

## Influence of NaCl concentration on pitting corrosion of extruded Al–Mg–Si alloy AA6060

*Extruded Al–Mg–Si alloys (AA6xxx series alloys) are the most common aluminum alloys for structural application due to reliable mechanical characteristics and corrosion properties. Spontaneously formed adherent aluminum oxide film on the surface protects Al and Al-alloys from corrosive attack in neutral media, but in chloride containing solutions, such thin and compact passive film is prone to breakdown.*

*In this study the corrosion behavior of commercial extruded Al–Mg–Si alloy AA6060 was investigated in NaCl solutions of different concentrations using anodic potentiodynamic polarization measurements under deaerated conditions at room temperature. It was shown that sensitivity to chloride attack increase with increasing Cl<sup>-</sup> concentration and depends on cathodic microconstituents in extruded Al–Mg–Si alloy.*

**Keywords:** pitting corrosion, commercial Al–Mg–Si alloy, deaerated NaCl

### 1. INTRODUCTION

Extruded Al–Mg–Si alloys (AA6xxx series alloys) are widely used for different kinds of aluminium products including profiles for structural applications in the automotive industry, sections for architectural applications and tubes for the heat transfer segments [1,2]. The major alloying elements in the heat-treatable 6xxx series are magnesium and silicon. Both elements are required for precipitation strengthening, which is commonly acquired by solutionizing and artificial aging [3-6]. Their recyclability, high strength-to-weight ratio and resistance to corrosion make them more and more used as replacement material for expensive AA2xxx and AA7xxx in aerospace industry and military applications [7].

Oxide passive layers composed of Al<sub>2</sub>O<sub>3</sub>, Al(OH)<sub>3</sub> and AlO(OH) grow spontaneously on Al and Al-alloys and provide good corrosion resistance in highly aggressive environments. However, different thermomechanical treatments applied to achieve required mechanical properties lead to destruction of the protective film so that Al-alloys are liable to suffer from various forms of corrosion, mainly pitting and intergranular attack, depending on the nature of anion in the neutral solution [8]. It is known that halide ions are aggressive for Al alloys. Physicochemical characteristics of the passive layers govern the adsorption of aggressive ions such as Cl<sup>-</sup>, their penetration and accumulation in imperfections of the protective film. Therefore, such processes are considered as one of the triggering factors in the nucleation of pitting [9-13].

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In order to demonstrate the effect of NaCl concentration on pitting corrosion, the object of this study was to obtain the breakdown potential of passive layer by following the anodic polarization behavior of commercial extruded profiles produced from heat treatable Al–Mg–Si alloy.

### 2. EXPERIMENT

#### 2.1. Sample composition and preparation

Extruded products of Al–Mg–Si alloy are commercially available as EN AW6060 and AA6060 [14]. From the hollow quadratic profile shown in Figure 1, the alloy samples for electrochemical measurements were cut into square shaped test plates of 80 x 50 mm and thickness of 2 mm. Investigated 6xxx alloy is characterized by the chemical composition (Al-98.72, Mg-0.45, Si-0.49, Fe-0.21, Mn-0.02); which correlate closely with those generally accepted as suitable one for extruding processes [15-18].

To remove surface contamination before each measurement, specimens were mechanically and chemically treated. The surface of sample was mechanically abraded using emery papers (grade 400, 500, 600 and 1000) on test face and rinsed with distilled water.

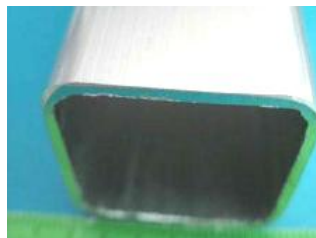


Figure 1 - Commercial hollow profile made of AA6060 alloy

The test plates were subsequently treated by immersion for 1 minute in a solution containing 0.1

mol dm<sup>-3</sup> NaOH at 40 °C, in order to remove the surface oxide layer and eventually incorporated impurities. Immediately after the rinsing in distilled water, the clean specimen was as quickly as possible placed in the electrochemical cell and then subjected to the experimental procedure.

