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THE EFFECT OF ELECTROPOLISHING IN A DEEP EUTECTIC SOLVENT (ETHALINE) ON THE SURFACE PROPERTIES AND CORROSION RESISTANCE OF ALUMINIUM–MAGNESIUM ALLOY

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Electropolishing of Al–Mg alloy (5 wt.% of Mg) in a deep eutectic solvent ethaline (a eutectic mixture of choline chloride and ethylene glycol) was investigated. Scanning electron microscopy and atomic-force microscopy revealed that the electrochemical surface treatment in ethaline provided a significant improvement of the surface characteristics of Al–Mg alloy. The amount of surface oxygen decreased after electropolishing of aluminium–magnesium alloy in ethaline as compared with the untreated surface. A removal of aluminium oxide film took place during electropolishing and no anodization was observed. The potentiostatic electropolishing of Al–Mg alloy in ethaline at the potential of +6 V (against Ag pseudo-reference electrode) and the temperature of 25°C allowed reducing the surfaces roughness coefficient. The study of corrosion behavior of Al–Mg alloy in 10 wt.% NaCl solution before and after electropolishing in ethaline was performed by using liner polarization resistance technique. It was established that the electrochemical polishing in ethaline caused an improvement in corrosion resistance of Al–Mg alloy. Thus, the deep eutectic solvent ethaline can be used as an environmentally friendly, resource-saving and inexpensive alternative to common hazardous acidic electrolytes for electropolishing of Al-based alloys.

Keywords: Al–Mg alloy, electropolishing, deep eutectic solvent, surface roughness, corrosion resistance.

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Introduction

Aluminium alloys are used in a wide range of applications due to their unique properties such as low density, enhanced corrosion resistance, high electric and thermal conductivity, good light reflection, easy machinability, and relatively low cost. In practical applications of the aluminium and its alloys, a proper surface finishing is often required. For producing smooth surfaces of Al-based alloys with attractive appearance and high corrosion resistance, some surface treatment techniques can be used: mechanical polishing, chemical polishing, thermal polishing and electropolishing [1]. It should be noted that electrochemical polishing is the most efficient method of improving surface characteristics of Al-based alloys. This method involves not only a decrease in the roughness of surfaces, but also changes in surface layer composition, which can improve corrosion resistance and other surface properties of alloys.

However, most common electrolytes for electrochemical treatment of Al and Al-based alloys are very corrosive. Such polishing electrolytes contain strong mineral acids (phosphoric, perchloric, nitric, sulfuric acids and their mixtures) and some toxic additives (alcohols, CrO₃, etc.) [2–9]. Thus, the development of new environmentally friendly processes for electrochemical polishing of Al and Al-based alloys avoiding the use of toxic and hazardous chemicals is a topical issue in modern surface engineering. An efficient electropolishing of Al and its alloys can be carried out in a new type of ionic liquids, the so-called deep eutectic solvents [10,11]. These solvents are a new generation of ionic liquids, which have a wide range of attractive properties, such as environmental safety, affordability, chemical and thermal stability, wide window of electrochemical stability, relatively high conductivity, etc. [12].

In the present work, we investigated the process of electropolishing of Al–Mg alloy by using ethaline, a deep eutectic solvent that is a eutectic mixture of choline chloride and ethylene glycol. We described the effect of electropolishing process in ethaline on the surface morphology of Al–Mg alloy, its roughness and corrosion behavior.

Materials and methods

A choline chloride-based deep eutectic solvent ethaline was used in this work as an electrolyte for electropolishing of aluminium–magnesium alloy. Ethaline is a eutectic mixture of ethylene glycol and choline chloride at the molar ratio of 1:2, respectively. The synthesis of ethaline and specifics of its storage were described in details in our previous works [11,13–15].

The samples of Al–Mg alloy ($S=4\text{ cm}^2$) were used for electropolishing. The alloy contained 95.0 wt% of Al and 5.0 wt.% of Mg.

The Al–Mg samples before all tests were polished with 600 grit black silicon carbide abrasive papers, washed with distilled water, and then etched in HCl solution (1:1) for several seconds. After that, they were washed with distilled water and finally dried in hot air flow.

All electrochemical experiments were conducted in a thermostated (25°C) three-electrode glass cell using potentiostat Metrohm Autolab PGSTAT302N (Netherlands) controlled by a personal computer with Autolab NOVA software. To study the electropolishing process, the samples of Al–Mg alloy were used as working electrodes, platinum grid was an auxiliary electrode and silver wire served as a pseudo-reference electrode. The scan rate in cyclic voltammetry was equal to $5\text{ mV}\cdot\text{s}^{-1}$.

