SELF-HEALING CORROSION PROTECTIVE COATINGS BY TIO_2 PARTICLES AND A PH-SENSITIVE ORGANIC AGENT ON A MAGNESIUM ALLOY

A. Yabuki [1] and M. Sakai [1]

[1] *Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima, Hiroshima, 739-8527, Japan – e mail: ayabuki@hiroshima-u.ac.jp*

Keywords: corrosion, coating, self-healing, pH-sentitive, magnesium

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.

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]. 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. 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. 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.

2. MATERIALS

A 12 x 12 x 1 mm magnesium alloy AZ31 substrate was used for the test. The substrate was cut from a plate material. The plate was abraded with emery paper #2000, followed by a thorough rinse in water, and air drying. TiO_2 particles of a rutile structure with a mean diameter of 270 nm (Tayca Co.) were dispersed in deionized water to prepare a 1 wt% TiO_2 particle solution. Casein from milk (α-casein) (Sigma-Aldrich Co.) was also dispersed in deionized water to prepare a 1 wt% casein solution. Either acetic acid (liquid, ≥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 TiO_2 particle solution using a micro dip coater with a withdrawal speed of 10 mm s^{-1}. The TiO_2-coated specimen was calcined at 120 ˚C for 30 min in air. The specimen was immersed in a casein solution, pH12, at 35 ˚C for 4 h, then the pH of the solution was changed to 7, 5 or 4.

3. METHODS

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, a frequency response analyzer, 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. 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. 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.

4. RESULTS

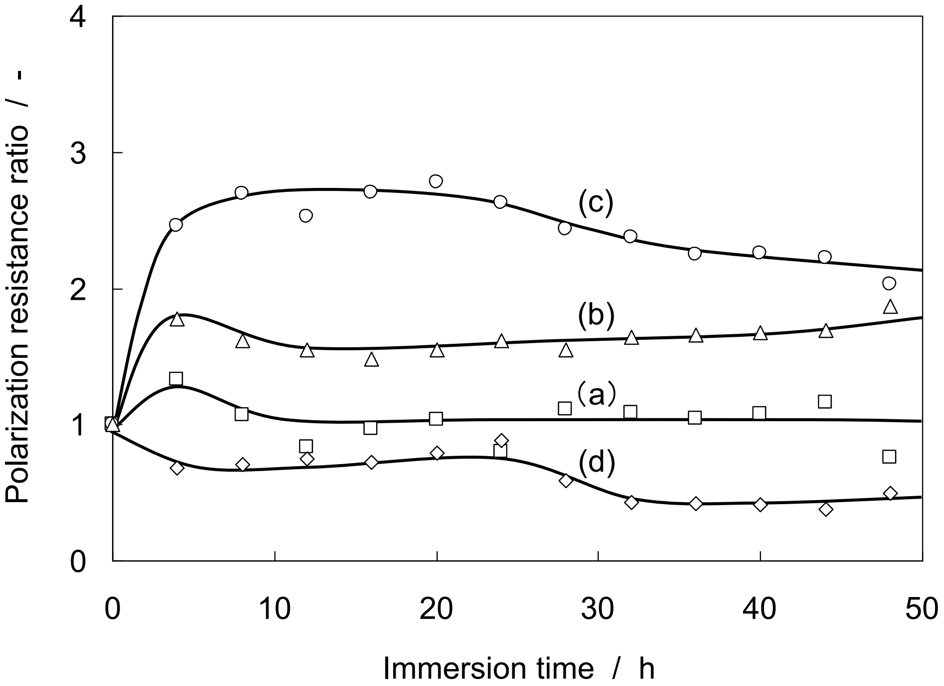

Figure 1: Polarization resistance ratio of scratched specimens coated with TiO_2 particle and TiO_2 particle-casein coatings prepared under various conditions; (a) TiO_2 particle coating, (b), (c) and (d) TiO_2 particle-casein coatings prepared by changing the pH from 12 to 7, 5, and 4, respectively.

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. 1. 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. 1a). 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. 1b). The resistance of the scratched specimen prepared by changing the pH from 12 to 5 increased within the 4 h immersion, resulting in more than twice the initial resistance (Fig. 1c). 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. 1d). 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.

The scratched portions of specimens coated with TiO_2 particle-casein — 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 Figures 2a, 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 Figure 2b 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 Figure 2c. 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. 1).

