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Metallic Protective Coatings of Magnesium Metal in Ionic Liquids

A Thesis

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بسم الله الرحمن الرحيم

وَيسْألُونَكَ عَنِ الرُّوحِ قُلِ الرُّوحُ
مِنْ أَمْرِ رَبِّي وَمَا أُوتِيتُم مِّن
الْعِلْمِ إِلَّا قَلِيلًا (٨٥)

صَدَقَ اللهُ العَظِيم

سورة الاسراء
الآية ٨٥

الإهداء

بسم الله الرحمن الرحيم
(وقل أعملوا فسيرى الله عملكم ورسوله والمؤمنون)
صدق الله العظيم

إلهي لا يطيب الليل إلا بشكرك ولا يطيب النهار إلى بطاعتك ..ولا تطيب اللحظات إلا بذكرك.. ولا تطيب الآخرة إلا بعفوك..

الى من منحني ينبوع العلم والمعرفة و النور .. الى من علمني ومن ازال غيمه جهل عني مررت بها برياح العلم الطيبة الى أستاذي الفاضل المشرف على رسالتي (أ. د . هادي محمد علي عبود) المحترم أطال الله في عمره وأدامه منهلا للعلم والمعرفة.

إلى روح من أحمل أسمه بكل افتخار .. الى من انار دربي وساندني واوصلني الى ما انا عليه اليوم .. أرجو من الله أن يتغمده برحمته ويسكنه فسيح جناته
(والدي العزيز)

إلى ملاكي في الحياة .. إلى معنى الحب و الحنان والتفاني .. إلى بسمة الحياة وسر الوجود.. إلى من كان دعائها سر نجاحي وحنانها بلسم جراحي إلى أغلى الحبايب
(امي الحبيبه)

الى من بهم أكبر وعليهم أعتمد وبهم استمد عزتي وإصراري ,الى من بوجودهم أكتسب قوة لا حدود لها.. إخوتي...
(علي وغادة وسيف وسرى وادم)

إلى عزي وسندي في الدنيا ...إلى رفيق دربي ونور حياتي
(زوجي الحبيب)

الى كل اقربائي واصدقائي الذين ساندوني وشجعوني طوال سنوات الدراسة
الى صديقاتي واخواتي الذين دعموني ووقفوا معي على طريق النجاح
(دعاءياسين-الاء بدر-ازل اسامه-عبير عرفان)

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٢٠١٧

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Summary

Magnesium is a reactive element, poor corrosion resistance and highly unstable, which have limited its industrial applications. One of the most effective ways to improve the corrosion resistance of Mg and its alloys is to form a coating on the surface to isolate them from the environment. This can be achieved by forming or applying some type of functional barrier layer. There are several surface coating treatment techniques, including electrochemical plating (electroplating), conversion coating, anodizing, hybrid coatings, and vapor-phase process.

In present work, conversion coatings and electroplating on pure magnesium metal have successfully achieved by using three ionic liquid; hydrate ammonium alum/urea, hydrate aluminum nitrate/urea and aluminum chloride/urea ILs were used to form corrosion protection conversion coating layers on the surface of pure Mg metal. The process was performed at room temperature by immersing Mg metal in each ionic liquid for 40 min.

Metal electroplating was applied to magnesium metal and consequently aluminum metal was successfully deposited on uncoated and prior conversion coated magnesium metal from $AlCl_3$/urea ionic liquid. The conversion-coated layers were acted as initial preparation for Al deposit and to promote plating.

The surface morphology of conversion and electrodeposited layers were examined by Scanning Electron Microscope (SEM), cross-sectional SEM and Atomic Force Microscopy (AFM) whilst the chemical compositions were inspected with Energy Dispersive X-ray analysis (EDXA) and X-ray diffraction (XRD).

The corrosion behavior has been evaluated by galvanostatic polarization experiments in 3.5 wt% NaCl aqueous solution.

The three conversion coating layers were homogenous uniform and covered the whole substrate with a nanoscale particle size, roughness, and average height. They were well adhered to the substrate with reasonable allocation, while the average thickness were about (2-5) µm. The EDXA and XRD results showed that aluminum oxide and mixed metal oxides ($MgAl_xO_x$) complex have been presented in the three conversion coating layers formed on the Mg metal surface.

The Al deposited layers on uncoated and conversion coated Mg metal were gray compact and rather rough metallic coating with about (30-50) µm thickness. The corrosion resistance of pure Mg metal was improved by the conversion coating established from the three ionic liquids and the Al electrodeposited layers from aluminum chloride/urea IL. The corrosion potential was shifted to more positive values and the corrosion current has significantly lower value compared to uncoated Mg metal.

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Abbreviations

Abbreviation	Name
SHE	**Standard hydrogen electrode**
IL	**Ionic Liquid**
RTILs	**Room temperature ionic liquids**
DES	**Deep eutectic ionic liquid**
$AlNH_4(SO_4)_2.12H_2O$	**Hydrate ammonium alum**
$Al(NO_3)_3.9H_2O$	**Hydrate aluminum nitrate**
$AlCl_3$	**Aluminum chloride**
$CO(NH_2)_2$	**Urea**
$[C_2H_5N]^+ [H_3NO_3]^-$	**Ethylammonium nitrate**
[BMIM]PF$_6$	**1-butyl-3-methylimidazolium hexafluorophosphate**
[BMIM]BF$_4$	**1-butyl-3-methylimidazolium tetraflouroborate**
[EMIM]I	**1-Ethyl-3-methylimidazolium iodide**
BF_4^-	**Tetraflouroborate anion**
PF_6^-	**Hexaflourophosphate anion**
[EtNH$_3$][NO$_3$]	**Ethyl ammonium nitrate**
$(CF_3SO_2)_2N^-$	**Bis(trifluoromethanesulfonyl) amide**

$[NTF_2]^-$	**bis(trifluoromethanesulfonyl) amide**
$[dPP]^-$	**Diphenylphosphate**
$[P_{6,6,6,14}]^+$	**Trihexyl tetradecyl phosphonium**
AFM	**Atomic force microscopy**
SEM	**Scanning electron microscopy**
EDAX	**Energy dispersive X-ray analysis**
XRD	**X-ray diffraction**
E_{corr}	**Corrosion potential**
i_{corr}	**Corrosion current density**
ba	**Anodic Tafel slope**
bc	**Cathodic Tafel slope**

Chapter One

Introduction

Introduction

1.1 Magnesium metal and its alloys

1.1.1 Properties and uses

Magnesium is the eighth most abundant element on the earth and the lightest structural metal [1] (Its density is 1.74 g·cm^{-3}, only 2/3 that of aluminum and 1/4 that of iron) [2].

It has a moderately low melting temperature making it easier to melt for casting. Some of the most common alloyed elements in commercial magnesium alloys are aluminum, zinc, cerium, silver, thorium, yttrium, and zirconium; also, it can be alloyed with rare earth elements, which increase the strength of magnesium especially at high temperatures [3].

At room temperature magnesium and its alloys are difficult to distort due to the crystal structure which is hexagonal close packed **Figure (1-1)**. This structure limits its ability to deform because it has fewer slip systems at lower temperatures. [4]

Mg and its alloys have many advantageous properties such as [2]:

- High specific strength.
- Hot formability.
- Excellent machinability.
- Good electromagnetic shielding characteristics.
- High dimensional stability.
- High damping capacity.
- Good biocompatibility.
- Recyclability.

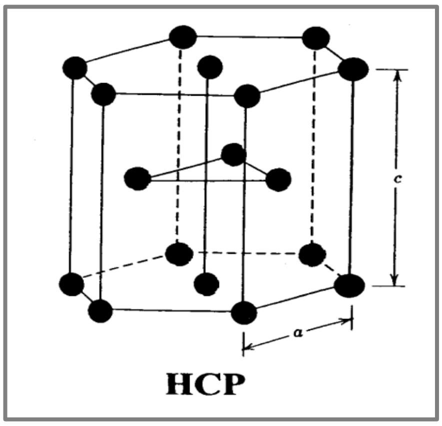


Figure (1-1): Example of hexagonal close packed crystalline structure

Magnesium and its alloys has been used as a “structural” component in aerospace, automotive, electronics due to its superior mechanical properties make them have the potential to replace steel and aluminum in many applications. On the other hand, due to its very low electrode potential (E = -2.37V vs. SHE), it can also be used as a sacrificial anode to protect other metals [5]. But most of the engineering applications of magnesium are limited due to its corrosion rate, even though they are already using in a number of applications including [1]:

- Automobile parts, **Figure (1-2)**.
- Computer and mobile components.
- Sporting goods.
- Aircraft and aerospace equipment.
- Household equipment.
- Implanted materials.
- Biomaterials and other fields.

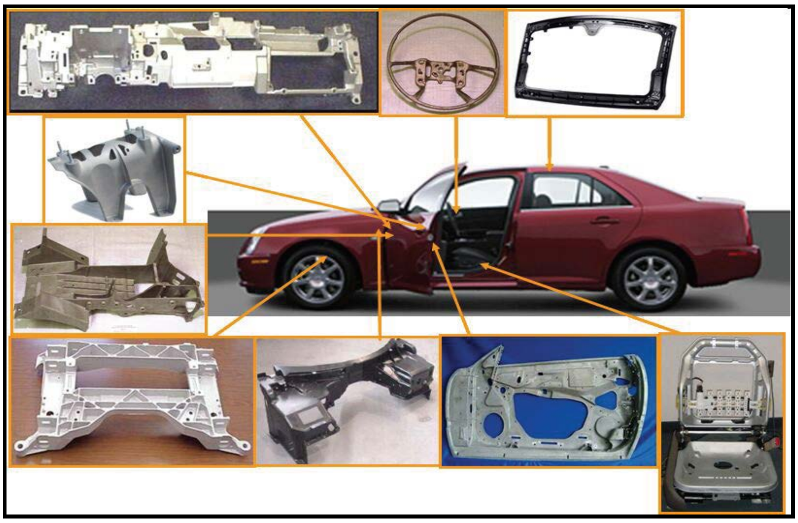


Figure (1-2): Automotive applications for Magnesium alloys

1.1.2 Corrosion behavior

Despite its many beneficial properties, magnesium remains a reactive element prone to a number of undesirable properties including poor corrosion and wear resistance, poor creep resistance, and high chemical reactivity, which have limited its wider industrial applications [6].

Pure magnesium corrodes rapidly in humid atmospheric and/ or acid, neutral and weak alkaline solutions where anions such as Cl^-, Br^-, F^-, I, SO_x^{2-} and NO_3^- promote local and generalized corrosion [7-13]. Additionally compounds like alcohols, ethers, and phenols also can attack magnesium.

Moreover, Mg rapidly develops oxide/ hydroxide /carbonate films (Unlike other active light metals, such as Al and Ti Mg alloys do not form a naturally passivating oxide film) [14,15]. These films are porous, poorly bonded and inhomogeneous, unable to provide satisfactory protection to the underlying metal against corrosion [16].

1.1.3 Mechanism of corrosion

There are two major reasons for the poor corrosion resistance of magnesium; Firstly, the very electronegative potential of Mg (the standard potential of Mg^{2+}/Mg is -2.366V vs. S.H.E. at 25°C) [17], makes it very prone to galvanic corrosion that can be initiated by internal coupling components with more noble potential (e.g. impurities [18] or second phases of alloy) or by external coupling with various metals.

Galvanic corrosion occurs when two metals/alloys having differing compositions, and thus standard electrode potentials, are electrically coupled in the presence of an electrolyte. This coupling results in the formation of a galvanic cell, which preferentially corrodes the more reactive, or electronegative, of the two metals [19,20].

Secondly, the quasi-passive hydroxide film[21] with a formula of $Mg(OH)_2$ is found to be not as stable as other metal oxide films such as aluminum, nickel and chromium oxide that provide better corrosion properties, **Figure (1-3)**. It's found to be slightly soluble in water with hydrogen evolution as $Mg^{+}(aq)$ and $Mg^{2+}(aq)$ and does not provide protection over long periods. However, it also breaks down in the presence of aggressive ions like chlorides [20, 22,23].

Formation of $Mg(OH)_2$ and magnesium dissolution in aqueous environments proceeds electrochemically accordingly to the following reactions:

$Mg \longrightarrow Mg^{2+} + 2e^{-}$ (anodic reaction) .... (1)

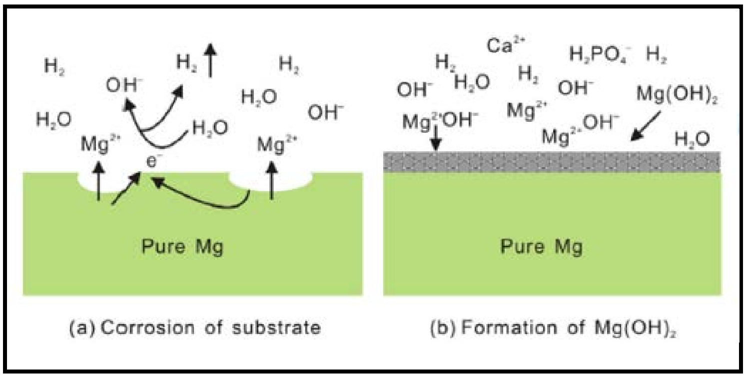
$2H_2O + 2e^{-} \longrightarrow H_{2\,(g)} + 2OH^{-}$ (cathodic reaction) .... (2)

$Mg^{+2} + 2OH^{-} \longrightarrow Mg(OH)_2$ (product formation)..................(3)

$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$ (overall reaction)............. (4)

During corrosion of magnesium, there are two important key points; Firstly, hydrogen evolution observed (4) that were associated with both the cathodic reaction (2) which balances the anodic reaction of magnesium dissolution (1). Overall in reaction (4), 1 mole of hydrogen gas is generated for 1 mole of magnesium dissolved.

