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The Role of Microstructure on the Corrosion Behaviour of as cast AlCu4MgSi and MgAl2Si Alloys

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Abstract

In this work, the effect of the microstructure on corrosion behavior of selected Mg- and Al-based as cast alloys, was evaluated. The electrochemical examinations were carried out, and then a morphology of corrosion products formed due to local polarization on materials surface, was analyzed. It was documented that the presence of Mg₂Si phase plays an important role in the corrosion course of Mg-based alloy. A selective etching was observed in sites of Mg₂Si precipitates having “Chinese script”- like morphology. Analogous situation was found for Al-based alloy, where the key role was played by cathodic θ-CuAl₂ phase.

Keywords: Metallography, Corrosion resistance, Aluminum alloys, Magnesium alloys, Al-Cu-Mg-Si alloy, Mg-Al-Si alloy

1. Introduction

A cathodic protection is one of the most efficient and simple way to protect materials against corrosion. Its basics principles include an application of galvanic anodes (as protectors) having a more electronegative potential than a protected structural material. The potential difference between the anode and material should be high enough to ensure a formation of protective cathodic current. The higher difference in these values contributes the better protective current.

The efficiency of cathodic protection is mostly determined by applied anode (its type, chemical composition, or shape) as well as by a conductivity of corrosion environment. In a sea water environment, the most popular cathodes are made of aluminum and zinc alloys in as cast state, having different mass and shape

depending on protected surface geometry and its pre-assumed lifetimes [1,2]. In some short-term applications (e.g. upon a maintenance of hulls), magnesium alloys are also applied as the anodes [1]. On the other hand, objects that work underground are protected only by using magnesium [2].

A galvanic anode should fulfill presumed requirements in terms of passivation, polarization and self-corrosion. It should not be susceptible to passivation, and should also undergo only a small polarization. It means that an anode's potential should not be significantly increased due to applied current, because it limits the anode/construction potential, and thus to a current of cathodic protection. The anode should also exhibit a negligible self-corrosion [2].

Aforementioned conditions are fulfilled by zinc, aluminum and magnesium alloys. Additionally, alloying elements are introduced to these alloys in order to hinder their passivation and

self-corrosion [2]. On the other hand, the alloying results in a precipitation and formation of intermetallic phases that strongly affect an intensity and course of corrosion.

In this work, two as cast alloys from Al-Cu-Mg-Si and Mg-Al-Si systems that are applied as cathodic anodes, were investigated. A corrosion-assisted destruction mechanism of these alloys under exposition to 5% NaCl solution, was discussed. The results obtained for zinc alloy, have been already described in [3]. Presently obtained results are of high practical importance due to a wide interest in using of Zn-based, Al-Mg-based and Al-Si are considered as very attractive for a transport industry [4,5].

2. Materials and methods

The chemical compositions of Al-based alloy was evaluated by a glow-discharge optical emission spectroscopy (GDOES) by using LECO GDS500A device. The chemical composition of Mg-based alloy was examined by scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDX) by using Phenom World ProX microscope. The content of each particular element was determined by using the ZAF correction and normalization to 100 %. The obtained chemical compositions of investigated materials are listed in Table 1.

Table 1.
Chemical compositions of investigated materials

Alloy	Al	Mg	Cu	Si	Mn	Fe	Zn	Cr
AlCu4MgSi	balance	0,75	4,06	0,46	0,68	0,66	0,22	0,04
MgAl2Si	1,82	balance	-	0,75	-	-	-	-

Light microscope (Leica DM 6000 M) and SEM/EDS (Phenom World ProX) were applied to characterize microstructure of examined materials on etched and non-etched metallographic specimens. Macroscopic evaluations were performed by using Leica M205 C stereoscopic microscope.

