

CORROSION RESISTANCE OF ALUMINIUM ALLOY USED IN THE AUTOMOTIVE INDUSTRY

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Abstract

The results of corrosion resistance of aluminum alloy 5754 used as a construction material in the automotive industry has been presented in the paper. The samples of aluminum alloy were exposed to acetic salt spray, containing copper chloride as a corrosion initiator, according to ISO 9227: 2012 and the following methods: linear polarization, potentiodynamic cyclic voltametry according to PN-EN ISO 10271: 2012 and impedance spectroscopy according to PN-EN ISO 16773: 2009. In order to correlate the tests as a corrosive environment at temperature 50 °C acetic salt solution was used. Obtained results have been developed in terms of corrosion mechanism, extension and type of acetic corrosive environment. It has been found that tested material is not resistant to corrosion in a acetic acid corrosion environment. The literature research shows that aluminum alloy 5754 has good corrosion resistance properties which are required for many structural components in the automotive industry.

Keywords: Corrosion resistance, salt chamber, electrochemical research, impedance spectroscopy, aluminum alloy

1. INTRODUCTION

Automotive materials can have an important impact on the environment. The use of lightweight materials can help reduce vehicle weight and improve fuel economy. Automotive manufacturers are making efforts to reduce vehicle weight which may lead to a gradual decrease in the amount of steel and cast iron used in vehicle and the corresponding increase in the amount of alternative materials like aluminum and plastics. Recently, development effort to apply wrought aluminum is becoming more active than applying aluminum castings. Forged wheels have been used where the loading conditions are more extreme and where higher mechanical properties are required. Wrought aluminum is also finding applications in heat shields, bumper reinforcements, air bag housings, pneumatic systems, sumps, seat frames, side impact panels, to mention but a few. Aluminum alloys have also found extensive application in heat exchangers [1, 2].

Aluminum is actually a very active metal meaning that its nature is to oxidize very quickly. When oxygen is present in the air, soil or water aluminum instantly reacts to form aluminum oxide. The aluminum oxide layer is chemically bound to the surface and it seals the core aluminum from any further reaction. Aluminum's oxide film is tenacious, hard and instantly self-renewing. Therefore, aluminum has excellent corrosion resistance in a wide range of water and soil conditions because of the tough oxide film that is formed on its surface. Although aluminum has a huge advantage when compared to other metals, it is not always completely impervious to corrosion. Its protective oxide layer can become unstable when exposed to extreme pH levels. When the environment is highly acidic or basic, breakdown of the protective layer can occur and its automatic renewal may not be fast enough to prevent corrosion [3].

Pitting corrosion is defined as localized accelerated dissolution of metals that occurs as a result of a breakdown of the protective passive film on the alloy surface. In an aggressive environment, typically containing halide ions, pits initiate and grow in an autocatalytic manner, where the local environment within the pits becomes

more aggressive because of decrease in pH and increase in chloride concentration, which further accelerates the pit growth. The pit growth usually takes a variety of shapes, simply divided into isotropic and anisotropic groups. If are anisotropic and are called microstructural orientated pitting. The variation in pit shape could mainly depend on the microstructure of metals or alloys such as alloy composition and aspect ratio of grains. Even though there are some differences in pitting corrosion between stainless steels and Al alloys, for example hydrogen bubbles form at the active pit surface in Al alloys, both materials basically share a similar mechanism. In general, pitting corrosion involves three stages: pitting initiation, metastable pitting, and pitting growth. Addition of alloying elements can significantly increase the mechanical strength of Al alloys by precipitation hardening. Due to the limited solubility of many elements of aluminium, alloying elements are often distributed not only in the Al solid solution but also in fine precipitates and coarse intermetallic particles. It plays a crucial role in corrosion behaviour of Al alloys. The micro galvanic coupling between the matrix and intermetallic particles is generally believed to result in pitting corrosion and further develop intergranular cracking into the deep structure of Al alloys. Zn, Mg and Cu as alloying elements have different effects on the pitting potential, on passivation potential and dissolution kinetics of Al alloys. Thus there was no influence of Mg on pitting corrosion, little or no effect on the repassivation potential by changing the dissolution kinetics [4, 5].

The results of corrosion studies of alloy 5754 gat. PA11 were presented. The objective of the study was to evaluate the alloy Al-Mg for corrosion resistance tests. The alloy according to literature has average tensile strength, high fatigue strength and high resistance to industrial corrosion atmosphere and marine condition. Thus, it is used in many industries for example: shipbuilding, chemical, food, nuclear, building and automotive industry.