### 2.2. Electrochemical measurements

The corrosive medium was deaerated NaCl solution (with concentration varying between 0.35 wt.% and 5 wt. %). Bubbling of high purity nitrogen (5N) through the electrolyte was performed 30 min before measurements started and subsequently continued (over the solution) during the experiments. All the tests were conducted at ambient temperature (293 ± 1) K and at natural acidity. The pH 5.5 was measured in 3.5 wt.% NaCl solution, and no significant change was noticed by changing the NaCl concentration.

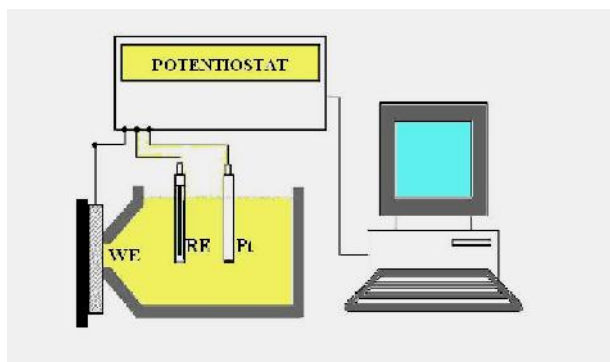


Figure 2 - Scheme of 3-electrode cell used for electrochemical measurements

Three-electrode electrochemical cell shown schematically in Figure 2 was used for the electrochemical testing. A circular section of alloy AA6060 (3.14 cm<sup>2</sup>) was used as the working electrode WE, while commercial Pt-electrode and SCE (saturated calomel electrode) were used as counter and reference electrode, respectively. Electrochemical measurements were carried out using a computer controlled potentiostat (PARSTAT 2273), managed with appropriate software. After the stabilization of open circuit potential,  $E_{ocp}$  and subsequent Tafel polarization measurements (not shown here), the anodic potentiodynamic polarizations curves were recorded (scan rate: 5 mV/sec) in order to detect the pitting potential, where breakdown of passive layer results in pitting corrosion.

The reproducibility of the presented data was generally checked by duplicate or triplicate measurements and typical results are reported.

### 2.3. Metallographic observations

Observations by optical microscope and SEM/EDS analyses were used to characterize the surface morphology and microstructural constituents in extruded alloy AA6060, respectively.

## 3. RESULTS AND DISCUSSION

The representative anodic polarization curves registered for AA6060 alloy in deaerated NaCl solutions of various concentrations at 293K are presented in Figure 3. Their typical shape with no active oxidation peak during the anodic scan is characteristics of passive behavior and reflects the stability of air-formed oxide on the surface of AA6060. However, at certain anodic potential denoted as  $E_{pit}$  on the plots presented, the destruction of passivating layer is marked by sudden increase of the current flowing along the passive region. Determination of  $E_{pit}$  values is critical issue for structural Al-alloys experiencing a variety of corrosive environments in service: The lower the  $E_{pit}$ , the higher pitting susceptibility [19].

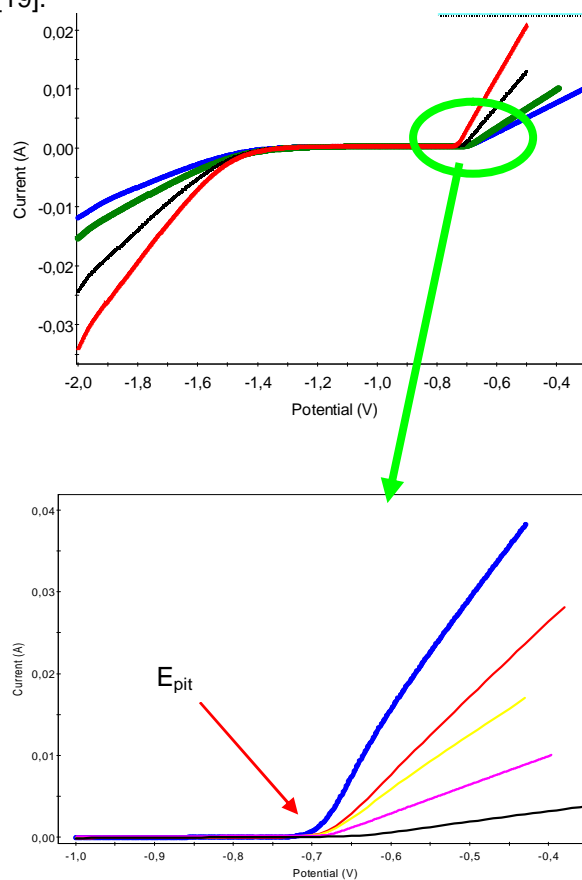


Figure 3 - Anodic polarization curves of alloy AA6060 in deaerated NaCl solutions at 293K

The shift of breakdown potential  $E_{pit}$  to more negative values in Figure 3, clearly suggests the higher pitting susceptibility of alloy AA606 in solutions with higher Cl<sup>-</sup> concentration.

