Corrosion Science 53 (2011) 829-833

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Self-healing coatings of inorganic particles using a pH-sensitive organic agent

Akihiro Yabuki*, Mariko Sakai

Faculty of Engineering, Hiroshima University, 1-4-1, Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan

ARTICLE INFO

Article history: Received 13 August 2010 Accepted 17 November 2010 Available online 23 November 2010

Keywords: A. Magnesium A. Organic coating B. EIS B. SEM

1. Introduction

Corrosion-protective coatings are needed to improve the resistance of magnesium and its alloys, since these materials have limited application in corrosive environments because of their poor corrosion resistance [1-4]. Recent reports cite various surface treatment techniques for their enhancement of corrosion resistance for magnesium and its alloys: chemical conversion coatings [5-8], anodizing [9-11], electrodeposition [12], polymer coatings [13], sol-gel coatings [14], cold sprayed coatings [15], plasma-splayed coatings [16], and micro-arc oxidation [17,18]. With excellent anti-corrosion properties, chromate conversion coatings are used as a surface treatment for magnesium and its alloys. An important requirement of these types of coatings is the ability to self-heal, so that if the coating suffers mechanical damage, and degradation of the bare metal surface by corrosive species in the environment begins, the damaged surface is automatically repaired by a chemical component within the coating. It is well understood that the repairing effect of the film in chromate conversion coatings is due to the hexavalent chromium ion, which has high reactivity. Environmental concerns, however, have necessitated the reduction and discontinuation of this process in recent years.

The addition of cerium, molybdic acid, phosphoric acid and colloidal silica to coating solutions reportedly was effective as an alternative technology for chromate conversion coatings [19–26]. Several new approaches based on the encapsulation of inhibiting compounds prior to their addition to corrosion-protection systems have been suggested [27]. A porous oxide interlayer doped with an organic corrosion inhibitor increased the active corrosion-protec-

* Corresponding author. Tel./fax: +81 82 424 7852. E-mail address: ayabuki@hiroshima-u.ac.jp (A. Yabuki).

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ABSTRACT

A self-healing corrosion protective coating was developed using TiO_2 particles and casein as pH-sensitive organic agents that is also environmentally friendly materials. A film structured of TiO_2 particles was formed on a substrate (magnesium alloy) by dip-coating followed by immersion in a casein solution. Casein was inserted and fixed in the particle film by changing the pH of the casein solution. The polarization resistance of the scratched specimen prepared by changing the pH of the solution from 12 to 5 increased with testing time, and a deposited film consisting of TiO_2 particles and casein was observed after the test.

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tion ability of thin hybrid sol-gel films on an aluminum alloy substrate [28,29]. Inhibitor-containing oxide particles were also used as nanocarriers of a corrosion inhibitor [30]. Nanocontainers that regulated the storage and release of a corrosion inhibitor were constructed with nanometer-scale precision by use of the layer-by-layer (LbL) method [31]. The development of such self-healing anti-corrosion coatings based on LbL-assembled nanocontainers was demonstrated [32-34]. A novel, layered double-hydroxide (LDH)-based nanocontainer of a corrosion inhibitor allowed the controlled release of vanadate ions from the nanocrystalline LDHs [35]. Self-healing polymer coating systems based on an electrospun coaxial healing agent were demonstrated for polysiloxane-based healing agents and an acrylate matrix [36]. The release of organic inhibitors from a hybrid sol-gel matrix can be described as a pH-dependent triggered release mechanism [33,37]. The key to the development of self-healing coatings is the ability to control both the storage and release of the inhibitors added to a coating.

Natural organic materials, such as starch, casein, cellulose, tannin, lignin, etc., are potential environmentally friendly inhibitors of corrosion. Electrodeposition of a casein coating for zinc reportedly prevents corrosion [38]. Casein is agglomerated and dispersed, depending on the solution pH [39]. The properties of casein are suitable as a pH-sensitive agent for the application of corrosionprotective coatings.

