

# **Corrosion behavior of the AlSi5Cu2Mg alloy with varying Zr addition**

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**Abstract:** The aim of this paper was to analyze the impact of varying *zirconium* additions (0.05; 0.10; 0.15 and 0.20 wt. % Zr) on corrosion behavior of the *AlSi5Cu2Mg aluminum* alloy. Potentiodynamic polarization corrosion tests in 3.5 % *NaCl* solution demonstrated that the addition of Zr improved the thermodynamic corrosion stability of the *AlSi5Cu2Mg* alloy by shifting the corrosion potential to more positive values for all as-cast samples. The addition of Zr to the as-cast alloys also improved corrosion kinetics by lowering the corrosion current density.

**Keywords:** corrosion, *AlSi5Cu2Mg*, zirconium

#### INTRODUCTION

The automotive sector has undergone tremendous transformation recently. Automotive manufacturers are compelled to develop technical solutions to lower emissions and enhance fuel efficiency as a result of ever-stricter emission standards laws.

Aluminum alloys are among the irreplaceable materials used in the automotive industry. Due to their favorable weight ratio and strength properties, *aluminum* alloys are used in the production of engine parts (cylinder heads, engine blocks, and pistons) and body parts. With the advent of electromobility, their applications expanded to include the manufacture of electric motor housings, battery trays/covers. This fact affects research centers that must develop new *aluminum* alloys that will meet the ever-tightening criteria for advanced castings in the automotive industry.

In addition to a whole range of mechanical, physical, and tribological properties, *aluminum* alloys for castings in the automotive industry must also meet the requirements for sufficient corrosion resistance. The evaluation of the corrosion resistance of automotive parts is especially important for the castings of electric car battery trays, which are located on the car chassis and are thus directly exposed to a corrosive environment (water, road salt, etc.) [1, 2].

There are several standardized tests to evaluate the corrosion resistance of aluminum alloys. One of them is the potentiodynamic polarization test, on the basis of which it is possible to characterize corrosion mechanisms, corrosion speed, and the susceptibility of the material to corrosion in a defined corrosion environment. The measurement is carried out in closed corrosion cells, which are connected to a laboratory potentiostat. In most cases, this is a threeelectrode connection. A connection of this type is formed by the observed surface of the tested material, which serves as a working electrode, a *platinum* mesh as a counter electrode, and a reference electrode, most commonly a saturated calomel electrode (SCE), which has a potential shift of +0.2446 V in comparison to the standard hydrogen electrode (SHE). By the potentiodynamic polarization test, a metallic material is characterized on the basis of the dependence of current density and potential. During the test, the potential of the tested material shifts in the

Tab. 1. Chemical composition of the experimental alloys with varying Zr addition

Chemical composition [wt. %]											
Zr addition [wt. %]	Si	Cu	Mg	Fe	Mn	Ti	Sr	Zr	Al		
0	5.47	1.91	0.29	0.18	0.02	0.013	0.01	0.0009	Bal.		
0.05	5.67	1.91	0.29	0.19	0.02	0.013	0.01	0.05	Bal.		
0.10	5.65	1.92	0.29	0.19	0.02	0.014	0.01	0.10	Bal.		
0.15	5.55	1.91	0.29	0.19	0.02	0.014	0.01	0.12	Bal.		
0.20	5.43	1.90	0.29	0.18	0.02	0.014	0.01	0.19	Bal.		

anodic (or cathodic) direction - the sample gradually acts as a cathode and an anode. The potential of the tested material immersed in the electrolyte settles at a certain value with respect to the reference electrode, which corresponds to the corrosion potential  $E_{corr}$ . Corrosion potential  $E_{corr}$  is defined as the potential at which the rate of oxidation of the material is the same as the rate of reduction of one of the components of the corrosion environment. Polarization tests are based on measuring the current response due to a change in the potential (polarization) of the working electrode in a specified range and at a certain speed. Polarization caused by an external controllable source imposes a potential different from its equilibrium potential on the tested material via a current. Anodic polarization shifts the potential of the electrode towards more positive values - the electrode then behaves as an anode and electrons are released. By cathodic polarization, the potential of the electrode is shifted to more negative values, and a reduction reaction occurs [3, 4].

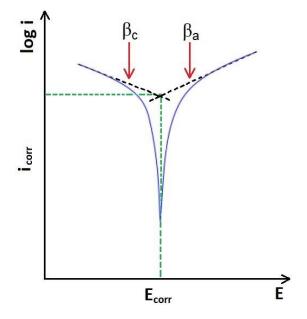


Fig. 1. Tafel analysis of the potentiodynamic curve [5]

The output from the potentiodynamic polarization test is a potentiodynamic curve, which is interpreted in semi-logarithmic coordinates. The anode and cathode partial curves are subsequently extrapolated by *Tafel*  analysis of the potentiodynamic curve (Fig. 1) and their slopes  $\beta_a$  and  $\beta_c$  are determined. The intersection of the linear part of the curves determines the values of the corrosion potential  $E_{corr}$  and the corrosion current density  $i_{corr}$  [5].

