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CORROSION TESTING OF AN AL-ZN-MG-CU ALLOY AFTER DIFFERENT HEAT TREATMENT REGIMES BY THE APPLICATION OF ELECTROCHEMICAL METHODS

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Abstract: *The corrosion tendency in the 7000 series aluminium alloys changes depending on the content of alloying elements, thermal and thermo-mechanical treatments, etc. An alloy of this type applied in the production of weapons and military equipment has been investigated by applying different electrochemical methods. A degree of the precipitation hardening (aging) of the alloy has been evaluated by measuring its electrical resistivity. The corrosion potential measurements ($E_{corr.}$) gave information about the distribution of the alloying elements between the solid solution and the precipitation phases. The polarization measurements, performed in the 0.5 M NaCl solution, have shown a more positive value of the pitting potential ($E_{pit.}$) and a greater corrosion resistance for the two-step aged alloy. The electrochemical impedance spectroscopy (EIS) has also shown that the two-step aged alloy has better corrosion properties (a higher value of polarization resistance, R_p, and a lower value of capacitance, C_{dl}) comparing to the one-step aged alloy. These results enable a deeper insight into the effects of both heat treatment and alloying elements, primarily copper, on the corrosion resistance of the tested alloy.*

Key words: *aluminium alloys, precipitation hardening, corrosion, electrochemical methods, EIS*

1. INTRODUCTION

Papers should be written in English language. Papers should be typed using Microsoft Word for Windows; A4 page format (210x297mm).

Although the 7000 series (Al-Zn-Mg-Cu) aluminium alloys have maximum strength, they are prone to corrosion and stress corrosion cracking (SCC). However, the tendency of these alloys to corrode in localized forms changes depending on the content of alloying elements as well as on mechanical, thermal and thermo-mechanical treatments [1-6]. The precipitation hardening of the 7000 series aluminium alloys is achieved by the segregation of GP zones that are transformed through the intermediate η' phase into the equilibrium phase $MgZn_2$ [7-10]. The maximum strength is obtained in the structure where there is a mixture of GP zones and η' precipitates. In the state of maximum strength, however, the 7000 series alloys are prone to SCC. In the over-aged state, these alloys are characterized with a good resistance towards both SCC and exfoliation corrosion. In the partially over-aged state, the alloys show a slightly lower resistance to SCC and high resistance to exfoliation corrosion, while in the state of maximum strength the alloys are sensitive to both types of corrosion [7, 10-13].

The 7000 series aluminium alloys not intended for welding contain copper. The addition of copper has a beneficial effect on hardness, by increasing the volume fraction of the hardening precipitates. It was found that copper is incorporated in GP zones, making them more stable even at higher temperatures [7, 14]. Also, copper atoms replace zinc atoms in the hardening precipitate η' ($MgZn_2$), particularly at temperatures above 150°C [14, 15], making the precipitate nobler. All this provide conditions for the increased resistance of these alloys to the localised forms of corrosion.

The 7000 series aluminium alloys in the over-aged state achieved by two-stage aging are characterized by high resistance to corrosion and SCC. However, the aging time is relatively long, and the hardness of the alloys is significantly reduced (15% compared to the state of maximum hardness). Based on the results reported in [16, 17], a two-stage aging process, performed in a much shorter period of time, was proposed. The tensile properties of the alloy in this state remain unchanged when compared to the state of maximum hardness. The electrochemical and corrosion characteristics of the alloy in the state of maximum hardness as well as in the state after a two-stage aging process were investigated in this study.

2. EXPERIMENTAL PART

2.1. Material and heat treatment

The chemical composition of the tested aluminium alloy is given in Table 1.

Table 1. Chemical composition of the Al-Zn-Mg-Cu alloy (wt.%):

Zn	Mg	Cu	Mn	Cr	Zr	Al
7.2	2.15	1.46	0.28	0.16	0.12	Rest

The heat treatment of the alloy was performed in accordance with the following regimes:

– Homogenization annealing at 460^{o}C/1h, quenching in water at room temperature, followed by precipitation hardening at 120^{o}C/24h (one-stage aging, indicated in this paper with TA).

– Homogenization annealing at 460^{o}C/1h, quenching in water at room temperature, precipitation hardening at 100^{o}C/5h, and then at 160^{o}C/5h (two-stage aging, indicated in this paper with TB).

2.2. Measurement of electrical resistivity

The measurements were performed on the TA and TB samples. The method of measurement is included in ASTM B193 standard. Electrical resistivity was measured by a microohmmeter in accordance with the manufacturer's instructions. The value of the measured electrical resistivity (ρ) was recalculated into electrical conductivity (χ=1/ρ), as well as into the IACS% factor, using the equation:

$$IACS = \frac{\chi}{\chi_{Cu}} \cdot 100\% \tag{1}$$

Where: χ is the value of the electrical conductivity of the tested alloy, and χ_{Cu} is the electrical conductivity of pure copper (58.34 MS/m).