In the present study, a self-healing corrosion-protective coating for magnesium alloy AZ31 was developed using an environmentally friendly material. The coating used TiO_2 particles and casein as a pH-sensitive organic agent. A film structured from TiO_2 particles was formed on a magnesium alloy plate by dip-coating, which was followed by immersion in a casein solution to insert the casein into the particle film. Changes in the polarization resistance of the coatings, scratched by a knife-edge, were monitored, and the





surface appearance of the specimen was observed after the corrosion test to elucidate the self-healing property of the coatings. The surface appearance of the scratched specimen was observed using FE-SEM.

2. Experimental

2.1. Materials

A $12 \times 12 \times 1$ mm magnesium alloy AZ31 (96.3 wt.% Mg-2.8 wt.% Al-0.81 wt.% Zn) substrate was used for the test. The substrate was cut from a plate material (Timminco Metals, A Division of Timminco Limited). The plate was abraded with emery paper #2000, followed by a thorough rinse in water, and air drying. TiO₂ particles of a rutile structure with a mean diameter of 270 nm (Tayca Co.) were dispersed in deionized water to prepare a 1 wt.% TiO₂ particle solution. Casein from milk (α -casein) (05-1900-5, Sigma–Aldrich Co.) was also dispersed in deionized water to prepare a 1 wt.% casein solution. Either acetic acid (liquid \ge 99%) or sodium hydroxide (granular or saturated solution) was then added to adjust the pH of the casein solution. A polished substrate was dip-coated in the TiO₂ particle solution using a micro dip coater (MD-0408-S1, SDI Co.) with a withdrawal speed of 10 mm s^{-1} . The TiO₂-coated specimen was calcined at 120 °C for 30 min in air. The specimen was immersed in a casein solution, pH 12, at 35 °C for 4 h, then the pH of the solution was changed to 7, 5 or 4.

2.2. Evaluation of the self-healing properties of coatings

An artificial defect was created on the coated specimen using a knife-edge on a scratch tester (IMC-1552, Imoto Machinery Co., Ltd.). The load for the scratch was 10 g to expose the substrate. The scratched specimen was connected with a conductive wire on one side and mounted in a sample holder of polyvinylchloride with an exposure area 6 mm in diameter, then immersed in a 0.5 mM NaCl corrosive solution. The solution was air-saturated using an air pump, and maintained at 35 °C. The impedance of the specimen in the corrosive solution was measured at intervals of 4 h for 48 h using a platinum counter and Ag/AgCl reference electrodes connected to a potensiostat (HABF-5001, Hokuto Denko Co.), a frequency response analyzer (5010A, NF Co.), and a personal computer. Sine wave voltages (10 mV rms) at frequencies from 20 kHz through 10 mHz were superimposed on a given electrode potential. A computer software program was used to control the measurements through a General Purpose Interface Bus (GPIB) interface. The difference in impedance measured at low and high frequencies was used to measure the polarization resistance, since the phase shift was almost zero at low and high frequency ranges. A bare aluminum alloy substrate was also scratched and the resistance was measured for comparison. The surface appearance of the specimens was observed after the corrosion test, using a field emission-scanning electron microscope (FE-SEM, JSM-6340F) at an accelerated voltage of 20 kV, to confirm the self-healing properties of the coatings. The scratched area of the specimen was analyzed after the corrosion test using an Energy Dispersive X-ray Fluorescence Spectrometer.

3. Results and discussion

3.1. pH-sensitive properties of the coatings and the coating materials

The condition of a casein solution at various pH values is shown in Fig. 1. Casein was precipitated in a beaker at a pH lower than 4.6. When the pH of the solution increased to 5, the casein solution whitened in the entire beaker. As the solution pH increased further, the solution was transparent, although it was slightly cloudy. This indicated that the casein was dispersed in the high pH solution, and the casein particles became smaller [40]. In order to insert and fix casein in the coatings, the pH of the solution was controlled. The casein solution was maintained at a high pH to insert the casein in the coatings, and then the pH of the solution was decreased to fix the casein.