In order to reveal this correlation more exactly, dependence between logarithm of Cl<sup>-</sup> concentration and  $E_{pit}$  is modeled by linear regression analysis. As a measure of goodness of fit, the high value of regression coefficient ( $R^2 = 0.9335$ ) is

used. The straight line obtained is shown in Figure 4 and can be presented by equation:

$$E_{pit} = a + b \log (c_{Cl^-})$$

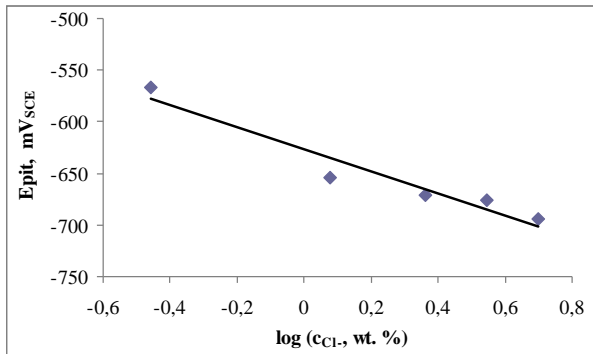


Figure 4 - Breakdown potential of alloy AA6060 in dependence on NaCl concentration in deaerated solutions at 293K

Comparing results here obtained to the recent literature, it was found that linear relationship  $E_{pit} =$

$f \log (c_{Cl^-})$  is also established for high purity Al [20], and for aluminum alloys in non-deaerated chloride solution [21, 22].

Besides the chloride concentration, another important factor associated with pitting is the presence of intermetallic particles in the bulk of aluminium matrix [23-26]. During extrusion of heat treatable Al-Mg-Si alloys, these microconstituents change the shape, quantity and distribution in order to achieve a desired level of mechanical properties. However, their influence on corrosion behavior can be detrimental [27-29].

Metallographic observations and SEM/EDS analyses of extruded alloy AA6060 under study have shown that the two main intermetallic phases exist. Dark particles in Figure 5 and Figure 6 are phases composed from Mg and Si ( $Mg_2Si$ ), while elongated white phases are iron-containing particles characterized by Fe-content higher than that of surrounding Al-matrix [30].