Secondly, in net reaction (4), H^+ is consumed and OH^- is formed favoring the formation of $Mg(OH)_2$ (3) and shifting the Mg by alkalization of the medium[24].



(a) Corrosion of substrate (b) Formation of $Mg(OH)_2$

Figure (1-3): Formation of magnesium hydroxide

1.1.4 Improving corrosion resistance of Magnesium

The methods used for increasing the corrosion resistant of magnesium and its alloys are many and varied. These methods could be generally classified as: [31]

- Modification of the metal by alloying and/or surface modification.
- Modification of the environment by using inhibitors and/or by change metal environment potential by cathodic or anodic protection.

There were mainly two approaches for achieving better corrosion resistance for Mg metal; alloying and surface treatments. It has been reported that alloying Mg with several metals such as Al, Be, Ca, Cu, Li, Mn, Ni, Re, Si, Ag, Th, Sn, Zn, Zr and Y changes both the mechanical properties and corrosion behavior. In which, these alloying elements either applied alone (binary alloys) or together with other metals (ternary alloys) are mainly aimed to change desired mechanical properties.

However, alloying Mg is mainly aimed to achieving better mechanical properties but it does not provide a sufficient corrosion protection in aggressive environments [13], therefore many industrial surface treatments are developed to increase its corrosion resistance.

1.2 Surface treatment for corrosion resistant of Mg and its alloys

To protect magnesium and its alloys from being corroded many industrial surface treatments are developed to increase its corrosion resistance but, due to its high partiality to galvanic coupling and its very anodic nature; these treatments have to be pore-free to avoid aggressive attacks of electronegative anions such as chlorides [26].

One of the most effective ways to improve the corrosion resistance of Mg and its alloys is to form a coating on the surface to isolate them from the environment, either by forming or adding some type of functional barrier layer. The coating may also form a good base for subsequent organic coatings [27]. Several surface coating treatment techniques, including electrochemical plating (electroplating), conversion coatings, anodizing, hybrid coatings, and vapor-phase process have been developed. Although these coatings are usually found to enhance corrosion resistance, due to their electrochemical activity, many challenges are reported for these processes. It is found to be very difficult to achieve compact and pore- free coatings with multi-step preparation. Another import challenge to consider is that the presence of heavy metals reduces the recyclability of the metal [26].

1.2.1 Chemical conversion coating

The field of conversion coating technology for Mg is significantly less advanced than that of Al/principally due to Al being the major of the aerospace industry. Chemical conversion coatings are adhesive, insoluble, inorganic crystalline or amorphous surface films, formed via a non-electrolytic chemical reaction between the metal surface and the dipping solution. They are preferable because of their adherent nature, high speed of coating formation and frugal that can be formed using simple equipment and without the application of any external potential. It has been widely adopted in industrial processes sometimes used on their own or as surface preparation for following coating [27,28].

In conversion coating process a portion of the base metal is converted into one of the components of the resultant protective film, which is much less reactive to subsequent corrosion than the original metal surface. This film imparts an equal potential to the metal surface, neutralizing the potential of the local anodic and cathodic galvanic corrosion sites.

The following is a summary of conversion coatings on magnesium by coating type [29].

- Chromate Coatings
- Phosphate Coatings
- Fluoride Conversion Coatings

- Stannate Conversion Coatings
- Rare Earth Conversion Coatings
- Hydrotalcites coating
- Ionic Liquid Conversion Coatings
- Multi-Elements Complex Coating
- Vanadate Coatings
- Organic conversion Coatings

Many factors influence the quality of conversion coatings such as [30,31]:

— Composition of the base Mg alloy.

— Pretreatment processes.

— Composition of the conversion formulations.

— Posttreatments.

— Some parameters, such as temperature, pH, immersion time, and degree of agitation.

These can all influence the structure, composition, and performance of conversion coatings. The surface pretreatment process has a major impact on the ultimate coating efficacy. The careful and selective choice for pretreatment procedure is essentially for a proper coating formation.

We focus on the using of ionic liquids as conversion coating on Mg and its alloy which is discussed with details in section 1.5.

1.2.2 Anodizing[32]

Anodizing is a successful technology for corrosion protection of magnesium alloys; it is an electrolytic process producing a thick and stable oxide film on the part. It can also be used to improve paint adhesion to metals or as a passivity treatment. Two types of anodizing coating has been reported oxygen precipitation and film forming.

1.2.3 Plating[6,17,33]

Plating is a successful coating method that can be divided into two categories: electroplating and electroless plating. The process is that a metal salt in solution is reduced to its metallic form and deposited on a surface of the substrate. The difference between electroplating and electroless are that in electroplating the electrons are supplied by an external power source versus a chemical reducing agent in the solution.

The electrochemical method has been discussed in details in section 1.6.

1.2.4 Sol-Gel[34,35]

Sol-Gel is another successful coating process, an advanced technique that synthesizes high quality oxide thin films and powders. It is often used instead of electroless plating as electroless plating can only achieve a relatively uniform metallic layer.

1.2.5 Cold Spray[36,37]

A new coating technique that is still in development, it has using aluminum particles which are proving to be very successful for protection of magnesium parts. This new coating technique may be the best new coating for magnesium alloys that is environmentally friendly and long lasting.

Table (1-1) a summary of the advantages and disadvantages to all coating type are outlined [38]:

Coating Type	**Advantages**	**Disadvantages**
Chemical Conversion	Most effective and provides good corrosion resistance.	Cr^{6+} in chromate bath is a highly toxic carcinogen limiting its uses.
Phosphate Treatments	Similar to chemical conversion in protection, but it is chromate Free	Produce rough grains can cause cracks; existing heavy metal ions in solution can cause environmental pollution.
Anodizing	Can evolve paint adhesion to metals.	Coatings are brittle and apt to cracking or shedding.
Plating (electro and electroless)	Improve corrosion resistance depending on what material is plated on surface.	Plating films have a weak adhesion to magnesium alloys. Galvanic corrosion may occur depending on type of metal used.
Sol-Gel	Can achieve better coating layer than electroless plating.	Potential issues with galvanic corrosion depending on material used.

Paint	Provides a final coating when used in combination of other coating techniques.	Does not provide protection when exposure to chipped or cracked.
Cold Spray	Improved good adhesion and corrosion resistance when high purity aluminum is used as sprayed material.	Still a new technology, not widely tested.

1.3 Ionic liquids

1.3.1 General definition

Ionic liquids (ILs) are salts with a melting point below 100 °C, consisted entirely of ions [39]; typically, at least one of the cation or anion has a bulky, asymmetric structure, **Figures (1-4 and 1-5)**. Therefore these compounds have low lattice energy and hence low melting points. Some of ILs are liquids at room temperature called (Room Temperature Ionic Liquids), while others are liquids below room temperature called (deep eutectic solvent) [40].

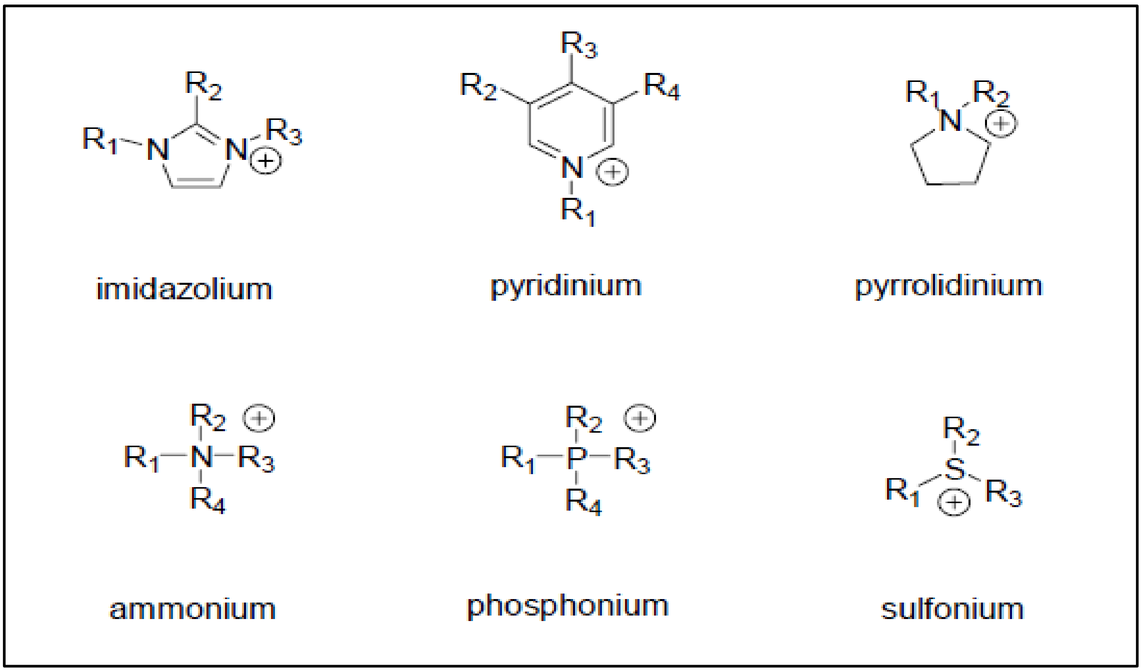


Figure (1-4): Most common cations used in ionic liquids

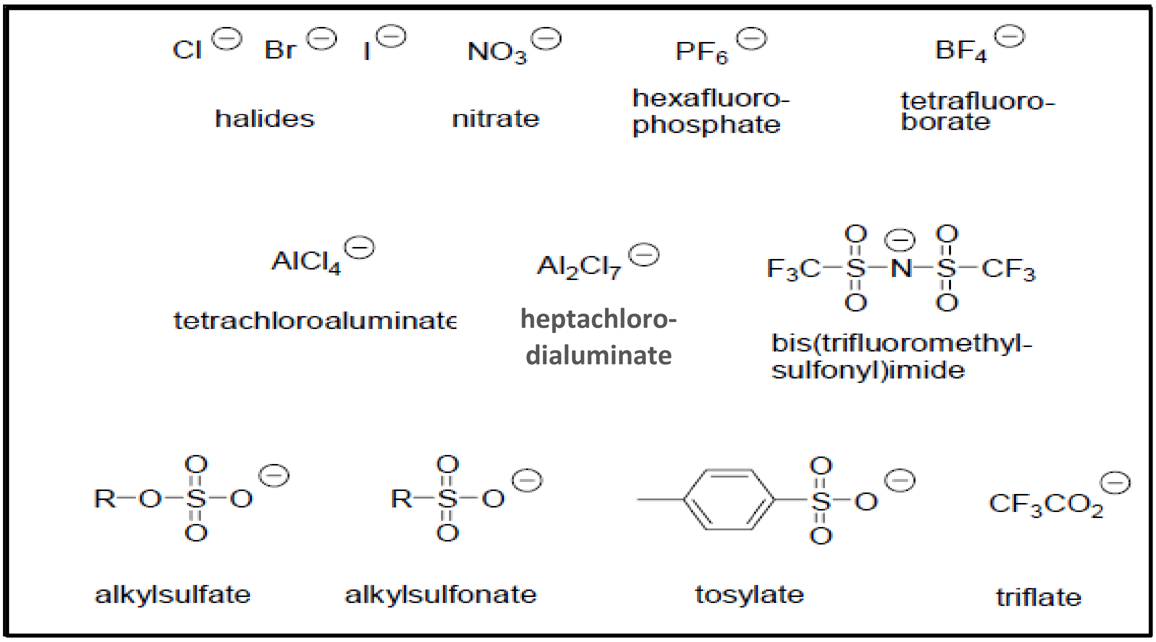


Figure (1-5): Most common anions used in ionic liquids

1.3.2 A Brief history

The first ionic liquid prepared is generally credited to Walden as preparing [41] ethylammonium nitrate $[C_2H_5NH_3]^+$ $[NO_3]^-$ IL which has a melting point of 12 °C. This compound is highly reactive and this is why it has not been widely used. The first generation of ionic liquids was prepared using $AlCl_3$ but these had limitations due to their reactivity with water.

Hurley and Wler [42] prepared an ionic liquid by mixing and warming 1-ethyl pyridinium chloride with aluminum chloride.

Osteryoung et al. [43,44] and Hussey et al. [45,46] in 1970s and 1980s respectively also worked on organic chloride–aluminium chloride ambient temperature ionic liquids and were the first to produce a major review of room temperature ionic liquids [47]. In 1992, the first air and moisture stable ionic liquids reported by Wilkes and Zaworotko [48] were they based on the 1-ethyl-3 methylimidazolium cation with either tetrafluoroborate (BF_4^-) or hexafluorophosphate (PF_6^-) as anions.