TiO₂ particle coatings were applied on the substrate as a container to fix the casein. Since the gap between TiO₂ particles with a mean diameter of 270 nm was on the order of 100 nm, casein particles of the same size could be inserted in the TiO₂ particle coatings. Fig. 2 shows the surface appearance of TiO₂ particle-casein coatings prepared under various conditions: (a) TiO₂ particle coating, (b), (c and d) TiO₂ particle-casein coatings, which were prepared by changing the pH of the casein solution from 12 to 7, 5 and 4, respectively. The TiO₂ particle coating was densely applied by dip coating, and a gap between particles was observed (Fig. 2a). Casein film was observed on the TiO₂ particle-casein coatings. The casein film formed on coatings prepared by changing the pH from 12 to 4 was deposited over a wide area (Fig. 2d). The casein film formed on the coatings by changing the pH from 12 to 7 and 5 (Fig. 2b and c) was inserted in the gaps between particles, although the size was small $-3-4 \mu m$ in mean diameter. The thickness of the coating was approximately $2 \mu m$, as measured by observation of cross-sections of the coatings. Thus, the casein could be coated on the TiO₂ particle coating by controlling the pH of the casein solution.

3.2. Self-healing properties of the coatings

The typical electrochemical impedance spectroscopy of scratched specimens of substrates coated with TiO_2 particles and casein prepared by changing the pH from 12 to 5 after 4 and 8 h immersions are shown as Cole–Cole plots in Fig. 3. The plots for the scratched specimens were nearly semi-circular, although the plot of the composite coating was not semi-circular at low frequencies. For the scratched TiO_2 particle casein-coated specimens, the difference in impedance at high and low frequency, i.e., the diameter of the depressed semicircle corresponded to the polarization resistance of the coating. Each of the scratched specimens coated with TiO_2 particles and casein showed a similar plot. The polarization resistance ratio normalized to the polarization resistance at 5 min was calculated from measured resistances.

The polarization resistance ratios of the scratched specimens coated with TiO_2 particles and casein, or with TiO_2 particles alone, are shown in Fig. 4. The resistance ratio of the scratched specimen coated with TiO_2 particles alone increased slightly, but it was almost the same as the initial resistance following the 8 h immersion (Fig. 4a). The resistance ratio of the TiO_2 particle-casein coating prepared by changing the pH from 12 to 7 increased soon after immersion, and was almost 1.5 after 8 h immersion, after which it was constant (Fig. 4b). The resistance of the scratched specimen prepared by changing the pH from 12 to 5 increased within the 4 h



Fig. 1. Condition of casein solution at various pH levels.



Fig. 2. Surface appearance of TiO₂-casein coatings prepared under various conditions; (a) TiO₂ particle coating; (b–d) TiO₂ particle-casein coatings prepared by changing the pH from 12 to 7, 5, and 4, respectively.



Fig. 3. Cole–Cole plots of scratched specimens coated with $\rm TiO_2$ particles and casein prepared by changing the pH from 12 to 5 after 4 and 8 h immersion.

immersion, resulting in more than twice the initial resistance (Fig. 4c). On the other hand, the resistance ratio of the scratched specimen prepared by changing the pH from 12 to 4 decreased soon after immersion in corrosive solution, and the ratio was approximately 0.5 after 28 h immersion (Fig. 4d). As a result of polarization resistance, casein that was coated onto the TiO_2 particle coating, prepared by changing the pH from 12 to 7 and 5, increased the resistance, which was a self-healing effect. However, the scratched specimen prepared by changing the pH from 12 to 4 in the casein solution showed no increase in the resistance ratio, although the casein film was observed over a wide area, as indicated in Fig. 2. This assumes that the casein in the coating prepared



Fig. 4. Polarization resistance ratio of scratched specimens coated with TiO_2 particle and TiO_2 particle-casein coatings prepared under various conditions; (a) TiO_2 particle coating; (b), (c) and (d) TiO_2 particle-casein coatings prepared by changing the pH from 12 to 7, 5, and 4, respectively.

by changing the pH from 12 to 4 was only on the surface, and that it was not inserted into the coating. The resistance ratio of the coating prepared by changing the pH from 12 to 4 was lower than that of the coating with TiO_2 particles alone. This might be caused by the activated surface of the substrate after immersion in the solution at pH 4, as the scratched part retained the effect, although the surface was plastically deformed by the knife edge.

