



Effects of various anode materials on the corrosion resistance of calcareous films deposited with an oyster shell waste-recycled solution

Jeonghyeon Yang¹ · Hui-Hun Kim² · Beom-Soo Kim³ · Yeonwon Kim[†]

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Abstract: The favorable role of calcareous coatings that improve the effectiveness of cathodic protection in submerged marine structures is generally recognized. However, although selection of anode materials has a significant effect on deposits, related studies have not been conducted extensively. Further, a method of supplementing calcium, which is the main component of calcareous film, in seawater has not been investigated. Thus, in this study, the calcareous films were electrodeposited using four anodes of STS, Al, Zn, AZ31 in the $\text{Ca}(\text{HCO}_3)_2$ solution where calcium hydrogen carbonate was prepared from oyster shell waste. The surface morphology, structure, and elemental composition analyses of the calcareous films were conducted through X-ray diffraction (XRD), scanning electron microscope (SEM), and energy dispersive X-ray spectroscopy (EDS), respectively, and corrosion resistance was evaluated through 3% NaCl immersion test and anodic polarization experiments. Consequently, it was determined that the corrosion resistance of the calcareous thin film using Mg was higher than others.

Keywords: Electrodeposition, Calcareous film, Waste oyster shell, Corrosion resistance, Cathodic protection

1. Introduction

The favorable role of calcareous coatings that improve the effectiveness of cathodic protection in submerged marine structures is generally recognized. Such calcareous deposits are caused by an increase in the pH of the electrolyte adjacent to the metal surface owing to the cathodic current, and reduction in the solubility limit of most inorganic compounds such as CaCO_3 , MgCO_3 and $\text{Mg}(\text{OH})_2$. Several research groups have reported that calcareous deposits suppress the diffusion of dissolved oxygen to metal surfaces and reduce the required current density for cathodic protection. It is also reported that the overall magnitude of uniform corrosion is reduced even in the absence of cathodic protection [1]-[3].

High-performance epoxy coatings protect ship ballast tanks for at least 10 years, but many reports on decoration of ship ballast tank coatings show that the localized areas, such as corners and joint welds, are susceptible to corrosion owing to the poor coating adhesion and irregularities of coating thickness. In addition, the negative impact of toxic paints on the marine

environment require alternative approaches to develop more environment-friendly corrosion protection methods.

Recently, several studies have been conducted on the formation of calcareous deposits on steel surfaces submerged in seawater [2]-[5], such as ballast water tanks, using an electrochemical calcareous deposit method [6]. These calcareous coatings are primarily formed at the area of the defective epoxy coating with the cations of Mg and Ca naturally present in seawater. Thus, they have several advantages over conventional epoxy coatings, providing a very promising technology for corrosion protection of ship ballast tanks.

Intensive oyster shells are mostly abandoned, while only certain oyster shells are reused as soil conditioners and chicken feed [7]. Therefore, recycling of these discarded oyster shells is required. However, to this date, the use of oyster shell waste has been limited and more recycling routes are needed to prevent shell waste and reduce environmental problems. Thus, in this study, we performed the experiment using oyster shell waste-recycled solution [8]-[10]. The surface morphology, structure, and

[†] Corresponding Author (ORCID: <http://orcid.org/0000-0001-5638-4339>): Professor, Division of Marine Mechatronics, Mokpo National Maritime University, 91, Haeyangdaehak-ro, Mokpo-si, Jeollanam-do, 58628 Republic of Korea, E-mail: k.yeonwon@mmu.ac.kr, Tel: +82-61-240-7237

¹ Professor, Department of Mechanical System Engineering Gyeongsang National University, E-mail: jh.yagi@gnu.ac.kr, Tel: +82-55-772-9107

² Researcher, Department of Mechanical System Engineering Gyeongsang National University, E-mail: k2h040@gmail.com, +82-55-772-9107

³ Professor, Department of Mechanical System Engineering Gyeongsang National University, E-mail: kimbs@gnu.ac.kr, Tel: +82-55-772-9107

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elemental composition analyses of the calcareous films were conducted through X-ray diffraction (XRD), scanning electron microscope (SEM), and energy dispersive X-ray spectroscopy (EDS), respectively, and corrosion resistance was evaluated through 3% NaCl immersion test and anodic polarization experiments. In addition, to identify the supplementary role of anode materials in providing a source of soluble ions, we conducted the experiments using several anodes of STS, Zn, Cu, AZ31 materials.