Furthermore, a direct current electrochemical experiments including measurements of open circuit potential E_{OCP} and recording of $i=f(E)$ curves upon polarization tests carried out in triple electrodes setup. This setup was composed of container, ATLAS 0531 potentiostat and a computer driver. The supporting electrode was made of austenitic steel, while the reference electrode was saturated Ag/AgCl. The surface of investigated electrode (a sample) was equal to 0.785 cm^2 . Before experiment, each sample was stabilized upon 20 min. exposure at room temperature in 5 % NaCl solution. After that, a sample was polarized in the same solution in anode direction under the rate $dE/dt = 1 \text{ mV/s}$. The pH value of applied NaCl solution was equal to 7.5. The initial potential value was set as 200 mV lower than that of E_{OCP} . Polarization curves were recorded for three samples of each investigated materials. After that, they were used to determine corrosive potential E_{corr} and corrosion current density I_{corr} .

3. Results and discussion

3.1. Microstructural study

The MgAl2Si alloy had a microstructure typical for cast magnesium alloys alloyed with Si and Al (Fig. 1). Beside the δ solid solution, precipitates of Mg_2Si phase having „Chinese script” morphology and globular $\text{Mg}_{17}\text{Al}_{12}$ (the β phase) precipitates with a local form of “deteriorated eutectic” (Fig. 2), were observed. The identification of these two phase components in Mg-Al-Si alloys is also confirmed by the results reported by other authors [4-7].

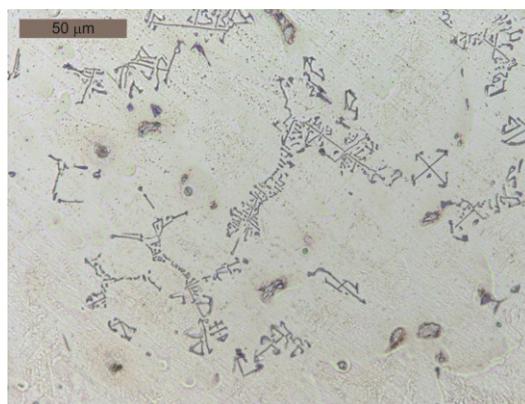


Fig. 1. Microstructure of as cast MgAl2Si alloy. Mg_2Si phase in the form of „Chinese script” and $\text{Mg}_{17}\text{Al}_{12}$ (phase β) visible in the background δ solid solution.
Light microscope. Sample of etching

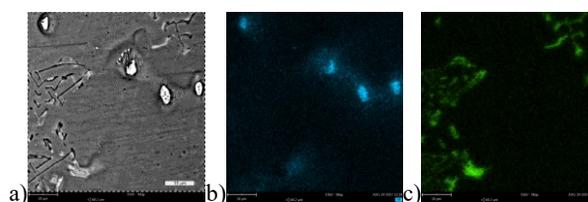


Fig. 2. Microstructure SEM of as cast MgAl2Si alloy (a) and the corresponding EDX maps for (b) Al, (c) Si. SEM/EDS

In the case of AlCu4MgSi cast alloy, the presence of $\theta\text{-CuAl}_2$ phase and iron enriched AlFeMnSi one, was documented (Fig. 3, Fig. 4). The latter is commonly observed in almost all aluminum alloys, as the effect of primary iron contamination that is too expensive to be completely removed. The low solubility of iron in aluminum leads to the formation of intermetallic phases.

The CuAl_2 precipitates are typically found in copper containing as-cast alloys, and have been already described previously [8, 9]. Two kinds of such precipitates were observed:

large blocky-like, and dispersive formed due to a rapid quenching and heterogeneous nucleation [9].

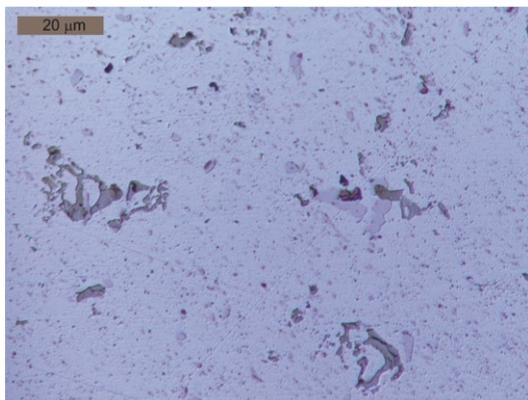


Fig. 3. Microstructure of as cast AlCu4MgSi alloy. Light microscope. Sample of etching