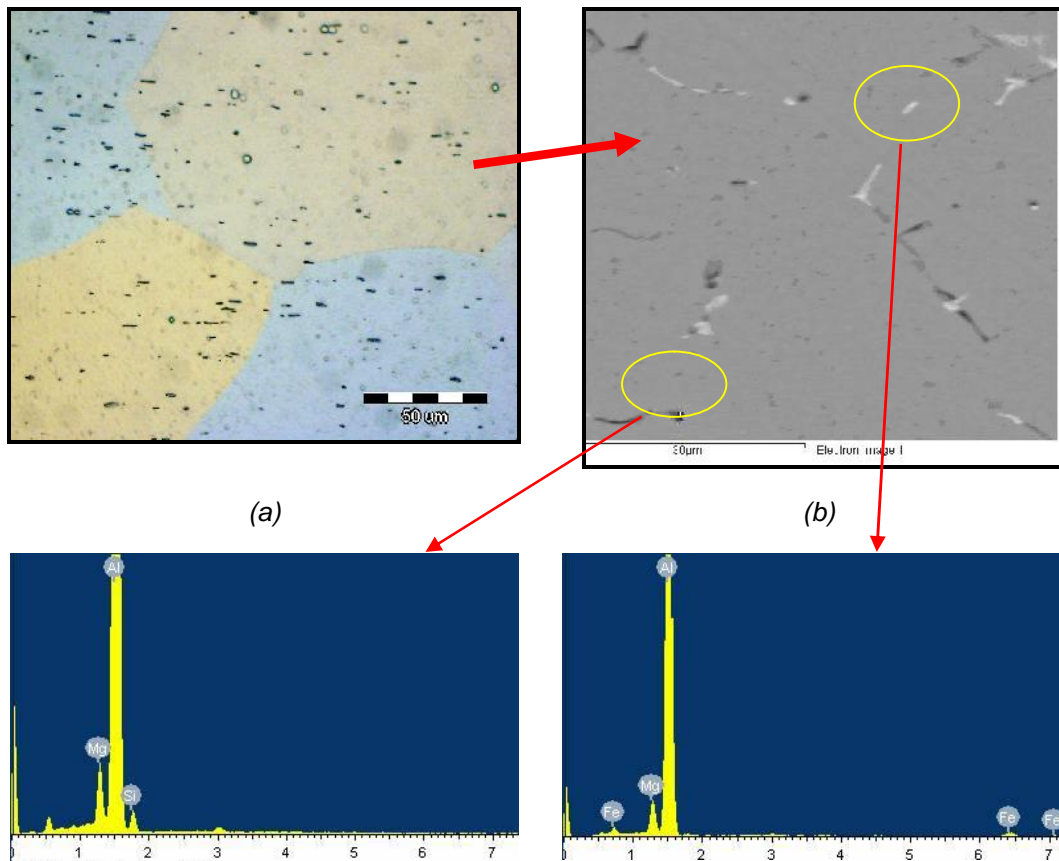


Figure 5 - Microscopic images of commercial Al-Mg-Si alloy AA6060: (a) OM- transversal section, etched in Barker reagent, polarized light, tint filter; (b) SEM/EDS micrography of intermetallic phases on the surface of extruded profile

Figure 6 presents the outer layer of extruded Al-alloy AA6060 and surface distribution of secondary phases identified.

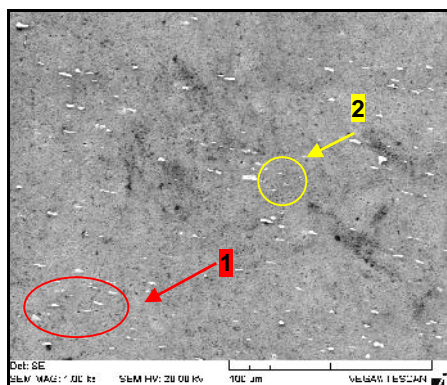


Figure 6 - SEM image of intermetallic particles on the surface of extruded AA6060; detail 1: bright Fe-rich phases; detail 2: dark Mg-rich phases

Both Fe-rich and Mg-rich intermetallic particles contribute to the heterogeneity of the surface, so that local micro-galvanic couples are formed when alloy AA6060 is in contact with the NaCl electrolyte. Chemical composition and electrochemical nature of intermetallics can be correlated with difference in potential between the matrix and these particles: they can be either nobler or more active with respect to Al. The potential of  $Mg_2Si$  particles is lower than the one of aluminium, while Fe-rich phase is nobler than Al-matrix [31,32]. Therefore, the exposure of AA6060-alloy to the aggressive chloride medium results in specific electrochemical activity: Fe-rich particles behave as cathodes and induce local anodic dissolution of surrounding aluminium matrix, i.e. pitting corrosion process. The extent of this process is under the strong influence of chloride concentration, as it is shown in Figure 4.

#### 4. CONCLUSION

In this study the corrosion behavior of commercial extruded Al-Mg-Si alloy AA6060 was investigated in deaerated NaCl solutions at room temperature. The results obtained indicate significant role of the chloride concentration on the pitting corrosion of alloy AA6060. The following conclusion can be drawn:

During the anodic potentiodynamic polarization, specimens show passive behaviour in solutions containing chloride ions in the concentration range 0.35 wt.%-5 wt.%.

Detrimental influence of  $Cl^-$  on pitting resistance of AA6060 is characterized by passive film breakdown at  $E_{pit}$ -potential.

Increasing the NaCl concentration shifted  $E_{pit}$ -potential to more negative values, suggesting the lower resistance to pitting.

$E_{pit}$ -dependence on  $Cl^-$ -ion concentration follows the linear relationship in the interval 0.35 wt. %-5 wt. %.

