

ELECTROCHEMICAL BEHAVIOUR OF ALUMINUM ALLOY EN AW-2024 IN CITRIC ACID

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ABSTRACT

The electrochemical behaviour of the aluminum alloy EN AW-2024 in 0.05 M citric acid has been studied at different values of the pH, by the methods of the open circuit potential and chronoamperometry. The results show that with the increase in the pH of the medium, the values of the E_{ocp} of the studied alloy deviate in a more negative direction. The values of the magnitude of the current of the EN AW-2024 alloy in a 0.05 M solution of citric acid at pH 2 and 12 are the highest, due to which a higher risk of corrosion exists with them.

Keywords: corrosion, aluminium alloy, citric acid, electrochemical techniques.

AIMS AND BACKGROUND

The first applications of aluminum and its alloys in food industry date back to the beginning of the 20th century, when they were initially used for manufacturing brewing equipment and household utensils, and later went deeper and were used to make equipment for factories, food containers and many more. Their wide use in this industry is due to a number of valuable properties of aluminum, such as good thermal conductivity (7–12 times higher than the one of the steels), good possibility to press and draw, and last but not least, aluminum is not toxic. In most cases of contact with food, it does not react and does not change the taste of the food or its appearance. Alcohol, liqueur and wines make an exception, and in these media, aluminum is susceptible to corrosion. At room temperature it is stable in dilute or highly dilute organic acids such as acetic acid, but destroyed in formic, oxalic and chloroacetic acids¹.

The literature review shows that there is a lack of sufficient data on the electrochemical behaviour of aluminum alloys in organic acids, contained in a number of food products. One of them is citric acid ($\text{C}_6\text{H}_8\text{O}_7$), which is a weak organic acid, found mainly in citrus fruits. It is a natural preservative, used to add a sour taste to foods and drinks. It finds application also in medicine, textile and food industry and

due to its wide use, it is of interest to study the corrosion behaviour of aluminum and its alloys in citric acid. In the scientific literature, there are few studies related to the corrosion of aluminum and its alloys in citric acid²⁻⁴.

The aim of this paper is to study the electrochemical behaviour of the aluminum alloy EN AW-2024 in 0.05 M citric acid at pH values from 2 to 12.

EXPERIMENTAL

Materials and methods. Aluminum alloy EN AW-2024 with a composition (mass %) of 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 balance of Al was used for the corrosion studies. Measurements were performed in 0.05 M citric acid (Fluka). The Mettler Toledo laboratory pH meter (Five Easy) was used to determine the pH of the medium. Appropriate pH values (from 2 to 12) were achieved by adding small amounts of NaOH and a very small amount of HCl to the solution. All solutions were prepared with double-distilled water.

Electrochemical measurements. Electrochemical measurements were carried out using a Palm Sens portable electrochemical workstation (Palm Instruments, BV, The Netherlands) in a three-electrode cell – a working electrode of the studied aluminum alloy, an auxiliary electrode of platinum and a reference electrode of saturated Ag/AgCl. All studies were performed at room temperature. The working electrode had an area of 1 cm², the rest of the electrode surface was varnished.

Prior to the electrochemical measurements, the working electrode was immersed in the corrosion medium for 15 min. The open circuit potential (OCP) of the working electrode was recorded as a function of time for 600 s.

RESULTS AND DISCUSSION

Open circuit potential (OCP). The EN AW 2024 aluminum alloy electrode was immersed in 0.05 M citric acid and the OCP values were measured over time until a steady state was reached. When comparing the potential-time curves of the studied aluminum alloy, it was found that the behaviour of the alloy at pH 2, 4 and 6 differs from that at pH 10 and 12.

Figures 1 and 2 show the potential-time curves, illustrating the two types of behaviour. The obtained results show a change in the surface of the alloy during the immersion period in citric acid at the different pH values of the medium.

The results for the cases of immersion in citric acid with pH 2, 4, and 6 (Fig. 1) show that initially the E_{OCP} value shifts in a positive direction, which is due to passivation of the alloy surface. Then the E_{OCP} values remain relatively constant throughout the study, which is probably due to a rapid formation of an oxide layer on the alloy surface.

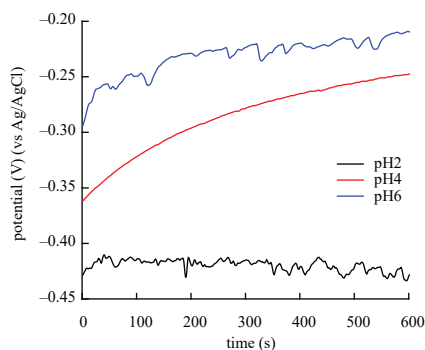


Fig. 1. Open circuit potential of aluminum alloy EN AW 2024 in 0.05 M citric acid at pH 2, 4 and 6

The shape of the potential-time curves in the citric acid solution with pH 10 and 12 (Fig. 2) shows a rapid shift of the potential in the negative direction in a relatively short time (30–40 s). This may be due to a relatively strong dissolution of the oxide layer formed before the immersion in the considered solution, as well as to the passive layer formed during OCP, and/or dissolution of the metal in places with structural defects in the oxide layer.