2. TESTED MATERIAL

The aluminum alloy 5754 (EN AW-5754, PN PA11, ISO AIMg3) was selected for the research in form of sheet-metal, 1000 x 2000 mm size and 1 mm thickness. The chemical composition of tested alloy included: 95.5 % Al, 3.3 % Mg, 0.34 % Fe, 0.23 % Mn, 0.19 % Si, 0.11 % Zn, 0.037 % Cu, 0.029 % Cr, 0.023 % Ti, 0.01 % Ni, 0.01 % Pb. The results were obtained by use of Spectrometer WD-XRF (X-ray fluorescence with wavelength dispersion) ZSX type Promus II, produced by Rigaku company.

The aluminum alloy 5754 was studied for corrosion resistance in salt spray chamber and accelerated electrochemical tests. The material was subject to metallographic assesment (**Figure 1**), hardness measurement by Brinell method according to PN-EN ISO 6506-1:2014 [6] and measurement of surface roughness according to PN-EN ISO 4288:2011 [7] to correlate the corrosion results with the material parameters. The hardness measurements were made in five places. The average values with the standard deviation were calculated. The result presents as follows: 58.2 ± 1.0 HBW 2.5/62.5. The measurements of surface roughness were made in fifteen palces by using contact profilometer with elementary section 0.8 mm and measuring section 4 mm. The average values of *Ra* (arithmetical mean roughness value), *Rz* (mean roughness depth) and *Rt* (total height of the roughness profile) with uncertainty of measurement $\pm 0.02 \mu\text{m}$ were calculated. The results present as follows: *Ra* 0.4 μm , *Rz* 2.5 μm , *Rt* 3.3 μm .

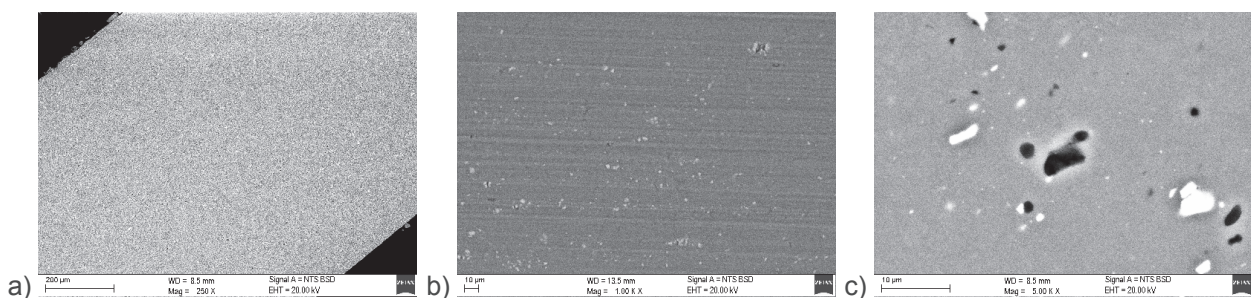


Figure 1 The intermetallic precipitates at SEM microscope magnification a) 250x, b) 1000x, c) 5000x

The analysis of the material in the SEM microscope shows the places with intermetallic precipitates phase (**Figure 1**). The black areas, like in **Figure 1c**, indicate the presence of silicon whereas white areas shows iron and manganese presence. The rest of surface that looks chemical homogeneous contain 1.45 % O, 3.21 % Mg and 95.34 % Al.

3. INVESTIGATION METHOD AND ANALYSIS RESULTS

3.1. Resistance to acetic acid salt spray test - CASS Test

The copper-accelerated acetic acid salt spray test is the method in which an acidified 5 % NaCl solution with the addition of copper chloride and acetic acid is atomized under controlled environment. The test consists in subjecting test specimen (plates 70 x 140 x 1 mm) to continuous operation salt spray produced by spraying solution at temperature 50 °C and pressure 1 bar. The solution concentration of salts were 50 g / l NaCl and 0.26 g / l CuCl₂·2H₂O in deionized water with conductivity lower than 20 μS / cm. The pH of the initial solution was 3.1 by adding of acidic acid. Before conducting the CASS test the corrosivity of the chamber was tested. Thus, the loss of mass of the steel reference specimens (after 24 h of the test average weight loss of the plates under angle 25° was 55 ± 15 g / m²) was checked and amounted to 47 g / m². The determination of the corrosive level of the chamber is designed to check the correct operation of the chamber, the reproducibility and repeatability of test results. In addition, pluviometric constant was fixed at 1.2 ml / h (the collection of salt spray for a minimum 16 h test should be in the range of 1.5 ± 0.5 ml / h). Test specimens of aluminium alloy 5754 have been tested in salt chamber for 144 hours. Plates no. 6.1-6 were removed from the chamber every 24 h. The interpretation of the results was based on visual appearance of plates surface with pitting corrosion. Corrosion results have been presented in **Figure 2**.

