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M. NABIAŁEK³, D.C. ACHITEI^{1,2}**CORRELATION BETWEEN MICROSTRUCTURE AND ELECTROCHEMICAL PROPERTIES OF Al-Si ALLOYS**

The composition and structural modification of aluminium alloys influence their strength, tribological properties and structural stability. The phase composition of the structure as well as the characteristics of the elementary cell of each identified phase was established by X-ray diffraction, and the main objective was to determine the compositional phases, microstructure and microcomposition of the alloy. Based on the cyclic voltammograms it can be said that on the OCP interval (+1.5 V... -1.1 V), after the breakthrough potential is an intensification of the anodic process by the pronounced increase of the current density, in these conditions the Al-Si alloy has low values which means that it has a better corrosion resistance.

Keywords: aluminium alloys; microstructure; X-ray diffraction; corrosion; Evans diagrams

1. Introduction

Aluminium offers a wide range of properties that can be engineered precisely to the demands of specific applications through the choice of alloy temper and fabrication process. Worldwide demand for aluminium is around 29 million tons per year. About 22 million tons is new aluminium and 7 million tons is recycled aluminium scrap. The use of recycled aluminium is environmentally and economically compelling. It takes 14,000 kWh to produce 1 tonne of new aluminium [1]. On the contrary, it only takes 5% of it to re-melt and recycle a ton of aluminium. There is no difference in the quality between new and recycled aluminium alloys. By utilising various combinations of its advantageous properties such as corrosion resistance, strength, lightness, formability and recyclability, the aluminium is used in almost all applications.

Aluminium is a metal with special mechanical properties and has introduced a revolution to many technological fields. It has a specific strength and is an easy reason why it is so used in many technological fields. Aluminium is approximately one third the density of steel, making it light weight in comparison [2-3]. It is comparatively strong and has good properties of elasticity, especially when alloyed [4-5]. It resists corrosion, because an oxide layer forms on contact with air, which prevents further corrosion.

Surface finishes can be applied, including anodising, paint and powder coating. Corrosion is a process of degradation of materials due to chemical or electrochemical reactions with various substances. Corrosion is most often an undesirable phenomenon that causes great economic losses and it is very important to know this process as well as the means of prevention [6-10].

Corrosion is possible in most materials through chemical reactions.

A smaller class of corrosion phenomena is electrochemical corrosion, which occurs through electrochemical reactions and affects only metals, because electrochemical reactions take place through electric current leaks and only metals allow these current leaks, through the free electrons they possess [11].

In general, metals are significantly affected by chemical corrosion only at high temperatures, and under normal conditions electrochemical corrosion predominates. It is used by the construction industry for structural purposes, when the right cross-sectional structure and alloy is applied. Aluminium can be cast, extruded, rolled, machined and cold or hot formed [12-14].

Therefore, in this paper is present the correlation between microstructure and electrochemical properties of Al-Si alloys. The objectives of this work have been achieved in order to provide a complete characterization of aluminum-based alloys (chemical, structural and electrochemical).

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2. Experiment

This paper presents the chemical, structural and electrochemical analysis of a special equipment, high pressure water discharge gun, which must provide optimal protection against various types of corrosion, oxidation and wear. By carrying out this work, the resistance capacity of this equipment is tested, which can be used daily or in irregular time intervals, which requires a careful analysis.

Analyses to determine the chemical composition of the alloy were performed on a Foundry Masters optical spectrometer, using the Al analysis base, with an accuracy of $\pm 3\%$. The subjected sample was cut from the high pressure water discharge gun and prepared by lathe cutting.

The determination of the chemical composition, by quantitative spectral analyzes, was performed at 3 different points on the prepared surface. Based on the measured percentages, the specific software performs an arithmetic mean of the recorded values, which can be found on the analysis bulletin.

