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Effect of native air-formed oxidation on the corrosion behavior of AA 7075 aluminum alloys

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ABSTRACT

The effect of native air-formed oxidation on the corrosion behavior of AA 7075 aluminum alloy and selective corrosion of anodic Mg_2Si precipitates was presented. Oxidation of Mg_2Si leads to formation of $Mg(OH)_2$ protrusions depleting magnesium in this precipitate as shown by AFM, SEM and EDX results. Spectroscopic studies prove that composition changes occurring within the passive layer may be a cause of observed improvement of electrochemical properties under prolonged exposition to air. Influence of cathodic phases containing AlFe(Cu,Mn,Cr) is limited in these conditions.

1. Introduction

Corrosion resistance of the aluminum alloy AA 7075 is mostly connected with the presence of many types of intermetallic phases, such as Al_7Cu_2Fe, $(Al,Cu)_6(Fe,Cu)$, $Al_{23}CuFe_4$, Al_2CuMg, $Al_{12}(Fe,Mn)_3Si$, Mg_2Si. It was noticed however, that they usually show a deviation from stoichiometric composition [1]. Phases consisting of Al, Zn and Mg are anodic, while those containing Al, Cu, Fe and Mn are cathodic relative to the aluminum alloy matrix [2–4]. This situation promotes the formation of corrosion micro-cells and initiates the local corrosion process.

The influence of intermetallic precipitation mostly depends on the difference between electrochemical potentials between the phase and the matrix of the aluminum alloy, implying different local corrosion mechanisms [5]. It was reported by Blanc and Mankowski [6] that presence of intermetallic precipitates on the metal surface leads to passive layer inhomogeneities and increases the susceptibility to pitting corrosion. Vuelvas et al. [7] and Boag et al. [8] show directly that pitting corrosion of aluminum alloys depends on electrochemical character of intermetallic precipitates and anodic dissolution of Al–Mg phase. Luo et al. [9] and El-Amoush [10] reported that not only pitting corrosion, but also intergranular corrosion is affected by structure heterogeneity leading to formation of galvanic micro-cells while Pao et al. [2] proves its influence on fatigue corrosion.

Anodic precipitates play a major role in local corrosion of aluminum alloys. Mg_2Si is the most significant precipitate of 7xxx alloys due to its strongly anodic character versus alloy matrix. It is currently known that this phase is the place of pitting initiation. Research carried out by Birbilis et al. [4,11] has shown that the Volta potential of Mg_2Si is 200 to even 500 mV lower as compared to the alloy matrix. Such a big difference between the potentials influences considerable activity of the galvanic cell occurring in the alloy microstructure. A majority of studies prove that especially during exposure to NaCl solution, this precipitate undergoes selective corrosion resulting in magnesium dissolution [12]. During the corrosion process, an increase in the potential of this precipitate occurs due to the falling magnesium content. The decrease in the magnesium content is accompanied by the appearance of oxygen, which may indicate the formation of corrosion products in the form of oxides or hydroxides [13].

Zeng et al. [14] concluded that local corrosion resulting in dealloying and selective solubilization of magnesium leads to enrichment of anodic precipitates with silicone and causes increase of the Volta potential, eventually turning the remains of Mg_2Si phase into a cathode. Selective solubilization of magnesium leads to the formation of a layer of magnesium hydroxide $Mg(OH)_2$ and hydrated $SiO_2 \cdot nH_2O$. Their presence on the surface of Mg_2Si accounts for the relatively low corrosion activity of this phase. The enrichment of the anodic phase in silicon and the formation of a hydroxide layer prevent further pitting propagation within Mg_2Si and, at the same time, it enriches the corrosion resistance of the alloy to a certain extent.

$Mg(OH)_2$ may constitute an additional barrier hindering further solubilization of the anodic intermetallic phase. *In-situ* AFM tests confirm the corrosion behavior of the Mg_2Si phase. At the first stage of pitting corrosion, a thin layer of deposits is formed which consists of $SiO_2 \cdot nH_2O$ and/or $Mg(OH)_2$, which inhibits further

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pitting propagation in the area of the occurrence of the phase rich in magnesium and silicone [15].

Resistance of the 7xxx alloys depends strongly on the size and distribution of particles forming intermetallic precipitation [16], making the corrosion process described above very complex. As was suggested by Zeng et al. [14], only after silicon becomes the dominant ingredient in Mg_2Si phase, the corrosion process begins to affect the alloy matrix.

This study is aimed at presenting the effect of native air-formed oxidation, similar to the one occurring during natural ageing process, on corrosion behavior of AA 7075 aluminum alloy and, in particular, microstructural changes in the Mg_2Si precipitate resulting from exposure under air conditions.

2. Experimental

2.1. Material and sample preparation

Two sets of identical samples from AA 7075 aluminum alloy were prepared. Cylinder samples have a diameter of 10 mm and a height of 5 mm. Chemical composition of the AA 7075 aluminum sample is presented in Table 1.

Before the experiment samples were subjected to grinding on 400 to 4000-grit sandpaper and next polished using diamond emulsion with 50 nm finish using a SiO_2 suspension until mirror finish was obtained. Next, samples were rinsed three times for 15 min in acetone on an ultrasound bath.