The analysis of pitting corrosion was carried out according to PN-EN ISO 11463:2010 [8]. On the surface of plate no. 6.1 pits occur with density 5 x 10⁴ / m² and depth 0.1 mm. Plates no. 6.2-6 show intensive propagation of existing pitting corrosion areas.

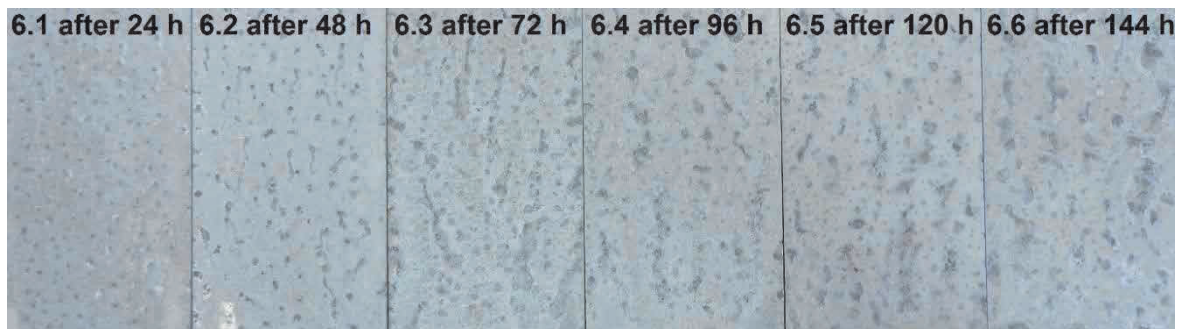


Figure 2 The visual appearance of plates surface with pitting corrosion

3.2. Electrochemical corrosion test

The electrochemical research of corrosion resistance was based on potentiostatic, potentiodynamic and impedance spectroscopy method in acetic acid corrosive solution (5 % NaCl with CuCl₂) oxygenated as a result of free contact with air at 50 °C. The research was done by use of PGSTST302N potentiostat, no. AUT83628 produced by ECO CHEMIE B.V. company. The instrument cooperates with program recording progress of study. The research was carried out in relation to the reference electrode. It was silver / silver chloride electrode (Ag, AgCl/Cl⁻) of + 222.4 mV potential compared to NEW at T = 25°C. The study was conducted by use of linear polarization method (with potential ranging from -0.1 V to 0.1 V, with 1 mA current, scanning rate 0.001 V / s), cyclic voltammetric method (in the range from -1.0 V to 1.6 V potential, scanning rate 0.1 V / s) and impedance spectroscopy (in the range from 10 mHz to 100 kHz frequency, amplitude 20 mV).

The results of research were calculated in Nova 1.7 software. The following parameters, as average of ten measurements, were established: open circuit potential OCP, corrosion potential E_{Cor} , corrosion current density j_{Cor} , corrosion rate V_p and polarization resistance R_p . All parameters were calculated for the electrochemical equivalent 9.08 g / mol, density 2.68 g / cm³ and tested area of surface was calculated individually for each sample. **Table 1** presents the measurement results of corrosion resistance in acetic acid corrosive solution (5 % NaCl with CuCl₂) at 50°C. The example of the polarization curve and potentiodynamic cyclic voltammetric curve in acetic acid solution at 50 °C is presented in **Figure 3**. The analysis of the material after electrochemical corrosion test in the SEM microscope shows **Figure 4**. The products of corrosion that appeared on surface included: 59.8 % Al, 38.14 % O, 1.44 % Mg and 0.62 % Si.

