Self-repairing Coating for Corrosion Protection of Aluminum Alloys: A Proof-of-Concept Using Cagelike Smart Particles

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ABSTRACT

The development of effective anti-corrosion pre-treatments for metallic substrates is an issue of great importance for durability of metal structures and components. In this work, we proposed and demonstrated the concept of self-repairing coating for corrosion protection of aluminum alloys, using cagelike oil core/silica gel shell particles. These micron-scale, cagelike smart microspheres with opened and closed pores were successfully fabricated, and at the same time encapsulated repairing agent (methyl methacrylate) and catalysts (potassium persulfate and sodium thiosulfate) into the microspheres respectively. Such smart particle composites (SPCs) were prepared based on an interfacial self-assembly process and sol-gel reaction. They were then self-assembled on the AA2204 aluminum alloy surface, followed by the application of a sol-gel film. The hybrid film worked as a primer coating featuring the self-repairing property. Both the EIS and SEM/EDS data demonstrated that the encapsulated repairing agent was released as a response to external stimulus (scratches) and polymerized to repair the coating defects.

By comparing the corrosion rate of AA2204 in three coating systems, the self-repairing effect is estimated to be 22% after 2-hr immersion in deoxidized 3% NaCl solution. This preliminary study demonstrated the feasibility of the self-repairing primer coating, which merits further investigation that may lead to a promising environmentally friendly alternative to chromate conversion coatings.

Keywords: Self-repairing coating; Cagelike smart particles; Metallic corrosion; Aluminum alloy
1. INTRODUCTION

Aluminum is an important material for transportation systems. For instance, it is extensively used in traffic structures such as luminaries, signal supports, and sign supports. Aluminum alloys are also widely used for automobile components. Aluminized steel (through thermal spray, hot-dip, etc.) is used for applications requiring corrosion resistance, such as culvert pipes, petroleum pipelines, and supports for telecommunication cables. Research has found that the combined action of sand abrasion and marine corrosion can lead to premature failure of the metallic coatings in the tropical coastal area, where the aluminum-coated steel performed 60 percent better than the zinc-coated steel (1).

The development of effective anti-corrosion pre-treatments for metallic substrates is an issue of great importance for durability of metal structures and components. Conventional chromate conversion coatings (CCC) work well for iron and aluminum alloys in terms of their corrosion protection performance. However, the strong oxidation properties of chromates make them a potential lung carcinogen responsible for the DNA damage (2). Due to the toxicity of hexavalent chromium (Cr\(^{6+}\)), numerous efforts have been spent to develop environmentally benign alternatives to CCC; and the most promising ones identified thus far have been rare-earth corrosion inhibitors (e.g., cerium oxide conversion coatings) and hybrid organic-inorganic materials (e.g., organically modified silicates).

Currently there is an urgent need to establish innovative design of protective coating systems that feature both excellent performance and environmental stewardship. To this end, one promising technology for primer coating is sol–gel derived thin films. Sol–gel films have good adhesion to both metallic substrates and organic top coats. Good adhesion of sol–gel films to metals derives from the formation of strong covalent Si–O–Me bonds. Sol–gel technology offers various ways to prepare functional coatings with chemically tailored properties (3,4). However, inorganic sol–gel derived films may not provide adequate barrier properties to prevent the ingress of corrosive species onto the metal surface, due to pores and cracks present in the film after the drying procedure. Furthermore, they cannot provide any active corrosion protection (5,6) or stop the propagation of corrosion once corrosion is initiated and defects in the coating occur.

Incorporation of nanoparticles in the hybrid sol–gel systems has been proven to enhance the corrosion protection properties, as a result of lower porosity, increased thickness, and reduced cracking potential along with improved mechanical properties. The corrosion resistance of the coating strongly depends on the concentration and size of the nanoparticles. Different strategies for nanoparticle introduction can be used, such as addition of nanopowders into the sol–gel system (7,8) and design of functional nano-structured materials through the use of controlled hybrid organic–inorganic interfaces (9,10,11,12).

A recently method developed for coating fabrication features the formation of functionalized silica nanoparticles \textit{in situ} in an aqueous sol–gel process and subsequent assembling and crosslinking of the nanoparticles to form a thin film. Known as the Self-assembled NAanophase Particle (SNAP) process (9), this new route was demonstrated to be a viable alternative to CCC and provide exceptional corrosion resistance and long-term coating performance. Nonetheless, such SNAP primer coating serves simply as a physical barrier for corrosion resistance, lacking the ability to leach corrosion inhibitors upon the coating defects or to minimize corrosion of the unprotected substrate areas as in the case of chromates.
One way to improve the self-repairing properties of such nanocomposite primer coating is the addition of corrosion inhibitor, which can suppress corrosion initiated at the coating defects (13). However, the inhibitors can also have a negative effect on the properties of the sol–gel film, decreasing its stability and consequently its barrier properties (14). Additionally, the release of inhibitors from coatings is relatively fast and not controllable.