2. Experimental method

A cold-rolled steel sheet (SPCC, KS D 3512) with a thickness of 0.1 mm and dimensions of 70 mm x 90 mm was selected as the substrate for the calcareous deposition. Specimens prepared for an electrodeposition were immersed into a $\text{Ca}(\text{HCO}_3)_2$ and the film properties were evaluated for each experimental condition. The $\text{Ca}(\text{HCO}_3)_2$ solution used was prepared by bubbling 20 L of water with oyster shell waste at room temperature ($\sim 22^\circ\text{C}$) at a flow rate of 5 L/min. in a CO_2 cylinder. Four types of STS, Al, Zn, and AZ31 were selected to observe the influence of the anodes at a fixed current density of 0.1 mA/cm² and 0.5 mA/cm², respectively. The details regarding composition of materials are listed in **Table 1**.

Table 1: Chemical composition of the anode materials

Contents (wt.%)	Pure Al	Pure Zn	Mg Alloy (AZ31)	STS304
Mg	-	-	-	0.08
Zn	-	-	Balance	-
Al	Balance	Balance	1.0	-
Mn	-	-	3.0	-
Si	-	-	0.2~0.5	2.0
P	-	-	-	1.0
S	-	-	-	0.045
Ni	-	-	-	0.03
Cr	-	-	-	8.0~10.5

The experiments were conducted for 1 hour, 3 hours, 6 hours, and 12 hours as shown in **Figure 1**. The morphology and surface composition element analyses were conducted through an energy-dispersive X-ray spectroscopy (EDS) and a scanning electron microscope (SEM), respectively. The crystal structure analysis of the calcareous deposited films was performed using the X-ray diffraction (XRD). To evaluate the corrosion resistance of

the calcareous deposited film, immersion tests and an electrochemical polarization tests were conducted in 3% NaCl solutions.

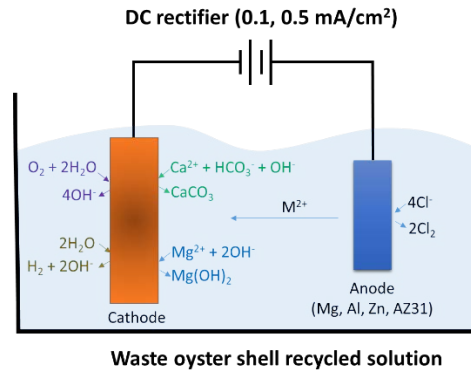


Figure 1: Schematic diagram for experimental setup of electrodeposition for calcareous films in the oyster shell recycled solution

3. Results and Discussion

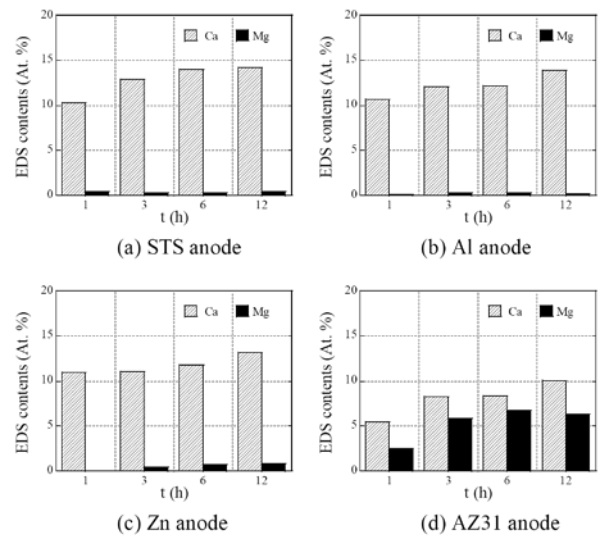


Figure 2: Variations in surface elemental composition of Mg and Ca for calcareous films deposited at 0.5 mA/cm² by various anode materials: (a) STS, (b) Al, (c) Zn, and (d) AZ31