TABLE 1

Chemical composition

Compound	Al	Si	Fe	Mn	Mg	Ni	Zn	Other
Mass (%)	94.30	2.24	0.84	0.60	0.50	0.24	0.17	1.11

In the TABLE 1 shows the elemental composition in mass percentages evaluated from the EDX spectra of the sample, which allow highlighting the presence on the surface of aluminum, but also of the alloying element, silicon, plus a number of alloying components. Based on the analysis bulletin obtained, the studied alloy falls into the class of Al-Si alloys

The characterization of the material was performed on X'Pert PRO MRD X-ray diffractometer, Malvern Panalytical, from UK, with a PreFIX concept that ensures the possibility of using several combinations of modules and an ease and speed of their positioning within the equipment. Depending on the nature of the samples to be analyzed, X-ray tubes with Co, Mo, Fe or Cr anodes can be used.

Corrosion behavior was monitored by rapid electrochemical tests and dynamic potentiometry. Open circuit potential measurements and dynamic polarizations were performed using a Volta Lab 21 potentiometer.

In order to calculate the corrosion rate of an alloy immersed in a corrosive environment it is necessary to know the instantaneous current density which is determined by the polarized resistance method [13]. This method is used to determine the corrosion current at the corrosion potential of a metal using for this purpose the linear polarization curve obtained for relatively small overvoltages. Data acquisition and processing was performed with Volta Master 4 software. A three-electrode cell was used, equipped with a stirring system, with the specification that the electrodes made in a cylindrical shape were mounted in Teflon supports that allow connection to the rotating electrode of the electrochemical system. A platinum electrode was used

as the auxiliary electrode and a saturated calomel as the reference electrode.

The electrochemical measurements were performed in a glass cell that is equipped with a platinum reference electrode and a saturated calomel (SCE). All experiments were performed at laboratory temperature ($25 \pm 1^\circ\text{C}$), using an electrochemical cell with 3 electrodes, connected to the Autolab Potentiostat PG STAT 302N, which has in its composition software Nova 1.10. The 0.3 M NaCl solution, which was the aggressive medium, was prepared from NaCl with bidistilled water, having a pH of 6.26 and an electroconductivity of 49.9 [mS/cm], measured at the Consort C861 electrochemical multimeter. Prior to each determination the working electrode was sanded with metallographic paper of different granules (80, 400, 1000, 1500) degreased and washed with bidistilled water.

To identify the corrosive effect on the surface layer, the Leica DMI5000 M metallographic microscope was used, with magnification orders of $100\times$ and $200\times$.

3. Results and discussion

3.1. Qualitative phase analysis by X-ray diffractometric investigations

X-ray diffraction is used in the identification and quantitative determination of various crystalline compounds, known as 'phases', which are found in powders and solids.

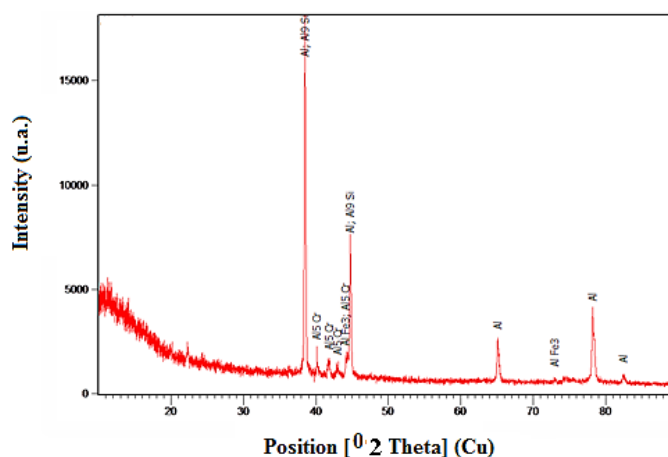


Fig. 1. X-ray diffraction

Fig. 1 shows the diffractogram obtained for the Al-Si alloy. In the sample are present as phases: Al_3Si with cubic crystal lattice, having the principal maximum at the angle $2\theta = 38.500^\circ$ and Al with cubic lattice lattice, having the principal maximum at the angle $2\theta = 44.490^\circ$. The conventional method used for qualitative structural analysis consists in comparing the structural data extracted from the diffraction spectrum of the investigated sample with the data characteristic of different known crystalline substances (phases, compounds). The structural data necessary for the comparison are taken from the ICDD (International Center

for Diffraction Data) (ICDD) sheets. The ICDD file system for indexing compounds, inorganic and organic phases, contains the complete structural data of about 500.000 compounds and phases, each given as a card or file.

