

Protection of HDG Steel Using ORMOSIL Coatings Enhanced with CeO₂(5-ATDT)-Ceramic Nanocontainers

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Abstract

First, we studied the anticorrosion efficiency of the corrosiveness inhibitors CeO₂, 5-amino-1,3,4-thiadiazole-2-thiol (5-ATDT), Ce(NH₄)₂(NO₃)₆ in hot-dip galvanized zinc (HDG) steel. The best protection is shown by the compound Ce(NH₄)₂(NO₃)₆ among the three. Second, CeO₂ ceramic nanocontainers were prepared, which were loaded with 5-ATDT. Third, organically modified silica (ORMOSIL) coatings were produced on hot-dip galvanized zinc (HDG) steel, which was reinforced with CeO₂(5-ATDT) nanocontainers. Finally, the anticorrosion protection of these composites was studied using the Frequency Response Analysis (FRA) method, and it was established to reinforce ORMOSIL with CeO₂(5-ATDT); inducing the phenomenon of “self-healing”.

Keywords: Corrosion, Hot-dip galvanized zinc, ORMOSIL, Nanocontainers, Inhibitors, Self-healing

1 Introduction

Galvanized steel is produced by hot steel immersion in a molten zinc tank. While steel is inside the furnace, iron reacts metallurgically with the molten zinc to form a tightly attached alloy coating that provides superior corrosion protection to steel. The term “galvanizing” is often misused to describe various zinc coatings for steel in the hot-dip galvanizing process. In addition to hot-dip galvanizing, several other zinc coatings are applied to steel, such as zinc-rich paint, zinc plated, plated zinc, and mechanical zinc. These zinc coatings are significantly different from the coating of the hot dip galvanizing process and can be unsuitable for many situations of environmental exposure [1].

When one exposes the metals to the atmosphere, they tend to come to the lowest energy state through corrosion; in other words, the metal rusts. Therefore, HDG is an excellent structural material used as a building material for cement strengthening due to its durability, low environmental impact, and long-term durability. However, corrosion is an unavoidable catastrophic event that can be highly costly for repairing

the structure and bringing about the loss of construction. Therefore, the answer to HDG corrosion is protective coatings, e.g., type ORMOSIL.

In recent years, ORMOSIL coatings have been produced to protect aluminum, copper, magnesium, and iron. It has been observed that integrating nanocontainers loaded with corrosion inhibitors improve their offered protection by observing the self-healing phenomenon [2]–[10]. Other kinds of inhibitors are potential candidates to be employed and deserve exploitation [11]. With this perspective, ORMOSIL coatings with CeO₂(5-ATDT) were produced in this study, and their anticorrosion ability was studied. FRA has been used for the determination of corrosion protection.

2 Chemicals and Equipment

We used N-(2-aminoethyl) – 3 -(trimethoxypropyl) propylamine (N-(2-Aminoethyl)-3-(trimethoxysilyl) propylamine, Z 6020, Sigma-Aldrich, St. Louis, United States), epoxy resin (epoxy resin “Araldite GY 257,” GY 257, Ciba-Geigy), and 2,2'-diaminodimethylamine

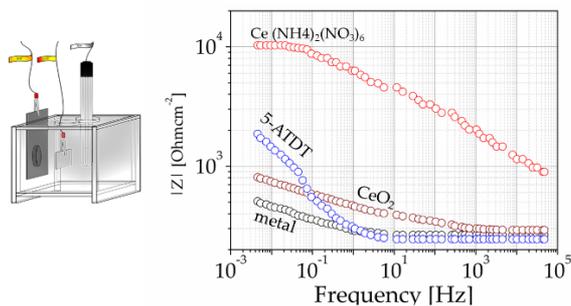


Figure 1: Nyquist diagram after 30 hours of exposure of HDG steel in a 0.05 M NaCl corrosive environment and the same corrosive environment with corrosion inhibitors.