The aim of this experimental research was to determine the impact of varying Zr addition on the corrosion behavior of the AlSi5Cu2Mg alloy.

#### 1 EXPERIMENTAL MATERIAL AND METHODS

AlSi5Cu2Mg aluminum alloy in a pre-modified state was used as an experimental material. This alloy is currently used to manufacture cylinder heads for gasoline engines. As part of the experiment, different experimental alloys with varying additions of Zr(0; 0.05; 0.10; 0.15 and 0.20 wt.% Zr) were made. Zirconium was added to the AlSi5Cu2Mg alloy in the form of AlZr20 master alloy. The chemical composition of the experimental alloys is shown in Tab. 1.

The experimental alloys were made by gravity casting into a metal mold with temperature of 200 °C. The casting temperature was  $780 \pm 5$  °C. 10 pieces of samples were made from each experimental alloy, of which 5 were subjected to evaluation of corrosion behavior in the cast state and 5 were subjected to heat treatment. For the purposes of heat treatment, the *T*7 mode was chosen, consisting of solutionizing at 500 °C for 6.5 hours, followed by rapid cooling in water at a temperature of 80 to 95 °C. Artificial aging took place at a temperature of 250 °C for 4 hours, followed by cooling in the air.

Corrosion testing of the experimental alloys was evaluated using potentiodynamic polarization (*PD*) tests in 3.5 % *NaCl* solution at laboratory temperature 20 °C. Measurements were performed in a threeelectrode cell system on a laboratory potentiostat Biologic *SP*300, with the sample connected as a working electrode, *platinum* mesh as a counter electrode, and a saturated calomel electrode (*SCE*) serving as a reference electrode. After 10 minutes of potential stabilization, samples were tested with potentials ranging from -200 mV to +500 mV vs. the open circuit potential (*OCP*) at a step rate of 1 mV·s<sup>-1</sup>. *EC Lab* 10.42 software was used to analyze measured *PD* curves using the *Tafel* extrapolation method, determining values of corrosion potential  $E_{corr}$ , corrosion current density  $i_{corr}$ , and *Tafel* coefficients *a* and *c*, as well as anodic and cathodic slopes of curves. Additionally, the corrosion rate  $r_{corr}$  was calculated. Samples were prepared by wet grinding with *P*1200 sanding paper. Each experimental alloy was exposed to the *PD* test and measurements were repeated five times [6, 7].

#### 2 POTENTIODYNAMIC POLARIZATION TESTS

Results of *PD* tests for a series of the experimental alloys are graphically presented in the form of representative *PD* curves in Fig. 2 and corresponding values of electrochemical characteristics obtained by Tafel analysis of the *PD* curves are presented in Tab. 2. This experiment presented two perspectives on the measured results: corrosion kinetics, as represented by the value of corrosion current density  $i_{corr}$ , and thermodynamics, as indicated by corrosion

potential values  $E_{corr}$  [8]. Data obtained indicated that heat treatment (HT) enhanced  $E_{corr}$  values for samples without Zr addition to more positive ones, pointing to the alloy's increased thermodynamic stability after HT. Regardless of Zr, the change in  $E_{corr}$  towards higher positive values was documented for as cast (AC) samples when inspecting the alloys with Zraddition. This suggested that the presence of zirconium, whether in solid solution or intermetallic phase, contributed to the improved thermodynamic corrosion response of the material to a corrosive environment. In comparison to their AC counterparts, the thermodynamic response of alloys with Zraddition appeared to be worse after HT. Furthermore, the  $E_{corr}$  values for each heat-treated experimental alloy revealed that the amount or form of Zr present effect on corrosion in the alloy has no thermodynamics, as no significant difference was observed among the heat-treated samples with Zraddition. This pattern was also seen in cast experimental alloys containing Zr.

However, in terms of corrosion kinetics, which is considered to be a more important factor when

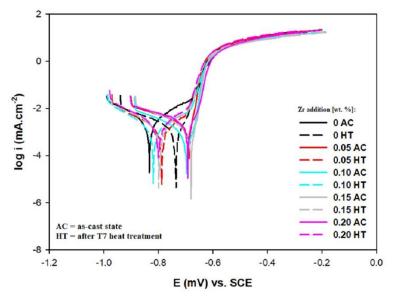


Fig. 2. Potentiodynamic curves measured in 3.5 % NaCl for various types of alloys

