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Comparative study on the Corrosion Behavior of Aluminum Alloy 2011 in Different Acidic Media

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Abstract. Electrochemical study, aiming at comparing the corrosion resistance of aluminum alloy 2011 in three different acid solutions (H_2SO_4 , HCl and HNO_3) has been carried out by means of employing cyclic voltammetry, open circuit potential and a digital microscope. Potentiometric technique has been applied to determine the corrosion behaviour of the alloy in the three acid solutions and to study its passivity over time. The metal surface morphology has been studied using a digital microscope. The obtained results indicate that the aluminum alloy 2011 corrodes to a greater extent in a hydrochloric acid solution than it does in a nitric and sulphuric acid solution. The results from the potentiometric tests show the formation of more stable passive films in the sulphuric than in the nitric and hydrochloric acid solution.

INTRODUCTION

Aluminum alloys are materials of great technological importance, finding application in a number of industries such as automotive, aerospace and chemical industry. Their wide use is due to a number of valuable properties such as low weight, high strength, hardness and ability to form an oxide protective layer of Al_2O_3 . This oxide layer forms spontaneously on the surface of the aluminum alloys in contact with aqueous solutions or air, though it can also be formed by anodic polarization, which increases its thickness [1-5]. The chemical resistance of the protective layer determines the corrosion behaviour of aluminum and its alloys. The nature (pH) of the corrosive medium, its composition, concentration, temperature and other parameters are essential for the rate of corrosion [6]. Certain mechanical or chemical influences can also lead to either removal or loosening of this layer, thus enhancing the extent of corrosion of the aluminum alloys. For example, the presence of aggressive ions, such as chloride ions, activates the corrosion process, disrupts the stability and integrity of the passive layer [7].

EXPERIMENTAL STUDY

Electrochemical measurements

The measurements were performed using samples, made of the following types of aluminium alloy 2011. The experimental samples were mechanically cleaned, washed in a detergent for five minutes, then rinsed with distilled water and dried.

The electrochemical measurements were carried out using a computer-controlled electrochemical workstation PalmSens (Palm Instruments, BV, The Netherlands), equipped with the software PS Trace 2.1. A three-electrode configuration was employed, with the aluminum alloy 2011 acting as a working electrode, a platinum panel - as the auxiliary electrode, and a saturated Ag/AgCl electrode as a reference. All tests were performed at $\pm 25^\circ$ C. Before the measurements the working electrode was immersed in the test solution (0.1M HCl, 0.1M H₂SO₄ and 0.1M HNO₃) for 15 min. The open-circuit potential (OCP) curves were recorded at the time of immersion of the alloy Al 2011 in the corresponding test solution, while the cyclic voltammetry was taken after 15 minutes stay in the acid. The exposed area of the working electrodes was 1 cm². The cyclic voltammetry measurements were initiated from -1.0 V to 1.5 V vs. Ag/AgCl, KCl with a potential scan rate of 0.010 V/s and then reversed with the same scan rate until one complete cycle was formed. The open-circuit potential (OCP) of the working electrode was recorded as a function of time for 1200s.

Surface analysis

The structure of the corroded surface of the aluminum alloy 2011 was investigated by a digital microscope (Digi Micro Scope 2,0M Pixels).

RESULTS AND DISCUSSION

Electrochemical measurements

The open circuit potential (OCP) variations of the aluminum alloy 2011 in different acid solutions, are presented in figure 1.

When comparing the values of the open-circuit potential OCP of the 2011 aluminum alloy samples it can be noticed that it occurs at a more negative value in 0.1M HCl (-0.590 V/Ag/AgCl) compared to 0.1 M H₂SO₄ (-0.450 V / Ag / AgCl) and 0.1M HNO₃ (-0.125 V/Ag/AgCl), which may be associated with the easier dissolution of the surface oxide layer under the action of the chloride ions.

In 0.1M HCl, the OCP value of the alloy quickly reaches a steady state and remains relatively constant during the measurement period, compared to the other two acids. In 0.1M HNO₃, the OCP value of the investigated alloy gradually decreases over time, which is evidence of corrosion, occurring on the alloy surface throughout the measurement period.

