

## Magnesium and Aluminum Oxides Formation Via Conversion Coating of Magnesium Metal in AlCl<sub>3</sub>/Urea Room Temperature Ionic Liquid

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### Abstract

A highly adherent conversion coating has fabricated on pure magnesium by the treatment with AlCl<sub>3</sub>/urea room temperature ionic liquid. The conversion coated surface was characterized by Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Energy Dispersive X-ray analysis (EDXA), and X-ray diffraction. The corrosion resistance of the uncoated and coated Mg metal was evaluated in 3.5 wt% NaCl solution. The coating was homogenous, rough, and was covered the entire magnesium substrate surface. The resulted coating was achieved in 40 min at room temperature as thin films of about 5µm thickness and composed of Al<sub>2</sub>O<sub>3</sub> and magnesium aluminum mixed oxide. Polarization study of the coated specimen showed decreasing in the corrosion potential with remarkable lowering of the corrosion current comparing to that of bare Mg metal. [DOI: [10.22401/JUNS.20.4.04](https://doi.org/10.22401/JUNS.20.4.04)]

Keywords: Mg metal, conversion coating, room temperature ionic liquid, Mg and Al metal oxide, corrosion protection.

### Introduction

Magnesium is the eighth most terrestrially abundant element and a cheap metal to extract. In recent years, magnesium and its alloys have become more interesting employed in industrial applications especially in the automotive and aeronautic transport industries [1]. These applications were attributed to the lightweight structural engineering components, low density of magnesium [2], their good machinability [3], high specific strength and inflexibility [4] which leading to weight reduction and thus significant cost-effective benefits in energy consuming and fuel economy [5]. In other hand, magnesium continued to form a passive, atmospheric surface film comprising a magnesium oxide/hydroxide and carbonate film [6]. This film is impressionable to attack when exposed to moist environments that may limit their commercial and industrial applications [7].

Wide and various chemical surface treatments [8], protective films, and coatings have been developed and utilized for improving magnesium's corrosion performance and provide a barrier between metal and environment [9]. These treatments included anodization [10], electroplating, conversion-coating [11] and vapor-phase processes. Conversion coatings for Mg are in most cases comprehend of chromates,

phosphates, metal oxides or other chemicals that are chemically bonded to the surface. Whereas effective chromate based conversion, coatings are highly toxic and hence undesirable for mass-market applications. Alternate coatings have recently developed using stannate, phosphate, permanganate, phosphate-permanganate and rare earth based chemistries [12].

Last decade, using ionic liquids (ILs) in the field of metal surface modification has become increasingly employed [13,14]. Ionic liquids are salts composed of organic cation and either an inorganic or an organic anion that are liquid below 100°C. They are generally nonvolatile, high thermal stability, wide and stable electrochemical window [15], nonflammable and can have a low toxicity, thus show promise as replacements for toxic molecular solvents [16]. Few works involved ILs treatment for corrosion protection of magnesium metal based on phosphates, for example trihexyl (tetradecyl) phosphonium bis (trifluoromethylsulfonyl) amide ([P<sub>6,6,6,14</sub>]<sup>+</sup>[NTf<sub>2</sub>]<sup>-</sup>) IL [17], ammonium phosphate IL [18] and halogen-free phosphonate ILs [19].

In this work, aluminum chloride/urea IL was used to explore it ability to form conversion coating for Mg metal. This ionic liquid was reported to an acidity nature and

contain the cationic species  $[\text{AlCl}_2.n\text{Urea}]^+$  and the anionic species  $\text{AlCl}_4^-$  as illustrated in the following equation [20]:



These species were expected to interact with magnesium to form a conversion coating in the same manner that occur with sulphate and nitrate ionic liquids. A paper under review has exhibited the ability of two recently reported ionic liquids (hydrate ammonium alum/urea and hydrate aluminum nitrate/urea ILs) [21-23] to form a thin film on the surface of pure Mg metal that increased its corrosion resistance in presence of active sulphate and nitrate.

## Experimental Section

### Materials and pre-treatment

Pure Mg metal sheet (99.95%, 1mm thickness), anhydrous aluminum chloride ( $\text{AlCl}_3$ ) (99.5% obtained from BDH), urea ( $\text{NH}_2\text{CONH}_2$ ) (99.5% obtained from THOMAS BAKER) and decane ( $\text{C}_{10}\text{H}_{22}$ ) (99.0% obtained from BDH). Specimens of (20 mm × 20 mm × 1.0 mm) dimension were prepared and grinded with successive grades of SiC paper, washed with distilled water, dipped in 4.5% diluent HCl, washed with distilled water, immersed in 0.5% aqueous NaOH solution, washed with distilled water, and finally rinsed with dichloromethane then propanol then air-dried.