Zr addition [wt. %]	Ecorr (mV)	icorr (µA.cm <sup>-2</sup> )	$\beta_a$ (mV·dec. <sup>-1</sup> )	$\beta_c$ (mV·dec. <sup>-1</sup> )	rcorr (µm∙year <sup>-1</sup> )
0 A C	-835	3.51	131	142	0.058
0 <i>HT</i>	-746	0.76	36	171	0.013
0.05 AC	-671	2.81	41	214	0.057
0.05 HT	-784	1.25	101	167	0.021
0.10 AC	-696	1.09	33	152	0.018
0.10 HT	-816	0.89	155	139	0.014
0.15 AC	-685	2.07	31	192	0.273
0.15 HT	-799	1.66	166	157	0.016
0.20 AC	-695	2.28	24	259	0.031
0.20 HT	-798	1.79	155	160	0.025

discussing the practical application of the alloy, microstructural changes related to heat treatment led to a suppression of corrosion current density  $i_{corr}$ , meaning that corrosion reactions were slower, and alloys degraded less intensely than their as cast (AC)counterparts. This was also reflected by lover values of corrosion rate  $r_{corr}$  for the alloys. The  $i_{corr}$  results of the as cast experimental alloys also showed that corrosion kinetics was tending to decrease with increasing Zr content compared to the 0 AC samples up to the 0.10 Zr and then it tended to increase with higher Zr content. However, icorr values for the 0.15 AC and 0.20 HT experimental alloys were still lower compared to the as cast alloy without Zraddition, indicating that Zr presented in the solid solution to a greater extent (compared to Zr excluded in the form of intermetallic phases) is more suitable for the corrosion resistance of the alloy. Since the  $i_{corr}$ values were directly proportional to the corrosion rate, Zr addition in carefully chosen range appeared to be rather beneficial for improvement of corrosion resistance of the studied AlSi5Cu2Mg alloy in 3.5 % NaCl solution. Similar conclusions were presented also in the study of Kim et al. [9], where authors proposed improved corrosion resistance of 1xxx series Al alloy after addition of Zr in aggressive salt solution. However, these findings could be applied only when evaluating the as cast experimental alloys, since the electrochemical values showed that the highest corrosion resistance, with regard to *i*corr, was obtained by the 0 HT alloy, showing that heat treatment offers more effective corrosion resistance than the presence of Zr in the alloy.

#### CONCLUSION

The aim of this research was to investigate the effect of varying additions of Zr on the corrosion properties of the AlSi5Cu2Mg aluminum alloy. Potentiodynamic polarization tests in 3.5 % NaCl solution revealed that the addition of Zr had a positive effect on the thermodynamic corrosion stability of the AlSi5Cu2Mg alloy due to a shift of the corrosion potential to a more positive value for all as cast samples. Moreover, the addition of Zr to the as cast alloys improved corrosion kinetics by lowering the corrosion current density, regardless of the form of its presence in the alloy. The highest corrosion resistance in 3.5 % NaCl with regards to corrosion current density was obtained by the alloy without Zr in heat treated state, meaning that heat treatment has a more significant impact on the corrosion resistance of the studied alloy than alloying with Zr.

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#### REFERENCES

[1] HAJDÚCH, P. - DJURDJEVIC, M. B. -BOLIBRUCHOVÁ, D. (2020): New trends in the production of aluminum castings for the automotive industry. Slévarenství, No. 1-2, pp. 5-7, ISSN 0037-6825.

[2] HOAG, K. - DONDLINGER, B. (2016): *Cylinder block and head materials and manufacturing*. Vehicular engine design, pp. 97-115.

[3] HADZIMA, B. - LIPTÁKOVÁ, T. (2008): Fundamentals of electrochemical corrosion of metals. EDIS – publishing house of the University of Žilina, ISBN: 978-80-8070-876-4.

[4] DZIKOVÁ, J. - KAJÁNEK, D. - NOVÝ, F. -PASTOREK, F. (2021): *Corrosion of metal materials*. EDIS – publishing house of the University of Žilina, ISBN: 978-80-8070-554-1757-8.

[5] ŠVECOVÁ, I. (2021): The influence of ferric intermetallic phases on the structure and properties of secondary aluminum alloys based on Al-SI-Mg. [dissertation thesis]. Žilina: University of Žilina, 2021. 132 s.

[6] MHAEDE, M. - PASTOREK, F. - HADZIMA, B. (2014): Influence of shot peening on corrosion properties of biocompatible magnesium alloy AZ31 coated by dicalcium phosphate dihydrate (DCPD). Materials Science and Engineering C, No. 39, pp. 330-335.

[7] GHALI, E. (2015): Corrosion Resistance of Aluminum and Magnesium Alloys: Understanding, Performance, and Testing. New Jersey, John Wiley & Sons, Inc. ISBN: 9780471715794.

[8] KAJÁNEK, D. - PASTOREK, F. - FINTOVÁ, S. - BAČA, A. (2017): Study of Corrosion Behavior of Dicalcium Phosphate-dihydrate (DCPD) Coating Prepared by Large Amplitude Sinusoidal Voltammetry (LASV) Technique on ZW3 Magnesium Alloy. Procedia Engineering, No. 192. pp. 399-403.

[9] KIM, Y. - PARK, J. - AN, B. - LEE, Y. - YANG, CH. - KIM, J. (2018): Investigation of Zirconium Effect on the Corrosion Resistance of Aluminum Alloy Using Electrochemical Methods and Numerical Simulation in and Acidified Synthetic Sea Salt Solution. Materials, No. 11.