(2,2'-Diaminodiethylamine, HS 943, Sigma-Aldrich, St. Louis, United States). We acquired the chemicals 5-amino-1, 3, 4-thiadiazole-2-thiol (5-ATDT), and $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ by Acros-Organics, New Jersey, United States. The production of the ORMOSIL coatings and CeO_2 nanocontainers was described in the literature [10]. We used the equipment described in the literature [12].

3 Inhibitor Evaluation

Corrosion resistance has been studied for the CeO_2 , 5-ATDT, and $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ inhibitors of electrochemical impedance spectroscopy (EIS) spectroscopy. Figure 1 shows the EIS spectra of all inhibitors from which steel was protected against NaCl corrosive solution after thirty hours of exposure. More specifically, the electrochemical cell is presented in the figure, while the corresponding Nyquist diagrams are demonstrated in Figure 1. The impedance of the Nyquist spectrum at low frequencies in the case of the solution without inhibitor (bare) shows a value of about $400 \Omega/\text{cm}^2$. The corrosion inhibitors (Figure 1) increase impedance value in the low-frequency range, higher than the minimum value obtained for the solution without an inhibitor. This proves that additional corrosion inhibitors have indeed achieved a degree of protection. However, the extent to which the increase in impedance is achieved varies depending on the effectiveness of each inhibitor. CeO_2 and ATDT are shown in the same diagram, and both substances have an excellent effect and an increase in impedance in the low-frequency range. In the case of $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$,

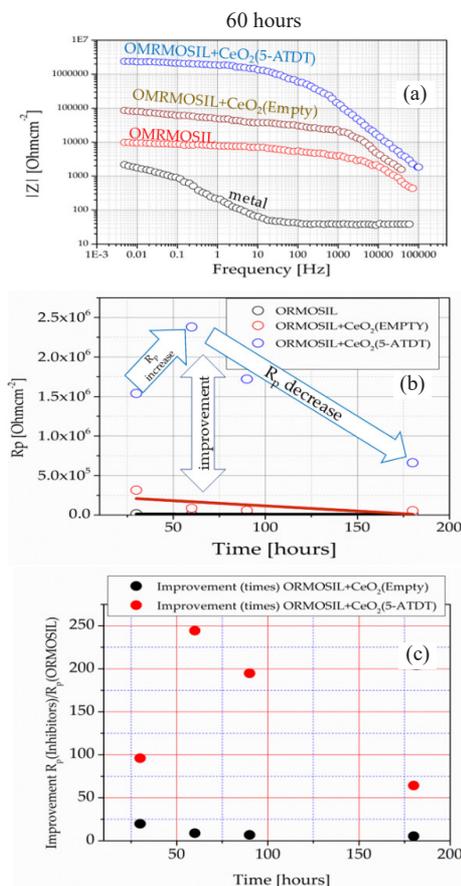


Figure 2: (a) EIS of all samples exposed to salt water for 60 h. (b) R_p of the HDG + ORMOSIL, HDG + ORMOSIL + CeO_2 (EMPTY) and HDG + ORMOSIL + CeO_2 (5-ATDT) coatings as a function of the exposure time in salt water. (b) Improvement of R_p of HDG + ORMOSIL + CeO_2 (EMPTY) and HDG + ORMOSIL + CeO_2 (5-ATDT) compared to R_p of HDG + ORMOSIL (c).

the protection appears more effective and stable throughout the scan and offers a higher impedance value than the solution without an inhibitor.

4 Anticorrosion Properties of The Coatings

The anticorrosion test procedure involves exposing the coated frames to 0.5 M NaCl solution for 30, 60, 90, and 180 h exposed area were 2 cm^2 . EIS assessed the coated samples' protective abilities and corrosion mechanism [10]. Figure 2(a) shows the EIS measurement

for 60 h for all samples. Figure 2(b) shows the R_p of the coatings HDG + ORMOSIL + CeO₂(EMPTY) and HDG + ORMOSIL, HDG + ORMOSIL + CeO₂(5-ATDT) as a function of the time of exposure to salt water. The R_p of the HDG+ORMOSIL, HDG+ORMOSIL+CeO₂(5-ATDT) coating is greater in all saline exposure times than in all other samples. R_p in these samples grows from 30 to 60 hours of exposure and decreases from 60 to 180 h, but never becomes smaller than the R_p of the other samples. This behavior is due to the release of 5-ATDT from the nanocontainers causing the “self-healing” effect [12].