The wide application of ionic liquids has been made in the field of air and water stable [49] and today around 300 types of different ionic liquids are commercially available. In fact, hundreds of ionic liquids have been reported with wide liquid temperatures, and one that remains liquid down to - 96 °C is known.

Recently new ionic liquids reported by Abood and co-workers in 2011[39] based on aluminum chloride and either urea, acetamide or trimethyl urea were prepared. These ionic liquids are relatively cheaper, less sensitive, easily prepared comparing with other chloroaluminate ionic liquids of i.e. imidazolium or pyridinium chloride. They offer higher stabilities with promising similar properties as catalytic feature for organic reactions and aluminum coating on metal substrate. Another sort of room temperature ionic liquids with exceedingly air and moisture stable characterization was synthesized by Abood [50], which based on hydrate ammonium aluminum sulfate /$AlNH_4(SO_4)_2.12H_2O$ or hydrate aluminum nitrate /$Al(NO_3)_3.9H_2O$ [51] also combined with urea or acetamide. These inorganic salts are easily handle, cheaper, greener and availability of these compounds in variable industrial applications such as water purification. This new green ionic liquids shown to exhibit interesting features as good media for some insoluble compounds in aqueous solvents such as metal oxides or silver sulfate also they was expected to be used in variable process such as metal coating.

Ohno focused his work on the synthesis of a series of polymerizable ionic liquids and their polymerization to prepare a new type of ion conductive polymers [52]. The polymer electrolytes that were prepared were made from mixing nitrite rubber [poly (acrylonitrile-cobutadiene) rubber] with the ionic liquid N-ethylimidazolium bis(trifluoromethanesulfonyl) imide and these were found to have a high ionic conductivity and good elasticity.

1.3.3 Synthesis of ionic liquids

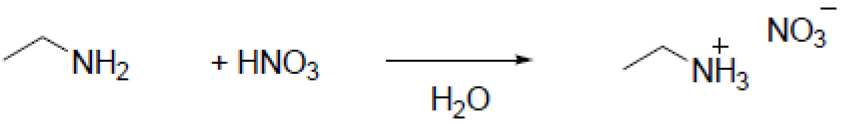
There are various approaches to prepare different types of ionic liquids such as [53]:

1. **Metathesis reactions:** It is offer the potential to preparation of relatively air and water stable ionic liquids which is based on replacement of cations/anions reaction. For example; 1-alkyl-3-methylimidazolium

cation was used with silver salts such as $AgNO_3$, $AgBF_4$ and $Ag[CO_2CH_3]$ where carried out in methanol.

$$[EMIM]I + Ag[BF_4] \longrightarrow [EMIM]^+[BF_4]^- + AgI$$

2. **Acid-base neutralization reaction:** The formation of an ionic liquid can also be prepared by protonating amine with an acid. The very first ionic liquid $[EtNH_3^+ NO_3^-]$ was synthesized from ethylamine and nitric acid (HNO_3) [54]. Protonation of amine is also used in the preparation of [Hmim][BF4] from N-methylimidazole and tetrafluoroboric acid [55].



3. **Direct combination of salts/Lewis acid- base ILs:** The most studied system is includes the chloroaluminates as a Lewis acid in the preparation of an ionic liquid. Other Lewis acids also can be used, such as $EtAlCl_2$ [56], BCl_3 [57], CuCl [58], $SnCl_2$, $GeCl_2$ [59] and $InCl_3$ [60].

   The composition of Lewis acid-based ionic liquids is generally mentioned as the mole fraction of monomeric acid present in the mixture which can be classified as basic, neutral or acidic ILs.

4. **Eutectic mixture:** Eutectic based liquids can be formed starting from an ammonium halide $[R'R_3N]^+X^-$ [53].

   These liquids can described by the general formula $R_1R_2R_3R_4N^+X._zY$, where the anion X^- is generally a halide (often Cl^-),

   $R_1R_2R_3R_4N^+$ a quaternary ammonium salt and Y are a complexing agent, where z is the number of molecules required.

Depending on the complexing agent, Y can be divided in to three eutectic types:

Eutectic Type I Y= MClx, M = Zn, Sn, Fe, Al, Ga, Ge, In.
Eutectic Type II Y= $MClx.yH_2O$, M = Cr, Co, Cu, Ni, Fe.
Eutectic Type III Y= RZ, Z = $CONH_2$, COOH, OH, etc.
Eutectic Type IV Y= Mixture of type I and Type III.

1.3.4 Physical and chemical properties of ILs

Ionic liquids have numerous unique properties such as:

- **Melting point:** Ionic liquids have melting points below 100 ºC and mostly they are liquid at room temperature [61].
- **Stability:** Several studies indicated that ILs are not 100% inert. Certain ionic liquids based on dialkyl imidozolium cations are generally more resistant than traditional solvents under certain harsh process conditions such as oxidation, photolysis and radiation processes [62].
- **Thermal Stability:** Ionic liquids are thermally stable up to temperatures of 450 °C. Most the ILs have extremely low vapor pressure which allow to remove water by simple heating under vacuum [61].
- **Viscosity:** Ionic liquids are more viscous than molecular solvents (their viscosities are ranging from 10 mPa s to about 500 mPa s at room temperature) [63, 64]. With increasing the temperature the viscosity of ILs is decrease. The viscosity of ionic liquids is determined by Van der Waals (VDW) [65] forces and hydrogen bonding. Electrostatic forces may also play an essential part.

- **Density:** The values of density of ionic liquid are ranging from 1 to 1.6 g/cm^3. It is influenced with the increase in the length of the alkyl chain in the cation and either by the identity of anions [63, 64].
- **Conductivity:** Ionic conductivities of the Ionic liquids reasonably great than those of organic solvents/electrolyte systems (up to 10mS cm^{-1}). While, it is usually lower than concentrated aqueous electrolytes at room temperature [66].

  The extensive constituent ions of ionic liquids reduce the ion mobility which leads to lower conductivities. Additionally, ion pair formation and/or ion aggregation also can reduce the conductivity [66].
- **Electrochemical window:** It is the electrochemical potential range over which the electrolyte is neither reduced nor oxidized at an electrode [67]. Unlike aqueous molecular electrolytes ionic liquids have wide potential windows (some of which are in the realm of 6V) make them interesting for electrochemistry [68].
- **Color:** High quality ionic liquids mixing $[\text{bmim}]^+$ cation and a various anions, such as $[PF_6]^-$, $[BF_4]^-$, $[CF_3SO_3]^-$, $[CF_3CO_2]^-$ and $[(CF_3SO_2)_2N]^-$ have been reported to be colorless, even though they are not 100% pure.

  The color of less pure ionic liquids generally ranges from yellowish to orange [69, 70].
- **Hygroscopicity:** The viscosity of the ionic liquids could be influenced by the water content that with increasing water content ionic liquids became less viscous. Hydrolysis problems can also occur [69].

- **Hydrophopicity:** The degree of polarity of ionic liquids can be diverse by adapting the length of the alkyl chain. Long chain has attracted some interest due to their liquid crystalline (LC) properties [69].

Furthermore, variation of the anions or the length of the alkyl groups allows fine tuning of the physicochemical properties of ILs, such as viscosity, conductivity, solvation, catalytic activity and melting points, etc.

In general, the properties of specific ionic liquids are determined by, and vary depending on the selection of the ionic constituents. Physical properties control by the cation of the salt whereas the anion has a greater effect on the stability and chemical reactivity; for example, $[\text{bmim}]\text{PF}_6^-$ is water immiscible, whereas $[\text{bmim}]\text{BF}_4^-$ is water soluble [71].

1.3.5 Applications of ionic liquids

During the last decade, there has been an increase in the number of publications on using of ionic liquids in various fields including extraction/separation, electrodeposition, and electrochemical analysis etc.[66]. Many different ionic liquids have been successfully used as solvents in different reactions, such as Diels-Alder [72, 73], Friedel-Crafts[74,75], Heck [76], hydrogenation [77], oxidation [78],alkylation [79], allylation[80], hydroformulation [81], esterification [82], dimerization [83] and polymerization reactions [84, 85] . Also enzyme catalysis [86, 87], acetylation [38] often leading to better selectivity, yield and reaction rates than with volatile organic solvents. Furthermore, phenomena such as nucleation, surface diffusion, and crystallization that associated with metal deposition can be accelerated when using ionic liquids [71], **Figure (1-6)**.

In addition, ionic liquids have shown outstanding potential as lubricants and lubricant additives including lubrication of light alloys [88-93], nanophase modifiers [94,95], electrolytes[96], corrosion inhibitors [97] or reagents in the formation of corrosion protective surface coatings [98].

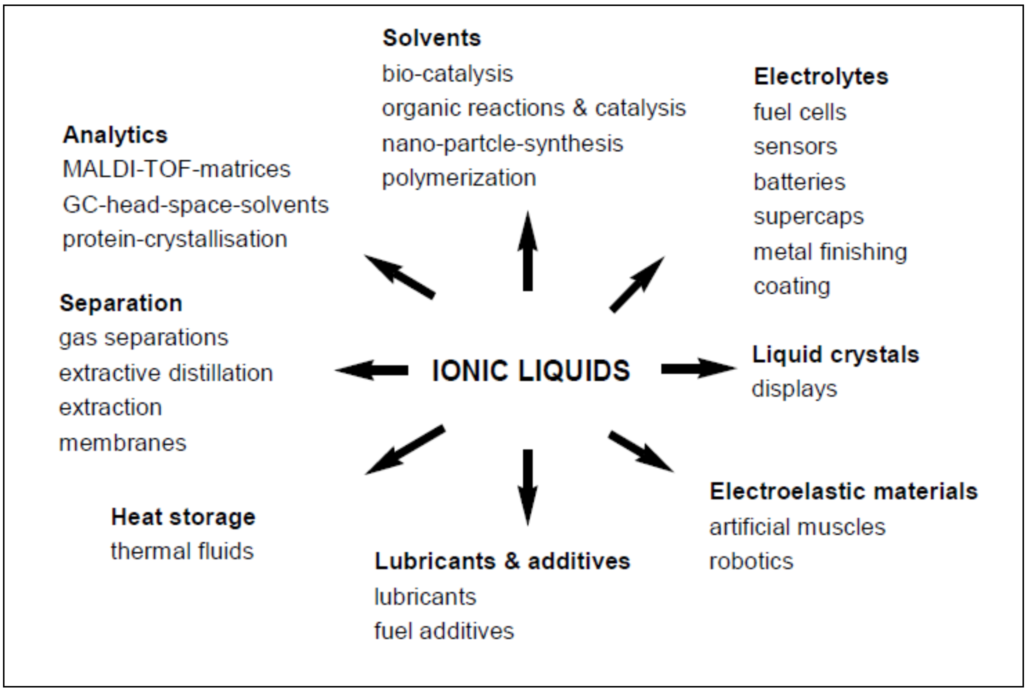


Figure (1-6): Summary of applications using ionic liquids

1.4 Conversion coating via ionic liquids on Mg and its alloys

Chemical conversion coatings are commonly applied to Mg alloys as paint bases for subsequence coating or in some cases as standalone protection. Traditional conversion coatings which based on hexavalent chromium compounds are commonly used but that are undesirable due to severe environmental risks [32].

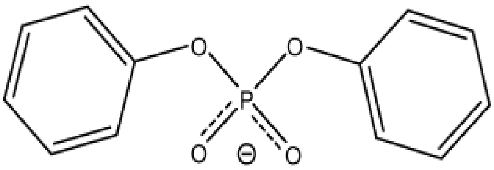
In recent years, the using of ionic liquids (ILs) in the field of metal surface modification has become interesting. Ionic liquids open a range of specific chemistries to which the substrate may be exposed that allowing tailoring the conversion coating which may formed. Comparing with traditional conversion chemistry, ILs have several advantages, such as higher flexibility in molecular design, hydrophobicity, and potentially better bonding to paints.

The researchers have investigated the possibility of using Ionic liquids to generate conversion coatings upon Mg and its alloys [98,99]. Almost all of the earliest studies involving IL treatments for corrosion protection focused on $[P_{6,6,6,14}]^+$ $[NTF_2]^-$ IL **Figure (1-7)**, due to its commercial availability and advantageous electrochemical properties[100]. A set of studies by Howlett, MacFarlane, Forsyth, et al. [100–111] have confirmed that ILs based on trihexyltetradecylphosphonium coupled with either diphenylphosphate or bis(trifluoromethanesulfonyl) amide **Figure (1-7)** shown to react with magnesium alloy surfaces, leading to the formation a surface film that can improve the corrosion properties via formation of a thin film (~10–100nm) [102]. In addition, combining the bis(trifluoromethanesulfonyl) amide $(CF_3SO_2)_2N^-$ anion with the trihexyl tetradecyl phosphonium $[P_{6,6,6,14}]^+$ cation provides a unique well-adhered, continuous, relatively defect free, and corrosion-resistant surface films ranging from nanometers to micrometers in thickness [109].