2.3. Corrosion potential measurements

Corrosion potential measurements of were performed on the TA and TB samples. The samples (working electrodes) were degreased by ethanol and then placed in the electrochemical cell with a saturated calomel electrode (SCE) as a reference electrode. The measurements were performed in the 3.5 wt. % NaCl solution. The changes in the corrosion potential were monitored at room temperature, in the presence of atmospheric air, during 60 min.

2.4. Polarisation measurements

The cathodic and anodic polarization curves of the TA and TB samples were obtained using the GAMRY Reference 600 Potentiostat / Galvanostat / ZRA in deaerated 3.5 wt. % NaCl at room temperature. A three-electrode cell arrangement was used in the experiments. The working electrode was the aluminium alloy sample, placed in a special holder. The counter electrode was a platinum mesh with a surface area considerably greater than that of the working electrode. The reference electrode was the SCE. A potential sweep rate of 0.5 mV s^{-1} was applied after the constant open circuit potential (OCP) was established (up to 30 min).

2.5. Electrochemical impedance spectroscopy measurement

For electrochemical impedance spectroscopy (EIS) measurements, the TA and TB samples were exposed to 3.5 wt. % NaCl for 48 h. A three-electrode cell arrangement was used as in the polarization measurements. The EIS data were obtained at the open-circuit potential using the GAMRY Reference 600 potentiostat / galvanostat / ZRA. The impedance measurements were carried out over a frequency range of 100 kHz to 10 mHz using the 10 mV amplitude of sinusoidal voltage. The impedance spectra were analyzed using the GAMRY Elchem Analyst fitting procedure.

3. RESULTS AND DISCUSSION

The tested aluminium alloy, aged according to the TA and TB regimes, is characterized with the appropriate structure, mechanical properties, corrosion resistance, electrical conductivity and electrochemical properties. Based on these indicators, the tendency of the alloy to localized corrosion was evaluated.

3.1. Electrical resistivity

The obtained results have shown that the TB sample has larger conductivity (36.71 IACS%) than the TA sample (32.56 IACS%) and the alloy sample immediately after homogenization annealing (29.65 IACS%). A supersaturated solid solution with a high concentration of vacancies was obtained after quenching. The fields of elastic strains around vacancies cause dissipation of electrons, so lower values of conductivity are obtained [18]. During the aging process, the clusters of zinc were formed at first, and after that the GP zones that grow gradually and transform themselves into the half-coherent phase η'. The elastic strains around the GP zones and the η' phase caused more electron dissipation, so low values of conductivity are obtained. With the appearance of the stabile η phase during two-stage aging, elastic strains decrease, and the alloy conductivity increases. The formed precipitates are getting coarser (their dimensions increase while their number decreases), and conductivity still increases with a prolonged time of aging (approximately 42 IACS% after 24 h). However, the mechanical characteristics of the alloy (hardness) decreased [7], and the resistance to exfoliation corrosion and the resistance to SCC are lowered as well. For a large number of the 7000 series Al alloys, the criteria of electrical conductivity for SCC and exfoliation corrosion can be found [19].

3.2. Electrochemical properties

In the test solution, at a constant temperature, the corrosion potential value of the tested aluminium alloy depends on the content of the alloying elements in the solid solution [13, 19]. As the content of alloying elements varies during the aging process, the value of the corrosion potential is changed in a predictable way due to the precipitation of certain phases.

The results presented in Figure 1 show that the corrosion potential has a higher value after two-stage (TB), than after one-stage aging (TA). This can be related to the kinetics of the precipitation hardening. The alloy in the TA thermal state has a larger concentration of zinc (more negative) in the solid solution, which results in a more negative value of the corrosion potential (E_{corr} = -795 mV). In the case of the TB thermal state (partially over-aged state), the enlargement of the straightening precipitates occurs at the expense of impoverishment of the solid solution in zinc, magnesium and copper. This is in accordance with the measurements of electrical conductivity. In this case, the solid solution has a more positive corrosion potential (E_{corr} = -775 mV) due to depletion in zinc and magnesium. The formed precipitates after two-stage aging have become more electrically positive than the precipitates after one-stage aging. The atoms of aluminium and copper are incorporated in ($MgZn_2$), replacing to some extent the atoms of zinc and forming $Mg(AlCuZn)_2$. It was shown [20, 21] that the content of copper in this precipitate is approximately 20 at. %. The electrochemical and corrosion characteristics of different precipitates and intermetallic compounds existing in commercial precipitation-hardened aluminium alloys have been studied [13, 20-27].