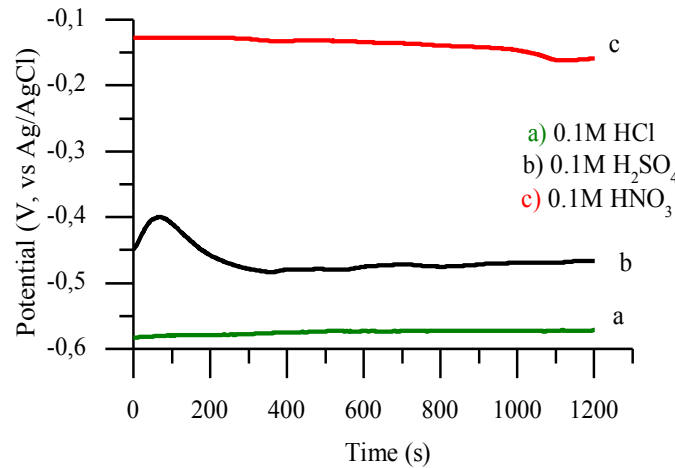


FIGURE 1. Open circuit potential of aluminum alloy 2011 in a) 0.1M HCl, b) 0.1M H₂SO₄ and c) 0.1M HNO₃ reference electrode Ag/AgCl, KCl

Initially, the OCP value in 0.1M H₂SO₄ deviates in a positive direction, reaching a maximum plateau in the first 100s, after which the value decreases with time and reaches a steady state. This indicates an initial rapid passivation process, in which an oxide layer is formed, and then dissolved [8].

Figure 2 shows the cyclic voltammograms CV of the 2011 aluminum alloy, taken in the presence of 0.1M solutions of HNO₃ and H₂SO₄. In the anode course of the cyclic voltammograms, availability of a peak (P₁) is observed at a potential of about -0.020 V/Ag/AgCl in 0.1M H₂SO₄ and at a potential of about 0.180 V/Ag/AgCl in 0.1M HNO₃. This peak has been described in other similar studies and is attributed to basic intermetallic inclusions in AlCuMg alloys, soluble in acidic media [9].

From the presented curves it can be seen that the aluminum alloy 2011 oxidizes at different rates in 0.1M HNO₃ and H₂SO₄. The value of the current in 0.1M HNO₃ (1.5 mA) increases linearly with increasing the potential, while in 0.1M H₂SO₄ the magnitude of the current is almost twice lower (0.6 mA) and it remains constant with increasing the potential, which is probably due to passivation of the alloy surface. The low value of the corrosion current in 0.1M H₂SO₄ suggests better corrosion resistance of the aluminum alloy in this acid [10]. The value of the current in 0.1M

HCl (above 18 mA) is the highest compared to the other two acids and also increases linearly with increasing the potential. Since the magnitude of the current is proportional to the corrosion rate, it follows that the following descending order can be constructed from the corrosion resistance of the alloy 2011 in acidic media: 0.1M H₂SO₄, HNO₃ and HCl. In addition, in 0.1M H₂SO₄ the value of the potential is by about 35 mV higher than that of the alloy Al 2011 in 0.1M HNO₃, i.e., the anodic dissolution of the studied alloy in 0.1M H₂SO₄ starts harder.

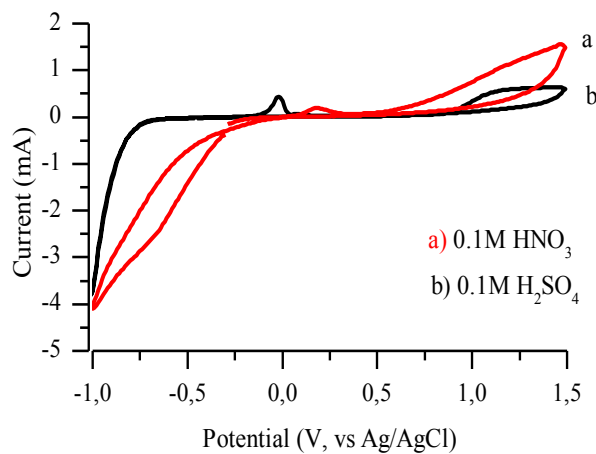


FIGURE 2. Cyclic voltammograms of Al 2011 0.1M in solution of HNO₃ and H₂SO₄, $v = 0.010$ V/s reference electrode Ag/AgCl, KCl

In the reverse (cathode) scan, the reduction of aluminum ions is at a potential of about -0.3V (vs Ag/AgCl) in 0.1M HNO₃ and at a potential of about -0.8V (vs Ag/AgCl) in H₂SO₄.