Corrosion behavior of untreated and electropolished aluminium–magnesium samples was estimated by the method of linear polarization resistance (LPR) measurements. To this end, the same electrochemical cell and potentiostat were used. The corrosion characteristics of Al–Mg alloy were studied in 10 wt.% NaCl aqueous solution. In the study of corrosion behavior, the Al–Mg alloy samples (electropolished and untreated) were working electrodes, a saturated silver chloride electrode served as a reference electrode and platinum grid was used as a counter electrode. The LPR measurements were realized at the scan rate of $1\text{ mV}\cdot\text{s}^{-1}$.

In all electrochemical measurements, an automated IR-compensation was implemented by means of a built-in compensator of the potentiostat.

The surface morphology of the samples before and after electrochemical treatment was estimated by scanning electron microscopy (Zeiss EVO

40XVP). The chemical composition of the surface was determined by energy dispersive X-ray spectroscopy (EDS) coupled with SEM microscope (Oxford INCA Energy 350). The atomic-force microscopy (AFM) (Bruker, Dimension Edge) was applied to characterize surface profile and determine roughness parameters. AFM investigations were performed in tapping mode using etched silicon probes (Bruker, RTESPA-300). Root mean squared roughness (R_q) was calculated from AFM data.

Results and discussion

The cyclic voltammogram recorded for Al–Mg alloy in ethaline at the temperature of 25°C and the scan rate of $5\text{ mV}\cdot\text{s}^{-1}$ is shown in Fig. 1. The potential scan was carried out from an open circuit potential (OCP) (about -0.980 V) in the anodic direction up to the potential of $+6\text{ V}$ and then returned to the OCP value.

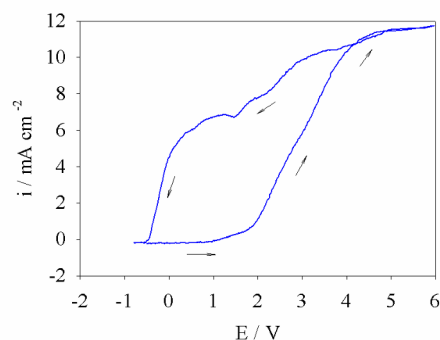


Fig. 1. Cyclic voltammogram of Al–Mg alloy recorded in ethaline (25°C, $5\text{ mV}\cdot\text{s}^{-1}$)

Active dissolution of Al–Mg alloy starts from an anodic potential of about $+1\text{ V}$. A plateau of anodic current is observed at the potential of about $+4\text{ V}$. Curves presented in Fig. 1 are very similar to those obtained for «pure» aluminium sample in ethaline [11]. Therefore, the main electrochemical process occurring during electropolishing of Al–Mg alloy is probably the anodic dissolution of aluminium.

It is well known that the best effect of surface leveling in electropolishing processes can be achieved if an electrochemical dissolution of metal occurs under diffusion control. Therefore, the anodic potential of $+6\text{ V}$ situated in zone of current plateau was chosen for further experiments to provide efficient electropolishing of Al–Mg alloy.

SEM images (Fig. 2) of the surfaces of Al–Mg samples unpolished and electropolished in ethaline showed that the anodic treatment results in defect-free and uniform surface morphology. According to the data of EDS analysis (Fig. 3 and Table 1), the

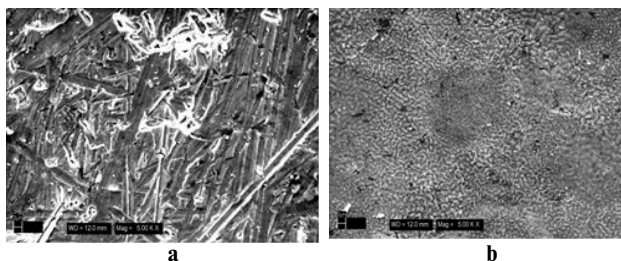


Fig. 2. SEM images of unpolished (a) and electropolished (b) Al–Mg alloy ($E=6$ V; $\tau=20$ min; $t=25^{\circ}\text{C}$)

amount of surface oxygen slightly decreases after electropolishing in ethaline as compared with the untreated surface. This behavior may indicate that a removal of aluminium oxide film takes place during electropolishing and newly formed protective oxide layer after electrochemical polishing has a denser structure. Thus, the EDS analysis confirms that no anodization is observed when Al–Mg alloy was electrochemically treated at the potential of 6 V in ethaline deep eutectic solvent.

