

Impact of the anionic composition parts of conventional acids on the galvanostatic anodic polarization of AA2024-T3 alloy

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Abstract: Nowadays, the aluminum alloys find various applications, such as production of lightened aircrafts, automobiles and stationary (i.e. pipelines) transport facilities, as well as high voltage, large distance energy transmission via aluminum cables. Recently, various sensor elements and alternative energy sources have been developed on the basis of anodized aluminum details. Furthermore, some aluminum alloys are widely used for packaging of nutrition products and soft drinks. However, the reliable use of these alloys demands elaboration of advanced surface treatment methods, in order to supply satisfactory durability and reliability of the respective aluminum products. In this sense, the present study provides information on the influence of the alloying elements and the anionic components of four commonly used acids: HNO_3 , H_3PO_4 , H_2SO_4 , and HCl on the AA2024-T3 surface morphology during galvanostatic anodic polarization in the corresponding media.

Keywords: AA2024-T3 surface morphology, anodic polarization, acidic electrolytes

INTRODUCTION

In order to ensure durability, reliability and a long service life, the aluminum details and constructions usually undergo multiple coating procedures in the respective industrial factories, hence obtaining multilayered coating systems [1 - 3]. In this sense, the preliminary surface treatment appears to be indispensable technological stage prior to the respective coating deposition and subsequent painting. In this sense, various techniques either for direct surface treatment or as intermediate coating deposition stage can be found in the literature. The purpose of the treatment in each of the tested acids in the present study depends on its anionic activity. For instance, the nitric acid is used for growth of passivation barrier oxide layer [4], and chemical surface modification [5, 6], whereas the phosphoric acid is employed in the intermediate stage of primer layer modification by phosphation [7, 8], applied generally on steels. Finally, the sulphuric acid alone [9], or in combination with H_3PO_4 is examined for anodizing of pure aluminum, in order to obtain regular porous oxide structures [10 - 12], with potential use as alternative energy generators [12], or even sensor elements [13 - 15].

Regardless of its reinforced mechanical properties, the AA2024-T3 alloy possesses enhanced susceptibility to local corrosion phenomena [16], such as pitting and intergranular corrosion due to the presence of various alloying elements with different electrochemical activities, relative to the basic aluminum matrix. Indeed, during the metallurgical post-treatments the intermetallic inclusions precipitate mainly in forms of S-phase Al_2CuMg , and θ -phase Al_2Cu [17], accompanied by secondary precipitates, such as: $\text{Al}_{20}(\text{Cu},\text{Fe},\text{Mn})_5\text{Si}(\text{Al}_8\text{Fe}_2\text{Si})$, $\text{Al}_{10}(\text{Cu},\text{Mg})$, $(\text{Al},\text{Cu})_{93}(\text{Fe},\text{Mn})_5(\text{Mg},\text{Si})_2$, $\text{Al}_3(\text{Cu},\text{Fe},\text{Mn})$, on the grain boundaries of the basic Al-matrix [18 - 20].

The variety of the intermetallic inclusions in the AA2024-T3 alloy and the distinguishable anionic activities of the respective acids have predetermined the aim of the present study, namely to investigate the impact of the anionic components of four common acids on the surface morphology of AA2024-T3 specimens, during galvanostatic anodic polarization at uniform conditions.

EXPERIMENTAL

Plates of AA2024-T3 alloy were anodized using galvanostatic anodic polarization regime, with applied current density of 15 mA cm^{-2} , for 2 hours in 15% wt. solutions of the mentioned acids (nitric, phosphoric, sulfuric and hydrochloric acid). A hydrodynamic regime was employed with solution agitation at 150 revolutions per minute, at room temperature. Each anodization process was carried out at least two times. Prior to the

respective anodic polarizations, all the metallic specimens underwent preliminary surface treatments, following a procedure, described in previous studies [6].

The obtained coatings were observed by Scanning Electron Microscopy. The SEM images were obtained using a scanning electron microscope TESCAN, SEM/FIB LYRA I XMU, at appropriate resolutions. Besides, in order to determine the depth of the acidic impact, cross-sectional observations were done as well. The dimensions of the investigated metallic plates are given in detail (Fig. 1).