The comparison of the electrochemical behavior of the 2011 aluminum alloy in the three studied acids shows that the oxide layer on the surface of the 2011 alloy in 0.1M H₂SO₄ has better protective properties than that, in 0.1M HCl and 0.1M HNO₃.

Surface analysis

Figure 3 presents the micrographs on the surface of the aluminium alloy 2011 at conditions, used in the present work.

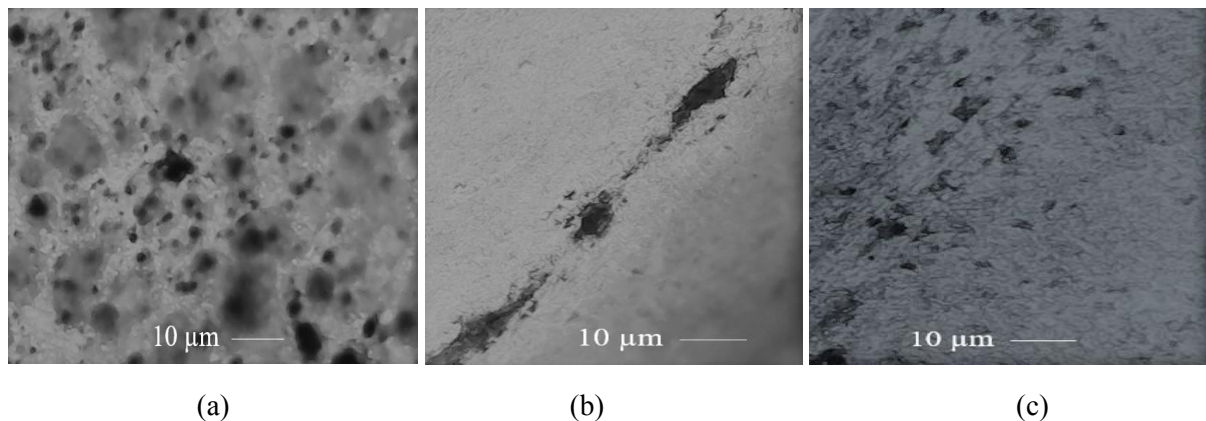


FIGURE 3. Micrography of aluminium alloy 2011 surface immersed in 0.1M (a) HCl, (b) HNO₃ and (c) H₂SO₄ by a digital microscope.

The surface morphology of the Al samples was examined after 768h of immersion into media of different solutions of acids. Pits can be seen on the surface of the specimens, corroded in 0.1M HCl. Fig.3a indicates that the aluminum alloy undergoes pitting corrosion in these media. Pitting is more extensive and localized in the solutions of 0.1M HCl than it is in H₂SO₄ and HNO₃. Under the extended immersion period of 768h in a medium, containing nitrate ions, the pits on the surfaces were found to be elongated and bigger in size, as shown in the micrograph in Fig.3b. The micrographs of the samples immersed in 0.1 M solutions of H₂SO₄ - Fig. 3c - show very few pits on the surfaces as compared to the samples, immersed in 0.1M HCl.

CONCLUSION

When comparing the values of the open circuit potentials (OCP) of samples of the aluminum alloy 2011 in the three studied acids it is noticed that in 0.1M HCl the OCP value is the most negative, compared to 0.1M HNO₃ and 0.1M H₂SO₄, which is a prerequisite for easier dissolution of the surface oxide layer and a higher risk of corrosion.

The cyclic voltammogram of the aluminum alloy 2011 in 0.1M solution of H₂SO₄ shows the lowest magnitude of the current, which implies better corrosion resistance of the studied alloy, compared to its corrosion resistance in 0.1M HCl and 0.1M HNO₃.

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