

Citric Acid as an Eco-Friendly Inhibitor for the EN AW-2024 Aluminum Alloy Corrosion in Acidic Medium

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ABSTRACT

The paper presents the results from a study on the possibility to use citric acid as an ecological inhibitor of corrosion in aluminum alloy EN AW-2024 in 0.5 M solution of H₂SO₄. The study has been carried out by using electrochemical techniques, such as open circuit potential and chronoamperometry. The results reveal that the presence of citric acid in the studied acid medium reduces the corrosion degree of the EN AW-2024 aluminum alloy. The inhibition efficiency increases together with increasing the concentration of the citric acid. The study shows that the citric acid can be used as an ecological inhibitor to fight corrosion in a solution of H₂SO₄.

Keywords: corrosion inhibition, aluminum alloy, citric acid, electrochemical technique.

INTRODUCTION

Aluminum alloys are used in industry owing to their high hardness, relatively low density and capability to form an oxide layer, protecting the metal surface from the environment. Because of their wide use, they are often in contact with natural or technological media, causing their destruction.

Corrosion is a natural process, leading to deterioration of the properties of metal materials as a result of their chemical or electro-chemical interaction with the environment. The costs, related to corrosion, can be both direct, such as replacement of corroded constructions and facilities, and indirect, such as interruptions of manufacturing processes, loss of effectiveness etc. (Revie et al., 2008; Roberge, 2012). When studying the costs of corrosion, it becomes clear that they reach up to 3–5% from the gross national income in the most developed countries in the world (McCafferty, 2010). The economic aspect, combined with the care for environment protection, are among the basic reasons for studying the ecological methods of corrosion protection.

There are a number of ways to protect metals from corrosion and one of them is related to using

corrosion inhibitors. These are the substances, which, when added in small amounts to a medium, considerably reduce or prevent the reaction of the metal to aggressive components in the medium (Popov, 2015). All corrosion inhibitors, as a whole, are divided into two groups – organic and inorganic. Compounds such as chromates, vanadates, molybdates, nitrates, nitrites and sulfates are used as inorganic inhibitors. However, despite of their proven inhibitory effect on corrosion in a number of metals and alloys (Gharbi et al., 2018), they are subject to a lot of criticism due to their toxicity and their replacement with safe substances is recommended.

The greater part of the used organic inhibitors, such as mono azo dyes (Al-Juaid, 2007); 1-pyrrolidine dithio-carbamate (Qafsaoui et al., 2015); sulfonic acid, sodium cumene sulfonate, and sodium alkyl sulfate (Maayta, 2006); polymethacrylate (Kalaivani et al., 2013) also pose a risk to human health and the environment, and therefore, in recent years, researchers' attention has been focused on studying the possibility of using ecological corrosion inhibitors. These are biodegradable, renewable and non-toxic substances, acting as inhibitors for various metal materials in

corrosive media such as HCl, H₂SO₄, H₃PO₄ and HNO₃. The ecological inhibitors, in their turn, are also divided into the same two groups according to their chemical composition: organic and inorganic. Salts of lanthanides are used as inorganic ecological inhibitors, (Arenas et al. 2001; Bethencourt et al. 1998; de Damborenea et al. 2014), while organic inhibitors include amino acids (Li et al. 2011; Salghi et al. 1997), biopolymers (Jmiai et al. 2017; Malik et al. 2011; Oukhrib et al. 2017; Verma et al. 2017), plant extracts (Deyab, 2015; Wisdom, 2018; Onukwuli et al., 2022; Sharma et al., 2019; El-Azaly, 2019) and some organic acids (Wysocka et al., 2018; Ibrahim et al., 2017).

Among the used organic acids, citric acid is indicated as one of the most effective inhibitors of corrosion in aluminum and its alloys in alkaline (Müller, 2004; Brito et al., 2013; Wysocka et al., 2017), neutral (pH 8) (Yurt et al., 2005), and acidic media (pH 2) (Solmaz et al., 2008). Due to the fact that sulfuric acid is one of the most frequently used reagents in technological operations, related to pickling and electrochemical etching of aluminum and its alloys, of particular interest to the industry is the study of the possibility of preventing the destruction and loss of valuable metal by using ecological inhibitors such as citric acid. The aim of the present study was to investigate the possibility of using citric acid as an ecological corrosion inhibitor for the EN AW-2024 aluminum alloy in the H₂SO₄ solution.

MATERIALS AND METHODS

The EN AW-2024 (AlCuMg2) Aluminum alloy, composed of (mass%) Cu 3.80–4.90; Fe 0.50; Mg 1.20–1.80; Mn 0.30–0.90; Si 0.50; Ti 0.15; Zn 0.25; Cr 0.10 and a residual of Al was used for conducting the corrosion measurements. The sulfuric and citric acid (Fluka) solutions were prepared with double-distilled water.