It has been reported that the corrosion protection properties of SNAP coatings on aluminum substrates can be significantly improved by β-cyclodextrin encapsulating of corrosion inhibitors within the coating matrix (15). The slow release of the inhibitor from the cyclodextrin/inhibitor complexes provides an effective long-term self-healing effect that protects the metallic substrates from corrosion.

Inorganic nanoparticles can also be a way to incorporate corrosion inhibitors into coating, preparing inhibitor nanoreservoirs for “self-repairing” films with controlled release properties. The particles (nanoreservoirs) store and slowly release inhibitors when a defect is formed in the sol–gel film. As such, it reduces the negative effect of inhibitors on the stability of the sol–gel matrix.

The design and synthesis of nano-structured materials extend the possibility of engineering “smart” primer coating that can be used to release repairing agents on demand when, for example, the coating is stressed or an electrical, mechanical or chemical control signal is applied to the coating. We reported a novel method to prepare cagelike smart particles (16,17). From previous studies, we have known that the method has several important advantages as follows. Firstly, the diameter of the particles and the pore size can be easily adjusted. Secondly, monodispersed particles can be made (18). Thirdly, the opened and closed state of the pore can be controlled. Finally, this technique is suitable for different organic, inorganic or their hybrid materials to form shell.

In this work, we proposed a novel approach for design of self-repairing anticorrosion primer coating by using the cagelike smart particles. We improved the previous method to fabricate cagelike oil core/silica gel shell particles, or smart particle composites (SPCs). The encapsulation of oil core is designed to be achieved during the formation of the cagelike particles. The cagelike particles were used as reservoirs for encapsulating repairing agent and chemical initiator, which provide self-repairing ability to the protective system after self-assembling into ordered coatings. The self-repairing effect was demonstrated using electrochemical and surface analytical tools, i.e., electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM) coupled with energy dispersive x-ray spectroscopy (EDS).

2. EXPERIMENTAL METHODS

Chemicals and reagents
Commercially available monomers: styrene (St) and methyl methacrylate (MMA) were obtained from Fisher Scientific Inc. and used without further purification. Poly(vinylpolypyrrolidone) (PVP), tetraethyl orthosilicate (TEOS), potassium persulfate, sodium thiosulfate, ethyl alcohol and concentrated sulfuric acid (98%) were also obtained from Fisher Scientific Inc. All the solvents were of analytical grade and were used as received. Deionized water (resistivity > 18.2 MΩ cm⁻¹) prepared by Milli-Q 185 system (Millipore, USA) was used for all experiments.
**Substrate preparation**
The AA2024 aluminum alloy was used as a substrate that was cleaned using the following procedure before being coated by the primer. The alloy surface was etched in the alkaline cleaner TURCOTM 4215 (50g/L) for 35 min at 65 ºC, then rinsed with distilled water followed by immersion in 20% solution of nitric acid for 15 min, rinsed again with distilled water and finally air-dried.

**Preparation of sol-gel solution**
TEOS was firstly dissolved in ethanol, and then distilled water and nitric acid were added to promote hydrolyzing of the TEOS. The molar composition of this mixture TEOS:H₂O:HNO₃:EtOH was 1:4:0.01:3. The mixture was vigorously stirred for 30 min at 50 ºC. Then the TEOS molecules became water-soluble and a transparent sol-gel solution was obtained.

**Preparation of cagelike smart particle composites**
The overall preparation procedure of the cagelike SPCs is illustrated in Figure 1.

