organic corrosion inhibitor and release it at the conditions of damage to the coating and exposed metal surface, providing self-healing of the localized corrosion attack.

The ability of the SNAP coating to store and release an organic corrosion inhibitor encapsulated in either its free molecular form or in the form of an inclusion complex with β-cyclodextrin has been examined by scanning vibrating electrode technique (SVET). For these measurements, the coatings were applied over the aluminum substrate with artificially pre-formed galvanic
copper/aluminum defects, as it is shown in Fig. 3 (SEM images a,b). For this purpose, the surface of AA 2024 was treated with CuCl₂ solution in order to obtain an artificial copper deposits much larger than copper-containing intermetallics of the aluminum alloy to induce an accelerated localized galvanic corrosion. As can be seen from the SEM images, these artificial copper deposits are randomly distributed over the substrate surface and evenly covered with SNAP material, and become imbedded within the coating film.

SVET is a relatively new electrochemical technique and has been developed specifically for the examination of localized corrosion [9,10]. The result of SVET measurements is a current density map derived from measurements of potential gradients in the solution, which represents a corrosion current flow associated with anodic and cathodic corrosion activity areas.

The current density distribution maps for SNAP coating without the addition of a corrosion inhibitor are shown in Fig. 4. The data indicate high anodic activity localized within the spot of the deposited copper and associated with a corrosion attack on the aluminum substrate. The pitting corrosion starts almost immediately after immersion of sample in dilute Harrison’s solution and with time leads to a rapid formation of pits shown in the optical microscopy image of the same sample in Fig. 5a.

The incorporation of corrosion inhibitors within the SNAP coating has a pronounced effect on the reduction of a corrosion attack on aluminum substrate as can be
seen from Figs. 6 and 7 that show the current density distribution maps of the SNAP coatings doped with MBI and MBT, respectively. As compared with the undoped SNAP coatings, the MBI-containing coatings demonstrate a significant (on the order of 50 times) decrease in the anodic corrosion current density upon initial immersion. Though the corrosion activity gradually increases with immersion time, it remains at relatively low level after 8 days of immersion in corrosive electrolyte. In the case of MBT-containing coatings, the initial corrosion activity is only 2–3 times less of that of the control SNAP coatings and it stays at almost the same level as immersion progresses, up to 48 h. In contrast to MBI, the MBT-doped coatings develop pits with piled-up brown-colored corrosion product, making further scanning on the sample surface difficult.

The coatings with the organic corrosion inhibitors encapsulated as inclusion complexes with β-cyclodextrin demonstrate significant improvement in corrosion protection properties for both inhibitors studied. As it is shown in Fig. 8, in the case of SNAP coatings with MBI/β-cyclodextrin complexes, no corrosion activity was observed for a long period of time (8 days) of immersion in the corrosive electrolyte. The surface of the sample remains practically unchanged, as it is shown in the optical microscopy image (Fig. 5b). In contrast, the SNAP coatings doped with MBT/β-cyclodextrin complexes after 10–30 min of immersion develop initial moderate corrosion activity (data are not shown), that progresses up to the current density 100–120 µA/cm², remains at this level for a short time (1–3 h), then declines within 24 h of immersion to the negligible level.
of corrosion activity. Once turned down, the corrosion activity stays at the lowest level for up to several weeks of immersion, thus indicating a self-healing effect of the inhibitor complexes.

4. Conclusions

The corrosion protection properties of the hybrid organo-ceramic coatings on aluminum substrate can be significantly improved by means of encapsulation of organic corrosion inhibitors within the coating matrix. We have demonstrated that improved corrosion protection is achieved when mercaptobenzothiazole or mercaptobenzimidazole is included in the coating in the presence or absence of \( \beta \)-cyclodextrin. The formulations that contain \( \beta \)-cyclodextrin demonstrate superior corrosion protection properties that can be explained by the act of slow release of the inhibitor from the cyclodextrin/inhibitor inclusion complexes followed by the self-healing of corrosion defects. Based on the overall positive corrosion reduction behavior of the studied systems, these surface treatments make it a promising corrosion protection approach and expend possible applications of the SNAP coatings.

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References