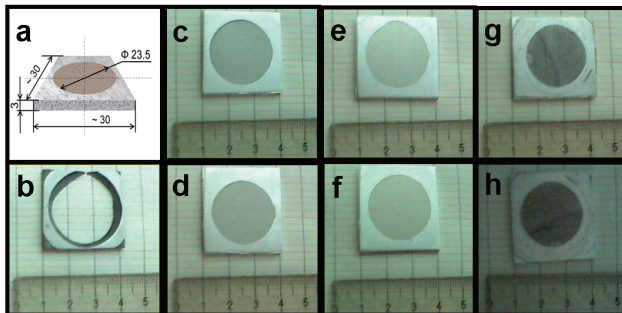
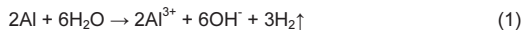


Fig. 1. Schematic view (a) and photographs (b – h) of the investigated metallic substrates: (b) – specimen treated in hydrochloric acid, (c, d) –in sulfuric acid, (e, f) –in phosphoric acid and (g, h) – in nitric acid, respectively

RESULTS AND DISCUSSION

The distinguishable impacts of each acid become evident yet from Figure 1. The complete dissolution of the specimen, treated in hydrochloric acid was achieved for about 30 minutes, remarking the extreme aggressive activity of the chlorine anions against this aluminum alloy. The photographs of the samples treated by sulfuric (b, c) and phosphoric (d, e) acids look relatively similar, but the differences between the activities of these acids become clear at the SEM observations, commented below. The specimens, treated by nitric acid (g, h) were darker in color due to the re-deposition of black metallic oxides, especially CuO, originated from the intermetallic inclusions, such as S-phase and θ -phase, and MnO₂ from the less active intermetallics.

The SEM images have rendered more clear images on the respective acid activity, as is well demonstrated in Fig. 2. The SEM topographical image of the comparative specimen (position a), submitted only to the conventional preliminary treatment procedure, reveals randomly distributed corrosion pits, originated from the predominant Al-dissolution adjacent to the intermetallic inclusions (IMI). On the interfaces between the intermetallic particles, and the surrounding Al-matrix grains galvanic elements appear, and cause Al-anodic dissolution (Eq. 1), as a result of the cathodic activity (Eq. 2) of the respective IMI.



Equation 2 also shows an additional local increase of the alkalinity around the IMI. These processes are accompanied by the simultaneous corrosion currents, which flow through the interface boundaries between the intermetallics and the neighboring Al-matrix grains. Also, the native oxide film is much more disrupted on these interface boundaries, due to the higher surface tension in these areas. Figure 2 represents high and low resolution (in the insets) SEM images of AA2024-T3 specimens after conventional preliminary treatment (a), according to ref. [6] and subsequent anodic polarization in sulfuric (b), phosphoric (c) and nitric (d) acids.

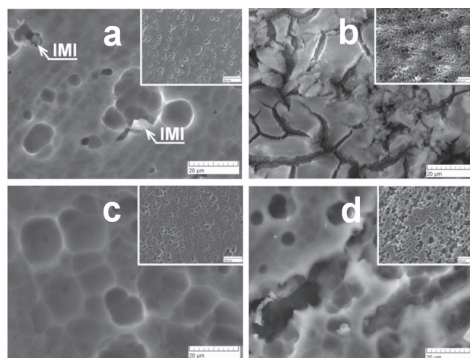
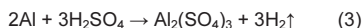
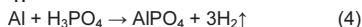


Fig. 2. SEM topographical images of the investigated surface, after the corresponding surface treatments: (a) - referent AA2024-T3 specimen; (b) - anodized sample in H_2SO_4 ; (c) - in H_3PO_4 and (d) - in HNO_3

The area, treated by H_2SO_4 has shown a highly cracked, continuous film, probably containing some $\text{Al}_2(\text{SO}_4)_3$, which covers the entire treated zone. Besides, the low resolution image in the inset of position (b), reveals a multitude of vertical channels throughout the entire film. The occurrence of these channels is an evidence for the hydrogen generation as a result of the irreversible formation of $\text{Al}_2(\text{SO}_4)_3$, according to reaction 3:



In contrary, in both cases of H_3PO_4 and HNO_3 no additional adhesive salt film was observed. The comparison between the insets of the referent surface (a) and the H_3PO_4 treated one (c) reveals a more frequent occurrence of corrosion pits. The anodic polarization in H_3PO_4 enhances the activity of the less active IMI, such as the mentioned in [18 – 20] and leads to a larger number of corrosion pits. However, the direct interaction between the $(\text{PO}_4)^{3-}$ and the aluminium, beneath the oxide layer defects, is a completely irreversible chemical process of passivation by formation of insoluble Al-phosphate, and proceeds following reaction 4:

