

Correlation between preliminary pretreatments and the behaviour of AA-2024 – aluminium alloy in 3.5% NaCl model corrosive medium

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Abstract: *The object of research in the present work is to follow how the surface preparations influence over the electrochemical behavior of Aircraft alloy AA2024. Preliminary, the corresponding samples have passed various mechanical, chemical treatments or combinations of them. Subsequently, the electrochemical behavior of pretreated samples in model corrosive media, consisted on 3.5% of NaCl was evaluated. The evaluation methods were based on electrochemical measurements as Linear Polarization and Electrochemical Impedance Spectroscopy. In addition, they were carried out after different exposure times, which permit to determine the rate of impact of the corrosive species over the metal surface. Optical and Atomic Force Microscopy were applied for additive observations, in order to obtain completed image for the processes and the nature of the corrosive impact, and its dependence on the method of preliminary preparation applied. After collection and analysis of the data obtained, it was found that the preliminary surface preparations possess a clear effect over the superficial morphology and the parameters of the corrosion process.*

Key words: *Preliminary treatments, AA2024 aluminium alloy, model corrosive medium 3.5%NaCl*

INTRODUCTION

Aluminum alloy 2024-T3 is a heat-treatable high strength alloy that is used for fuselage and structural material in aircraft design due to combination of remarkable mechanical properties and light weight [1-3]. At the same time, the inclusions which render their contribution to its enhanced mechanical properties, promote higher susceptibility to local corrosion attack. The latter is a consequence of defects which present as ruptures, cracks and lower thickness of the oxide layer over the superficial intermetallics. In addition, these inclusions form Galvanic couples, which fertilize the solubility of some of the alloy's components. The contradiction between the significant mechanical strength, and susceptibility to local corrosion have stimulated intensive research activities [1, 3, 4], which basic task is to improve the corrosion resistance of the alloy.

The corrosion mechanism of particularly 2024-T3 alloy is investigated and described in detail by Lamaka and ect [5], and Zheludkevich ect [6]. By other hand, large varieties of preliminary treatments prior the basic test procedures are described by different authors. Some of them proposed only mechanical preliminary treatment before rest research activities [7, 8], while others [9 – 12] suggest various techniques for preliminary chemical treatments. Simultaneously, a lack of reliable explications about the reasons or substantiations for the selection of one or other method or conditions of preparation is presented.

In this context, the aim of the present work is to compare several kinds of preliminary treatment, and to judge their impact over the superficial morphology and the parameters of the AA2024-alloy corrosion process. As a positive effect, the work will initiate further researches, which should lead to determination of the optimal conditions for preliminary treatment.

ENPERIMENTAL

Preliminary treatments

The samples, subjected to electrochemical evaluations, were divided into tree groups. Each one of these groups passed one of the below described procedures of preliminary treatment (table 1).

Table 1: Description of the procedures of the preliminary treatments

Group	Degreasing	Mechanical treatment	Chemical treatment
G1	Ethanol Ether 1:1; (5 min), room temperature	-----	-----
G2	Ethanol Ether 1:1; (5 min), room temperature	Polished by SiC emery paper, 500 – 1200 grids, subsequently	-----
G3	Ethanol Ether 1:1; (5 min), room temperature	Polished by SiC emery paper, 500 – 1200 grids, subsequently	Etched for 15 minutes at 60 °C in solution of NaOH (0.01M) in distilled water

Electrochemical tests

All electrochemical measurements were done by three-electrode electrochemical cell with volume equal to 100ml. The exposed circle zones of the samples, with surface area equal to 0,64 cm², were served as working electrodes (WE). Platinum Winkler's electrode and Ag/AgCl-standard electrode served as counter reference electrode and (CE and RE), respectively. The cell was connected to Autolab P/GSstat, 30/2 supported by Frequency Responce Analyser (FRA-2), during the measurements. Two basic electrochemical methods for characterizing of the corrosion processes were used, as follows: Electrochemical Impedance Spectroscopy (EIS), and Linear Voltammetry (LVA). The experiments are carried out at the following conditions:

EIS: Frequency's interval from 10⁵ – to 2x10⁻² Hz, with perturbation signal ±10 mV, according to Open circuit potential (OCP). LVA: Potential's interval, from (OCP – 0.050V) to (OCP + 0.500V), with scan rate equal to 0,001V/s. In addition, superficial observations, of the samples, after the corresponding preliminary treatments were done, in square areas with 49.5µm of linear size in resolution of 256 points per line, using AFM microscope Easyscan 2, product of Nanosurf (Switzerland).