![Diagram](image)

Figure 1: Schematic illustration of the preparation procedure of cagelike silica gel microspheres

The first step was to self-assemble surface-sulfonated polystyrene particles at water-oil (consisting of TEOS and MMA monomers) droplet interface. The surface-sulfonated polystyrene particles of 0.7±0.5 µm in diameter were prepared as reported previously (17). 0.05 g of the sulfonated polystyrene particles were dispersed into 15 ml deionized water using a high-intensity ultrasonic vibracell processor operated at 20kHz and up to 10 W for 2 minutes to form a homogeneous system. Then 1 g of oil phase (MMA/TEOS=17/3, mol/mol) was introduced and stirred continuously using a magnetic stirrer operated at 500 rpm. The turbid mixture gradually evolved into a creamy-white emulsion in appearance after 20 minutes. Then the sample was set
aside for 24 hours. During the reserving period, TEOS tended to diffuse into the interface of oil phase and water, leading to hydrolysis and condensation reactions of alkoxysilane precursors that were catalyzed by surface sulfogroup of the sulfonated polystyrene particles. After 24 hours, smart particles with silica gel shell were formed and at the same time the disengagement of adsorbed polystyrene particles left behind a porous shell.

The smart particles with a closed state of surface pores were prepared by using PS particles sulfonated for 60 hours followed by the encapsulation of MMA oil core. They were used as reservoirs for repairing agent.

The smart particles with an opened state of surface pores were prepared by using PS particles sulfonated for 9 hours. They were then dipped in a mixture solution of potassium persulfate and sodium thiosulfate (1/1.5, mol/mol) for 10 hours and then dried at room temperature for 10 hours. They were used as reservoirs for chemical initiator (catalyst).

Both types of cage-like particles were separated by using micro-infiltration film with a pore size of 1.5 μm. The product was collected by washing the film surface and through repeated centrifugation, then vacuum-dried at room temperature for 10 hours.

Preparation of anticorrosion primer coating on aluminum alloy

The anticorrosion primer coatings were produced by firstly dip-coating the cleaned AA2024 aluminum alloy substrates in 10 wt.% cage-like microspheres aqueous solution (with the ratio of repairing agent microspheres to catalyst microspheres at 30:1 by weight). The time of deposition in the solution was 3 minutes followed by controlled withdrawal with a speed of 18 cm/min. Then all samples were dried at room temperature for 10 hours. The sol–gel solution was subsequently applied on the top of the microspheres layer at a dipping speed of 18 cm/min and exposure time of 1 minute. Then samples were dried at room temperature for another 10 hours. For observing the morphology of microspheres layer, the samples used for SEM analysis had an exposition time of 1 second in the sol-gel solution. Several samples were scratched with a sharp knife-edge crosswise on the metal surface (the width of scratches: 20–50 μm) immediately before measurement. The scratched samples were immersed in a deoxidized 0.5 M NaCl solution at 45 ºC for 2 hours.

Characterization of anticorrosion primer coating on aluminum alloy

The localized surface morphology and chemistry of the primer coatings were assessed by means of SEM coupled with EDS, which were implemented on a Hitachi S-4100 system with beam energy of 25.0 keV.

A three-electrode cell was used for electrochemical testing of coated AA2024 samples, consisting of a saturated calomel electrode (SCE) as the reference electrode, a platinum mesh as the counter electrode, and the coated AA2024 substrate with an exposed surface area of 1 cm² as the working electrode. A Gamry Electrochemical Multiplexer ECM8 was used to monitor the open circuit potential (OCP) of coated AA2024 samples and to measure the EIS data. Two or more samples for each case were tested in order to ensure the reproducibility of test results. The EIS technique was used to estimate the evolution of the corrosion protection performance of the prepared coatings during immersion of the coated AA2024 samples in 0.5 M NaCl solution. At room temperature, EIS measurements were taken periodically by polarizing the coated AA2024 sample at ± 10 mV around its OCP and with sinusoidal perturbations having a frequency between 300 KHz and 5 mHz (10 points per decade). The Gamry analysis software was used to plot and fit the EIS data.
3. RESULTS AND DISCUSSION

3.1. Morphology of the cagelike smart microspheres
The SEM images of the obtained cagelike smart microspheres are shown in Figure 2. It can be seen that both cagelike microspheres with opened and closed pores were successfully obtained. The opened and closed state of the pores was adjusted by using PS particles subjected to different duration of sulfonation. The decrease in sulfonation time decreased the polarity of the microspheres surface, which in turn increased the contact area of the latex particles at the surface of oil droplet. As such, when the latex particles disengaged themselves from the silica gel shell, they left behind more opened pores.

