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Corrosion inhibition of 2024-T3 aluminum alloy in 3.5% NaCl by thiosemicarbazone derivatives

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ABSTRACT

Three thiosemicarzone derivatives, namely (E)-2-(2-hydroxybenzylidene) hydrazinecarbothioamide(MHC), (E)-2-(2,4-dihydroxybenzylidene)hydrazinecarbothioamide (DHC) and (E)-2-(2,3,4-trihydroxybenzylidene)hydrazinecarbothioamide (THC) were synthesized and their corrosion inhibition action on 2024-T3 aluminum alloy was studied in 3.5% NaCl solution. The surface morphology and surface composition of the corroded alloy were examined using FESEM, 3D profilometry, EDX spectroscopy and X-ray photoelectron spectroscopy. The synthesized inhibitors were found to provide corrosion protection on AA2024-T3 by forming an adsorbed layer of the complex on the alloy surface. They exhibited inhibition efficiency in the order, MHC < DHC < THC. Quantum chemical calculations corroborated the experimental results.

1. Introduction

Aluminum alloys, in general, find potential applications in automotive, aerospace industries, aviation industries, household appliances, ship buildings and military hardware due to their high strength, low density and high stiffness. 2024-T3 aluminum alloy, one of the widely used aluminum alloys in aerospace applications, possesses high strength to weight ratio and high damage tolerance resulting from the presence of copper and magnesium as the major alloying elements and suitable thermo mechanical processing [1]. Despite possessing advantageous mechanical properties, the utility of the alloy is limited by its high susceptibility to corrosion, arising out of the presence of the intermetallic particles which differ in their potentials from that of the alloy matrix [2–15].

There are number of reports available in the literature, discussing the corrosion mechanism of 2024-T3 aluminum alloy in aqueous media containing chloride ions [10,16–20]. The 2024-T3 aluminum alloy is mainly composed of three main intermetallic inclusions, namely, Al_2CuMg (S phase), Al_2Cu and Al_7Cu_2Fe. Al_7Cu_2Fe is the representative composition of different types of particles containing Al, Cu, Fe as major constituents; Mn and Si as minor constituents found in 2024-T3 aluminum alloy [21]. The role of these intermetallic inclusions have been investigated and found that the S phase acting as an active phase towards corrosion, while Al_2Cu and Al_2Cu_2Fe acting as noble phases [9]. The S phase particles, accounting for about 60% of the intermetallic particles in 2024-T3 aluminum alloys [17], are reported to be as initiation sites for localized corrosion of the alloy [17,22–29]. In the initial stages of corrosion, the active S phase undergoes dealloying corrosion with the chemical and electrochemical dissolution of Mg and Al from S phase, simultaneously enriching it with copper [30]. The dealloyed S phase, enriched with copper can act as an effective cathodic site for the preferential corrosion of alloy matrix [1,17]. Thus, an effective corrosion inhibition strategy for 2024-T3 aluminum alloy needs suppression of the dealloying of S phase and also protection of the alloy matrix from corrosion.

For many decades, chromate salts were used as corrosion inhibitors for aluminum alloys, as they form highly protective films on the alloy surface. However, the usage of chromate salts are discouraged for their toxicity; and alternatives to them are encouraged [31,32]. A number of rare earth element salts have been reported as efficient corrosion inhibitors for aluminum alloys [33–41]. The use of organic compounds as corrosion inhibitors on aluminum alloy surfaces, has been investigated and reported. The compounds used include triazoles [30,42–44], 2-mercaptobenzothiazole [45], 1-pyrrolidinedithiocarbamate [46], 8-hydroxyquinoline, salicylaldoxime and quinaldic acid [30]. Organic compounds consisting of hetero atoms, such as O, N or S and multiple bonds or aromatic rings act as good corrosion inhibitors on metal and alloy surfaces. The electron rich active sites on these molecules

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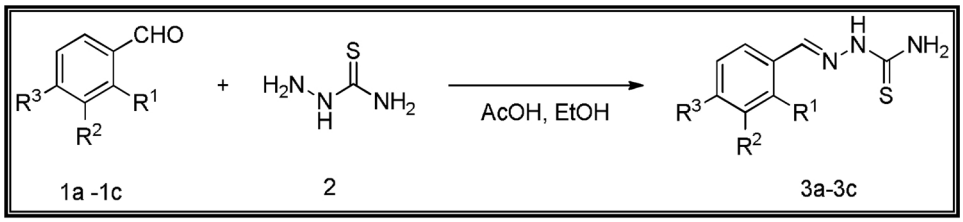


Compound 1	R^1	R^2	R^3	Compound 3
1a	OH	H	H	3a (MHC)
1b	OH	H	OH	3b (DHC)
1c	OH	OH	OH	3c (THC)

Fig. 1. The general scheme for the synthesis of inhibitor compounds.

facilitate easy adsorption of the molecules of these compounds on the metal/alloy surface [47,48]. Aromatic derivatives of thiosemicarbazone possess the combination of all the above bonding sites and are expected to act as good corrosion inhibitors.

In the present work, three different thiosemicarbazone derivatives have been synthesized. The inhibitive impact of the compounds on the corrosion of 2024-T3 aluminum alloy has been studied and reported.