Prior to the experiment, all samples were compared by means of scanning electron microscopy (SEM) to check on the quality of the polishing and cleaning process. An Energy Dispersive X-ray Spectroscopy (EDX) analysis was also conducted to compare their chemical composition with standard values [17]. No nonconformities were detected.

The samples were exposed to atmospheric air and the effect of native air-formed oxidation on corrosion behavior was checked in a closed air-conditioned laboratory at 22 °C with relative humidity of 50%. The exposure lasted 1, 7, 30 and 90 days. Additionally, each of the sets contained a reference sample, which is marked in this research as 0-day exposure. Due to the possibility of the modification of the passive layer, in particular during electrochemical analysis, each of the samples was used only once and afterwards did not take part in the experiment. This rule does not apply to the SEM/AFM analysis, which is non-destructive for the passive layer.

2.2. Conditions of research

The first of the sets of samples was used for electrochemical analysis that included the Electrochemical Impedance Spectroscopy (EIS) technique. EIS measurements were performed using Gamry Instruments CMS-300 system. Measurements were performed in a three-electrode system, in which a silver chloride electrode (Ag/AgCl) was the reference electrode and platinum mesh was the auxiliary electrode. The research was conducted in a borate buffer ($H_3BO_3 + Na_3BO_3$; pH 7.4). The working surface of the tested samples was 0.2 cm^2. Frequency of voltage excitation signal ranged from approx. 10 kHz to approx. 30 mHz with 10 points per decade. The amplitude of the voltage signal was 15 mV. The registration of the impedance spectra was performed with a stable value of corrosion potential. The stabilization time of the potential was 1 h.

Table 1
Chemical constitution of AA 7075 alloy, on the base of EDX measurements.

Al	Zn	Mg	Cu	Fe	Si	Mn	Cr
Bal.	5.5	2.4	1.3	0.4	0.4	0.2	0.2

Another set of samples was used in a physicochemical analysis including micro- and spectroscopic techniques. SEM analysis was performed using an S-3400N microscope manufactured by Hitachi. Micrographs were taken in the secondary electron mode for 20 kV accelerating voltage. The microscope was equipped with EDX detector manufactured by ThermoFisher Scientific. EDX was used to assess the chemical composition of the sample (averaging from the surface area of 2 mm^2) and to determine the composition of the individual phases in the AA 7075 alloy. To implement the latter objective, the accelerating voltage was reduced from 20 to 10 kV to eliminate signals from depths beneath analyzed phases.

An integrated measurement system, NTEGRA Aura, manufactured by NT – MDT was used for tests using atomic force microscopy. Micrographs were made in contact mode. The pressure of the probe blade on the surface was 170 nN, which allowed to obtain an extremely small contact area between the blade and the surface of the sample. Additionally, the original software allowed determination of the roughness profile.

The physicochemical analysis was supplemented with the determination of changes in the passive layer during the experiment using the X-ray Photoelectron Spectroscopy technique (XPS). An XPS Escalab 250Xi spectroscope manufactured by ThermoFisher Scientific was used. The diameter of the spot of the radiation source was 200 μm. Depth profiling using an ion gun (500 V) was performed. The energy and etch time was determined empirically to obtain the profile for the entire thickness of the passive layer.

3. Results

SEM microstructure, representative for alloy samples is presented in the top left of Fig. 1. Below, bottom left image presents the same fragment of the sample after 90-day exposure period. Significant changes were observed here for the Mg_2Si phase, the surface of which is covered by a layer of protrusions (magnified on the bottom right). The results of the point-based EDX analysis for the matrix and both phases are presented on the top right of Fig. 1. As a result of the exposure to atmospheric air, far-reaching and irreversible changes occurred in the Mg_2Si phase.

Atomic Force Microscopy (AFM) in the contact mode was utilized in order to provide detailed topographic information of sample surface. Fig. 2 shows AFM results for the same area of the investigated sample as was investigated with SEM/EDX for 0-day exposure (Fig. 2a) and 90-day exposure (Fig. 2c) with a close-up and contrast adjustment of the Mg_2Si phase. This phase initially does not differ significantly from the matrix in terms of the depth. Roughness profiles were prepared in the “scan 1” area for the AlFe(Cu,Mn,Cr) phase and “scan 2” for the Mg_2Si phase to present changes in vicinity of the phases as a result of experiment (Fig. 2b and d, respectively). By comparing both micrographs an increase in roughness on the surface of the analyzed sample can be noticed.

The results of impedance analysis performed for various exposure times are presented in Fig. 3. Electric parameters of the sample were estimated with R(QR) electric equivalent circuit, consisted from electrolyte resistance R_s, resistance of the passive layer R_f and constant phase element (Q, n) which describes the dielectric properties of the passive layer. Calculated values of the electric equivalent circuit components are given in Table 2. Electric parameters were calculated using ZSimpWin software.

XPS with depth profiling was used to determine changes in the passive layer as a result of natural oxidation process. High resolution XPS analysis was performed for magnesium, aluminum and oxygen only, guided by EDX analysis. The other elements were not included. Ion gun etching was made in accordance with the formula presented in Table 3, to obtain information within the