Table 1

Results of EDS analysis of the surface chemical composition of Al–Mg alloy before and after electropolishing in ethaline ($E=6$ V; $\tau=20$ min; $t=25^{\circ}\text{C}$)

State of the sample	Element content, wt. %			
	Al	Mg	C	O
Unpolished	86.04	4.03	3.25	6.68
Electropolished	91.68	4.35	1.53	2.44

The surface smoothing of the Al–Mg alloy after electropolishing in ethaline was evidenced by independent AFM measurements. Figures 4 and 5 show that the surface morphology of Al–Mg alloy after electropolishing in ethaline becomes much more uniform: deep scratches and defects of the surface practically disappear. Smoother and more even

surfaces of aluminium-magnesium alloy electropolished in ethaline demonstrate lower surface roughness coefficients (Table 2).

Table 2

Calculated values of surface roughness (R_q) determined by AFM analysis

State of the sample	R_q , nm
Unpolished	283.9
Electropolished	244.3

Corrosion behavior of aluminium-magnesium alloys before and after its electrochemical polishing in ethaline was estimated by means of LPR method. LPR measurements showed that the electrochemical anodic treatment of Al–Mg alloy in ethaline leads to a considerable shift of all segments of the polarization curve (including Tafel regions) towards more positive values of electrode potential (Fig. 6). Parameters characterizing corrosion of Al–Mg alloy in 10 wt.% NaCl solution were calculated from Tafel regions of voltammograms and are summarized in Table 3.

As can be seen from Table 3, the electrochemical polishing of aluminium–magnesium alloy results in an increase in the value of corrosion potential (E_{corr}) and a decrease in the corrosion current density (i_{corr}) and the corrosion rate (CR). The results here show clearly that less rough and more uniform surface of Al–Mg alloy electropolished in ethaline exhibits higher corrosion resistance than the unpolished sample. The newly formed dense protective oxide layer after electropolishing can also contribute to the improvement in the corrosion resistance. It is known that the constant b_a , which directly characterizes the kinetics of anodic metal dissolution in a corrosion process, decreases when the surface becomes rougher or partially coated with

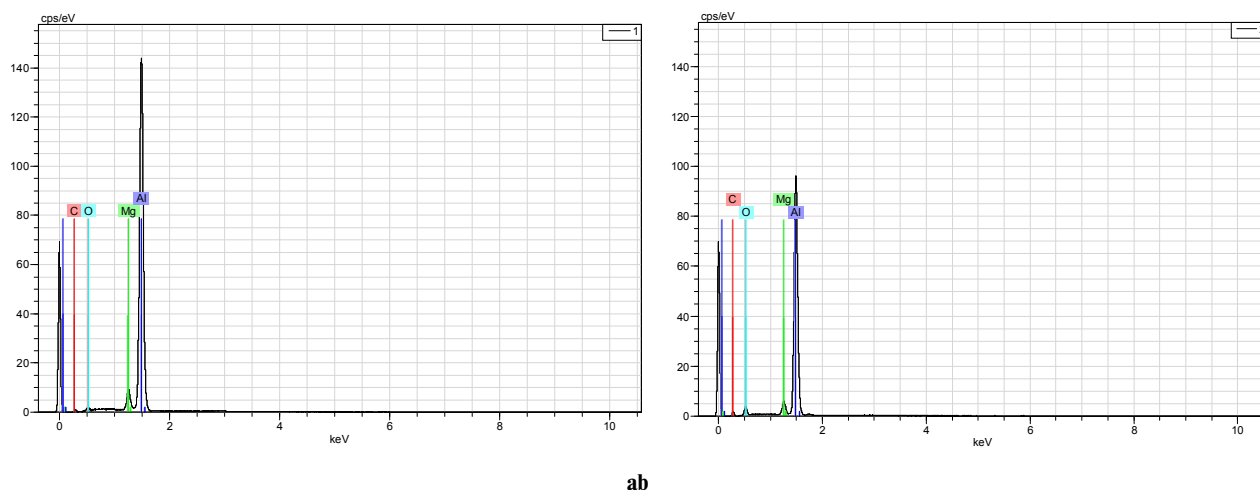


Fig. 3. EDS spectra of unpolished (a) and electropolished (b) Al–Mg alloy ($E=6$ V; $\tau=20$ min; $t=25^{\circ}\text{C}$)