3.2. Characterization of electrochemical behaviour

The corrosion current determined in this way represents the corrosion current that occurs at the metal/medium interface when the metal is immersed in the solution and can be measured directly by electrochemical methods.

The measurements were performed at a temperature of 25°C and the electrolyte was naturally aerated, the linear polarization curves were recorded at an electrode potential scanning speed of 1 mV/s in a potential range ± 150 mV in an open circuit of potential. Cyclic polarization curves were recorded at a speed of 10 mV/s in the potential range $-700 \dots +1500$ mV. The corrosion potential at the corrosion current E , the Tafel branches (ba and bc) the polarization resistance (R_p), the corrosion current density (j_{cor}) and the corrosion speed (V_{cor}), were evaluated using the facilities of the Volta Master 4 software.

Electrochemical tests (potential dynamic polarization, EIS-electronic impedance spectrometry) were used to detect pores and bubbles in the deposited polymeric layers as well as their effects on the corrosion resistance behavior for a short immersion period.

3.3. Corrosion behavior of Al-Si alloy

The anodic behavior of the Al-Si alloy over a potential range up to 1.00 V, starting with the open circuit potential (OCP) of the sample is shown in the Fig. 2.

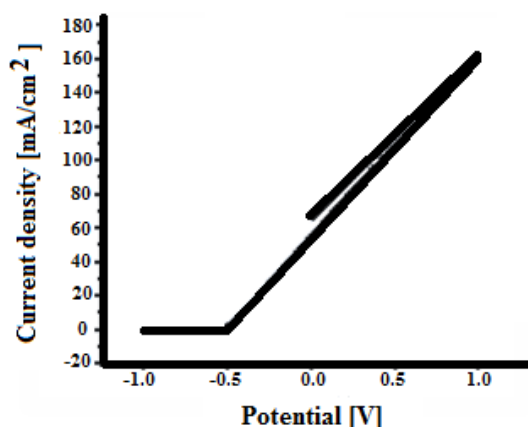


Fig. 2. Dependence of the current density on the potential applied in the field of Al-Si alloy

There is a linear dependence of the current density on the potential for this test, which shows that the corrosion process is continuous throughout the field. The cyclic polarization curve is specific to an alloy undergoing widespread corrosion.

Based on the cyclic voltamograms it can be said that on the OCP interval ($+1.5 \text{ V} \dots -1.1 \text{ V}$), after the break through potential an intensification of the anodic process takes place by the pronounced increase of the current density, in these conditions the Al-Si alloy has small values which means it has better corrosion resistance.

A quantitative estimation of the corrosion process of the alloy in the considered environment can be achieved by plotting the potential dynamics curves on the range $\pm 0.15 \text{ V}$ with respect to the OCP at a low sweep speed of the potential.

From these data the Evans diagrams are constructed which give the possibility to calculate the corrosion parameters. Fig. 3. shows the Evans diagrams for the Al-Si alloy in the 0.3M NaCl solution, the potential modification speed being 1 mV/s.

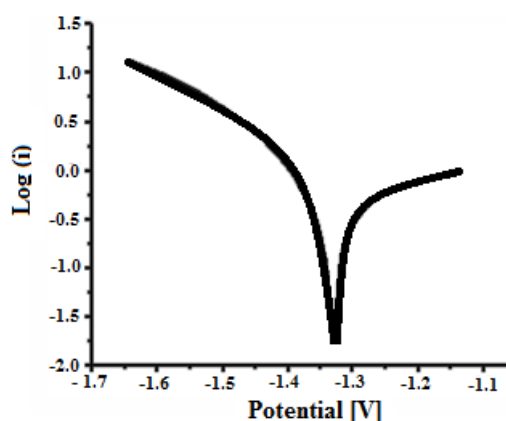


Fig. 3. Evans diagrams for Al-Si alloy in 0.3M NaCl solution

Based on the data obtained from the potential dynamics curves, using Volta Master 4 software, the Tafel coefficients were obtained. (b_{a,sib_c}), corrosion potential, ($E_{cor, calc}$) defined at the intersection of the Tafel straight lines (anodic and cathodic branch, corrosion current density (j_{cor}), corrosion rate (v_{cor}) and polarization resistance (R_p), presented in the TABLE 2.