Table 1 The measurement results of corrosion resistance of aluminum alloy 5754 in acetic acid solution

Established parameters	aluminum alloy 5754
OCP (V)	-0.712
E_{cor} (mV)	-704.73
j_{cor} (μ A / cm ²)	288.12
V_p (mm / rok)	3.19
R_p (Ω / cm ²)	31.89

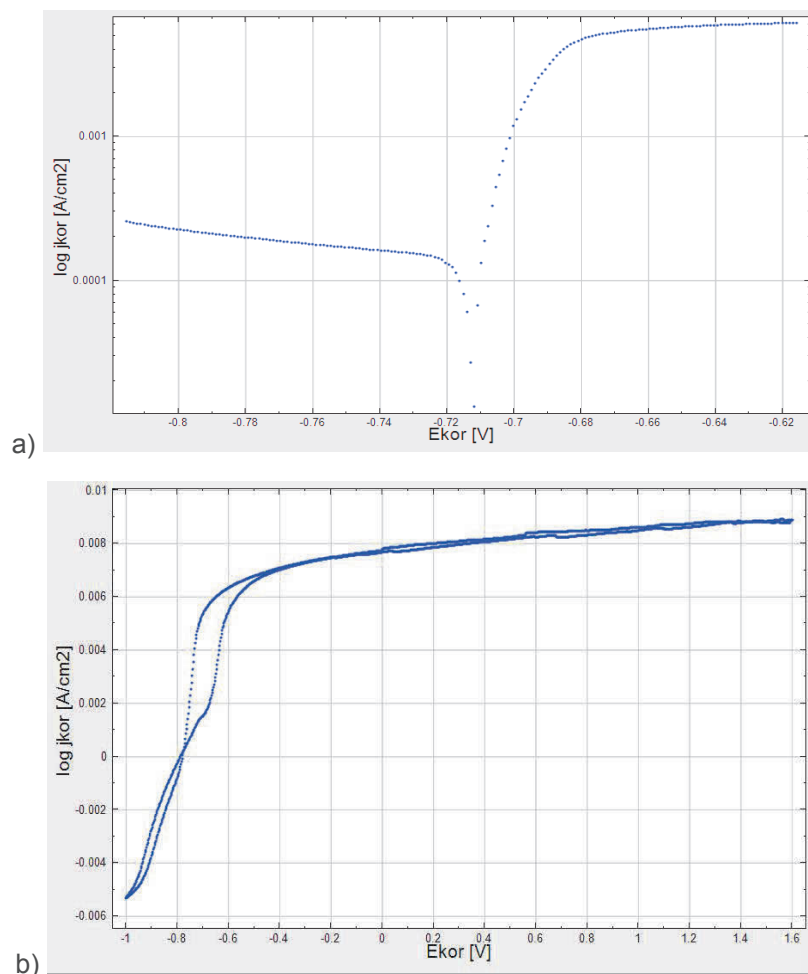


Figure 3 Examples of a) the polarization curve, b) the potentiodynamic cyclic voltammetric curve of aluminum alloy 5754 in acetic acid solution

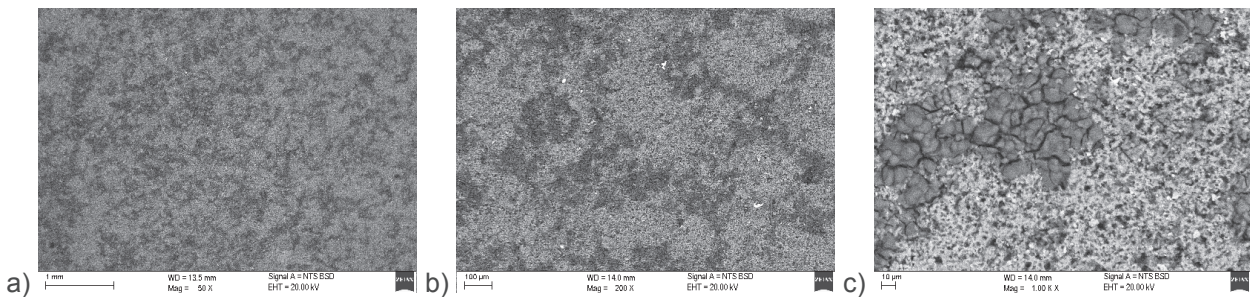


Figure 4 The surface of aluminum after electrochemical test with products of corrosion, magnification a) 50x, b) 200x, c) 1000x

The electrochemical impedance spectroscopy technique (EIS) can provide information about the electrochemical investigation process occurring on the surface of the test sample. The measurements were carried out in the frequency range from 10 mHz to 100 kHz by stimulating the sample with sinusoidal current of 20 mV amplitude. The measurement value during the EIS test is the impedance of the test electrode - sample of aluminum alloy 5754. The impedance is characterized by two values which are presented as the dependence of the real part of Z' impedance and the imaginary part of Z'' impedance (Nyquist diagram). Based on the impedance measurements obtained, parameters have been received: R_p 1.07 Ω / cm^2 (resistance associated with the transfer of charge across the boundary sample of aluminum - acetic acid solution), R_s 5.42 Ω / cm^2 (resistance of acetic acid solution) and CPE 17.4 μF (capacitance of a fixed-phase element associated with the double electrical layer). Substitute electrical system was used to analyze experimental data of corrosion system presented in **Figure 5** and the spectrum impedance for the substitute system is shown in **Figure 6**.