The β -Mg₂Si phase was not detected, which may also form in these alloy taking into account its chemical composition. Zheng et al. [8] have documented that the formation of either CuAl₂ or Mg₂Si is determined by the Cu/Mg content ratio. They showed that a formation of Mg₂Si phase requires low values of Cu/Mg ratio. Silicon was detected only in iron enriched AlFeMnSi precipitates. The CuAl₂ phase plays a role of strong cathode in the investigated alloy [10].

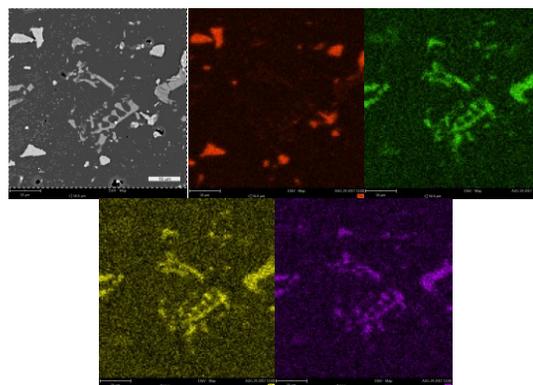


Fig 4. Microstructure SEM of as cast AlCu4MgSi alloy (a) and the corresponding EDX maps for (b) Cu, (c) Fe, (d) Mn, (e) Si

3.2. Electrochemical study

All three polarization curves obtained for each particular materials showed similar courses and curves differed slightly in the corrosion potential E_{corr} , what confirmed a high homogeneity of materials. For both alloys (Al and Mg-based) of anodic polarization curves pointed towards a high intensity of occurred corrosion related processes. Exemplary curves are shown in Fig. 5, while values of basic electrochemical parameters are listed in Table 2.