TABLE 2

Corrosion parameters of Al-Si alloy analyzed in aqueous 0.3MNaCl solutions

Parameters	Measurement units	Sample
Segment	[mV]	150
Atomic mass	[g]	55.85
-OCP	[mV]	514
b_a	[mV/dec]	-299.5
b_c	[mV/dec]	176.6
$-E_{cor, calc}$	[mV]	-1317.1
j_{cor}	[mA/cm ²]	1.1344
v_{cor}	[mm/an]	13.26
R_p	[ohm.cm ²]	137.65

Due to the active layer of aluminum oxide that covers the metal upon exposure to air, aluminum has an increased resistance to corrosion. The overall degradation of the aluminum alloy was found to be mainly controlled by mechanical wear while wear accelerated corrosion little contributed

($-OCP = 514 \text{ mV}/j_{cor} = 1.1344 \text{ mA}/\text{cm}^2$). Age-hardened alloys exhibited less wear due to their increased hardness.

TABLE 2 also shows the surface of the sample, (S) immersed in an aggressive environment, which played the role of the working electrode. The experimental results obtained, both by the OCP value and by the corrosion rate, confirm that the Al-Si alloy is corrosion resistant.

3.4. Optic Microscopy

In order to confirm the conclusions of polarization studies, as well as to understand the mechanism of electrochemical corrosion of Al-Si alloy, the microstructure of surfaces was analyzed by light microscopy.

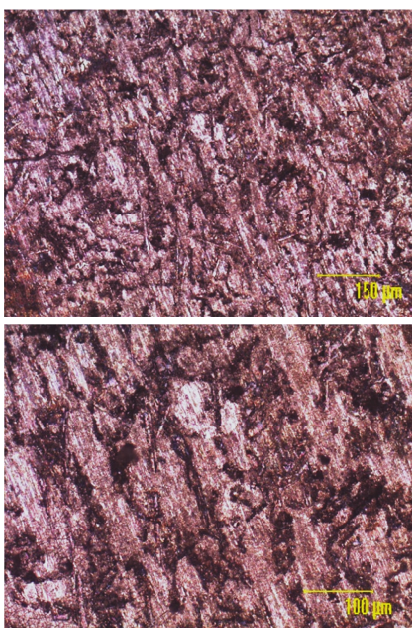


Fig. 4. Microstructure of Al-Si alloys 100 \times , 200 \times magnification

The sample analyzed at the magnification power of 100 \times and 200 \times , made of aluminum-based alloy, was subjected to the study of electrochemical corrosion, using 0.3 M NaCl as corrosive medium. The SEM micrographs obtained for the Al-Si alloy indicate that the chemical attack (0.3 M NaCl) takes place superficially, uniformly on the entire surface of the alloy and only locally appear a series of superficial corrosion points, very small and randomly distributed on the surface. The behavior of the investigated alloys is consistent with the results of potential dynamic measurements that indicate low values for instantaneous corrosion rate (TABLE 2).

4. Conclusion

Design to durability without regard to effect, local corrosion, lead to premature and unexpected failures in the many technical applications. Based on the cyclic voltamograms it can be said that

on the OCP interval (+1.5 V... -1.1 V), after the break through potential there is an intensification of the anodic process by the pronounced increase of the current density, in these conditions other Al-Si has small values which means it has better corrosion resistance. The microscopic metallographic obtained for other Al-Si are consistent with the results of potential dynamic measurements that indicate low values for instantaneous corrosion rate.

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