### Ionic liquids and conversion coatings

Aluminum chloride/urea IL was prepared by progressively addition of a proper amount of both anhydrous aluminum chloride and urea in mole ratio of (1.2:1) with continuous stirring in glove box under nitrogen gas until faint yellow liquid was formed [14,20]. Conversion coatings on pure magnesium metal were conducted as per the following sequence steps in ionic liquid at 25°C:

- Immersion the sample in aluminum chloride/urea IL at room temperature in close atmosphere.
- After 40 min, the sample was rinsed immediately with dichloromethane then with propanol then dried with air.
- Finally the dried samples were stored in a desiccator for subsequent analysis.

## Measurements

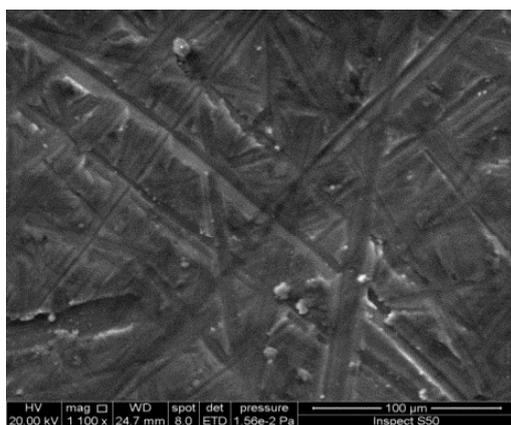
The surface morphologies of the samples were investigated with the high-resolution field emission scanning electron microscopy (SEM) (INSPECT S50, AA2000) and atomic force microscopy (AFM) (Angstrom Advanced Inc.) contact mode used to analyzed topography of samples. The X Flash 6110 Bruker (EDXA) was used in conjunction with (SEM) for determination of the composition of coating layer. The crystalline and phase identification of samples were determined by X-ray Diffractometer (Bruker-D2 phaser). The corrosion behavior of the conversion coated samples was examined in 3.5% NaCl solution at room temperatures by (WENKING M Lab multichannel) and (SCI-M Lab Potentiostat) while the corrosion measuring system was measured using (GmbH Bank Electronics-Intelligent controls, Germany 2007). The data obtained from potentiostate measurements were replotted using Origin6 software.

## Result and Discussion

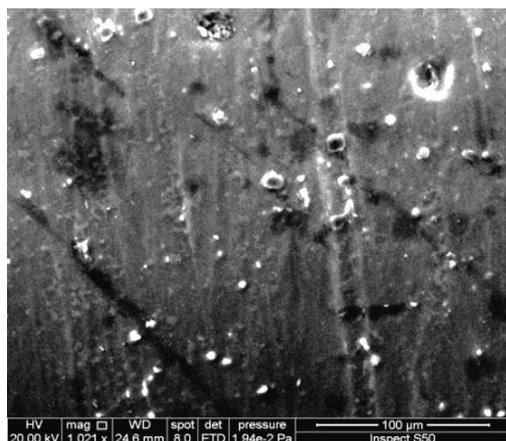
### Pre-treatments and post-treatment of magnesium substrates

The pre-treatments procedure have carried out on pure Mg samples thought to offer a clean surface with a more homogeneity and subsequently to promote adhesion and film formation, in which an aqueous sodium hydroxide solution has been utilized as a degreasing bath. Following alkaline cleaning a chemical pickling by using hydrochloric acid was used in order to perform a chemical etching on Mg surface.

Examination of pure and pre-treated Mg metal surface shown that the micro-incision of bare Mg metal were disappeared Fig.(1) and a rather smooth surface was formed. In addition, EDXA result Fig.(2) did not show a presence of chloride ion or any other contaminates on the surface of substrate after the treatment with HCl solution. This is contrast to phosphoric acid pickling which induced the formation of a magnesium phosphate film [24].