![Figure 2: SEM images of cagelike silicon microspheres with closed (a) and opened (b) pores](image)

![Figure 3: Schematic illustration of the self-assembling of SPCs and self-repairing of primer coating on aluminum alloy](image)
3.2. Performance of Primer Coatings: Self-Repairing and Corrosion Protection

The cagelike microspheres can self-assemble into ordered film on the substrate surface by capillary forces. The degree of orderliness of these microspheres self-assembled on the surface of AA2024 alloy depends on both the size monodispersion of microspheres and the initial condition of the alloy surface. The concepts of self-assembling of SPCs and self-repairing of primer coating on aluminum alloy are illustrated in Figure 3. Firstly, repairing agent particles and catalyst particles self-assemble in matrix before the sol–gel solution is applied on the top of the microspheres layer and form the primer coating. When a scratch occurs, it is expected to rupture the particles and thus release both the repairing agent and the catalyst. The repairing agent fills into the scratch plane through capillary action. When the repairing agent is in contact with the catalyst through the cracked particles or the surface pores of catalyst particles, its polymerization is triggered and the polymerized repairing agent bonds the scratch faces together.

![Figure 4: SEM images of the scratched coating samples before (a) and after (b) immersion in deoxidized 3% NaCl solution at 45 ºC for 2 hours](image)

SEM and EDS provide information on surfaces and thus shed light on the localized morphology and chemistry of scratched coating samples before and after immersion in deoxidized salt brine for some time.

As shown in Figure 4, the SEM images demonstrated that two types of particles self-assembled into some ordered layer through which the scratch run through. Figure 4a shows that some cracked particles existed in the scratch and the surface of the scratch was coarse. In contrast, Figure 4b shows that several glossy agglomerations formed in the scratch (as indicated by the arrowhead) and the surface of the scratch became smoother, subsequent to the immersion in deoxidized 3% NaCl solution at 45 ºC for 2 hours, indicating the release of repairing agent by the externally applied mechanical force and possibly a subsequent polymerization of the repairing agent for self-repairing of the primer coating.

To prove these, EDS data were obtained to analyze the elemental composition of the agglomeration in scratch and of the coating surface, respectively (as shown in Table 1). Table 1 shows that the coating surface mainly consisted of Si, C and O, which was consistent with the chemical composition of the silica gel shell. There was little signal of Al in the coating surface, indicating good coverage of the substrate. The signal of S in the coating surface might be derived
from the presence of the chemical initiators, potassium persulfate and sodium thiosulfate. The agglomeration in scratch mainly consisted of C and O and had much less Si. In addition, the relative elemental content of C to O for the agglomeration in scratch was similar to that of PMMA, suggesting that the agglomeration was mainly PMMA with some cracked particles.

Table 1: EDS data of the coating surface and of the agglomeration in scratch, compared with the calculated composition of PMMA

<table>
<thead>
<tr>
<th>Element content (wt.%)</th>
<th>C</th>
<th>O</th>
<th>Na</th>
<th>Al</th>
<th>Si</th>
<th>S</th>
<th>K</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating surface</td>
<td>21.57</td>
<td>14.97</td>
<td>8.39</td>
<td>1.05</td>
<td>31.67</td>
<td>14.52</td>
<td>3.21</td>
<td>4.61</td>
</tr>
<tr>
<td>Agglomeration in scratch</td>
<td>55.09</td>
<td>20.61</td>
<td>6.90</td>
<td>0.40</td>
<td>9.36</td>
<td>5.32</td>
<td>1.01</td>
<td>1.31</td>
</tr>
<tr>
<td>PMMA</td>
<td>67.61</td>
<td>22.54</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

It is also noted that in Figure 4b the released repairing agent did not fill in the entire scratch and close the space between the faces. That can be attributed to the fact that the scratch was more than 20µm wide, whereas the repairing agent particles were less than 2 µm in diameter (as shown in Figure 2a). The current design seems to be a system to self-repair micron-level defects in the primer coating, but not the larger defects. In our laboratory, experiments are under way to address this issue, by adjusting the size of the SPCs and the strength of the silica gel shell.

Furthermore, the current design used potassium persulfate and sodium thiosulfate as the catalysts to initiate the polymerization of MMA. This served the purpose of demonstrating the feasibility of the self-repairing coating concept. For practical application, however, we plan to encapsulate repairing agents other than MMA (most likely siloxanes) to obtain better corrosion resistance of the polymerized repairing agent layer; and to encapsulate catalysts that do not entail an oxygen-free environment to polymerize.

EIS provides information on interfaces and thus sheds light on the properties of the primer coating layer on the surface of AA2024. The complex impedance of the coated alloy depends on the frequency of the externally applied AC polarization signal, allowing the representation of the system using an equivalent circuit with typically resistors and capacitors to characterize different interfaces. As such, EIS was also used to evaluate the level of corrosion protection offered by various primer coatings on AA2024.