The electrochemical measurements were conducted by means of a computer-controlled Palm Sens work station (Palm Instruments, BV, The Netherlands) in the three-electrode cell. The alloy under investigation was used as a working electrode, a platinum conductor served as an auxiliary electrode, and in the role of a reference electrode, a saturated Ag/AgCl electrode was used. All tests were performed at room temperature. The working electrode had an area of 1 cm², the rest of the electrode surface was varnished.

The open circuit potential was measured after immersing the working electrode in a 0.5 M solution of H₂SO₄ until reaching a stable state (600 seconds). Similarly, measurements were carried out in the presence of 0.0025, 0.0050, 0.0075 and 0.01 mM citric acid. A chronoamperometric measurement was made for 60 seconds. The inhibition efficiency (η %) was also calculated from the following equation:

$$\eta\% = \frac{I_{corr} - I'_{corr}}{I_{corr}} \cdot 100 \quad (1)$$

where: I_{corr} and I'_{corr} are the corrosion current values in the absence and presence of the inhibitor, respectively.

RESULTS AND DISCUSSION

Open circuit potential (E_{OCP})

Figure 1 presents the potential-time curves, which illustrate the change in the surface of the oxide layer on the alloy during the test. When comparing the curves of the studied aluminum alloy, it was found that the behavior of the alloy in the presence of 0.5 M H₂SO₄ differs significantly from that after adding citric acid.

When the aluminum alloy is immersed in 0.5 M H₂SO₄, the potential value quickly deviates in the negative direction and this continues throughout the entire duration of the test, i.e., the alloy actively dissolves in the test solution. This is probably due to the aggressive sulfate ions in the solution, dissolving the surface of the alloy. The observed fluctuations in the potential indicate instability of the processes, occurring on the surface of the alloy, which is characteristic of pitting corrosion. The shape of the potential-time curves for the aluminum alloy EN AW 2024 in 0.5 M H₂SO₄ in the presence of 0.0025, 0.0050, 0.0075 and 0.01 mM of citric acid show an initial shift of the potential in the negative direction (for about 70–120s). This is possibly related to the rapid dissolution of the oxide layer, formed before the immersion into the studied solution, as well as to the passive layer, formed during E_{OCP} , and/or to the dissolution of the metal in sections with structural defects in the oxide layer. The value of the E_{OCP} then shifts in the positive direction and remains relatively constant throughout the test. It is observed that at 0.01 mM citric acid, the value of the E_{OCP} is by 0.005 V more positive compared to

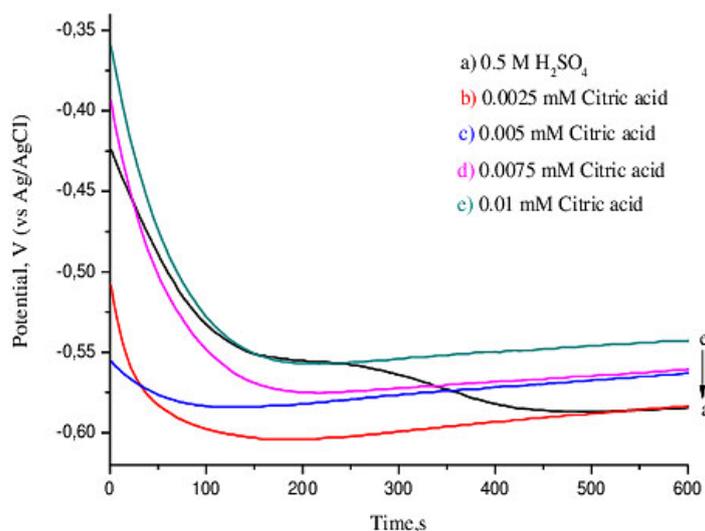


Figure 1. Open circuit potential of EN AW 2024 alloy in 0.5 M H_2SO_4 in the absence and in the presence of citric acid

that of the E_{OCP} in 0.5 M H_2SO_4 , i.e., as the concentration of the citric acid in the H_2SO_4 solution increases, the risk of corrosion decreases due to the adsorption of the citric acid on the surface of the alloy.

Chronoamperometric measurement

The chronoamperometric curves of the EN AW 2024 aluminum alloy in 0.5 M H_2SO_4 in the absence of citric acid (Fig. 2a) show fluctuations of the current, directly related to the formation and destruction of the passive layer.