RESULTS AND DISCUSSION

Electrochemical Impedance Spectroscopy

As could be seen from fig. 1, Bode plots reveal that the maximum of phase shift appears at larger frequency range, and consequently the oxide layer possesses different thickness and structure. At the lowest frequencies range, the logarithm of the total impedance for G1 possesses the highest values, and consequently at this particular case, the charge transfer reaction is much more hindered than in the rest of cases.

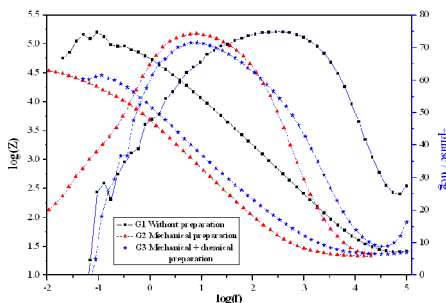


Fig. 1. Bode plots for after 2 hours of exposure in 3.5% NaCl solution for AA2024, passed different approaches of preliminary treatment

Consequently, the oxide layer of G1 is much thicker and distinguishable than those of the rest samples. This phenomenon could be explained when the high temperature of the industrial process are taken in account. Thus, the oxide layer grown after removing of the superficial metal from the alloy is much thinner, because of the room temperature of the laboratory's treatments.

Linear Voltammetry: Figure 2 shows that sample G2 has the most negative value of the corrosion potential, and the highest current at the anodic branch. Both of these features of its curve could be explained, having in account the particular removal of the oxide layer, and simultaneously larger denuded intermetallic areas, enhancing electrochemical corrosion, by forming of electrochemical couples [4].

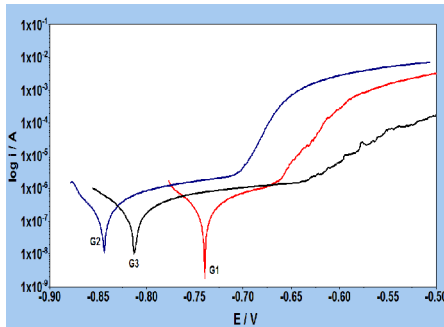


Fig. 2. Polarization curves 2 hours of exposure in 3.5% NaCl solution for AA2024, passed different approaches of preliminary treatment

The current of the anodic branch of sample G3, is almost two orders of magnitude lower than the rest two samples, which could be explained by the particular removal of Mg from the S-phases (Al_2CuMg) [4] by the etching treatment.

Sample G1: For the needs of the present article, this group serves as base of comparison with the rest two groups. That is the reason that this group will be not subjected under detailed description in the present work. Fig. 1 demonstrates the overlapping of OCP and R_p , and their development with the exposure time. Schematically, its superficial morphology is shown on fig. 4, position- a, respectively.

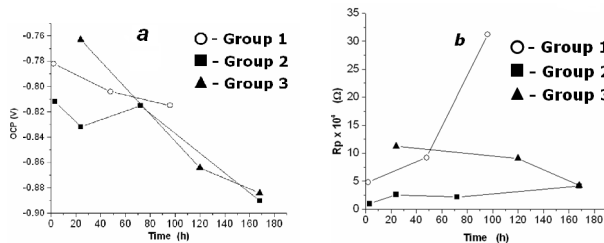


Fig. 3. Development of the average mean values for: (a) - Open circuit potential and (b) - Polarization resistance.

Sample G2: The polish surface treatment leads to lower initial value for R_p , coupled with more negative value of OCP, compared with those of G1 (see fig. 3). The initial R_p of G2 is $0.965 \times 10^4 \Omega \cdot \text{cm}$, while the G1 possesses $4.80 \times 10^4 \Omega \cdot \text{cm}$. The corresponding values of initial OCP for G1 is -0.782 V , and OCP for G2 is -0.812 V . The changes of both of

these parameters look surprising, because it should be rather expectable that the polishing decreases the surface area. The surface area decreasing could lead to increase of the resistance, combined by decrease of the number of exposed superficial inclusions, such as S-phases. Reasonable explication of both of these facts is that the polishing of G2 is performed at room temperature. As consequence, the thick oxide layer was removed due to this procedure. It is well known, that in the metallurgic industry the Al-alloys are hot rolled. At the industrial process of their production, they obtain thick oxide protective layer. The sample G2 has lost this thick layer during polishing at laboratory's conditions. Afterwards, the new layer formed immediately after polishing is thinner, and more defective, because it is formed at room temperature. Consequently, R_p of G2 is lower, than of G1. In addition, the lower thickness of the oxide layer leads to higher exposed areas of the intermetallic inclusions. By other words, it means larger intermetallic area appeared at the alloy's surface. The consequence should be higher superficial Mg inclusions, which lead to more negative values of OCP (see fig. 4 position b).