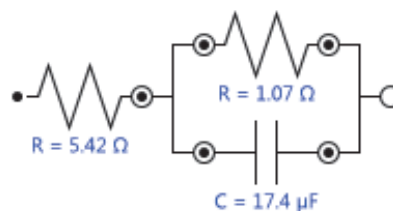


Figure 5 Model of substitute electrical system for combination aluminum alloy - acetic acid solution

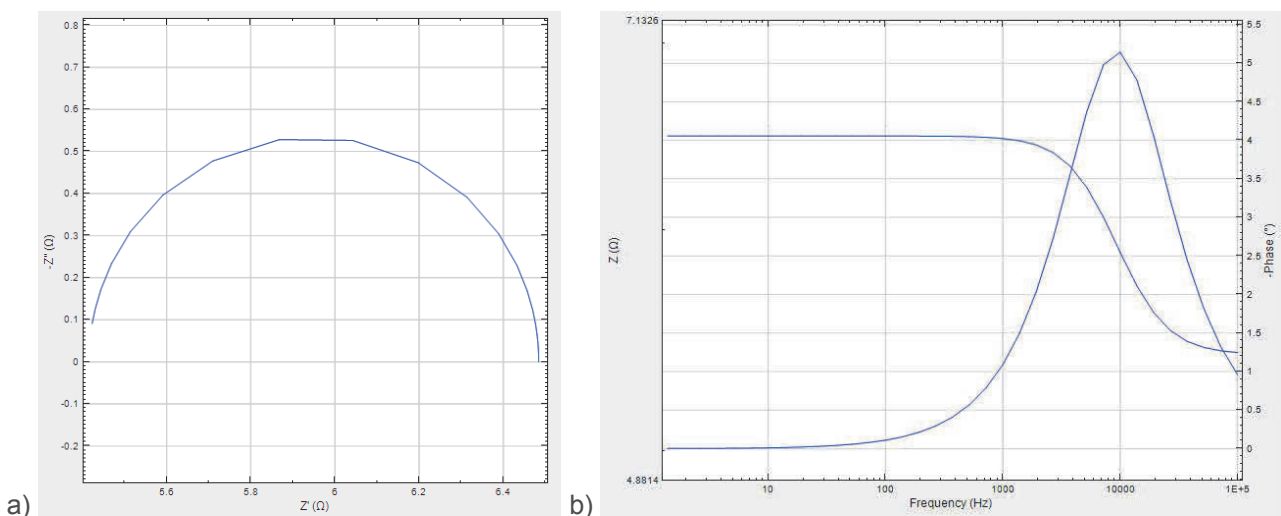


Figure 6 Spectrum impedance for substitute electrical system a) Nyquist diagram, b) Bode diagram

4. SUMMARY AND CONCLUSIONS

Based on the results, it can be concluded that aluminum alloy 5754 tends to produce a passive protective layer which is rapidly dissolved in the acetic acid solution. It is presented in **Figure 3**. The observations confirm the value of corrosion rate in that case amounts to 3.19 mm / year. During corrosion tests the pitting corrosion of aluminum alloy 5754 simultaneous lack of spontaneous repassivation of the formed pits was observed. The intermetallic precipitates such as silicon or iron-manganese were the likely place of pitting corrosion on aluminum plates. Probably, the Cu^{2+} ions attack the intermetallic precipitates that dissolve strongly as a result of electrochemical cell creation.

Matching the electrical substitution system to surface phenomena of aluminum alloy 5754 gives an opportunity to present a description of the corrosion mechanism in contact with corrosive medium as acetic acid solution. The electrical substitution system created in the work consisted of two resistors and a fixed-phase element (**Figures 5, 6**).

To sum up it may be concluded that:

- 1) Aluminum alloy 5754 is not suitable for use in acetic acid environments where copper ions are presented.
- 2) The aluminum alloy 5754 is susceptible to pitting corrosion, under condition, with a tendency to propagate deep into the material and it may lead to the material perforation.

ACKNOWLEDGEMENTS

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