Figure 2 shows the variations of the surface EDS elemental composition of Mg and Ca for calcareous films deposited at 0.5 mA/cm² by various anode materials. It can be observed that the overall amount of Ca components in the calcareous film increases with deposition time. In contrast, a relatively large amount of Mg was detected in the thin film using the AZ31 anode material. The Mg component showed a tendency to increase in

proportion to the time, and unlike the cases of using Al and Zn anode materials, each component of Al and Zn did not exceed 1% of the total amount, whereas the film using AZ31 anode material contained more than 6% of Mg in the film. When electrodeposited for 12 hours, the total of Mg and Ca components exceeded about 16%. This compositional change is much greater than that in the calcareous electrodeposition coating in natural seawater [11][12].

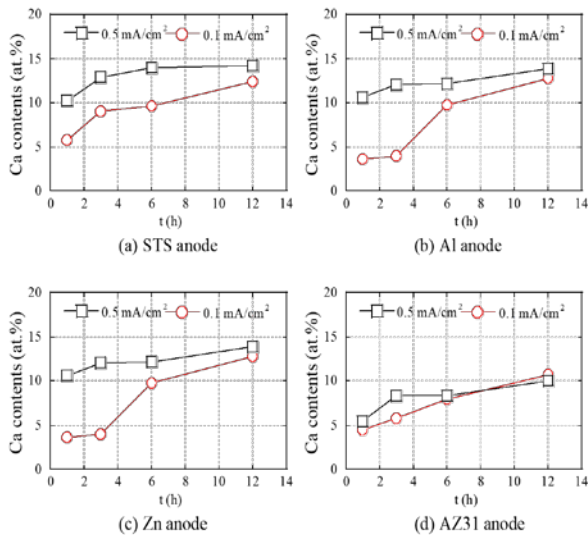


Figure 3: Comparison of variations in Ca elemental composition at current densities of 0.1 and 0.5 mA/cm² in calcareous films deposited using various anodes of (a) STS, (b) Al, (c) Zn, and (d) AZ31

Figure 3 shows the variation in Ca content in the calcareous films deposited with respect to time on using various anodes such as STS, Al, Zn, and AZ31. In the cases of all anodes, the Ca content was higher at 0.5 mA/cm² than that at 0.1 mA/cm². In addition, a higher increase in Ca content was shown in the initial 1 hour under the condition of current density of 0.5 mA/cm². However, a relatively low Ca content was observed in the films using the AZ31 compared to the films using other anodes, and there was no significant difference even at current densities of 0.1 and 0.5 mA/cm². It is attributed to the competitive reaction of dissolved Mg from the AZ31 anode with others like calcium hydrogen carbonate.

Figure 4(a) shows SEM images of the calcareous films formed using various anode rods. The overall trend was that the size of crystallites on the surface became finer when the electrodeposition time was increased in all anode cases. Generally, it is known that grain sizes are limited by the fact that crystallites grow from several nucleation centers only until they touch an adjacent grain or amorphous materials. At low deposition rate, grains do not coalesce at the grain boundaries to form larger grains. Thus, the results indicate that the growth rate increases as the deposition time increases. This is because the high growth rate prevents crystalline growth. Comparing the size differences of grains for each type of anode, Al anode showed the largest grain and the rest were similar. Comparing the surface grain size for each current density of 0.1 and 0.5 mA/cm², it can be