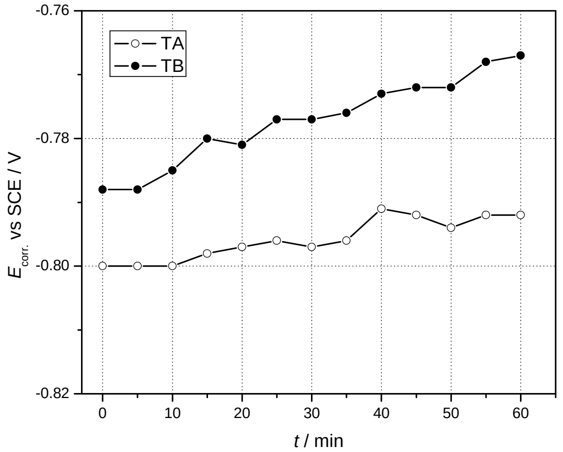

Figure 1. Time dependence of E_{corr} of the aluminium alloy in the TA and TB state.

The polarization curves of aluminium alloy after one-stage and two-stage aging are shown in Figure 2. It can be seen that the alloy after two-stage aging has a more positive value of the pitting potential (E_{pit} = -775 mV) with regard to the one-stage aged alloy (E_{pit} = -800 mV). Also, the value of the corrosion current density for the alloy in the TB state is lower than for the alloy in the TA state, whereas the anodic and cathodic curves are shifted to the lower current density for the alloy in the TB state.

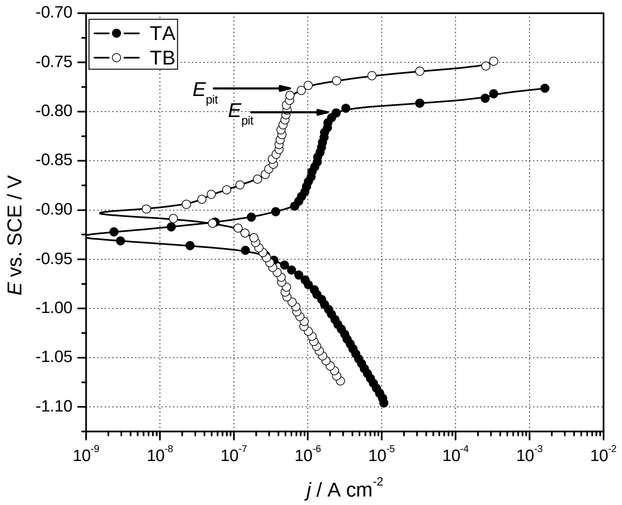

Figure 2. Polarisation diagrams of the aluminium alloy in the TA and TB states in deaerated 3.5 % NaCl at room temperature.

In the 7000 series aluminium alloys, pitting occurs due to the local dissolution of the matrix or to the dissolution of intermetallic compounds [28]. The intermetallic compounds containing Cu and Fe are cathodic with respect to the matrix and promote the matrix dissolution while Mg-rich intermetallics are anodic with respect to the matrix and dissolve preferentially. The explanation for the alloy's behaviour after two-stage aging probably lies in the fact that the difference in the electrode potentials between the intermetallic compounds and the solid solution has been decreased as well as the electrode potential difference between the precipitates and the solid solution. It was noticed that two pitting potentials exist, with the appearance of the second pitting potential at current densities higher than 1 mA cm^{-2} [21, 29, 30]. The nature of these pitting potentials is considered in details [17, 29, 30]. In the 7000 series aluminium alloys with similar copper content as in the tested alloy, the equalization of corrosion and the pitting potential occurs in the presence of oxygen [21].

The Nyquist complex plane plots of aluminium alloys in TA and TB state obtained by the EIS measurements are shown in Figure 3. The alloys in both thermal states show almost ideal Nyquist semicircle after one hour in 3.5 wt. % NaCl. The polarization resistance, R_p, of the alloy in the TA state is lower (which corresponds to a higher corrosion rate) with regard to R_p of the TB state (Table 2). After 24 h, a so-called Warburg's diffusion tail has appeared on the Nyquist diagram for the TA sample. A similar diffusion tail has appeared for the TB sample, also, after 48 h. However, the value of R_p was higher for the TB sample that corresponds to a lower corrosion rate.