The $[P_{6,6,6,14}]^+$ cation shown to have several desirable merits including stability at potentials between -3.2V and 2.6V vs. Fc/Fc^+, higher thermal stability compared to nitrogen based ionic liquids [98,112], and a lack of reactivity with magnesium alloys [100, 102], making it a good choice for ionic liquid treatments of magnesium. Whereas, the $[NTF_2]^-$ anion is known to be decomposed at 2.0V vs. Fc/Fc$^+$ in the presence of water, oxygen and reductive meta substrates. In addition, this IL is relative hydrophobicity (the maximum water content in this IL is around 1wt. %) that the treatments are able to be conducted open to the atmosphere at room temperature [101,104].

Trihexyl(tetradecyl) phosphonium ($P_{6,6,6,14}$)

bis(trifluoromethanesulfonyl) amide $(Tf)_2N$



Diphenyl Phosphate (dpp)

Figure (1-7): Structures of the anion and cation of ILs

In present investigation, three types of ionic liquids have been used. The first is hydrate ammonium alum mixed with urea which offered a room temperature ionic liquid with highly moisture and air stable characterization. This ionic liquid expected to be used in variable process such as metal coating and it offer good dissolving medium for some water insoluble compounds [50,113].

In addition, it was reported that the presence of water molecules of $NH_4Al(SO_4)_2.12H_2O$/urea ionic liquid composition were not free due to their interaction with the ions present in the initial solid lattice. Mole ratio of (1:5) of ionic liquid was prepared in this work, which was reported to have lowest melting point and low viscous [113].

The second ionic liquid used in this work was hydrate aluminum nitrate/urea IL. The novel binary deep eutectic solvent (DES) systems, $Al(NO_3)_3.9H_2O$/ urea found to have freezing points at the lowest rang of 3℃ with a mole ratio of 1:1 to 1:1.5 respectively as shown in **Figure (1-8)** accord with prior publication [51]. The mole ratio of 1:1.2 was used in this work as it has the lowest melting point. The acidity value of $Al(NO_3)_3.9H_2O$/urea IL (which was reported as more as for $AlNH_4(SO_4)_2.12H_2O$) [114] suggested to form an acidic species of Lewis type with cationic charge $[Al(NO_3)_2.nUrea]^+[Al(NO_3)_4]^-$ as comparable type to those reported in aluminum chloride/urea ionic liquid [51,115]

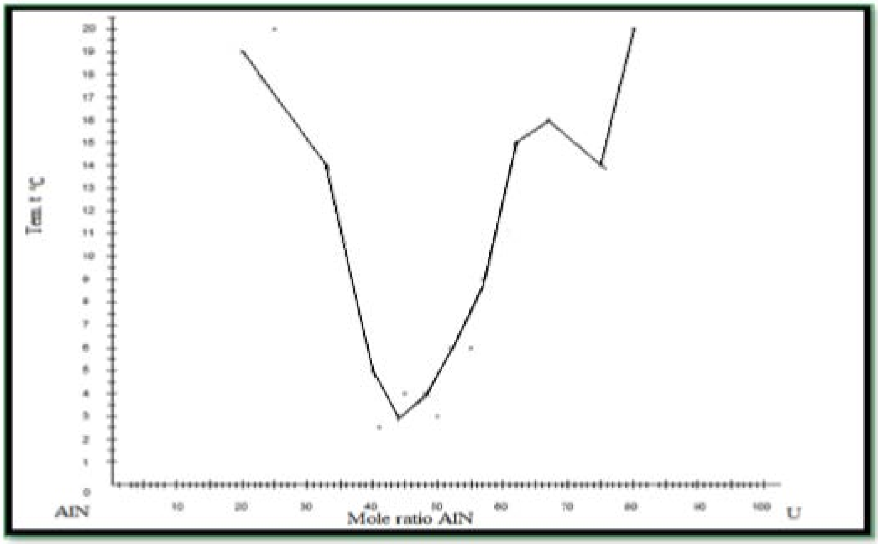
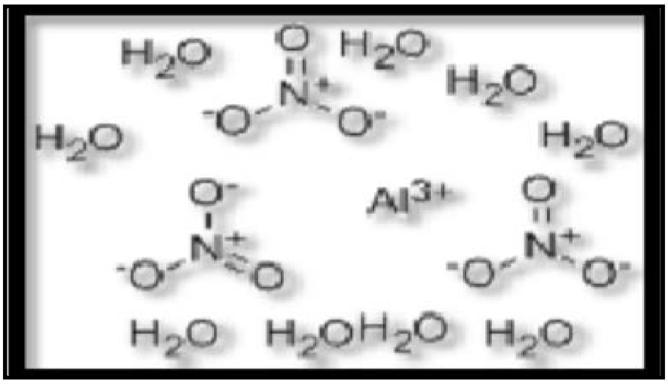


Figure (1-8): Concentration phase diagrams of $Al(NO_3)_3.9H_2O/CO(NH_2)_2$ system plot versus temperature

Water molecule believed to interact with both ions as shown in **Scheme (1-1)**. This ionic liquid shown several useful properties such as lower melting point (3°C), low cost and easy to prepare and could be considered as a green solvent because it has a low vapor pressure and stable to air and moisture.

Previous examinations of ionic liquid suggested an equation of ionic liquid formation as follows [51]:

$$Al\,(NO_3)_3.9H_2O + nUrea \longrightarrow [Al\,(NO_3)_2.nUrea.nH_2O]^+[\,Al(NO_3)_4]^-$$



Scheme (1-1) structure of $Al(NO_3)_3.9H_2O$

The third ionic liquid has prepared by slowly mixing of $AlCl_3$ with urea under nitrogen gas that caused the formation of a faint yellow liquid. This ionic liquid was reported to contain the cationic species $[AlCl_2.nUrea]^+$ and the anionic species $AlCl_4^-$ as illustrated in the following equation[115]:

$$2AlCl_3 + nUrea \longrightarrow [AlCl_2.n\,Urea]^+ + AlCl_4^-$$

Due to the strong Lewis acid nature of aluminum chloride and the Lewis base nature of urea, these salts were found to react immediately in the solid phase and the forming mixture has evolved heat due to the exothermic reaction, thus the reaction did not required external heating [115].

1.5 Metallic film deposition from ionic liquids

Selection of the metallic film deposition method, either electro-or electroless deposition is dependent on the geometry and application of the substrate. Several excellent studies and reviews exist on the use of ionic liquids in the deposition of metallic films [112].

Moreover, the unique physicochemical properties of ionic liquids make them interesting candidates for the electrodeposition of reactive metals, semiconductors and polymers that cannot be plated from aqueous baths [52, 71, 112,116], they show capability of electrodepositing several metals such as aluminum, zinc, chrome, copper, iron, and nickel.

There are several advantages that ionic liquids have over aqueous baths made their properties critically important such as [116]:

- Electroplating of a range of metals impossible to deposit in water due to hydrolysis e.g. Al, Ti, Ta, Nb, Mo, and W as well as various alloys including aluminum/chrome, zinc/tin, and copper/palladium.
- Possible direct electroplating of metals (water-sensitive substrate materials such as Al, Mg and light alloys) with good adherence.
- During electroplating with ionic liquids, negligible gaseous hydrogen is produced/a major problem during water electrolysis wherefore coatings will have better mechanical properties.
- Metal ion electrodeposition potentials in ionic liquids are much closer together compared with water, enabling easier preparation of alloys and the possibility of a much wider range of possible electroplated alloys, which are difficult or impossible in water.

- The electrodeposition of metals from ionic liquids is a novel method to product a nanocrystalline metals and alloys that giving improved properties compared to microparticles (e.g. thermal and electrical conductivity, transparency, uniformity and low friction).

Concerning magnesium- based substrates, electroplating from ionic liquids has been investigated [68,116,118-128], whereas no extensive investigations have been conducted regarding electroless deposition from ionic liquids particularly on magnesium and its alloys.

Among coating options aluminum and zinc are likely the most desired as they resist both pitting and corrosion while remaining quite cost effective. Furthermore, both aluminum and zinc cohabit more peacefully with magnesium than most other metals, as seen by their inclusion in many magnesium alloys, such as AZ91D (8.3–9.7 wt% Al, 0.35–1.0 wt% Zn), AZ31 (nominally 3wt% Al, 1wt% Zn), AM60 (5.5–6.5 wt% Al), and ZE41 (3.5–5.0 wt% Zn). The deposition of any metal on magnesium is complicated by the substrate's high reactivity and the formation of corrosive galvanic couples between it and other metals in the presence of aqueous solutions, which can cause severe pitting in the metal.

1.5.1 Electrodeposition of metals on Mg and its alloys from ionic liquids

Metal electrodeposition is considered as one of the most effective ways to produce corrosion and wear resistant coatings on magnesium and its alloys. The process mechanism for electroplating could be summaries in three steps [38]:

1. Cations are gathered at the substrate surface (which acts as cathode) by concentration diffusion.
2. Displacement reaction occurs and the cathode and the cations are wasted.
3. Film is formed by the deposition of metal crystal on the substrate surface.

Aluminum serves as an excellent metal for corrosion protection according to its merits [68,122]:

(a) Al is a lightweight metal.

(b) The electrochemical potential of Al is close to that of Mg thus it is relatively easy to be electrodeposited on Mg or Mg alloys compared with other metals, such as Ni and Cu.

(c) Its ability to resist pitting.

(d) Its ability to form Mg–Al intermetallic compounds between the film and substrate after proper heat treatment, which are confirmed to have good corrosion resistance and can aid with coating adhesion.

(e) Good recycling because Al is a primary alloy element for the AZ series Mg alloys widely used.

There are some common preparation methods of Al coatings or depositions such as hot-dipping technology, thermal spraying, and physical or chemical vapor deposition, except for plating. The plating has advantages, such as cheap instruments, a smooth deposition with a low porosity, and room operating temperature. The electroplating of Al on the surface of magnesium alloy would not only prevent Mg substrate from corrosion, but also not obviously increase its mass. Additionally, both anodic oxidation technology and electrolytic coloring technology of Al alloys have been applied in the production industry, which have the potential to be directly used for the Al layer [123]. The high reactivity of aluminum due to the rather negative standard potential of Al/Al(III) couple (-1.67V vs. SHE), prohibiting deposition from aqueous solutions, likewise it requires deposition baths to be aprotic, organic solvents are eligible however they are proving undesirable characteristic such as flammability and volatility [97].

ILs which can serve as solvents and supporting electrolytes make them an attractive alternative to organic or toxic solvents in the electroplating industry [108]. Within the last few years, studies have been published concerning the electroplating of magnesium and its alloys from ionic liquids. This process enables a dense and thick aluminum film to be uniformly coated the magnesium alloy substrate using an ionic liquid as an electrolyte. Set of papers by J.-K. Chang, I.-W. Sun, et al. [68, 120, 124, 125] outline the electrodeposition of aluminum on the AZ91D magnesium using the first-generation type 1 eutectic ionic liquid $AlCl_3$–EMIC. The authors investigate the possibility to achieve a dense and adhesive protective Al layer on Mg and its alloys in $AlCl_3$ based ILs which exhibit adjustable Lewis acidity. Room temperature Aluminum chloride-alkylimidazolium chloride or bromide IL mostly used in which the $Al_2Cl_7^-$ precursor, that is the dominant species in the ionic liquid can be electrochemically reduced to the metallic form according to the following reaction:

$$4Al_2Cl_7^- + 3e^- \longrightarrow Al + 7AlCl_4^-$$

From the recent researches [120-127] is clarified that the using of varied organic base in the preparation of ionic liquid can influence the quality and morphology of Al layer on Mg alloy. In addition, the existence of different metals with various proportions on the alloy substrate such as Mg_xAl_y

resulting in a non-uniform surface potential across the substrate, due to intermetallic species formed at the grain boundaries [112].

The methods related to electroplating aluminum on magnesium and its alloys from ionic liquids inclusive a surface pre-treatment of the magnesium and a surface post-treatment of the aluminum coated magnesium alloy to remove residual whit of ionic liquids, **Figure (1-9)**. The surface pre-treatment comprised at least one step to produce a clean surface and free of residues and foreign materials suitable for a subsequent electroplating operation and for control of nucleation and adhesion. The post-treatment of the magnesium alloy surface includes rinsing, stabilization of the surface, followed by drying the surface of the magnesium alloy.