Regarding sample G3: It reveals the opposite features of G2, at the initial exposure period. Figure 3-a clearly demonstrates that G3 possesses the most positive value of OCP at the initial exposure period (-0,763V). In addition, position b of this figure shows that the highest value of R_p also belongs to this sample ($11,28 \times 10^4 \Omega$). Both of the initial values are evidence, that the chemical treatment has the opposite influence of the mechanical, and also it is more significant. These facts could be explained, assuming that Mg is already not presented on the modified surface after chemical treatment. The alkaline solution could cause expense of all Mg from the metal surface, because of the processes which pass during the preliminary superficial treatment, due to the intensive attack by OH^- , originated by the corresponding NaOH solution [4]. These ions attack the aluminium from both of S-phase inclusions, and the surrounding Al-matrix. The Al-dilution leads to exposition of larger zones of S-phase, and consequently leads to increase of Cu surface, exposed to the solution. Larger cathodic zones, appeared by the above mentioned processes, provoke more intensive O_2 – reduction, (over Cu-cathodic parts) which leads to fertilization of the respective anodic process (dissolution of Mg and Al). The latter process additively increases of OH^- concentration. Namely, these ions fertilize the Al-dissolution. As a result this process passes with liberation of electrons, which are expending during the cathodic OH^- generation processes. Thus, when AA2024 is in contact with NaOH solutions, the dissolution of Al, and Mg is even higher than in the case of pure metallic Al. The reason is the presence of Cu- cathodic areas, which act as promoters of this process (see fig. 4, position c). Consequently, the Mg is completely expended, and it is not represented on the alloy's surface, even before the electrochemical tests.

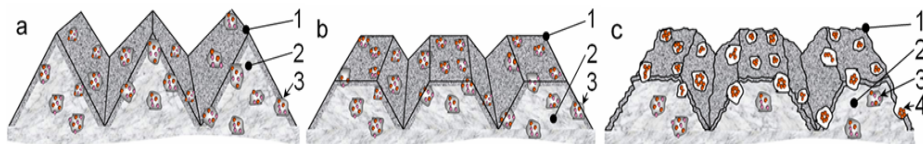


Fig. 4. Schematic views of superficial morphologies of the samples; a – as received; b – after polishing; c – after polishing and etching

Superficial observations

The images obtained via AFM (see fig. 5); undoubtedly confirm the simple models of the preliminary treated surfaces. The "as received" sample reveals clearly laminar superficial structure (fig. 5a), while the mechanically treated one represents nodular morphology (fig. 5b). The third-one represents concave forms, which are originated from the partial dissolution of Al, preferably in the S-phases, where the oxide layer is more

defective and thinner. In that case, after the initial dissolution of Al from the inclusions, posterior dissolution of Al from the surrounding part of the matrix occurs.

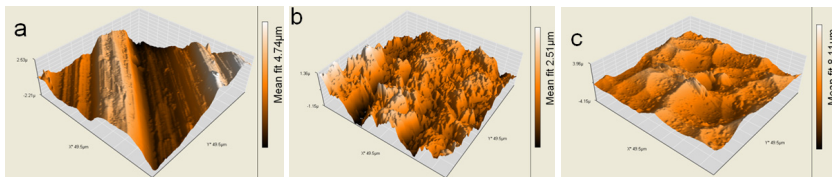


Fig. 5. AFM of superficial morphologies of the samples; a – as received; b – after polishing; c – after polishing and etching

CONCLUSION

On the base of the experiments carried out the following conclusions could be extracted:

- 1 – The preliminary treatment has significant influence over the features, and further behaviour of the alloy in corrosive medium.
- 2 – Mechanical treatment decreases the values of R_p , because of destruction of the thick oxide layer, obtained during the hot rolling technology.
- 3 – Chemical treatment by NaOH leads to disappearance of Mg from the superficial composition of the alloy. Consequently, it leads to its chemical and topological surface modification, making it noble for next technological treatment.

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Докладът е рецензиран.