Figure 5 depicts the EIS data in the form of Bode plots, for the primitive coating (A), for the scratched coating (B), and for the scratched coating after immersion in deoxidized 3% NaCl solution at 45 ºC for 2 hours (C). Two well-defined time constants can be observed for all three systems. The time constant at high frequencies (~10^5 Hz) can be ascribed to the capacitance of the coating layer, \( C_{coat} \). The time constant around 10^1 Hz can be associated with the presence of an intermediate layer (\( C_{oxide} \)), which is due to interaction of Al-OH groups with Si-OH forming Al-O-Si covalent bonds as described elsewhere (19). A plateau on the impedance curve between the two time constants reveals a resistive response (\( R_{coat} \)), as a function of the pore structure of the coating layer. At lower frequencies, another resistive response (\( R_{oxide} \)) was detected, as a function of cracks potentially formed in the intermediate oxide layer.

In the low frequency range, the impedance values for coating A were more than one order of magnitude higher than the impedance values measured for coating B, evidencing the corrosion protection properties of the primitive coating. The coating C had impedance values between coating A and coating B, signifying the self-repairing property of the coating.
Figure 5: Bode plots obtained for the primitive coating (A), for the scratched coating (B), and for the scratched coating after immersion in deoxidized 3% NaCl solution at 45 ºC for 2 hours (C).

Table 2: Parameters of the coating/substrate systems obtained by fitting the experimental EIS data with three different equivalent circuits

<table>
<thead>
<tr>
<th></th>
<th>Coating A</th>
<th>Coating B</th>
<th>Coating C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{\text{solut}}$ (Ω cm$^2$)</td>
<td>9.27±0.39</td>
<td>8.07±0.41</td>
<td>6.85±0.16</td>
</tr>
<tr>
<td>$R_{\text{coat}}$ (Ω cm$^2$)</td>
<td>2387±20</td>
<td>9.15±2.93</td>
<td>155.3±3.1</td>
</tr>
<tr>
<td>$Q_{\text{coat}}$ (μS cm$^{-2}$)</td>
<td>22.6±0.6</td>
<td>183.8±27.6</td>
<td>37.6±2.3</td>
</tr>
<tr>
<td>$n_{\text{coat}}$</td>
<td>0.80±0.01</td>
<td>0.78±0.03</td>
<td>0.87±0.01</td>
</tr>
<tr>
<td>$R_{\text{oxide}}$ (Ω cm$^2$)</td>
<td>437.8±64.3</td>
<td>43.1±3.1</td>
<td>83.0±10.8</td>
</tr>
<tr>
<td>$Q_{\text{oxide}}$ (μS cm$^{-2}$)</td>
<td>11.9±0.9</td>
<td>204.5±31.3</td>
<td>155.7±25.2</td>
</tr>
<tr>
<td>$n_{\text{oxide}}$</td>
<td>0.86±0.01</td>
<td>0.75±0.03</td>
<td>0.90±0.04</td>
</tr>
<tr>
<td>$R_{\text{polar}}$ (Ω cm$^2$)</td>
<td>260.2±37.1</td>
<td>2.27±0.51</td>
<td>10.2±1.7</td>
</tr>
<tr>
<td>$Q_{\text{dl}}$ (mS cm$^{-2}$)</td>
<td>11.4±0.29</td>
<td>55.9±9.9</td>
<td>36.6±4.4</td>
</tr>
<tr>
<td>$n_{\text{dl}}$</td>
<td>0.20±0.02</td>
<td>0.33±0.09</td>
<td>0.39±0.04</td>
</tr>
<tr>
<td>$W$ (mS cm$^{-2}$)</td>
<td>12.9±1.4</td>
<td>124.0±26.8</td>
<td>435.4±244.1</td>
</tr>
</tbody>
</table>

Impedance spectra in Figure 5 were fitted using three different equivalent circuits for coatings A, B and C, respectively, which were suggested in literature (20). The equivalent circuits were chosen on the basis of the number of time constants and the goodness of fits. Constant phase elements (Q) instead of capacitances were used in all fittings. Such modification is obligatory when the phase angle of capacitor is different from −90º. Table 2 presents
parameters of the coatings A, B and C. The used equivalent circuits provided the adequate fitting of the experimental results and the good estimation of parameters.