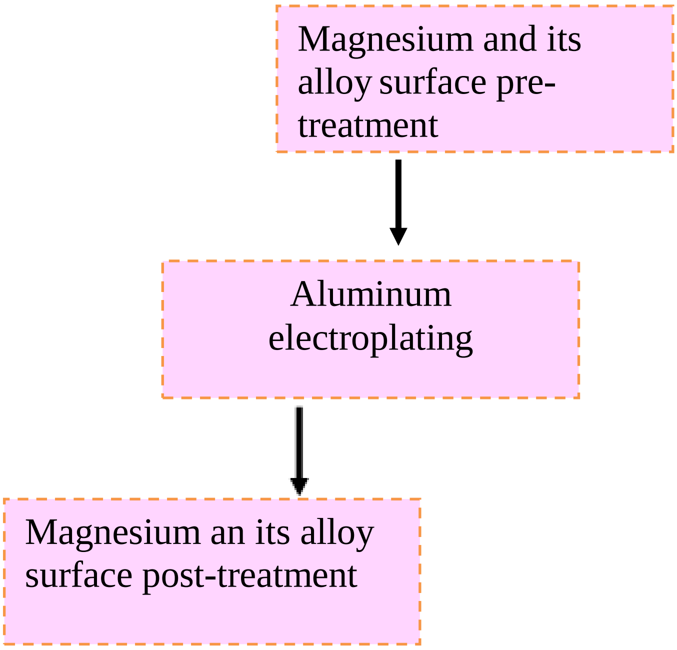


Figure (1-9) Electrodeposition process outlines

1.6 Aim of the present work:

Magnesium metal and its alloys are known to have important industrial applications due to several advantageous that they have. However, they are normally suffering from the corrosion set back. To protect the metal from being corroded:

- Mg metal was reacted with three ionic liquids: hydrate ammonium alum/urea, hydrate aluminum nitrate/urea and aluminum chloride/urea ionic liquids and formed conversion coating layers.
- Study the ability of electrodeposition of a protective aluminum layer on bare and previous coated Mg metal in aluminum chloride/urea IL from which aluminum metal was successfully deposited on copper in previous studies.
- Comparing the ability of deferent coating layers to protect Mg metal from corrosion which have been achieved on its surface.

Chapter Two

Experimental part

Experimental part

2.1 Chemicals

All the chemicals used in current work were of the highest purity available and supplied without further purification, **table (2-1)** shows the reagents, their purities, and suppliers.

Table (2-1): Specification of the chemicals

No.	Compound	Formula	Purity %	Company
1	Ammonium aluminum sulfate dodecahydrate	$NH_4Al(SO_4)_2.12H_2O$	99.5	BDH
2	Aluminumnitrate nonahydrate	$Al(NO_3)_3.9H_2O$	98.5	BDH
3	Anhydrous aluminum Chloride	$AlCl_3$	99.5	BDH
4	Urea	NH_2CONH_2	99.5	Thomas Baker
5	Acetone	CH_3COCH_3	99.5	Thomas Baker
6	Sodium Hydroxide	NaOH	99	BDH
7	Hydrochloric Acid	HCl	37	BDH
8	dichloromethan	CH_2Cl_2	99.8	ROMIL-SA
9	Propan-1-ol	$CH_3CH_2CH_2OH$	99.5	BDH

2.2 Practical Methods

2.2.1 Surface conversion coating using ionic liquids

2.2.1.1 Preparation of ionic liquids:

Three ionic liquids have been used to form the conversion coatings on pure magnesium metal were prepared by the following:

a. **Hydrate Ammonium alum/urea IL:** Prepared by mixing a proper amount of $NH_4Al(SO_4)_2.12H_2O$ and urea in mole ratio of (1:5). Milled and heated with gentle stirring gradually from room temperature to 80°C for 3 hrs. until clear colorless liquids were obtained[113], **Figure (2-1a)**.

b. **Hydrated aluminum nitrate/urea IL:** $Al(NO_3)_3.9H_2O$ mixing and milled with urea in mole ratio of (1:1.2) and heated gradually from room temperature to 80°C for 3 hr. with gentle stirring to produce colorless liquid [51], **Figure (2-1b)**.

c. **Anhydrous aluminum chloride/urea IL**: It was prepared by progressively addition of a proper amount of both $AlCl_3$ and urea in mole ratio of (1.2:1) with continuous stirring in glove box under nitrogen gas until faint yellow liquid was formed, **Figure (2-1c)**. It was noticed that an elevation in temperature when the salts were reacted which was reported to be 75°C in accord with prior publication [39, 115].

(a) (b) (c)

Figure (2-1): Photographs of (a) hydrate ammonium alum/urea IL (b) hydrate aluminum nitrate/urea IL (c) aluminum chloride/urea IL

2.2.1.2 Materials and pretreatment

The materials used in this work were pure Mg metal specimens with 1mm thickness and surface area of 5cm^2. They were prepared by grinding with successive grades of SiC paper, washed with distilled water, dipped in 4.5% diluent HCl then washed with distilled water; and again immersed in 0.5% NaOH solution, washed with distilled water. Finally rinsed with acetone and kept in desiccator to be used in the corresponding experiments.

2.2.1.3 Preparation of the thin layer

Conversion coatings on pure magnesium metal conducted as per the following sequence steps at 25˚C:

- Process performed at room temperature by immersion the samples in hydrate ammonium alum/urea IL, hydrate aluminum nitrate/urea IL in open atmosphere and aluminum chloride/urea IL in closed atmosphere **Figure (2-2)**.

- After 40 minutes, water rinsed then the samples were dried either with air when the specimen treated with hydrate ammonium alum/urea IL or with dry N_2 gas when the specimen treated with hydrate aluminum nitrate/urea IL while the sample treated with aluminum chloride/urea IL rinsed with dichloromethane and propanol then left to dry with air.
- The coated samples were stored in a desiccator for subsequent analysis.

(a) (b) (c)

Figure (2-2): Photographs of Mg metal specimens immersed in (a) hydrate ammonium alum/urea IL (b) hydrate aluminum nitrate/urea IL (c) aluminum chloride/urea IL

2.2.2 Electrodeposition of aluminum on conversion coated magnesium metal in aluminum chloride/urea ionic liquid

2.2.2.1 Materials and pretreatment

Conversion coated Mg metal samples, which previously prepared by immersion in $NH_4Al(SO_4)_2.12H_2O$/urea IL and $Al(NO_3)_3.9H_2O$ /urea IL as mentioned in 2.2.1.3 used as cathode. The anode was aluminum mesh with 30mm diameter which prepared by abraded with iron brush, rinsing with deionized water then dipped into 0.5% HCl also deionized water; immersed in 0.5% NaOH, wished with deionized water and finally rinsed with acetone and left to dry.

2.2.2.2 Electrodeposition process

A constant voltage of -0.6 was applied for 4hrs by using a power supply (Thurlby 15V-4A, England power supply) to control the current and the potential of electrodeposition process which was connected to two electrodes; conversion coated Mg electrode as cathode and aluminum mesh as anode. $AlCl_3$/urea ionic liquid, which was prepared as mentioned in 2.2.1.1 used as electrolytic bath. After the completion of electrodeposition process, the post-treatments performed on the deposited sample which were included immersed in dichloromethane then propanol, and then left to dry on air.

2.2.3 Electrodeposition of aluminum on pure magnesium metal in aluminum chloride/urea ionic liquid

2.2.3.1 Martials and pretreatment

The materials used in this work included pure Mg metal specimen with 1mm thickness and surface area of $5cm^2$, which was prepared as aforementioned in 2.2.1.2. Aluminum mesh with 3cm diameter, prepared by the same steps illustrated in 2.2.2.2. The electrocleaning process that has been used to prepare a clean metal surface was anodic electrocleaning. It was carried out by applying a positive potential of 1V for 1 min to Mg specimen.

2.2.3.2 Electrodeposition process

A pure Mg electrode was used as cathode and aluminum mesh as anode while a constant voltage of -0.6 was applied for 4hrs, aluminum chloride/urea ionic liquid was used as electrolytic bath. The post-treatments were applied to deposited sample included immersed in dichloromethan and propanol then left to dry by air.

2.3 Instrumentals and Techniques

2.3.1 Atomic force microscopy (AFM)

The surface topography of the coated samples was analyzed by atomic force microscopy (AFM) (AA2000, Angstrom Advanced Inc.) contact mode. The measurements carried out in the laboratories of Department of Chemistry /College of Science / Al-Nahrain University.

2.3.2 Scanning Electron Microscope (SEM)

The surface morphology of coated and uncoated metal was investigated by using a high-resolution field emission scanning electron microscopy (INSPECT S50), which carried out in the laboratories of Department of Physics /College of Science /Al-Nahrain University.

2.3.3 Energy dispersive X-ray analysis (EDXA)

The composition of coated layer was determined by the (X Flash 6110) Bruker EDX which conjunction with SEM. The measurements have executed in the laboratories of Department of Physics / College of Science / Al-Nahrain University.

2.3.4 Cross-sectional SEM

In order to determine the thickness of the coating layer, scanning electron microscopy (INSPECT S50) was used where the measurements carried out in the laboratories of Department of Physics /College of Science /Al-Nahrain University.

2.3.5 X-ray Diffraction analysis

The crystalline and phase identification of samples were determined using X-ray Diffractometer (bruker D2 phaser) performed in the laboratories of geology department/ College of Science /Baghdad University.

2.3.6 Corrosion test

2.3.6.1 Experimental Equipment

- **Potentiostat/Galvanostat device-M lab 200:** Potentiodynamic polarization measurements have fulfilled by using Potentiostat M Lab (WENKING M Lab multichannel and SCI-M Lab corrosion measuring system from Bank Electronics-Intelligent controls GmbH, Germany 2007). It was provide the electrochemical calculation such as Tafel line evaluation (cathodic and anodic regions). M Lab is adjusted by computer desktop Window XP.
- **Corrosion cell:**

  A container cell made of Pyrex with (1L) capacity comprise of two vessels, internal, that contain working solution and external, connecting with a thermostat device in order to adjust the temperature of the working solution by a thermometer inserted.

- **Corrosion electrodes:**

❖ **Working Electrode**

The coated Mg metal samples placed on a holder with a proper specific surface area of $1cm^2$ that was only being exposed to the salt solution.

❖ **Reference Electrode**

A saturated calomel electrode (SCE) was used as the reference electrode, which having a potential of 0.2444 V. The electrode was contacted with the examined solution through a Luggin capillary.

❖ **Auxiliary Electrode**

The auxiliary electrode used in the electrochemical cell was platinum electrode fixed opposite to the working electrode.

2.3.6.2 Corrosion test procedures

- **Open Circuit Potential Test**

Open circuit potential (OCP) is the potential of the working electrode that measured against the reference electrode by a high impedance potentiometer so there is no flowing of current between the working electrode and the reference electrode. To evaluate the open circuit potential value of coated Mg metal, the samples was immersed in the 3.5% NaCl solution for 900 second.

- **Tafel extrapolation**

The potentiostatic experiments were carried out using WINKING M Lab potentiostat/galvanostat. Polarization curve measurement were determined at a scan rate of 10 mV/s starting from a potential of about (-200) mV from the open circuit potential going towards anodic potential. This wide range of potential allows the determination of corrosion potential (E_{corr}), corrosion current density (i_{corr}), anodic (ba) and cathodic (bc) Tafel slopes from the polarization digram as shown in **Figure (2-3)** and the weight loss of coated Mg metal measured as grams loss in m^2 per day. All the measurements were studied in 3.5% NaCl solution at 25ºC with static conditions.

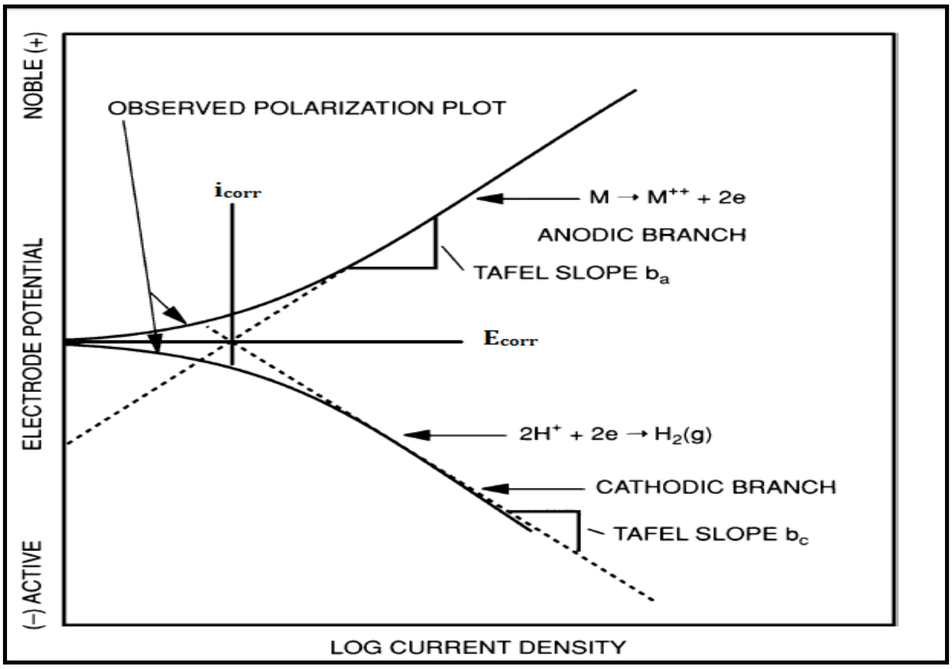


Figure (2-3): Cathodic and anodic polarization diagram

Chapter Three

Results &

Discussion

Results & Discussion

3.1 Conversion coatings formation

In this work, we investigated the ability of using three ionic liquids hydrate ammonium alum/urea, hydrate aluminum nitrate/urea and aluminum chloride/urea ILs to form a thin film on the surface of pure Mg metal. Attempting to electroplating pure magnesium with aluminum metal in these ionic liquids revealed the possibility of conversion coating magnesium metal with thin layer. Different conversion coatings were resulted from the treatment of pure magnesium metal with these three ionic liquids which photographs are shown in **Figure (3-1)**. The coatings were found to be homogenous uniform and covered the whole substrate. Magnesium plates were immersed in ionic liquids for 40 min until an equilibrium state was establish between the sample surface and ionic liquid. The time was chosen as the initially fast colorless gases evolution was halted and no bubbles were visually seen. It was noticed that the reaction of magnesium metal surface with aluminum chloride/urea IL was less intensive than the reaction with other ionic liquid used in this investigation, which was thought to be due the reaction of the water molecules presented in the initial solid lattice of hydrate ammonium alum/urea IL and hydrate aluminum nitrate/urea IL.