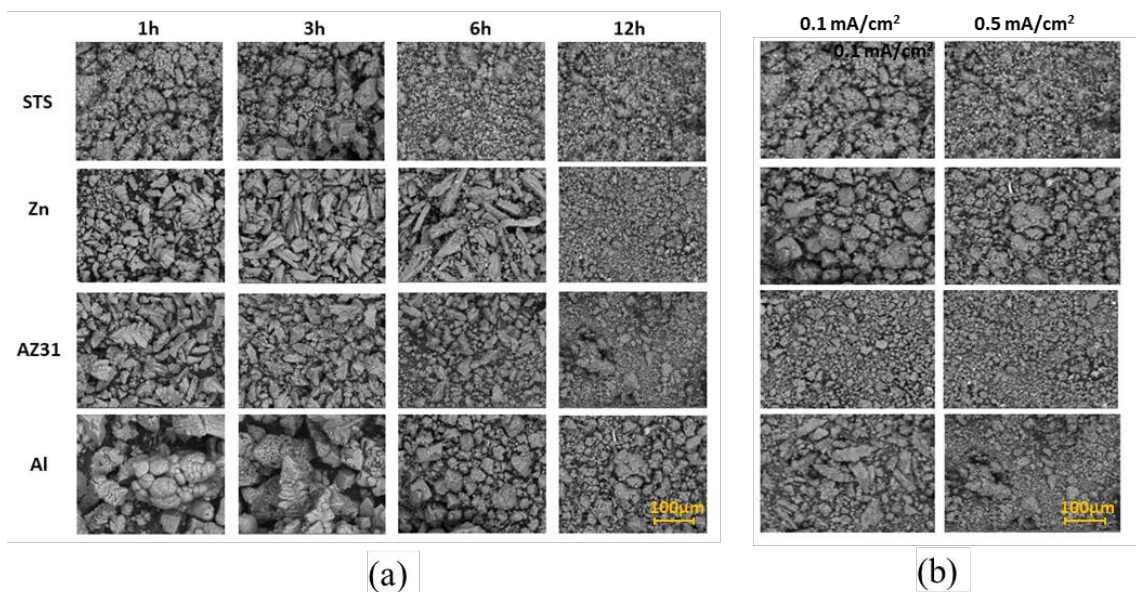


Figure 4: SEM images of calcareous films deposited with various anodes of STS, Al, Zn, AZ31 (a) after 1 h, 3 h, 6 h, 12h deposition at current density of 0.5 mA/cm², and (b) calcareous films after 12 h deposition at current densities of 0.1 and 0.5 mA/cm²

observed that Al anode also showed the largest grain size as shown in the **Figure 4(b)**.

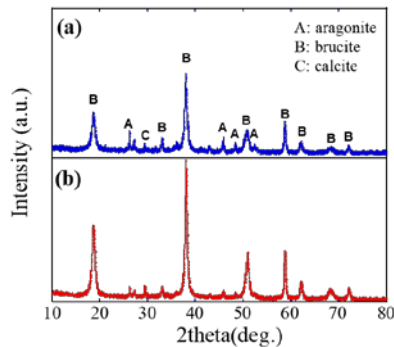


Figure 5: XRD pattern variations of calcaeous deposit films electrodeposited with the AZ31 material at a current density of 0.5 mA/cm^2

Figure 5 shows the XRD patterns of the calcaeous films formed using the AZ31 anode material. The current density was fixed at 0.5 mA/cm^2 . For the XRD data of 1h electroplating shown in **Figure 4(a)**, the intensive brucite $\text{Mg}(\text{OH})_2$ were detected at 18° , 38° with aragonite CaCO_3 at 26° , 48° . This can be explained by the sequential precipitation of calcium compound precipitated at lower alkali pH and the magnesium compound at higher alkali pH. It is known that the presence of magnesium ions leads to increase in the density of CaCO_3 by promoting structural change of calcite to aragonite. In contrast, for 6 h electroplating, predominant brucite $\text{Mg}(\text{OH})_2$ structure was observed. This is because of the continuous thickening of brucite $\text{Mg}(\text{OH})_2$ layer where a magnesium hydroxide preferentially precipitates compared with calcium carbonate, owing to a high constant alkali pH and rich magnesium ions [13][14].