Fe-rich intermetallic particles heterogeneously distributed in the surface of the samples were identified as cathodic phases which promote pitting corrosion by local anodic dissolution of Al-matrix.

#### Acknowledgments

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#### 5. REFERENCES

- [1] Sheppard, T., (1999) Extrusion of Aluminum Alloys, Kluwer Academic Publishers, Dordrecht, The Netherlands
- [2] Van Geertruyden, W. H., Browne, H. M., Misiolek, W. Z., Wang, P. T., (2005) Evolution of surface recrystallization during indirect extrusion of 6xxx aluminum alloys, Metallurg. Materials Trans. A, 36, 1049-1056.
- [3] Gupta, A. K., Lloyd, D. J., Court, S. A., (2001) Precipitation hardening in Al-Mg-Si alloys with and without excess Si, Mat. Sci. Eng. A, 316, 11-17.
- [4] Schikorra, M., Donati, L., Tomesani, L., Tekkaya, A. E., (2007) Microstructure analysis of aluminum extrusion: grain size distribution in AA6060, AA6082 and AA7075 alloys, J. Mech. Sci. Technol. 21, 1445-1451.
- [5] Chang, C.S.T., Wieler, I., Wanderka, N., Banhart, J., (2009) Positive effect of natural pre-ageing on precipitation hardening in Al-0.44 at% Mg-0.38% Si alloy, Ultramicroscopy, 109, 585-592.
- [6] Al-Fadhlah, K. J., Almazrouee, A. I., Aloraie, A. S., (2014) Microstructure and mechanical properties of multi-pass friction stir processed aluminum alloy 6063 Mater. Design 53, 550-560.
- [7] Jegdi, B. V., Živkovi, Lj. S., Popi, J. P., Bajat, J. B., Miškovi, -Stankovi, V. B., (2013) Electrochemical methods for corrosion testing of Ce-based coatings prepared on AA6060 alloy by the dip immersion method, J. Serb. Chem. Soc. 78, 997-1011
- [8] Allachi, H., Chaouket, F., Draoui, K., (2010) Protection against corrosion in marine environments of AA6060 aluminium alloy by cerium chlorides, J. Alloys Comp. 491, 223-229.
- [9] Radoševi J., Malina J., Doli N., Ljumovi P., Slavica - Mateši S. (2013) Susceptibility to corrosion of welded AlMgSi alloy EN AW 6060, Zastita materijala 54 (1) 3-7
- [10] Vargel, C., (2004) Corrosion of Aluminum, Elsevier Ltd., Amsterdam
- [11] Davis, J. R., (1999), Corrosion of Aluminum and Aluminum Alloys, ASM International, Ohio
- [12] Marcus, P., Maurice, V., Strehblow, H. H., (2008) Localized corrosion (pitting): A model of passivity breakdown including the role of the oxide layer nanostructure, Corr. Sci. 50, 2698-2704.
- [13] Malina J., Doli N., Unkić F., (2013) Mikrostrukturni aspekti lokalne korozije Al-slitina u lijevanom stanju, Zastita materijala 54 (3) 240-249