The conversion coating formed on pure Mg metal sample treated with hydrate ammonium alum/urea IL was white matt film while a bright silver film was formed by treatment with hydrate aluminum nitrate/urea IL. Due to their hydrophobic properties, working with these ionic liquids allowed experiments to be performed in open atmosphere. However, a dark gray layer was formed on Mg metal sample treated with aluminum chloride/urea ionic liquid.

The latter ionic liquid was reported as air and water sensitive, in which the treatment of Mg metal with this ionic liquid ought to be carried out in close atmosphere.

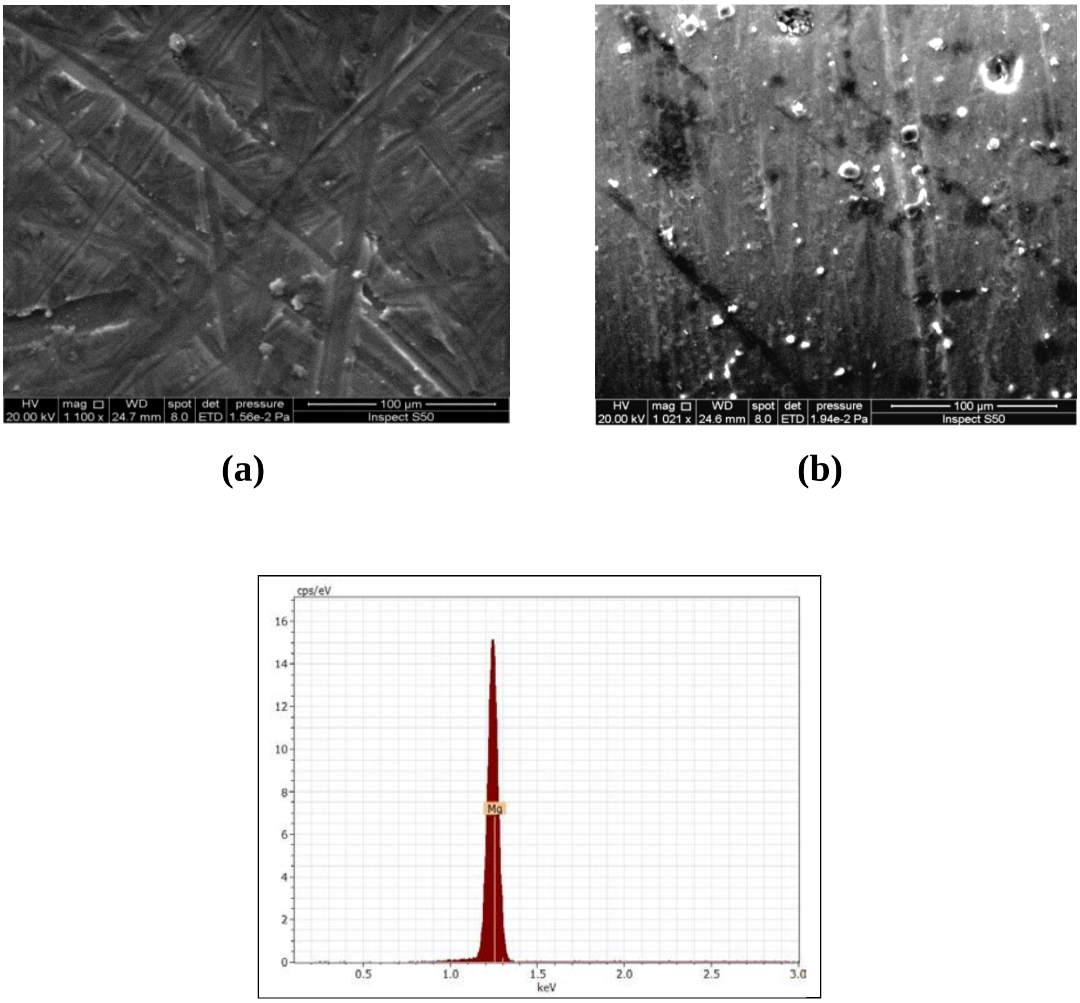
(a) (b) (c)

Figure (3-1): Photographs of conversion coatings obtained on pure Mg (a) treatment with ammonium alum/urea IL (b) treatment with aluminum nitrate/urea IL (c) treatment with aluminum chloride/urea IL

3.1.1 Pre-treatments and post-treatment of magnesium substrates

It was well known that chemical pretreatments could affect the surface roughness and the surface composition as well as the final corrosion resistance of the IL conversion coating [117]. On the other hand, the optimum surface pre-treatment procedures for initial preparation of Mg metal were still to be developed.

In general, the magnesium surface preparation included a mechanical polishing and buffing to a smooth finish, thereafter any grease, buffing compounds or organic contaminants were removed by solvent rinsing, or other suitable solvent emulsion cleaning. In this study, 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 etch on Mg surface. **Figure (3-2)** exhibits the Scanning Electron Microscope (SEM) and Energy dispersive X-ray analysis (EDXA) examination results of pure and pre-treatment magnesium metal specimen. From this micrograph photos it was disclosed that the micro-incision of pure Mg metal were disappeared and a rather smooth surface was formed. In addition, EDXA result did not show a presence of chloride ion or any other contaminates might be found on the surface of substrate due to the aggressive reaction occurred between the magnesium metal and the HCl solution. Otherwise, as stated in ref [138] by Xiaomei Yu, Mark R. Jaworowski, and et al. magnesium phosphate film was formed in the surface of substrate by using a phosphoric acid solution as a chemical pickling [128].



(a) (b)

(c)

Figure (3-2): (a) SEM image of pure Mg (b) SEM image of prepared Mg metal (c) EDXA spectrum of prepared Mg metal

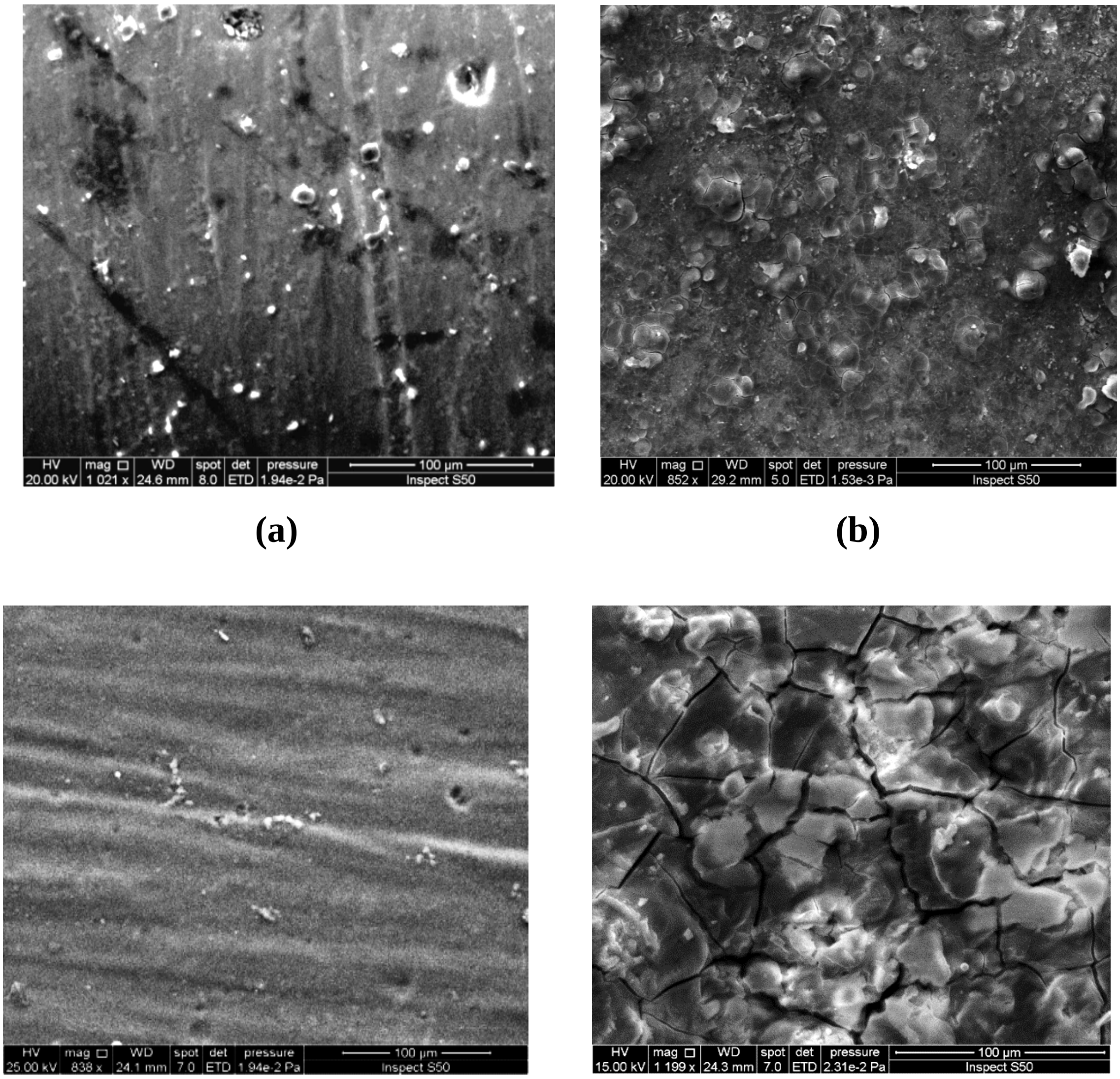
After the conversion coating process, The post-treatments have been employed on the coated Mg samples , included rinsing the samples with water then dried by either air in case of the treatment with hydrate ammonium alum/urea IL or by dry N_2 gas in case of the treatment with hydrate aluminum nitrate/urea IL. These treatments produce a clean smooth coating on the surface of pure magnesium metal. In this investigation, it was found that drying the sample, which was treated with hydrate ammonium alum/urea IL with N_2 gas gave a dully like form but when drying on air, an adhesive uniform white matte layer was obtained. In addition, it was noticed that yellow spots were formed on the surface of the Mg conversion coated by hydrate aluminum nitrate/urea when dried in open air while dried with N_2 gas give bright silver coating.

Furthermore, the sample treated with aluminum chloride/urea IL was required complete removed of all residual ionic liquid on the Mg surface after immersion, since this ionic liquid was sensitive to air, and can immediately react with moisture and forming hydrochloric acid which could damage the coating layer. Therefore, the conversion coating sample was rinsed with dichloromethane then propanol then dried on air, which showed the ability to dissolve the residual ionic liquid and did not reacted with the resulted coating. Finely, a rather compact adhesive coating was obtained.

3.1.2 Conversion coatings characterizations

The surface morphology of bare and coated magnesium metal samples have been examined by Scanning Electron Microscope (SEM). Surface observation result of the three conversion coatings that are shown in **Figure (3-3)**, these figures showed that the conversion coating caused a significant change in the morphology of the pure Mg metal. A typical island-like structure with many cracks has exhibited on the surface of coating layer formed on Mg metal surface treated with hydrate ammonium alum/urea IL **Figure (3-3b)**. Whereas, homogeneity appeared on the coating layer formed when immersion in hydrate aluminum nitrate/urea IL **Figure (3-3c)**. Close examination of the surface of Mg metal treated with hydrate aluminum nitrate/urea IL **Figure (3-3c)** look like that the ionic liquid has dissolved a thin layer of Mg metal surface producing only aluminum oxide adhered firmly on the surface of magnesium as was observed from EDXA examination shown in **Figure (3-7)**. In addition, thicker fine cracked surface with 'dry mud' morphology and a compact surface has been appeared on Mg metal surface when treated with aluminum chloride/urea ionic liquid **Figure (3-3d)**.