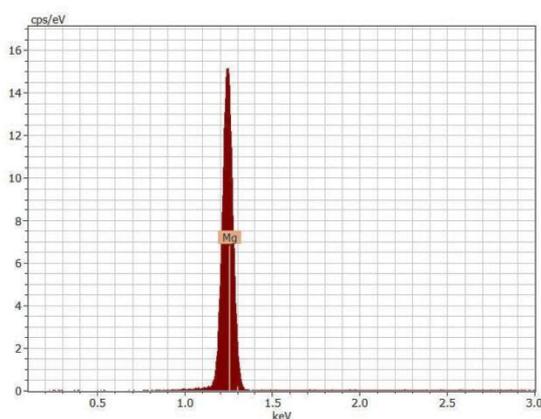


A



b

**Fig.(1): SEM images of (a) pure Mg (b) prepared Mg metal.**

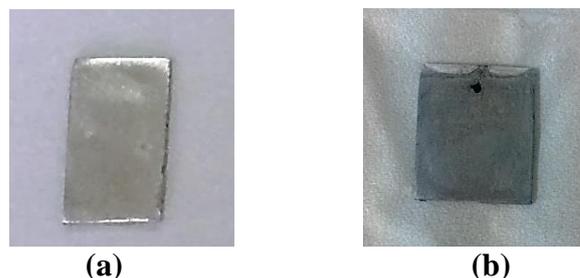


**Fig.(2): EDXA spectrum of prepared Mg metal.**

Residual ionic liquid on the Mg surface after immersion could be damaging the coating layer as it is sensitive to air and could react with moisture. The post-treatments have been established by rinsing the sample with dichloromethane then with propanol, which showed the ability to dissolve the residual ionic liquid and did not react with the resulted coating in which a rather compact adhesive coating was obtained.

### Conversion coatings formation

Magnesium plate was immersed in aluminum chloride/urea ionic liquid having a decane layer [14] for 40 min until an equilibrium state was established between the sample surface and ionic liquid. The decane layer was used to isolate and protect the ionic liquid from direct contact with air, as the ionic liquid is considered rather sensitive to air and moisture. The layer was formed on Mg metal substrate was dark gray, rather rough, homogenous uniform and covered the whole surface Fig.(3).



(a)

(b)

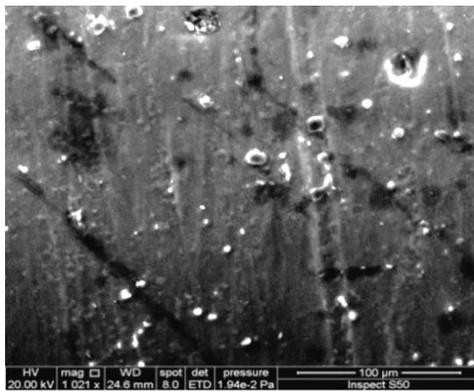
**Fig.(3): Photographs of (a) pure magnesium (b) conversion coatings obtained on pure Mg treated with aluminum chloride/urea IL.**

### Conversion coatings characterizations

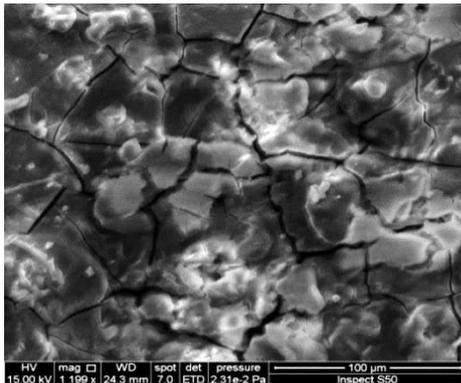
The surface morphology of bare and coated magnesium metal samples have been examined by Scanning Electron Microscope (SEM) Fig.(4). This figure showed that the conversion coating caused a significant change in the morphology of the bare Mg metal as well as a thick fine cracked surface with dry mud morphology of compact layer appeared on Mg metal surface.

The cross-sectional SEM images of coated magnesium indicated that the coating layer was well adhered to the substrate with average thickness of about 5 μm approximately Fig.(4).

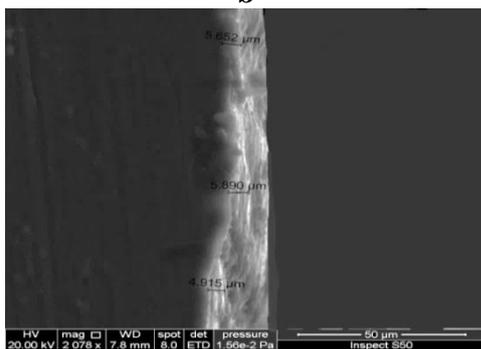
Fig.(5) and Table (1) showed the topographic properties of the immersed samples in aluminum chloride/urea IL which was examined by atomic force microscopy (AFM). The AFM examination indicated that the coating formed on Mg metal with nanoscale roughness of about (23.4 nm) and average height of about (177.54 nm) Table (1).