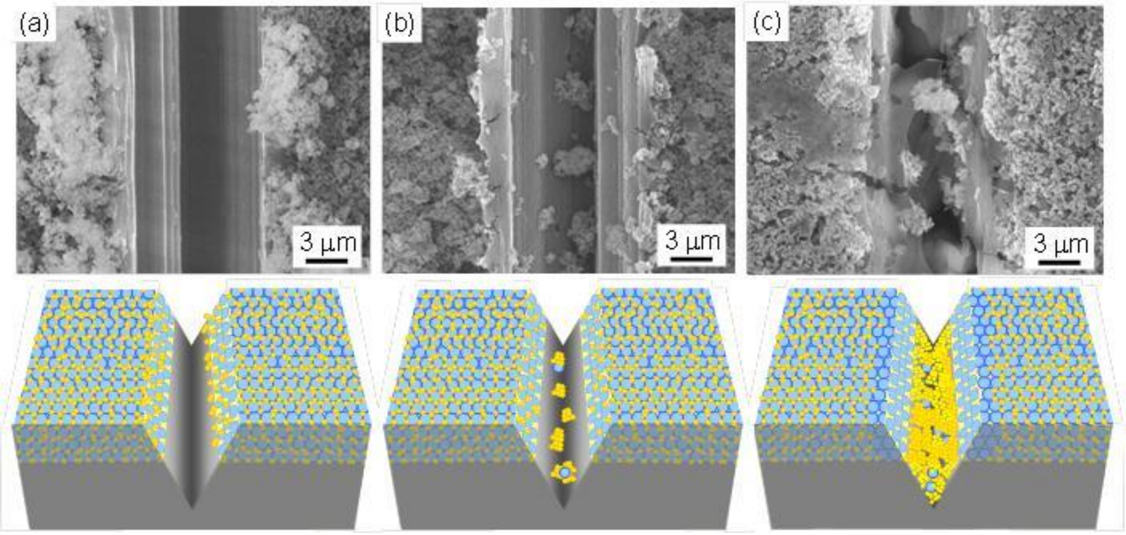

Figure 2: SEM images of the scratched area of specimens coated with TiO_2 particle-casein by changing the pH from 12 to 5 before the corrosion test (a), after 4 h immersion (b), and after 48 h immersion (c).

A schematic representation of the self-healing effect of the TiO_2 particle-casein coating is shown in Fig. 3. The self-healing effect is apparently due to the formation of a composite film that contains TiO_2 particles and casein. As 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. Negatively charged OH- ions were generated near the adherence between the coating and the substrate due to the cathodic reaction. Generated OH^- ions diffused in the coating and a local increase in pH near the TiO_2 particles promoted the release of casein from the surface of the TiO_2 particles. The released casein simultaneously took TiO_2 reservoir particles to the defect area. The casein and TiO_2 particles released from the coating gradually diffused onto the bare magnesium alloy substrate to form a barrier film, thereby repairing the defect.

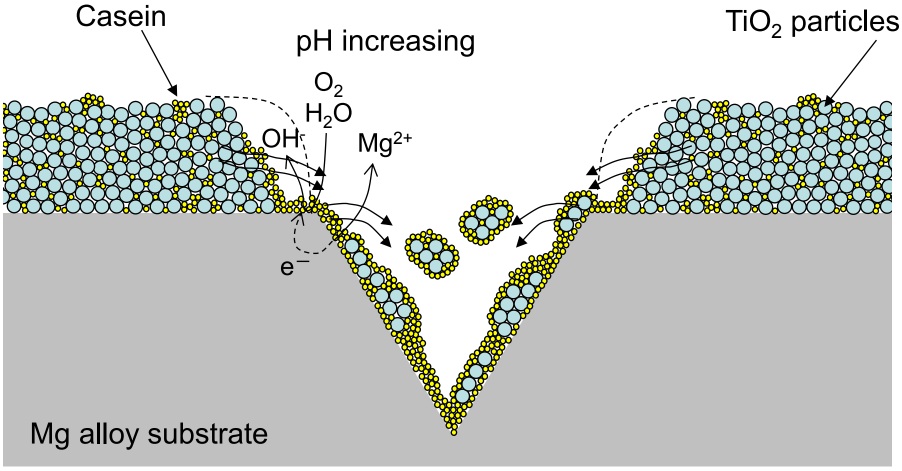

Figure 3: Self-healing mechanism of TiO_2 particle-casein coating.

5. CONCLUSIONS

The polarization resistance of the scratched specimen, coated with TiO_2 particles and casein by changing the pH from 12 to 5, increased with immersion time. A deposited film consisting of casein and TiO_2 particles was observed in the scratched area of the specimen. This was due to complementary roles: the TiO_2 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 TiO_2 particles. The self-healing effect of the coating appears to be due to the release of the casein and TiO_2 particles due to the increase in pH, and the subsequent formation of a film on the defect.

ACKNOWLEDGEMENTS

This research was supported in part by a Grant-in-Aid for Scientific Research (C), Japan Society for the Promotion of Science (No. 17560635).

REFERENCES

[1] G.L. Makar, J. Kruger, J. Electrochem. Soc. 137 (1990) 414-421.
[2] G. Song, A. Atren, D. St. John, X. Wu, J. Nairn, Corros. Sci 39 (1997) 1981-2004.
[3] R. Ambat, N.N. Aung, W. Zhou, Corros. Sci. 42 (2000) 1433-1455.
[4] G. Song, A. Atrens, M. Dargusch, Corros. Sci. 41 (1999) 249-273.