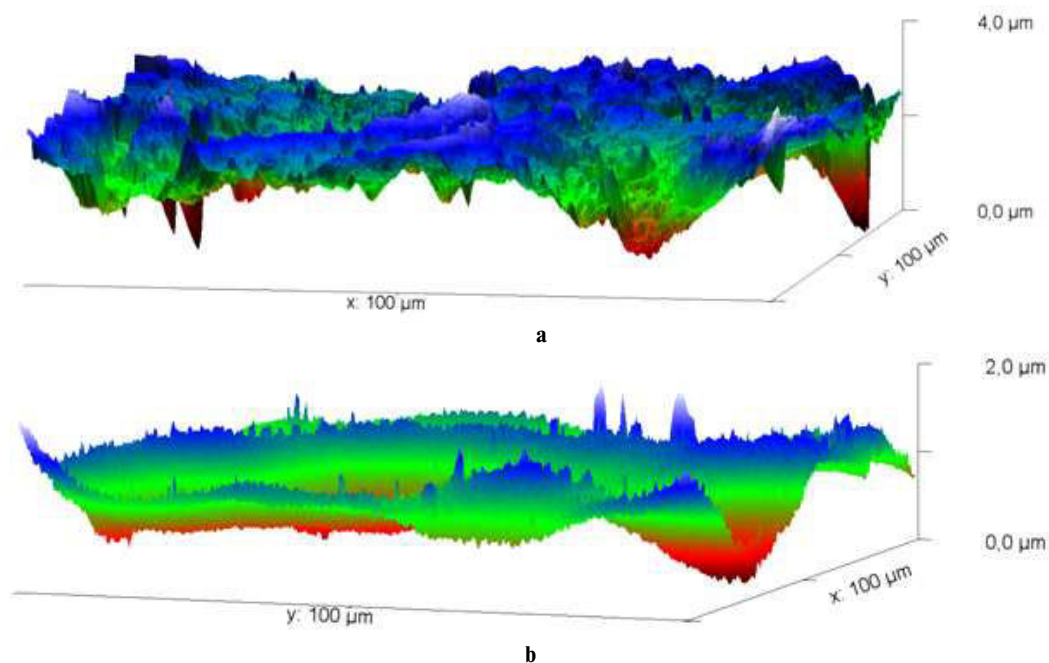


Fig. 4. Surface profiles of unpolished (a) and electropolished (b) Al–Mg alloy ($E=6\text{ V}$; $\tau=20\text{ min}$; $t=25^\circ\text{C}$)

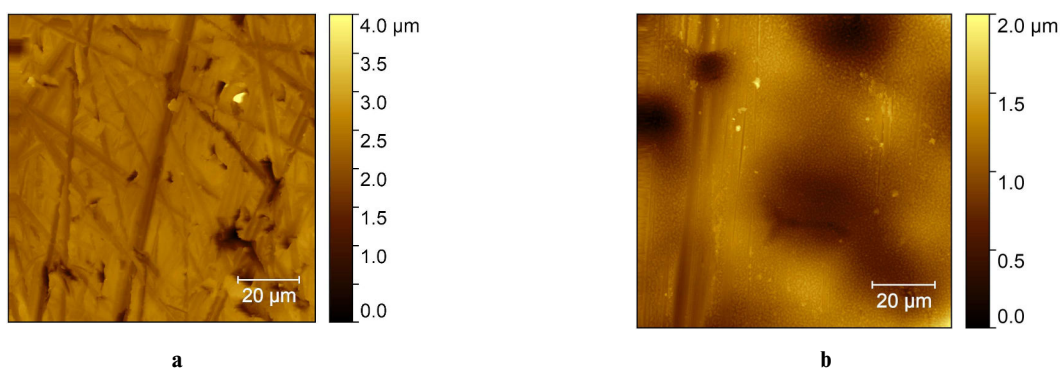


Fig. 5. AFM images of unpolished (a) and electropolished (b) Al–Mg alloy ($E=6\text{ V}$; $\tau=20\text{ min}$; $t=25^\circ\text{C}$)

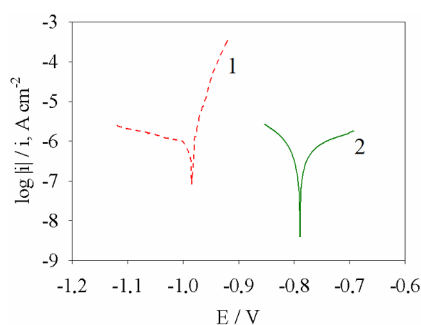


Fig. 6. Tafel plots for the corrosion of unpolished (1) and electropolished (2) Al–Mg alloy in 10 wt.% solution of NaCl (25°C). Electropolishing was carried out in ethaline ($E=6\text{ V}$; $\tau=20\text{ min}$; $t=25^\circ\text{C}$)

some passivating layers. In our case (Table 3), the electropolishing of Al–Mg alloy leads to a noticeable increase in the parameter b_a , which may be due to both a decrease in roughness and the removal of oxide layers on the polished surface of the Al–Mg sample.