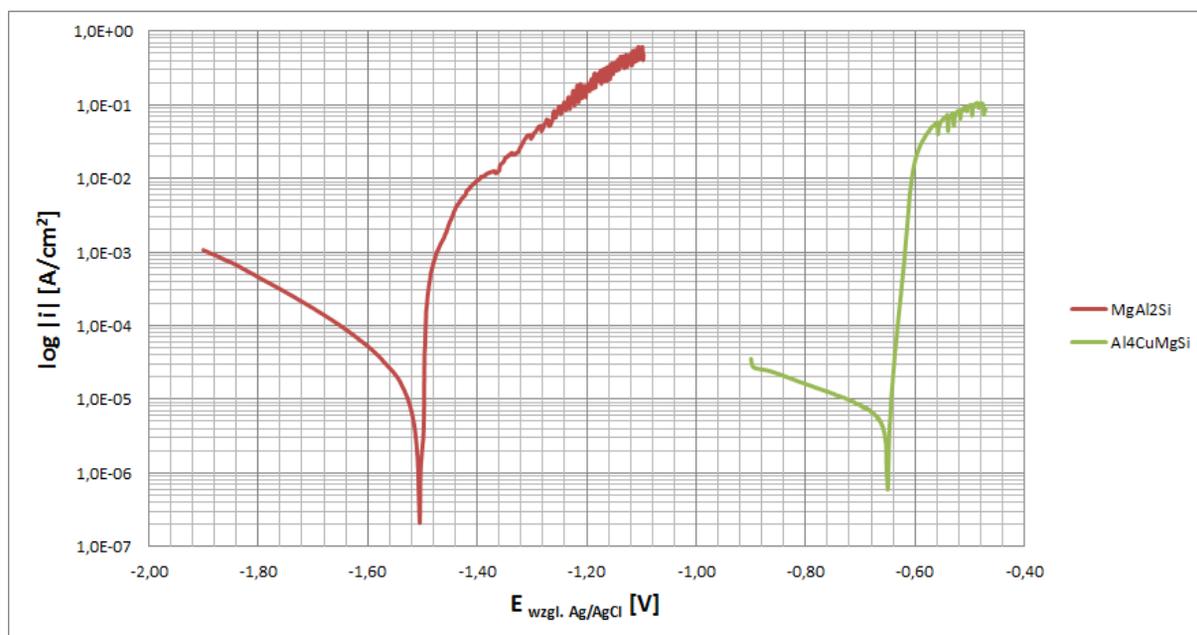


Fig. 5. Polarization curves of as cast MgAl₂Si and Al₄CuMgSi alloys

It was found that the MgAl₂Si alloy exhibits significantly lower value of corrosion potential E_{corr} , than that of AlCu₄MgSi

alloy. The lower E_{corr} value is also reflected by a higher polarization current for the Mg alloy. The corrosion potential of

aluminum alloy is more positive than that expected for non-alloyed aluminum, due to the presence of θ - CuAl_2 precipitates (strong cathodes).

A slightly lower I_{corr} value recorded for the aluminum alloy is also reflected by lower corrosion rate in examined environment.

Tabele 2.

Values of electrochemical parameters

Alloy	E_{OCP} [mV]	E_{corr} [V]	I_{corr} [$\mu\text{A}/\text{cm}^2$]
AlCu4MgSi	-0,63	-0,65	8,2
MgAl2Si	-1,48	-1,49	15,6

3.3. SEM observations after the electrochemical studies

The addition of alloying elements to Mg- and Al-based alloy result in a formation of intermetallic phases, that in turn are not neutral for the course of corrosion processes. In order to evaluate the nature of their impact, surfaces of both materials subjected to the electrochemical tests, were examined.

In the case of MgAl2Si alloy, the presence of Mg_2Si phase seems to be crucial for corrosion course. However, some discrepancies regarding the role of this phase, are reported in the literature. Some authors [4] have recognized its local cathodic activity, while the others [11] have pointed towards its anodic nature. Furthermore, some other works [4, 12] describe its negligible impact on the corrosion of Mg matrix, due to an electrochemical potential similar to that of pure magnesium. These discrepancies might be justified by the fact that behavior of Mg_2Si phase is strongly determined by pH of applied corrosive medium [5]. Moreover, a possible electrochemical polarity conversion due to a magnesium depletion at initial corrosion stages, was also documented [13].

Nevertheless, a formation of both blocky-like or Chinese script-like Mg_2Si precipitates, strongly affects the loss of continuity of surface oxide layer [4]. This finding was confirmed by microscopic observations of the MgAl2Si alloy surface after electrochemical tests. Some effects related to a selective oxidation were observed in sites where Mg_2Si phase was presented (Fig. 6). It might be associated either with the anodic nature of the phase or with a weakening of the surface passive layer.

Simultaneously, a formation pits filled by corrosion products and surrounded by rings, was observed (Fig. 7). It is a characteristic feature for the formation of stable pits [10]. It was not evidenced that these pits were related to the presence of some other phase constituents, which should be reflected in the chemical composition of the formed corrosion products. It was also confirmed by the results of EDX chemical composition analyses of corrosion products revealing only Mg, O and Cl.