5 Discussion

The cerium and 5-ATDT work against corrosion inhibitors with different mechanisms. Zinc substrates improve their corrosion resistance when immersed in solutions containing cerium [13]. This is due to the precipitation of cerium in the cathodic areas, which creates a coating of its oxides [2], [3]. Ce³⁺ oxidation in Ce⁴⁺ precipitates as insoluble CeO₂ in solution from dissolved oxygen in the cathodic regions. Cerium chloride and cerium nitrate are soluble in water. Cerium Ac and cerium sulfate have limited solubility in water. The solubility of the cerium compounds affects their chelating performance [14]. 5-ATDT acts as a corrosion inhibitor on zinc surfaces by creating protective gelatin [12]. The literature has proven that 5-ATDT performs excellently in aggressive media [15]. The results of the measurements relating to corrosion protection offered by the chemical substances CeO₂, Ce(NH₄)₂(NO₃)₆, and ATDT can be understood in the existing bibliography. Ce(NH₄)₂(NO₃)₆ protection appears effective and stable throughout the FRA scan and offers a higher impedance value than the solution without an inhibitor. The protective efficacy of CeO₂ is significantly less than that offered by the substance Ce (NH₄)₂(NO₃)₆. 5-ATDT has been added with an excellent effect and impedance increases in the low-frequency range. The resistance value takes its maximum value not by gradual increase, from the highest frequencies to the lowest, but is formed rapidly and abruptly in the range of the lowest frequencies. The differences may be due to the substances' solubility and the metal's protective surface formed by these processes.

The behavior of cerium in ORMOSIL coatings can be indulged in the roll of cerium inhibitor or in the condensation of the ORMOSIL coating that increases the barrier properties. When the cerium is complex in its matrix coatings, it cannot come out to offer the phenomenon of self-healing, but the barrier properties remain constant because it cannot get out of the coating. Specifically, one observes an improvement of 19.64 times in the 30 hours of exposure to salt solution and is reduced to 5.31 times for exposure to 180 h in the same salt solution [Figure 2(c)]. However, the coating behavior is entirely different when the nanocontainers are loaded with 5-ATDT. We observed at 30 hours of exposure to the salt solution an increase in R_p of 96.02 [Figure 2(b)]. When the exposure is increased to 60 h, the R_p becomes 244.37 times more extensive than what we get for the ORMOSIL coating. It is then reduced to 64.24 times after 180 h, which is still much greater than the corresponding R_p of the ORMOSIL coating. This is because the 5-ATDT inside the nanostructures is free to be released during corrosion to create protective gelatin on the HDG surface. After peaking at 60 h, the 5-ATDT gradually decreases with the result that the R_p [Figure 2(b)] is also reduced. This behavior can be attributed to the “self-healing” effect. The self-healing effect in protective coatings must also be considered in railway structures, as it has been done in other transport applications [5], [8]–[21].

6 Conclusions

This paper investigates the performance of the CeO₂, Ce(NH₄)₂(NO₃)₆, and 5-ATDT inhibitors in salt solutions concerning corrosion protection of HDG. In all three cases, one observes significant protection of the HDG metal. Furthermore, when CeO₂(5-ATDT) is incorporated into the ORMOSIL coatings, one observes a significant improvement in corrosion protection up to 244.37 times. This can be attributed to the “self-healing” phenomenon.

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Author Contributions

G.K.: conceptualization, investigation, research design, data analysis, writing, editing, and funding acquisition,

Conflicts of Interest

The author declares no conflict of interest.

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