Earlier, we demonstrated a positive effect of electropolishing in ethaline on the corrosion properties of some metals and alloys [11,14]. The data obtained in the present study indicate that this conclusion is valid in the case of Al–Mg alloy.

Conclusions

The electropolishing of Al–Mg alloy was performed for the first time by using choline chloride-based ionic liquids, ethaline. It was shown that the

Table 3

Corrosion parameters for unpolished and electropolished Al–Mg alloy samples in 10 wt.% NaCl solution calculated from Tafel plots

State of the sample	Corrosion parameter				
	E_{corr} , V	$ b_a $, V dec ⁻¹	$ b_c $, V dec ⁻¹	i_{corr} , A cm ⁻²	CR, $\mu\text{m year}^{-1}$
Unpolished	-0.984	0.025	0.291	$8.600 \cdot 10^{-7}$	9.55
Electropolished	-0.789	0.197	0.095	$5.765 \cdot 10^{-7}$	6.40

electropolishing of aluminium–magnesium alloy in ethaline (at the potential of 6 V, the temperature of 25°C and the treatment duration of 20 min) allows obtaining surfaces with an attractive appearance and significantly less roughness. The investigation of corrosion behavior of electrochemically polished Al–Mg alloy performed by means of liner polarization resistance method showed the enhancement of resistance to corrosive attack in 10 wt.% NaCl aqueous solution. More uniform and smother electropolished Al–Mg alloy surface with a dense protective oxide layer is characterized by a higher corrosion resistance than in the case of an unpolished sample. Thus, ethaline deep eutectic solvent can be successfully used as an eco-friendly medium for the efficient electropolishing of Al–Mg alloy.

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ВПЛИВ ЕЛЕКТРОПОЛІРУВАННЯ В НИЗЬКОТЕМПЕРАТУРНОМУ ЕВТЕКТИЧНОМУ РОЗЧИННИКУ (ETHALINE) НА ПОВЕРХНЕВІ ВЛАСТИВОСТІ І КОРОЗИЙНУ СТІЙКІСТЬ СПЛАВУ АЛЮМІНІЙ–МАГНІЙ

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Досліджено електрополірування сплаву Al–Mg (5 мас. % Mg) в низькотемпературному евтектичному розчиннику ethaline (евтектичній суміші холін хлориду і етиленгліколю). Сканувальна електронна мікроскопія і атомно-силова мікроскопія показали, що електрохімічна поверхневого оброблення в ethaline приводить до суттєвого покращення поверхневих характеристик сплаву Al–Mg. Кількість поверхневого кисню знижується після електрополірування сплаву алюміній–магній в ethaline у порівнянні з необробленою поверхнею. При електрополіруванні відбувається видалення шару оксиду алюмінію і не спостерігається анодування. Потенціостатичне електрополірування сплаву Al–Mg в ethaline при потенціалі 6 В (відносно Ag псевдо-електрода порівняння) при температурі 25°C дозволяє зменшити коефіцієнт поверхневої шорсткості. Дослідження корозійної поведінки сплаву Al–Mg в 10 мас. % розчині NaCl до та після електрополірування в ethaline було здійснено за допомогою методу вимірювання лінійного поляризаційного опору. Було встановлено, що електрохімічне полірування в ethaline приводить до підвищення корозійної стійкості сплаву Al–Mg. Таким чином, низькотемпературний евтектичний розчинник ethaline може бути використаний як екологічно-прийнятна, ресурсозберігаюча і дешева альтернатива звичайним шкідливим кислим електролітам для електрополірування сплавів на основі алюмінію.

Ключові слова: Al–Mg сплав; електрополірування; низькотемпературний евтектичний розчинник; поверхнева шорсткість; корозійна стійкість.

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Keywords: Al–Mg alloy; electroplating; deep eutectic solvent; surface roughness; corrosion resistance.

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