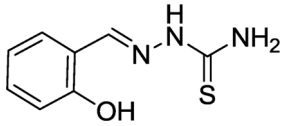
2. Experimental

2.1. Material and specimen preparation

The specimens of 2024-T3 aluminum alloy were used as substrates in the present study. The elemental composition of the alloy is as follows (wt%): (Al = 93.52, Cu = 4.24, Mg = 1.26, Zn = 0.08, Fe = 0.15, Mn = 0.65, Cr = 0.01 and Si = 0.06). The sample was abraded with 400, 800, 1200 and 2500 grade silicon carbide papers and finally polished on a polishing wheel, applied with legated alumina to get the mirror finishing. Then it was cleaned by sonicating in Milli-Q water for 10 min and dried at room temperature, before immersing in the corrosion medium.

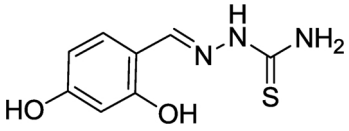
2.2. Corrosion inhibitors

2.2.1. (E)-2-(2-hydroxybenzylidene)hydrazinecarbothioamide (MHC)



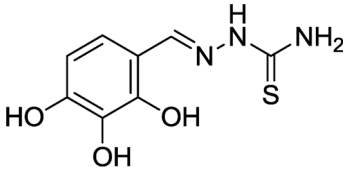
MHC was purchased from Sigma Aldrich.

2.2.2. (E)-2-(2,4-dihydroxybenzylidene)hydrazinecarbothioamide (DHC)



DHC was prepared as per the procedure reported in the literature [49]. A mixture of 2,4-dihydroxybenzaldehyde (1 g, 1 eq, 7.24 mmol) and thiosemicarbazide (0.66 g, 1 eq, 7.24 mmol) in 25 mL of absolute ethanol were refluxed for 12 h. The reaction mixture was cooled to room temperature, and the resulted precipitate was filtered and recrystallized with ethanol as a white solid (yield 85%). The compound was characterized by ^{1}H NMR, ^{13}C NMR and elemental analyses. ^{1}H NMR (DMSO): δ (ppm): 11.14 (s, 1 H, NHCS), 9.720 (s, 2 H, Ar-OH), 8.23 (s, 1 H, Ar-CH = N), 7.91(s, 1 H, NH),7.71 (s, 1 H, NH), 7.64 (d, 1 H, J = 8.4 Hz), 6.28 (d, 1 H, J = 2.4 Hz), 6.24(d, 1 H, J = 2.4 Hz and 8.8 Hz). ^{13}C NMR (DMSO): δ (ppm): 177, 160, 158, 140.8, 128.3, 11.73, 107.72, and 102.26. Elemental analysis: found (calculated) (%): C 46.10 (45.49), H 4.38 (4.29), N 20.08 (19.89) and S 15.44 (15.18).

2.2.3. Synthesis of (E)-2-(2,3,4-trihydroxybenzylidene)hydrazinecarbothioamide (THC)



THC was prepared by following the same procedure as above by the reaction of 2,3,4-trihydroxybenzaldehyde and thiosemicarbazide. The recrystallized yellow crystalline product was characterized by ^{1}H NMR, ^{13}C NMR and elemental analyses. ^{1}H NMR (DMSO): δ (ppm): 11.17 (s, 1 H, NHCS), 9.47 (s, 1 H, Ar-OH), 8.94 (s, 1 H, Ar-OH), 8.39 (s, 1 H, Ar-CH = N), 8.22 (s, 1 H, Ar-OH), 7.92 (s, 1 H, NH), 7.72 (s, 1 H, NH), 7.10 (d, 1 H, J = 8.8 Hz) 6.32 (d, 1 H, J = 8.8 Hz). ^{13}C NMR (DMSO): δ (ppm): 177.51, 148.73, 147.05, 142.65, 133.17, 118.70, 112.98, and 108.21. Elemental analysis: found (calculated) (%): C 43.14 (42.28), H 4.19 (3.99), N 18.47 (18.49) and S 14.21 (14.11).

The general scheme for the synthesis of inhibitor compounds are shown in Fig.1.

2.2.4. Corrosion media

A standard 3.5% NaCl solution was prepared by dissolving sodium chloride in Mili-Q water. 1 mM each of the synthesized inhibitor was dissolved in the standard 3.5% NaCl solution to evaluate their corrosion inhibition characteristics on AA2024-T3. The analyses were carried out at 30 °C (± 0.5 °C).

2.3. Electrochemical studies

The electrochemical measurements were performed using CH instruments electrochemical work station (CHI660E) in naturally aerated 3.5% NaCl solution in the absence and in the presence of different inhibitors. The corrosion cell set up employed was a three electrode cell comprising of the test coupon as working electrode (1 cm^2 exposure area), a platinum electrode as counter electrode and saturated calomel electrode used as the reference electrode.

The alloy coupons was immersed in 3.5% NaCl in the absence and in the presence of the inhibitor allowed to establish a steady state open circuit potential (OCP). The electrochemical impedance measurements were carried out at different immersion times in same 3.5% NaCl solution in the absence and in the presence of the inhibitors. The scanned frequency ranged from 100 kHz to 10 mHz with a small amplitude (10 mV) ac perturbation about the OCP. The corrosion characteristics