**a**

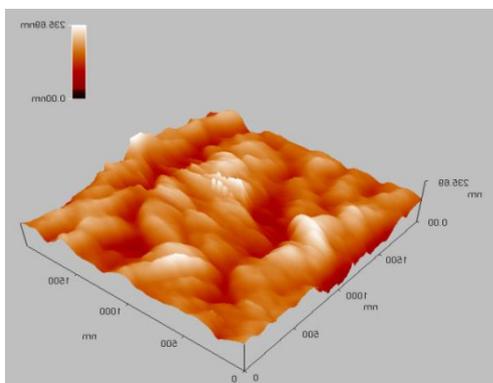


**b**



**c**

**Fig.(4): SEM images of Mg metal specimens (a) bare Mg (b) treated with aluminum chloride/urea IL (c) Cross-sectional SEM images of Mg metal specimen treated with aluminum chloride/urea IL.**



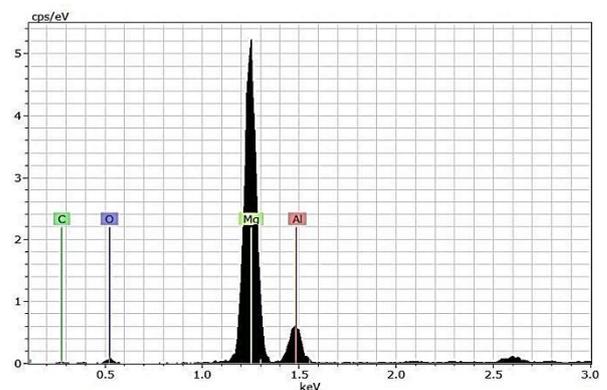
**Fig.(5): AFM images of Mg metal specimen treated with aluminum chloride/urea IL.**

**Table (1)**  
**AFM data of the conversion coatings on Mg metal.**

Sample	Total grain	Roughness [nm]	Avg. size [nm <sup>2</sup> ]	Avg. height [nm]
Treated with aluminum chloride/urea IL	149	23.4	26301.24	177.54

Elemental composition of the conversion coating layers formed by the treatment with aluminum chloride/urea was inspected by Energy dispersive X-ray analysis (EDXA) in which the composition peaks and weight % of different elements in the conversion coatings are shown in Fig.(6). It was disclosed that the thin film consisted of Al with (38.0227 wt%) and small proportions of O and C. In addition, the results of EDXA examination indicated that the coating layer compose of mixed oxides of MgO and Al<sub>2</sub>O<sub>3</sub> as exhibited in Table (2) which corresponding to the X-ray diffraction results showed in Fig.(7). Mixed oxide of Mg and Al (MgAl<sub>2</sub>O<sub>4</sub> and Al<sub>2</sub>O<sub>3</sub>) were detected by XRD examination on the surface of the Mg metal treated aluminum chloride/urea IL Fig.(7).

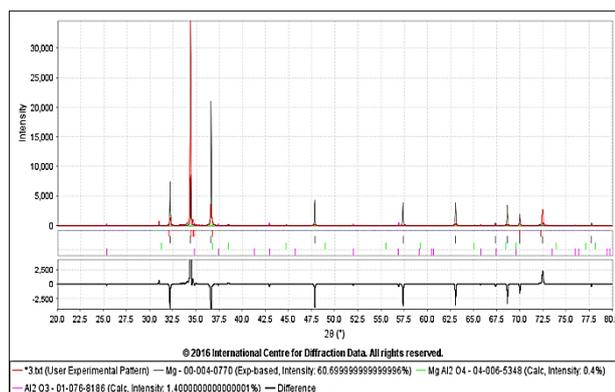
Although the presence of Cl<sup>-</sup> ions in solution promote local and generalized corrosion on Mg metal as reported in several researches [25], it was revealed that these ions have no effect on Mg metal probably they were restricted in this ionic liquid due to complex ion formation (i.e. AlCl<sub>4</sub><sup>-</sup>). On the contrary, a protective thin film was formed on Mg surface by using these ionic liquids.