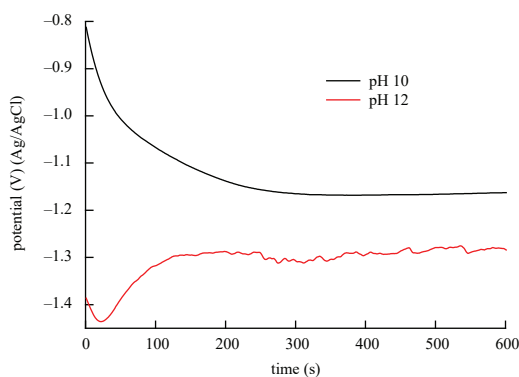


Fig. 2. Open circuit potential of aluminum alloy EN AW 2024 in 0.05 M citric acid with pH 10 and 12

It can be noted that the E_{OCP} values of the studied EN AW 2024 alloy in a citric acid solution at pH 10 and 12 are more negative than the E_{OCP} values at pH 2, 4 and 6, which, in turn, is one of the prerequisites for a higher corrosion risk for the alloy.

Chronoamperometric measurement (Chronoamperometry experiment). Chronoamperometric curves of aluminum alloy EN AW 2024 in 0.05 M citric acid at pH 2, 4 and 6 (Fig. 3) show constant fluctuations of the current, directly related to the formation and destruction of the passive layer. At pH 2, the current value (1.5 mA) is significantly higher compared to that, at pH 4 (4.3 μA), and at pH 6 (7.5 μA). At pH 2, the concentration of the hydrogen ions is higher and the dissolution of aluminum is under electrochemical control – a cathodic reaction of reduction of H^+ goes (release

of hydrogen gas), and an anodic reaction of aluminum oxidation (destruction of the alloy and passage of aluminum in the form of Al^{3+} into the solution).

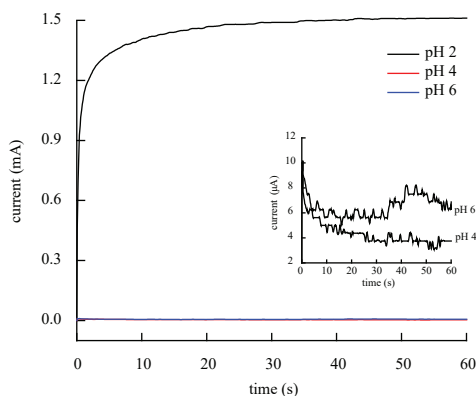


Fig. 3. Chronoamperometric curves of aluminum alloy EN AW 2024 in 0.05 M citric acid at pH 2, 4 and 6

At pH 4 and 6 the current decreases, probably due to the formation of the passive layer on the surface of the alloy at these pH values.

Depending on the pH of the medium, different complex ions (H_2Cit^- , HCit^{2-} and Cit^{3+}) can be present in the citric acid solution⁵, and therefore several reactions are possible when the aluminum surface is in contact with the citric acid. As a result of the interaction between the citric acid and the aluminum ions, a tetrahedral complex compound is formed, in which the aluminum cation is more stable and less reactive than the free aluminum cation. Most probably, at pH 4 and 6 these processes play an essential role and the formed chelate complex prevents the metal from destruction, by which the lower values of the current can be explained.

The chronoamperometric curves of the aluminum alloy EN AW 2024 in 0.05 M citric acid at pH 10 and 12 (Fig. 4) show that as the pH value increases from 10 to 12, the magnitude of the current increases and at pH 10 it is 0.1 mA, while at pH 12 – 0.7 mA.

The high value of the current at pH 12 is probably related to a strong destruction of the aluminum alloy, which takes place by an electrochemical mechanism – release of hydrogen and dissolution (oxidation) of the aluminum alloy in the form of aluminate ions AlO_2^- or $\text{Al}(\text{OH})_4^-$ ions⁶.

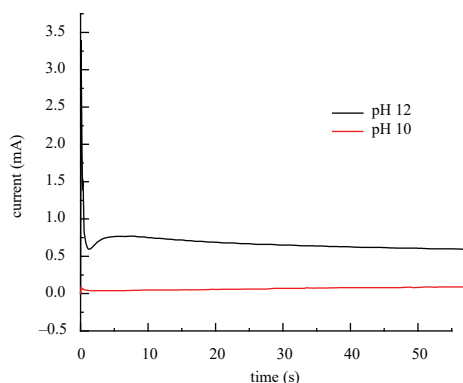


Fig. 4. Chronoamperometric curves of aluminum alloy EN AW 2024 in 0.05 M citric acid at pH 10 and 12

CONCLUSIONS

The electrochemical behaviour of the aluminum alloy EN AW-2024 in 0.05 M citric acid at different pH values was studied by the methods of the open circuit potential and chrono amperometry. The results show a deviation in the E_{OCP} values of the studied alloy in a more negative direction with an increase in the pH of the medium. At pH 2 and 12, higher values of the corrosion current were established, which is associated with a strong destruction of the alloy and with a higher corrosion risk at these pH values of the medium.

ACKNOWLEDGEMENTS

The author would like to thank the Research and Development Sector at the Technical University of Sofia for the financial support.

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Received 5 April 2023

Revised 15 May 2023