- [14] EN 755 - 2 : 2008 Aluminium and aluminium alloys. Extruded rod/bar, tube and profiles.
- [15] Hirsch, J., Skrotzki, B., Gottstein, G., (2008), Aluminium Alloys, Their Physical and Mechanical Properties, Wiley-VCH, Weinheim, Germany
- [16] Panchal V., Patel A., Shah N., (2012) Inhibition of Al-Mg alloy in hydrochloric acid using schiff bases as corrosion inhibitors, Zastita materijala 53 (1) 15-29
- [17] Kaufman, J. G., Rooy, E. L., (2004), Aluminum Alloy Castings: Properties, Processes, and Applications, American Society for Materials International, Materials Park, Ohio, USA
- [18] Altenpohl, D.G., (1998), Aluminum: Technology, Applications, and Environment, TMS
- [19] Trueba, M., Trasatti, S. P., (2010) Study of Al alloy corrosion in neutral NaCl by the pitting scan technique, Mat. Chem. Physics 121, 523-533
- [20] Soltis, J., Laycock, N. J., Krouse, D., (2011) Temperature dependence of the pitting potential of high purity aluminum in chloride containing solutions," Corr. Sci. 53, 7-10.
- [21] Abdallah, M., Zaafarany, I., Al-Karane, S. O., Abd El-Fattah, A. A., (2012) Antihypertensive drugs as an inhibitors for corrosion of aluminum and aluminum silicon alloys in aqueous solutions, Arabian J. Chem. 5, 225-234.
- [22] Zaid, B. Saidi, D., Benzaid A., Hadji, S., (2008) Effects of pH and chloride concentration on pitting corrosion of AA6061 aluminum alloy, Corr. Sci. 50, 1841-1847.
- [23] Yasakau, K. A., Zheludkevich, M. L., Lamaka, S.V., Ferreira, M.G. S., (2007) Role of intermetallic phases in localized corrosion of AA5083, Electrochim. Acta 52, 651-659.
- [24] Cavanaugh, M. K., Buchheit, R. G., Birbilis N., (2010) Modeling the environmental dependence of pit growth using neural network approaches Corr. Sci. 52, 3070-3077.
- [25] Birbilis, N., Buchheit, R. G., (2005) Electrochemical characteristics of intermetallic phases in aluminum alloys: an experimental survey and discussion, J. Electrochem. Soc. 152, B140-B151.
- [26] Zhu, H., Zhang, X., Couper, M. J., Dahle, A. K., (2009) Effect of primary intermetallic particles on surface microstructure and appearance of aluminium extrusions, Mat. Chem. Physics, 113, 401-406.
- [27] Birol, Y., (2004) The effect of homogenization practice on the microstructure of AA6063 billets, J. Mater. Process. Technol. 148, 250-258.
- [28] Schikorra, M., Donati, L., Tomesani, L., Tekkaya, A.E., (2008) Microstructure analysis of aluminum extrusion: Prediction of microstructure on AA6060 alloy, J. Mater. Process. Technol. 201, 156-162.
- [29] Kayser, T., Klusemann, B., Lambers, H.G., Maier, H. J., Svendsen, B., (2010) Characterization of grain microstructure development in the aluminum alloy EN AW-6060 during extrusion, Mater. Sci. Eng. A 527, 6568-6573.
- [30] Z. Brodarac, Z., Doli, N., Malina, J., (2013), Microstructural characterization of intermetallic phases in HAZ of MIG-welded EN AW-6060 alloy, 45th Int. Conf. Mining Metallurgy, Bor
- [31] Wloka, J., Bürklin, G., Virtane, S., (2007) Influence of second phase particles on initial electrochemical properties of AA7010-T76, Electrochim. Acta 53, 2055-2059.
- [32] El-Menshawly, K., El-Sayed, A. W., Mohammed E. El-Bedawy, M. E., Hafez A. Ahmed, H. A., El-Raghy, S. M., (2012) Effect of aging time at low aging temperatures on the corrosion of aluminum alloy 6061, Corr. Sci. 54, 167-173.

## IZVOD

### UTJECAJ KONCENTRACIJE NaCl NA PITING KOROZIJU EKSTRUDIRANE Al-Mg-Si LEGURE AA6060

*Ekstrudirane Al-Mg-Si legure (serija AA6xxx) naj eš e se koriste u konstrukcijske svrhe zahvaljuju i prihvatljivim mehani kim i korozijskim svojstvima. Spontano formirani sloj aluminijeva oksida na površini Al i Al-legura štiti od korozijskih ošte enja u neutralnim medijima, ali u otopinama koje sadrže kloride dolazi do proboja tankog i kompaktnog pasivnog filma. Kao posljedica tog procesa, nastaju na površini lokalna ošte enja i dolazi do pojave jami aste korozijske pitinga.*

*U ovom je radu prou avano korozijsko ponašanje komercijalne ekstrudirane Al-Mg-Si legure AA6060 u otopinama NaCl razli ite koncentracije, metodom anodne potenciodinami ke polarizacije u deaeriranim uvjetima pri sobnoj temperaturi. Pokazalo se da sklonost lokalnoj koroziiji raste s koncentracijom kloridnih iona i ovisi o katodnim mikrokonstituentima u ekstrudiranoj Al-Mg-Si leguri.*

**Ključne riječi:** piting koroziija, komercijalna Al-Mg-Si legura, deaerirana NaCl.

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