Two parameters that characterize the electrolyte/coating interface are the ionic resistance of the coating layer ($R_{\text{coat}}$) and the constant phase element (vs. capacitance) of the coating layer ($Q_{\text{coat}}$). $R_{\text{coat}}$ characterizes the porosity of the hybrid film and is a function of the resistance of electrolyte in interconnected pores, cracks and potentially air voids. As shown in Table 2, compared with coating A, $R_{\text{coat}}$ of coating B was significantly decreased as a result of the scratches on the hybrid film. Compared with coating B, coating C showed obvious increase in $R_{\text{coat}}$ after 2-hr immersion in deoxidized 3% NaCl solution, signifying the reduced number of interconnected pores, cracks and air voids in coating and the self-repairing property of the coating. Generally the capacitance of the dielectric film ($C_{\text{coat}}$), in this case $Q_{\text{coat}}$, is a function of the film thickness and the amount of absorbed water. As shown in Table 2, compared with coating A, $Q_{\text{coat}}$ of coating B exhibited obvious increase likely due to water absorption into the coating through the scratches and reduced film thickness. Coating C had $Q_{\text{coat}}$ values between coating A and coating B, signifying the self-repairing property of the coating.

The compactness and thickness of the intermediate oxide layer formed between the coating layer and the metallic substrate are also very important from the viewpoint of corrosion protection, since breakdown of this film would allow direct ingress of the corrosive species onto the AA2204 substrate. The properties of the oxide layer can be characterized by $R_{\text{oxide}}$ and $Q_{\text{oxide}}$. $R_{\text{oxide}}$ and $Q_{\text{oxide}}$ values for coatings A, B, and C followed similar pattern to those of $R_{\text{coat}}$ and $Q_{\text{coat}}$, suggesting that the intermediate oxide layer was repaired to some extent during the immersion process, possibly due to self-assembling of SPCs.

Two parameters that characterize the metal/electrolyte interface are the charge transfer resistance of AA2204 (mainly polarization resistance, $R_{\text{polar}}$) and the constant phase element (vs. capacitance) of the double layer on AA2204 ($Q_{\text{dl}}$). Interestingly, coating C had $R_{\text{polar}}$ and $Q_{\text{dl}}$ values between coating A and coating B, consistent with the trends observed for the other four parameters discussed above. Based upon the well-known relationship of polarization resistance with corrosion rate, the corrosion current density ($i_{\text{corr}}$) of AA2204 can be calculated as $B/R_{\text{polar}}$, with the Stern-Geary Coefficient ($B$) of 49.90 mV. By comparing the corrosion rate of AA2204 in the three systems, the self-repairing effect is estimated to be 22% after 2-hr immersion in deoxidized 3% NaCl solution (assuming that PMMA is as effective as the sol-gel coating for corrosion protection of AA2204). The self-repairing effect is expected to be enhanced if the scratches were not as wide as 20–50µm (which is the thickness of a typical blade), or if we used repairing agent particles larger than 2 µm in diameter, or if we used different types of repairing agent and catalysts to be encapsulated in the SPCs. At this stage of the research, it is unknown how long the self-repairing effect of the coating will last under the field conditions exposed by a typical transportation facility.

4. CONCLUSIONS

The development of effective anti-corrosion pre-treatments for metallic substrates is an issue of great importance for durability of metal structures and components. In this work, we proposed and demonstrated the concept of self-repairing coating for corrosion protection of aluminum alloys, using cagelike oil core/silica gel shell particles. These micron-scale, cagelike smart microspheres with opened and closed pores were successfully fabricated, and at the same time encapsulated repairing agent (MMA) and catalysts (potassium persulfate and sodium thiosulfate)
into the microspheres respectively. Such smart particle composites (SPCs) were prepared based on an interfacial self-assembly process and sol-gel reaction. They were then self-assembled on the AA2204 aluminum alloy surface, followed by the application of a sol-gel film. The hybrid film worked as a primer coating featuring the self-repairing property. Both the EIS and SEM/EDS data demonstrated that the encapsulated repairing agent was released as a response to external stimulus (scratches) and polymerized to repair the coating defects.

By comparing the corrosion rate of AA2204 in three coating systems, the self-repairing effect is estimated to be 22% after 2-hr immersion in deoxidized 3% NaCl solution. The self-repairing effect is expected to be enhanced if the scratches were not as wide as 20–50μm, or if we used repairing agent particles larger than 2 μm in diameter, or if we used different types of repairing agent and catalysts to be encapsulated in the SPCs. This preliminary study demonstrated the feasibility of the self-repairing primer coating, which merits further investigation that may lead to a promising environmentally friendly alternative to chromate conversion coatings.

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