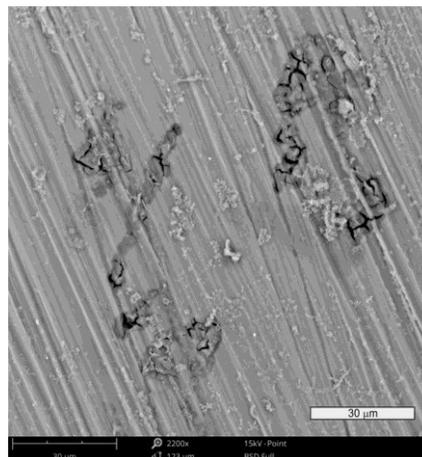
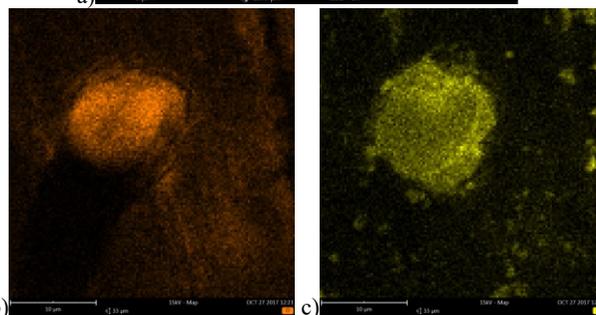
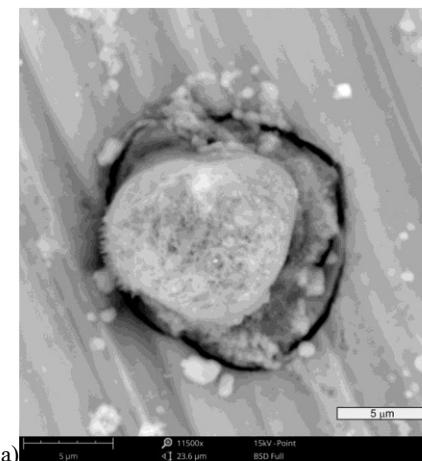
Fig. 6. Selective dissolution around Mg_2Si phase. SEM

Fig. 7. Corrosion pit containing chlorine and surrounded by ring (a) and the corresponding EDX maps for (b) O, (c) Cl. SEM/EDS

Although, the cathodic nature of $\text{Mg}_{17}\text{Al}_{12}$ (β) phase has been described in the literature [4, 14], the effect of this phase on the corrosion resistance of examined Mg-based alloy, was not clearly documented in this work. On the other hand, it has been noted in [4] that corrosion behavior of the β phase is strongly determined by a distance between its adjacent precipitates. It has been described that this phase becomes an active cathode when its high fractioned ensures low distance between neighboring particles. Otherwise, an increased corrosion in the β phase sites, takes place [4].

Copper is a basic alloying element in aluminum alloys. It has been already established that the θ - CuAl_2 phase in wrought alloys is a strong cathode able to locally support cathodic reaction. Its corrosion potential in NaCl solution, has been estimated to be around 150 mV higher than that of pure aluminum [11, 15]. The conducted microscopic observations confirmed an analogous effect of this phase on the occurrence of corrosion processes in the AlCu4MgSi alloy. A dissolution of α solid solution in areas located near CuAl_2 precipitates (Fig. 8, Fig. 9), was observed. By taking into account that the CuAl_2 phase was non-uniformly distributed in the volume of material (i.e. as fine submicron sized particles, as relatively large – up to 20 μm precipitates and as conglomerates), the formation of characteristic tunnels on the materials surface, was observed. An existence of tunneling corrosion features should be related to an initiation of corrosion in solid solution areas located near CuAl_2 precipitates, where the local copper content was depleted (Fig. 10). This effect originates from: (i) a preferential corrosion of low copper content sites and (ii) a galvanic interaction between CuAl_2 precipitates and the solid solution matrix.

Finally, no direct evidence for a significant effect of iron enriched AlFeMnSi phase on the corrosion course of the alloy, was found. This is in a good agreement with the results presented elsewhere [11].

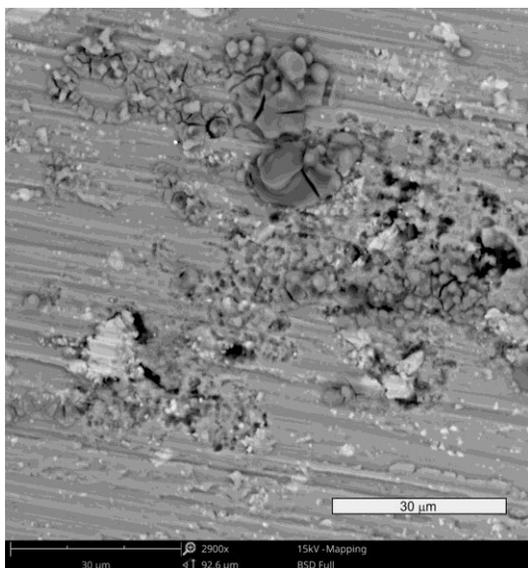


Fig. 8. Selective dissolution around cathodic CuAl_2 phase in microstructure of as cast AlCu4MgSi alloy. SEM