**Fig.(6): EDXA spectra of Mg metal specimen treated aluminum chloride/urea IL.**

**Table (2)**  
wt. % of elements and suggested compounds consist the coating layer formed by immersion in aluminum chloride/urea IL.

Element	[wt.%]	[norm. wt.%]	[norm. at.%]	Compound	[wt.%]	[norm. wt.%]
Magnesium	96.8631	48.7610	4 0.5209	MgO	160.6257	80.8592
Aluminum	20.1235	10.1302	7.58324	Al <sub>2</sub> O <sub>3</sub>	38.0227	19.1407
Oxygen	81.6618	41.1087	51.8958		4.01866E-09	2.023E-09



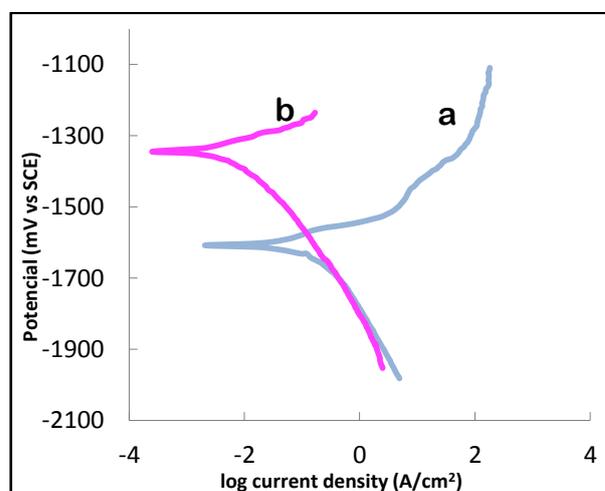
■ Mg      ■ Al<sub>2</sub>O<sub>3</sub>      ■ MgAl<sub>2</sub>O<sub>4</sub>

### Corrosion test

The corrosion behavior of the magnesium with and without coating have evaluated by galvanostatic polarization experiments. It is well known that the corrosion behavior of magnesium is very sensitive to the presence of Cl<sup>-</sup> ion thus three-compartment cell containing 3.5% NaCl solution have been used which, the coated Mg metal with 1cm<sup>2</sup> exposure area was used as working electrode, platinum electrode and saturated calomel electrode was used as counter and reference electrodes respectively. The corrosion resistance properties have been detected by polarization curves shown in Fig.(8). The Open circuits potential, corrosion potential (E<sub>corr</sub>) and corrosion current density (i<sub>corr</sub>) of the conversion coatings obtained from these curves were presented in Table (3). The pure Mg (curve a) showed a very negative potential of below -1.6V (vs. SCE) indicating its extremely active nature. As shown in Fig.(8), the corrosion resistance of pure Mg metal was improved by the conversion coating established from the treatment with aluminum chloride/urea IL. This treatment further shifted the corrosion potential to more positive values as well as significantly reducing the corrosion current in comparison with untreated Mg metal. From the results shown in Fig.(8), and

the values in Table (3), it was observed that the Mg metal sample treated with aluminum chloride/urea IL (curve b) showed highly corrosion resistant by shifting the potential to more noble values and extremely decreasing the corrosion current comparing to that of the pure Mg metal. The i<sub>corr</sub> value of the Mg metal sample treated with aluminum chloride/urea IL sample is (24) times greater than that of bare metal.

These results revealed that the immersion of pure Mg metal in this ionic liquid provides a significant ennoblement of the surface comparing with previously studies in other ionic liquids and aqueous solutions [17].



**Fig.(8): Polarization curves of (a) bare Mg (b) treated with aluminum chloride/urea IL in 3.5% NaCl.**

**Table (3)**  
**Polarization data of the conversion coatings on Mg metal in 3.5% NaCl solution.**

Samples	OCP, V	E <sub>corr</sub> , V (SCE)	I <sub>corr</sub> , μA/cm <sup>2</sup>
Bare Mg	-1.66	-1.59	44.51
Treated with AlCl <sub>3</sub> /urea IL	-1.27	-1.34	1.80

## Conclusion

Conversion coating of pure magnesium metal was successfully obtained in aluminum chloride/urea (1.2:1) mole ratio room temperature ionic liquids. The conversion coating resulted from the reaction of this ionic liquid and the surface of Mg metal was chemically bonded. The completion of adhesive coatings have been achieved at short time (40 min) and consisted of metals oxides of Mg and Al. This coating significantly reduced magnesium corrosion.

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