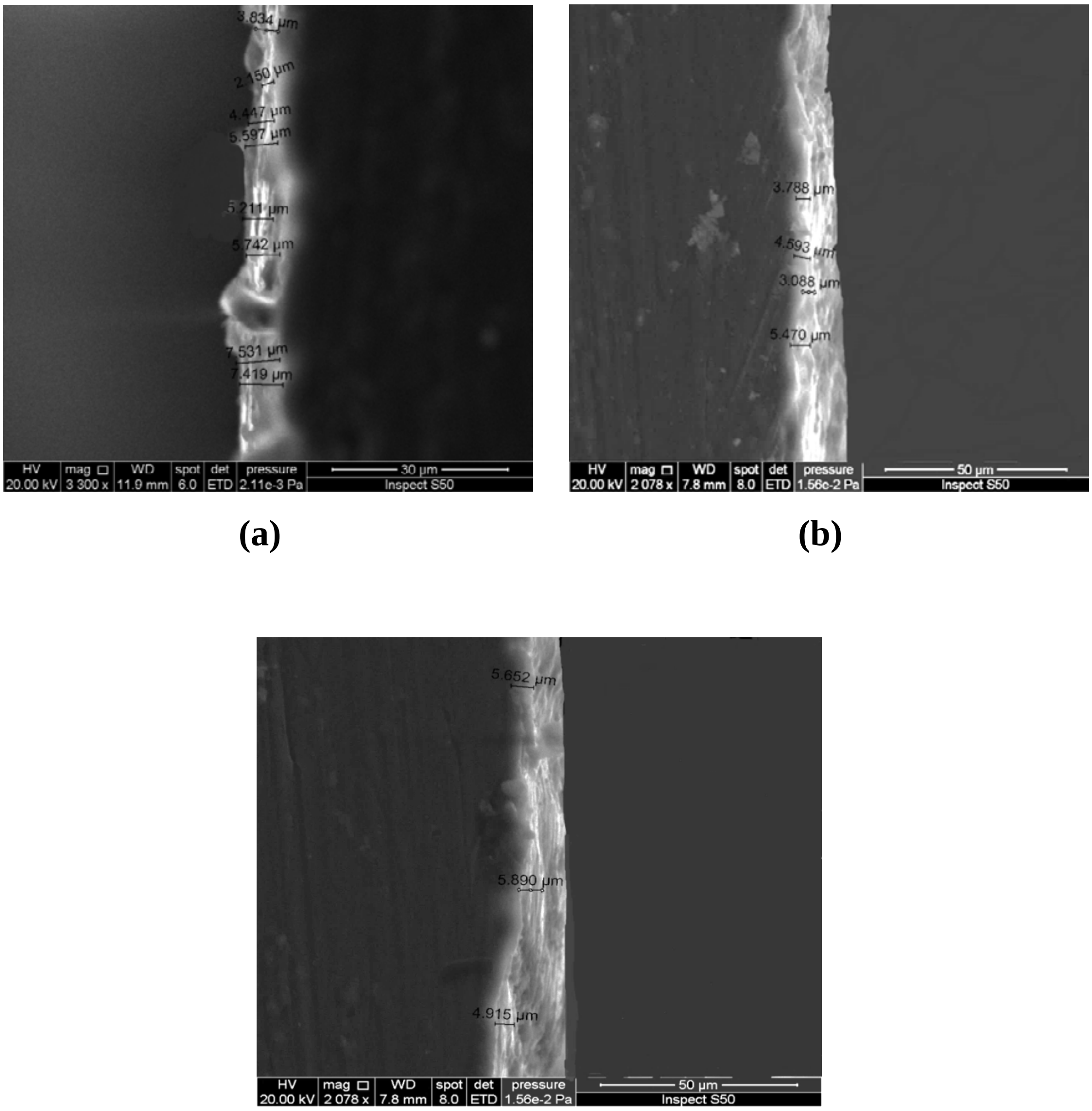
The cross-sectional SEM images of coated Magnesium have indicated in **Figure (3-4)**, showed that the three coating layer were well adhered to the substrate with reasonable allocation, while the average thickness were about **(2-5) µm**. In addition, the results showed that the layer obtained by the treatment with aluminum chloride/urea IL was relatively thicker and more compact as exhibited in **Figure (3-4c)**.



(a) **(b)**

(c) **(d)**

Figure (3-3): SEM images of Mg metal specimens (a) bare Mg metal (b) treated with hydrate ammonium alum/urea IL (c) treated with hydrate aluminum nitrate/urea IL (d) treated with aluminum chloride/urea IL



(a) **(b)**

(c)

Figure (3-4): Cross-sectional SEM images of Mg metal specimens (a) treated with hydrate ammonium alum/urea IL (b) treated with hydrate aluminum nitrate/urea IL (c) treated with aluminum chloride/urea IL

The topographic properties of the immersed samples in the three ionic liquids have been examined by atomic force microscopy (AFM) as shown in **Figure (3-5)**, while the data was tabulated in **Table (3-1)**.

The AFM examination indicated that the coatings formed on Mg metal showed a nanoscale roughness and average height. Yet the coating obtained from aluminum chloride/urea IL has relatively higher height and roughness than that obtained from both ammonium alum/urea and aluminum nitrate/urea ionic liquids respectively **Table (3-1)**.

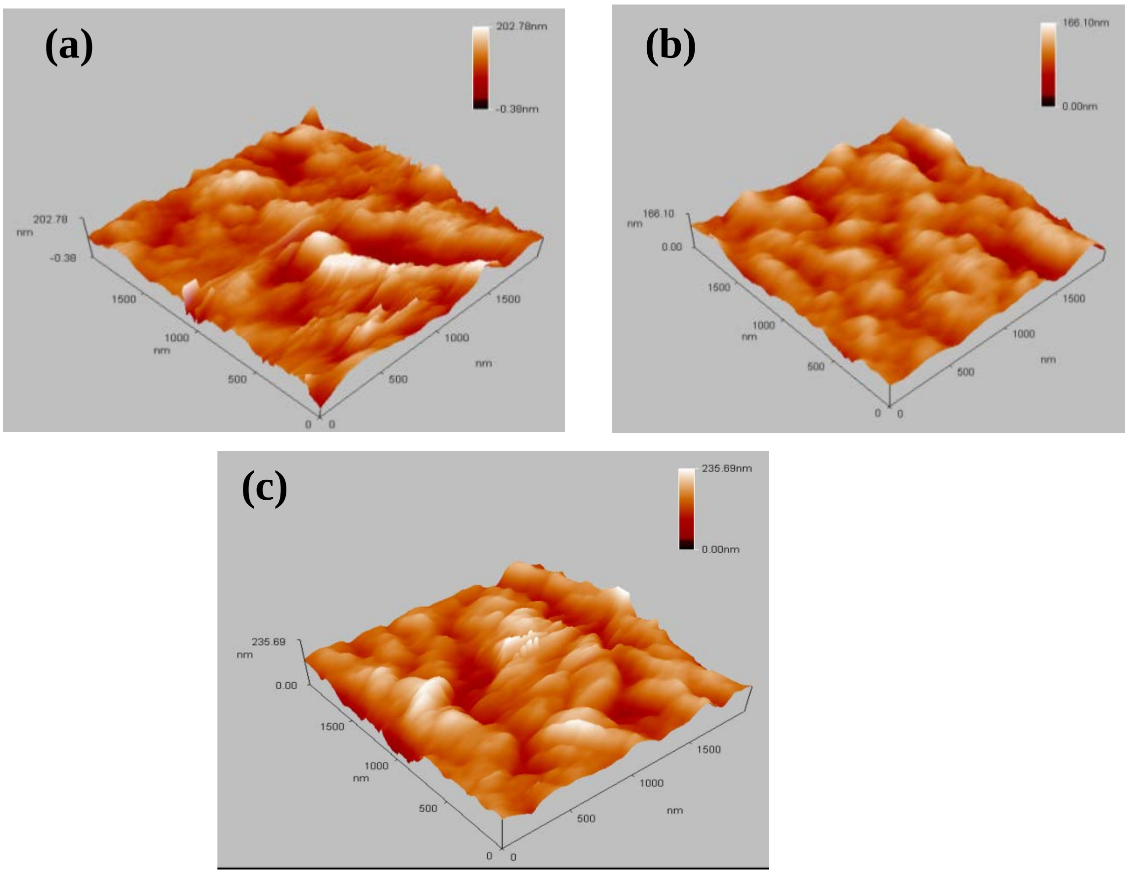


Figure (3-5): AFM images of Mg metal specimens (a) treated with hydrate ammonium alum/urea IL (b) treated with hydrate aluminum nitrate/urea IL (c) treated with aluminum chloride/urea IL

Table (3-1): AFM data of the conversion coatings on Mg metal

Sample	Total grain	Roughness [nm]	Avg. size $[nm]^2$	Avg. height [nm]
Treated with $NH_4Al(SO_4)_2.12H_2O$/urea IL	368	20.6	10569.32	139.25
Treated with $Al(NO_3)_3.9H_2O$/urea IL	224	14	17375.35	116.24
Treated with $AlCl_3$ /urea IL	149	23.4	26301.24	177.54

Elemental composition of the three-conversion coating layers have been inspected by Energy dispersive X-ray analysis (EDXA). The composition peaks and weight % of different elements in the conversion coatings are shown in **Figures (3-6, 3-7 and 3-8)**. From these figures it was disclosed that the thin films consist of Al, O, C with various weight ratio in both samples treated with hydrate ammonium alum/urea IL and aluminum chloride/urea IL, **Figures (3-6 and 3-8) and Tables (3-2 and 3-4)**. Whilst only Al was consisted the thin film formed by the treatment of Mg metal with hydrate aluminum nitrate/urea IL. It was clearly seen that the proportion of Al in the coating layer treated with Aluminum chloride/urea was the highest comparing with the other coating layers.

In addition, the results of EDXA have indicated that the coating layer formed on Mg metal surface by the treatment with aluminum chloride/urea IL was composted of MgO and Al_2O_3 mixed oxides as exhibited in **Table (3-4)**. These results corresponding to the X-ray diffraction results showed in **Figure (3-9)**.

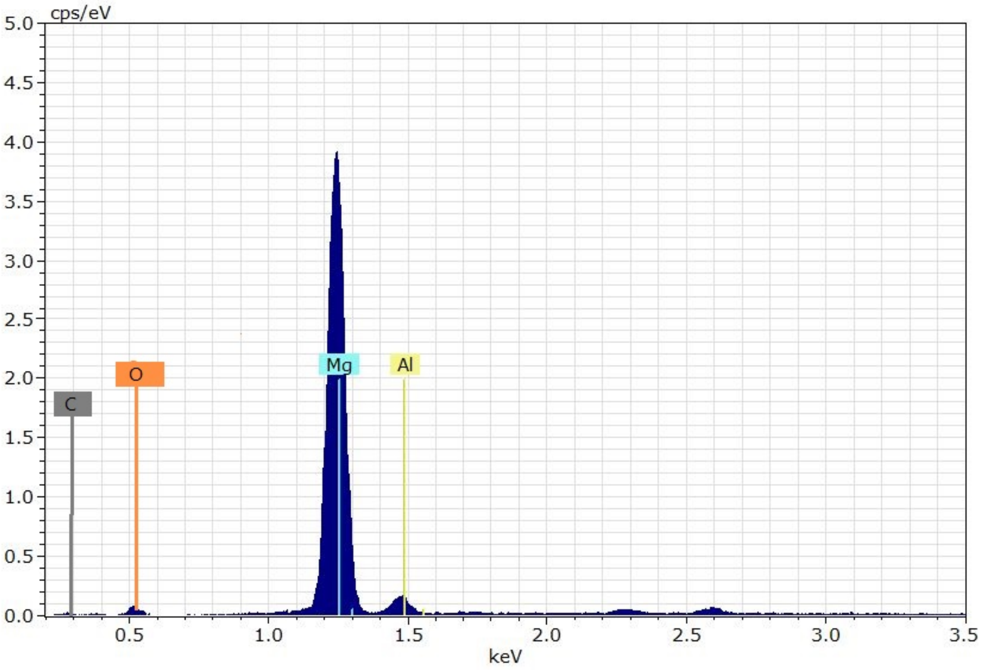


Figure (3-6): EDXA spectrum of Mg metal specimen treated with hydrate ammonium alum/urea IL

Table (3-2): wt. % of elements consist the coating layer formed by immersion in ammonium alum/urea IL

Element	[wt.%]	[norm. wt.%]	[norm. at.%]
Magnesium	53.6655	80.6442	76.3562
Carbon	3.84189	6.77328	11.0614
Oxygen	3.24667	5.87884	7.01746
Aluminum	3.77448	6.67199	4.93766

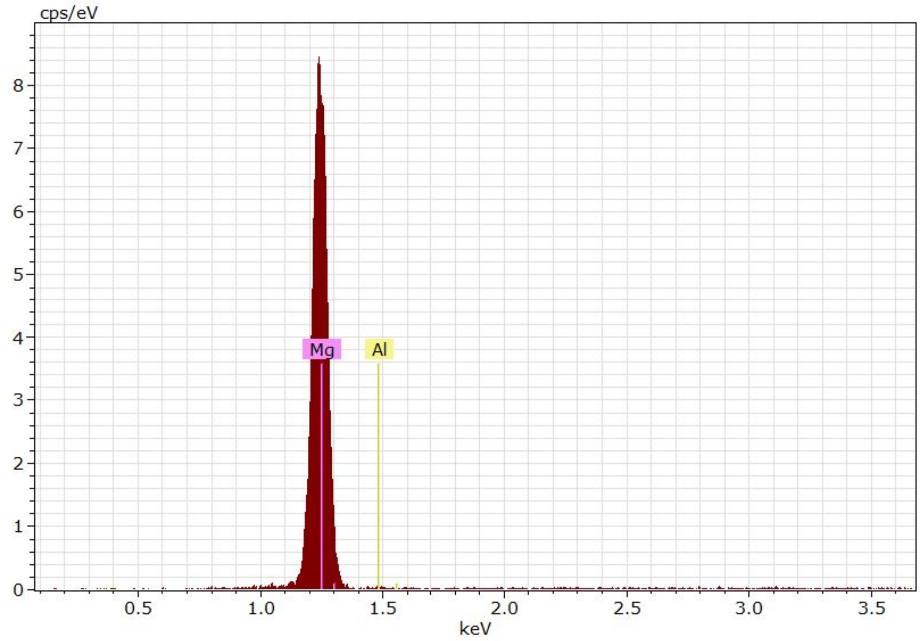


Figure (3-7): EDXA spectrum of Mg metal specimen treated with hydrate aluminum nitrate/urea IL