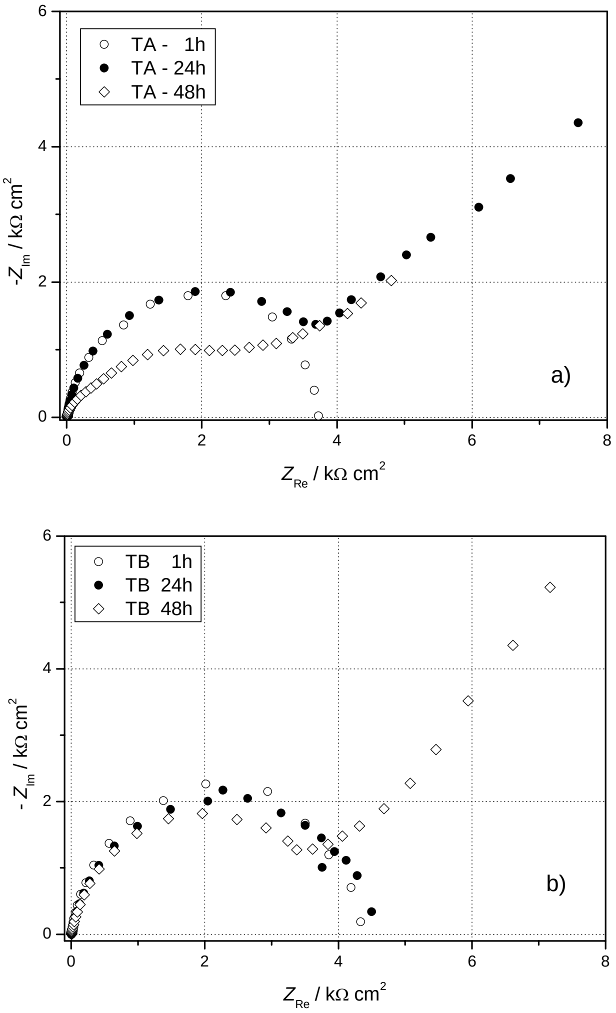

Figure 3. Nyquist plots of the aluminium alloys in 3.5 wt.% NaCl at room temperature after a) one-stage aging (TA), b) two-stage aging (TB).

At the surface of the tested samples a layer of dark corrosion products has been formed, probably consisting of aluminium hydroxide $Al(OH)_3$ [21]. The nature and conditions of corrosion products formation have been considered [21, 28].

The values of corrosion potential, E_{corr}, pitting potential, E_{pit}, polarization resistance, R_p and double layer capacitance C_{dl} of the alloys in both aging state are presented in Table 2. A significant increase in the double layer capacitance capacitance (C_{dl}) and a decrease in the polarization resistance (R_p) with time indicate lower corrosion characteristics of the alloy after one-stage aging. However, it should be kept in mind that the electrochemical conditions on the tip of a pit or a stress corrosion crack (decrease in pH, increase in the concentration of chloride ions, voltage drop, etc.) are significantly different from the electrochemical conditions at the alloy surface with a free access of electrolyte. Corrosion and electrochemical characteristics of different aluminium alloys with and without protective coatings have been investigated by EIS technique [31-34].

Table 2. The values of corrosion potential, E_{corr}, pitting potential, E_{pit}, polarization resistance, R_p and double layer capacitance, C_{dl}, for the aluminium alloys in 3.5 wt.% NaCl at room temperature after one-stage aging (TA) and two-stage aging (TB).

t (h)	Thermal State TA			
	E_{corr} (mV)	C_{dl} (μF cm^{-2})	R_p (kΩ cm^2)	E_{pit} (mV)
1	-795	12.5	3.86	-800
24	-775	22.7	4.18	-
48	-750	118.2	2.84	-
	Thermal State TB			
1	-770	7.9	4.33	-775
24	-755	28.7	4.56	-
48	-740	28.9	4.06	-

4. CONCLUSIONS

The corrosion resistance of a high strength 7000 series (Al-Zn-Mg-Cu) aluminium alloy was tested. The alloy was subjected to the standard one-step aging process as well as to a new two-step aging process. The testing was performed using several techniques that gave useful data related to the electrochemical behaviour and the structural state of the tested alloy. It has been shown that the alloy after two-step aging had considerably higher resistance to localized corrosion compared to the alloy after one-step aging.

The electrical conductivity measurements enabled the estimation of the alloy structural state, i.e. the type and degree of precipitation. The resistance to the localized types of corrosion (exfoliation, pitting and SCC) depends on the presence of different phases developed during the aging process.

The value of the corrosion potential depends on the distribution of the alloying elements (Zn, Mg, Cu) in the solid solution and in the precipitated phases such as the $Mg(AlCuZn)_2$ phase. The alloy in the TB state has more positive corrosion potential, compared to the TA state. Both these results and the results of the electrical conductivity measurements allow better understanding of the precipitation process in the tested alloy.

The polarization measurements have shown that the anodic and cathodic polarization curves of the alloy in the TB state were shifted to the lower values of the current density, and a more positive value of the pitting potential was achieved. The results of electrochemical impedance spectroscopy indicated better corrosion characteristics (higher values of polarization resistance and lower values of double layer capacitance) of the two-stage aged alloy compared to the one-stage aged alloy.

All the results presented enable a deeper insight into different forms of localized corrosion of the aluminium alloys after one-step aging as well as a new two-step aging.

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