The SEM images and EDX analyses of a cross-section of specimens coated with TiO_2 particle-casein prepared by changing the pH from 12 to 5 and 4 are shown in Fig. 5a and b, respectively. EDX analysis of carbon and magnesium was carried out at the cen-



Fig. 5. SEM images and EDX analysis of cross-sections of specimens coated with TiO₂ particle-casein by changing the pH from 12 to 5 (a), and from 12 to 4 (b). The center line is the scan line for EDX analysis.



Fig. 6. SEM images of the scratched area of specimens coated with TiO₂ particle-casein by changing the pH from 12 to 5 before the corrosion test (a), after 4 h immersion (b), and after 48 h immersion (c).

ter line of the figure. Carbon, which corresponded to casein, was recognized inside the TiO_2 particle-casein coating prepared by changing the pH from 12 to 5, and was especially concentrated at the interface between the coating and substrate (Fig. 5a). Magnesium was also detected at the interface. This indicates the dissolution of the magnesium substrate. On the other hand, no carbon was detected at the interface between the coating and the substrate of TiO_2 particle-casein coating prepared by changing the pH from 12 to 4, although it was observed on the surface of the coating (Fig. 5b).

The scratched portions of specimens coated with TiO_2 particlecasein – when the pH was changed from 12 to 5 – were observed. SEM images of the scratched area of the coating before the corrosion test, after 4 h immersion, and after 48 h immersion are shown in Fig. 6a, b and c, respectively. A deposited film was observed in the scratched area of the specimens, and consisted not only of casein, but also of TiO_2 particles. The film was enhanced as immersion time increased. As Fig. 6b shows, the TiO_2 particles seemed to move alone to the scratched area. However, a transparent film (thought to be casein) was observed at the edge of the scratched area shown in Fig. 6c. The TiO_2 particles may have been taken along by the casein, since they were difficult to move because of their size. Thus, it is noteworthy that the TiO_2 particles moved to form a deposited film at the scratched area. It appears that TiO_2 particles have two roles: as a component of the healing film and as a reservoir for casein as the healing agent. On the other hand, casein also has two roles, since it serves as a component of the healing film and as a courier of TiO_2 particles as healing components. These materials thus play complementary roles, so the TiO_2 particle-casein coating has self-healing properties, as indicated in the increased polarization resistance (Fig. 4).

A schematic representation of the self-healing effect of the TiO_2 particle-case coating is shown in Fig. 7. The self-healing effect is apparently due to the formation of a composite film that contains TiO_2 particles and case A a result of the defect in the coating, the bare magnesium alloy substrate was exposed to the corrosive solution, and then anodic dissolution occurred. The anodic process led to the generation of metal cations:

$$Mg \to Mg^{2+} + 2e^{-}. \tag{1}$$



Fig. 7. Self-healing mechanism of TiO₂ particle-casein coating.

Negatively charged OH⁻ ions were generated near the adherence between the coating and the substrate due to the following cathodic reaction:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-.$$
 (2)

Generated OH⁻ ions diffused in the coating and a local increase in pH near the TiO₂ particles promoted the release of casein from the surface of the TiO₂ particles. The released casein simultaneously took TiO₂ reservoir particles to the defect area. The casein and TiO₂ particles released from the coating gradually diffused onto the bare magnesium alloy substrate to form a barrier film, thereby repairing the defect.

4. Conclusions

A TiO₂ particle coating was applied to a magnesium alloy substrate, and the specimen was then immersed in a casein solution. By changing the pH of the casein solution, casein could be inserted into the film. The self-healing properties of the coatings were evaluated from the corrosion behavior of a specimen on which a defect had been created. The polarization resistance of the scratched specimen, coated with TiO₂ particles and casein by changing the pH from 12 to 5, increased with immersion time. A deposited film consisting of casein and TiO₂ particles was observed in the scratched area of the specimen. This was due to complementary roles: the TiO₂ particles acted both as a component of the healing film and a reservoir of casein, and the casein also acted as a component of the healing film and a courier of TiO₂ particles. The self-healing effect of the coating appears to be due to the release of the casein and TiO₂ particles due to the increase in pH, and the subsequent formation of a film on the defect.

Acknowledgement

This research was supported in part by a Grant-in-Aid for Scientific Research (C), Japan Society for the Promotion of Science (No. 21560747).

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