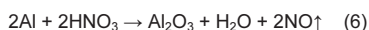


The competition between the electrochemical dissolution processes promoted by the applied external electric current, and the purely chemical process of aluminium phosphate formation leads simultaneously to two distinguishable features of the phosphate treated area, in comparison to the referent one: (1) – more frequent occurrence of corrosion pits, as a result of the electrical current applied, and (2) – lower depth of the corresponding pitting. The latter feature is a consequence of the uniform dissolution of the surface oxide layer. Consequently, during the anodic polarization in the presence of phosphate anions two different processes occur, as well: electrochemical dissolution adjacently to the less active IMI and partial chemical conversion of the oxide layer by formation of insoluble aluminium phosphate (Eq. 5):

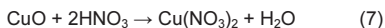


The resulting conjunction of these contradictive processes leads to the combination of larger number of corrosion pits and their relatively lower depth.

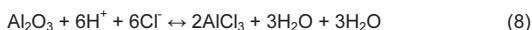
The most aggressive attack observed by the SEM images belongs to the nitric acid. It results in a sponge-like surface morphology, regardless of the passivating role of this acid described in the literature (eq. 6):



Obviously, another mechanism is involved in the sponge-like surface formation. It includes an intensification of the electrochemical corrosion processes of selective dissolution of the Al-grains around the IMI, described by Matter et al. [21]. This process happens, due to the uncovering of the cathodic Cu-containing precipitates, present in the alloy:



Namely, this chemical process of oxide layer dissolution suppresses the inactivation of the most active cathodic IMI, such as the S-, and θ - phases. By this manner, these cathodic areas remain uncovered and consequently active during the entire polarization process (i.e. 2 hours). This, namely, is the reason for the peculiar, tremendously irregular, sponge-like surface morphology obtained in the case of HNO_3 . Nevertheless, the most severe attack against the AA2024-T3 is registered for the hydrochloric acid. For about 30 minutes, this acid has dissolved a 3 mm thick metallic plate, so that for 2 hours, this acid is able to dissolve more than a 1.2 cm thick aluminum sheet, converting it to AlCl_3 (Eq. 8), or Keggin like $\text{Al}_x\text{Cl}_y\text{OH}_z$ products, as is proposed by Kozhukharov et al. [22].



In order to achieve a more complementary image about the depth of the anodic polarization assisted acidic attack, cross sectional observations were performed, as well. Figure 3 shows the cross sectional SEM images, acquired for sulfuric (a), phosphoric (b) and nitric (c) acids.

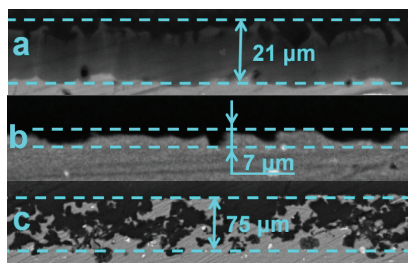


Fig. 3. SEM cross-sectional images of AA2024-T3 specimens, treated in the respective acids

The cross-sectional images (Fig. 3) completely confirm the topographical images in Fig. 2. The polarization in H_2SO_4 leads to formation of an Al sulfate film around the grain boundaries, whereas the nitric acid causes deep penetration (75 μm) via selective dissolution of the Al-grains adjacent to the IMI. The surface treated by the phosphoric acid looks smooth, but it is not clear whether it leads to efficient passivation or to an uniform chemical dissolution.

CONCLUSIONS:

The present research investigation has shown that the anionic part of the respective acids has a great importance for the mechanisms and reactions involving the alloying elements during anodic polarization of AA2024-T3 aircraft alloy. The Cl^- ions cause extreme attack, dissolving 1.2 cm alloy for 2 hours. The nitric acid causes selective dissolution, enhancing the electrochemical processes of the corrosion attack. The sulfuric acid leads to formation of a continuous film, including $\text{Al}_2(\text{SO}_4)_3$. The specimens, treated by the phosphoric acid possess the smoothest surface, but it is not clear whether it is a consequence of alloy passivation by formation of insoluble AlPO_4 or uniform dissolution of the surface layers.

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