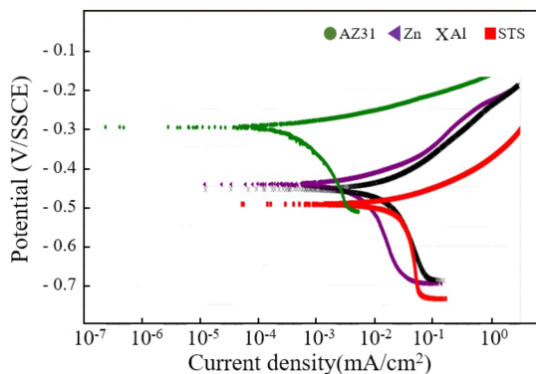


Figure 6: Anodic polarization analysis of the calcaeous films deposited using various anode materials of Zn, Al, STS, AZ31 at a current density of 0.5 mA/cm^2

Figure 6 shows the results of anodic polarization analysis of calcaeous films deposited using various anode materials such as STS, Zn, Al, and STS, at a current density of 0.5 mA/cm^2 . The lowest corrosion current density was measured for AZ31. It seems to be due to the improvement of corrosion resistance by the adsorption of calcium carbonate and a relatively large amount of magnesium compounds. The Zn and Al showed higher corrosion current densities than the AZ31, and the STS showed the highest corrosion current density. It is believed that the high potential difference between the cathode and anode (e.g., SPCC cathode and AZ31 anode) play an advantageous role in the formation of a calcium carbonate and a magnesium compound on the substrate. In the immersion test also, the AZ31 sample showed the highest corrosion resistance as shown in **Figure 7**, which were consistent with anodic polarization test results.

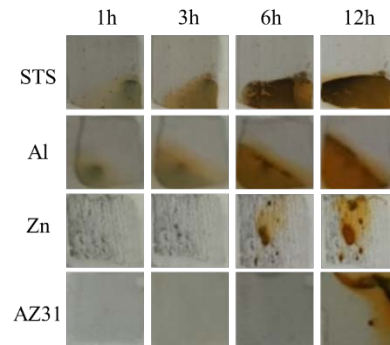


Figure 7: Optical surface photos of the calcaeous deposited films obtained using various anodes for different immersion times in 3% NaCl solution

4. Conclusion

The calcaeous film was electrodeposited using four anodes of STS, Al, Zn, AZ31 in the $\text{Ca}(\text{HCO}_3)_2$ solution where calcium hydrogen carbonate solution was prepared from waste oyster shells. The SEM observation showed that the surface morphology were dense and fine at high current densities and long electrodeposition times. In particular, a large amount of Mg was detected in the calcaeous film using the AZ31 anode material. It is believed that the additional Mg adsorption of the calcaeous film played a role in obtaining high corrosion resistance. The results of XRD analysis confirmed that most of the surface structure was brucite and aragonite. The polarization and immersion tests verified that the films using the AZ31 anode material had relatively higher corrosion resistance than others. It shows that a higher active material such as Mg is advantageous for the formation of a high-

performance calcareous film through electron injection into the target substance of cathodic protection. These results are expected to be utilized for practical applications of calcareous thin films and recycling of waste oyster shell.

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Author Contributions

Conceptualization, J. Y. Yang; Methodology, J. Y. Yang; Software, H. H. Kim; Formal Analysis, H. H. Kim; Investigation, B. S. Kim; Resources, B. S. Kim; Data Curation B. S. Kim; Writing-Original Draft Preparation, H. H. Kim; Writing-Review & Editing, J. Y. Yang; Visualization, Y. Kim; Supervision, Y. Kim; Project Administration, Y. Kim; Funding Acquisition, Y. Kim.

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