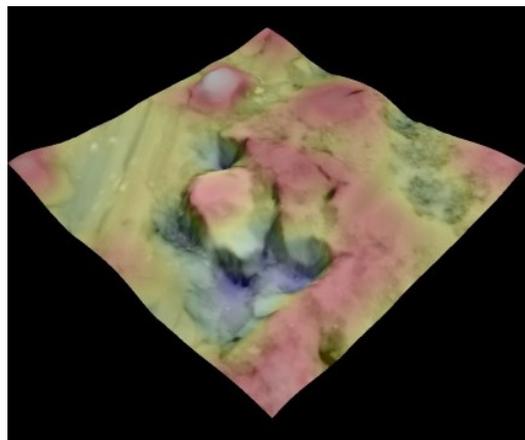


Fig. 9. Selective dissolution of solid solution around CuAl_2 precipitates. Image 3D. SEM

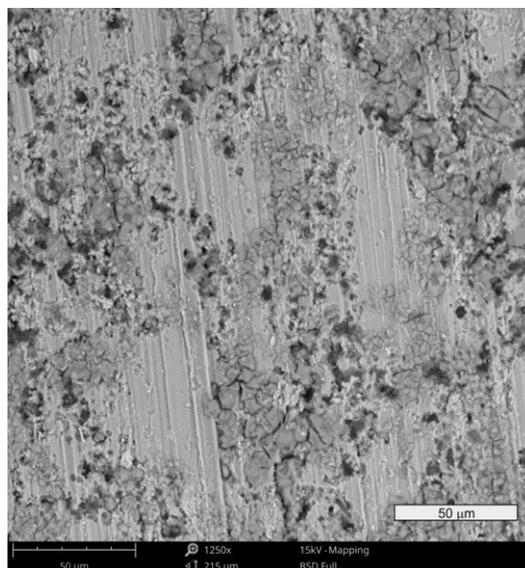


Fig. 10. The surface as cast AlCu4MgSi alloy after electrochemical tests. Selective dissolution of as cast AlCu4MgSi alloy and tunneling corrosion. SEM

4. Conclusions

The main purpose of the presented research was to evaluate morphological features of surface corrosion products formed on the investigated materials, due to an occurrence of local corrosion. It is important, from the viewpoint of recognizing involved mechanism, and especially the role of intermetallic phases existed in materials' structures. The high importance of the conducted research is also justified not only by a possible usage of the investigated materials as galvanic anodes, but also due to their potential applications in the transport, automotive and aerospace industry. The cathodic protection is the most popular method of protecting the hulls of ships against corrosion [1]. The use of light alloys for automotive components is an important issue to reduce

vehicle weight and associated fuel consumption leading to a reduction in air pollutants emission. Nowadays, magnesium alloys are successfully used in the drive system of automobile engines [7]. There are also reported that corrodible characteristic of magnesium alloys can be used to their utilization on degradable fracturing ball applied to the oil industry [5].

In the case of as cast MgAl₂Si alloy, a strong effect of the Mg₂Si intermetallic phase on the corrosion course, was documented. A selective dissolution of material's surface in the vicinity of well-developed Chinese script like precipitates points towards either the anodic nature of Mg₂Si phase or a weakening of surface passive layer.

The examinations of as cast AlCu₄MgSi alloy revealed a crucial role of θ -CuAl₂ cathodic phase. The dissolution of solid solution matrix was observed in regions neighboring precipitates of this phase. The corrosion mechanism associated with action of these cathodic participates, is usually assisted by a depletion of near particles areas, what in turn leads to a more intensive selective dissolution of the matrix.

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