These fluctuations of the current are due to constantly occurring processes of formation and

dissolution of defects on the surface of the alloy, which indicates its electrochemical instability in the studied corrosion medium. Due to the instability of the passive layer, it is partially destroyed over time and anodic oxidation and current increase occur in the corresponding sections.

After the addition of 0.0025 mM citric acid to the studied corrosion medium, a slight decrease of the current at the end of the measurement was observed. As the citric acid concentration increases from 0.0050 до 0.01 mM, the value of the current decreases significantly and the citric acid exhibits its inhibition efficiency. The corrosion parameters, including the open circuit potential (E_{OCP}), corrosion current (I_{CORR}), inhibition efficiency (η) and

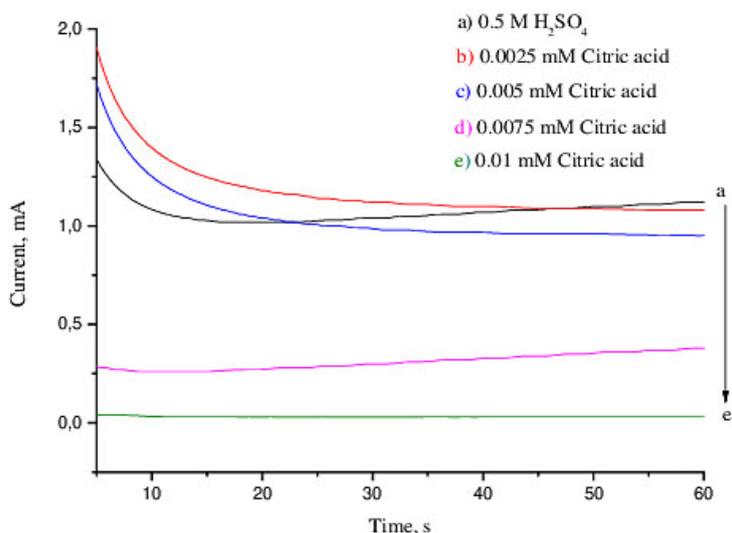


Figure 2. Chronoamperometric curves of the EN AW 2024 aluminum alloy in 0.5 M H_2SO_4 in the absence and presence of citric acid

Table 1. Corrosion parameters of the EN AW 2024 aluminum alloy in 0.5 M H₂SO₄ in the absence and presence of citric acid

| c (mM) | E _{ocp} vs Ag/AgCl (V) | I _{corr} mA/cm ² | η % | θ |
|--------|---------------------------------|--------------------------------------|-------|--------|
| 0 | -0.580 | 1.12 | - | - |
| 0.0025 | -0.580 | 1.08 | 3.57 | 0.0357 |
| 0.0050 | -0.570 | 0.96 | 14.28 | 0.1428 |
| 0.0075 | -0.560 | 0.38 | 66.07 | 0.6607 |
| 0.01 | -0.540 | 0.04 | 96.42 | 0.9642 |

surface coverage (θ) of the aluminum alloy EN AW 2024 in 0.5 M H₂SO₄ in the absence and presence of citric acid, are given in Table 1. The obtained data illustrate that the magnitude of the corrosion current decreases significantly with increasing the citric acid concentration (1,12 mA cm² in the absence of an inhibitor and 0.04 mA cm² in the presence of 0.01 mM citric acid), probably due to the formation of a barrier film on the surface of the alloy. At the same time, the inhibition efficiency increases along with the citric acid concentration and reaches the maximum of 96.42% at 0.01 mM citric acid.

Since the magnitude of the current is proportional to the corrosion rate, it follows from the values of the corrosion parameters in Table 1 that the corrosion rate decreases with increasing the citric acid concentration.

The decrease in the corrosion rate is due to the strong complex-forming properties of the Al³⁺ ions and the formation of chelate complexes (Hidber et al 1996, Katoh et al., 1968, Powell et al., 1996)].

The inhibitory mechanism of the citric acid is probably due to its adsorption on the metal surface (Solmaz., 2008) and the chemical reaction between the citric acid and the Al³⁺ ions, resulting in formation of a tetrahedral complex compound. The chelate complex is thermodynamically stable, and the aluminum cation in it is much less reactive than the free Al³⁺ cation, which prevents the destruction of the metal.

CONCLUSIONS

The inhibition efficiency of citric acid on the corrosion of the aluminum alloy EN AW-2024 in a sulfuric acid solution was studied. The inhibition efficiency increases along with the citric acid concentration, while the magnitude of the corrosion current decreases. The obtained data give the opportunity for successful use of citric acid as an eco-friendly corrosion inhibitor for the EN AW-2011 aluminum alloy in 0.5 M H₂SO₄.

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