Table (3-3): wt. % of elements consist the coating layer formed by immersion in aluminum nitrate /urea IL

Element	[wt.%]	[norm. wt.%]	[norm. at.%]
Magnesium	105.9831	99.26556	99.33793
Aluminum	0.784143	0.734441	0.662068

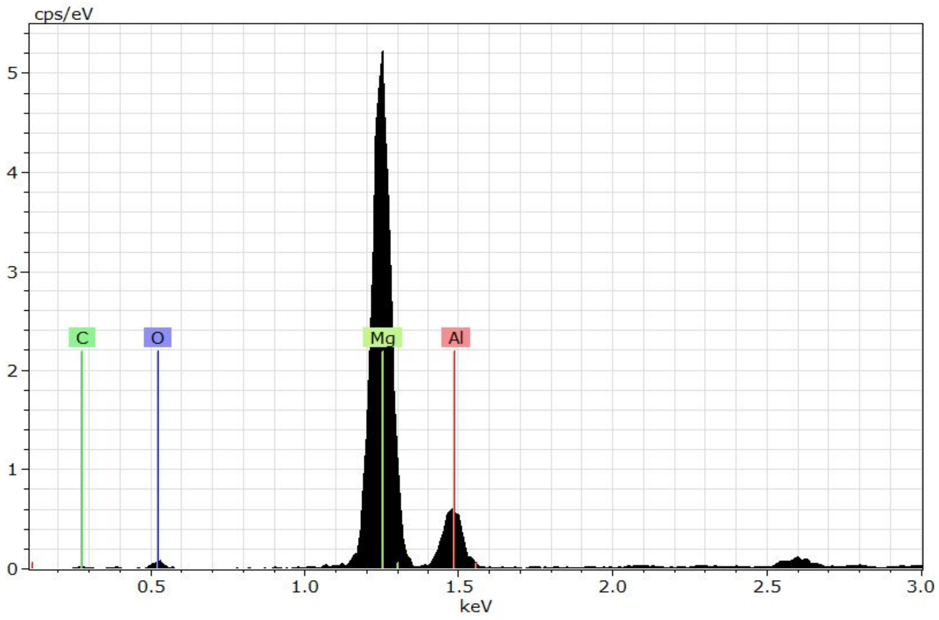


Figure (3-8): EDXA spectrum of Mg metal specimen treated with aluminum chloride/urea IL

Table (3-4): 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_2O_3	38.0227	19.1407
Oxygen	81.6618	41.1087	51.8958		4.01866E-09	2.023E-09

As exhibited in mixed oxide of Mg and Al oxide ($MgAl_2O_4$ and Al_2O_3) were detected by XRD examination on the surface of the Mg metal treated with hydrate ammonium alum/urea IL **Figure (3-9a)** and aluminum chloride/urea ILs **Figure (3-9c)**. Whereas only a thin aluminum oxide-rich layer was observed on the surface of substrate treated with hydrate aluminum nitrate/urea IL **Figure (3-9b)**.

In general, the conversion coating mechanism could elucidate as follows:

The substrate aimed to be protected is immersed in a electrolyte (which act as anode) that react with the surface of the Mg metal altering the metal ion concentration at the metal-solution interface, therefore the anodic behavior and the reactivity of the substrate in a given environment takes a critical role. The localized change in composition causes precipitation from the solution onto the surface of the substrate forming the coating film that chemically bonded to the metal surfaces. In this work, pure magnesium metal samples have immersed in three different ionic liquids and a reaction has been occurred between the metal surface and the immersion solutions. The EDXA and XRD results shown that aluminum oxide and mixed metal oxides ($MgAl_xO_x$) complex have been presented in coating layers formed on the Mg metal surface. Additionally, the cross-section SEM indicated that these films were highly adhesive on that surface which gave an evidence for chemically bonded films.

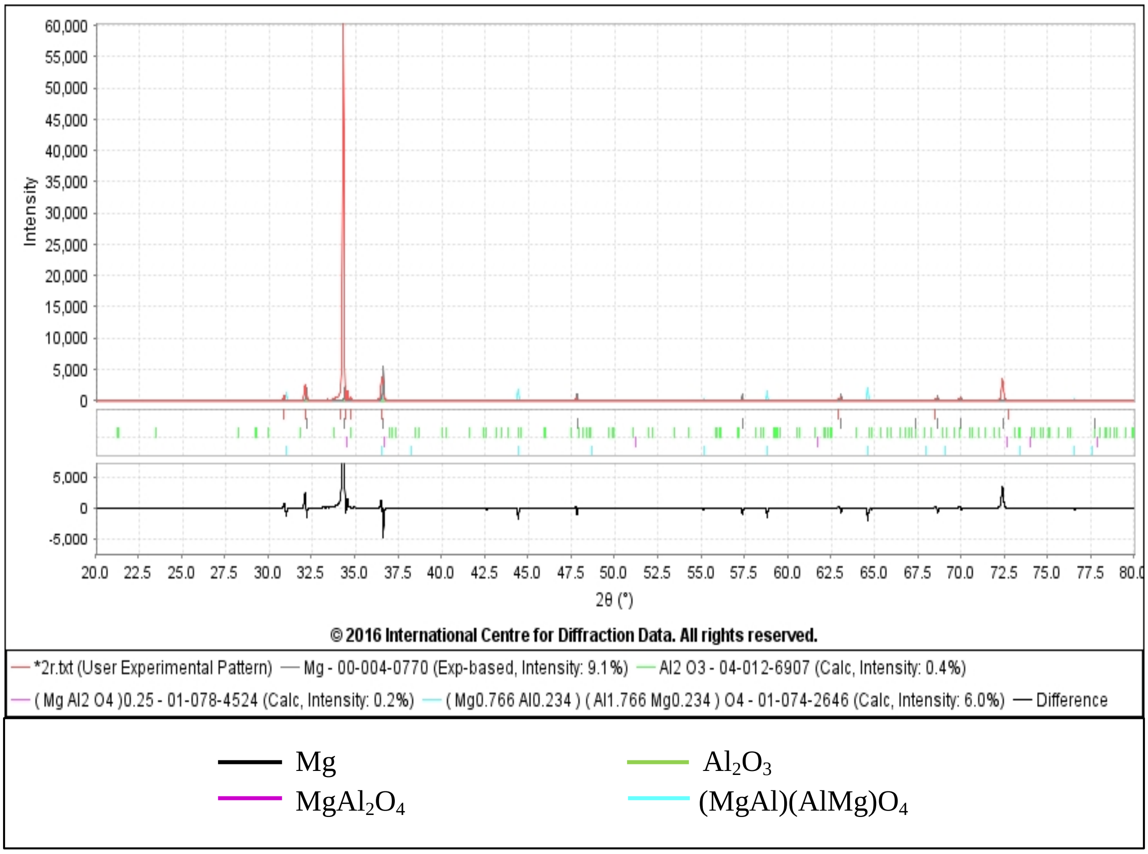


Figure (3-9a): XRD spectra of Mg metal specimen treated with hydrate ammonium alum/urea IL

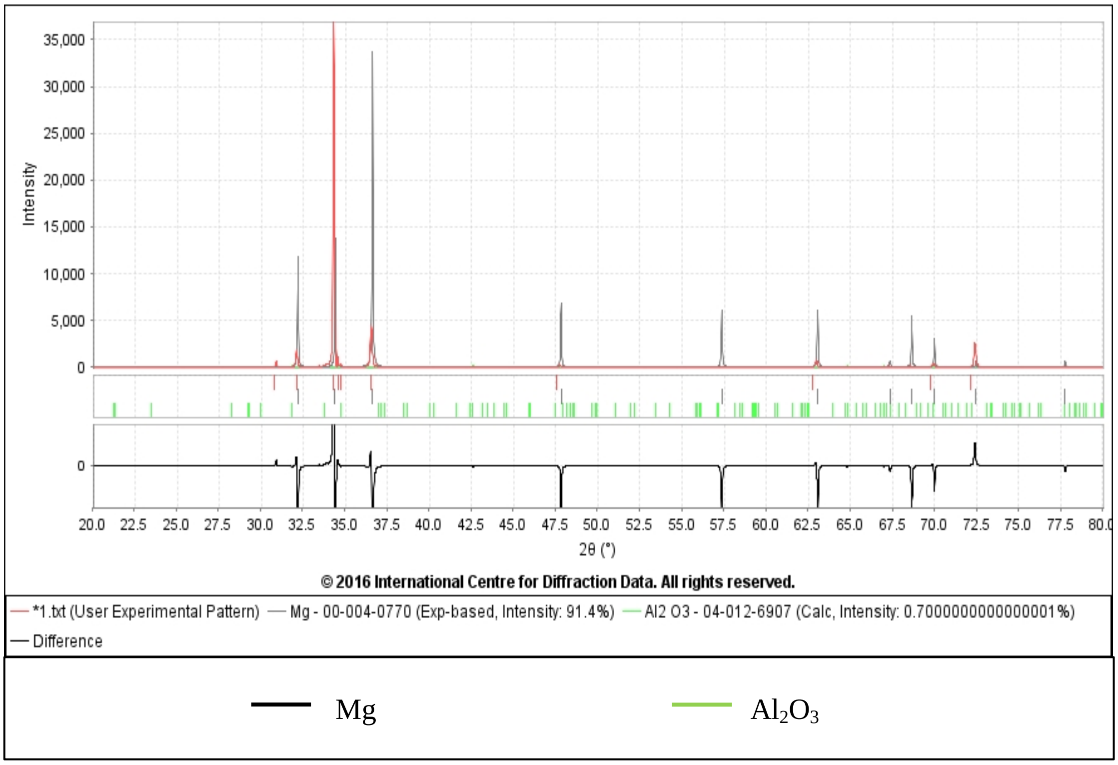


Figure (3-9b): XRD spectra of Mg metal specimen treated with hydrate aluminum nitrate/urea IL

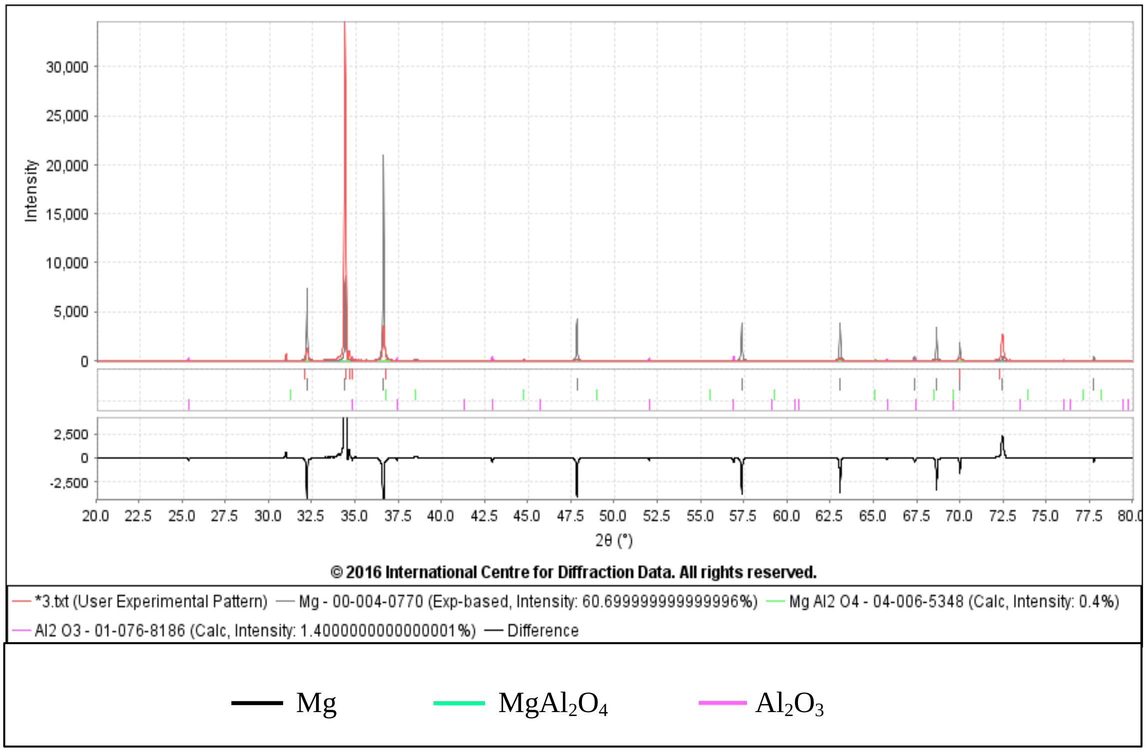


Figure (3-9c): XRD spectra of Mg metal specimen treated with aluminum chloride/urea IL

Although the presence of SO_4^{2-}, NO_3^- and Cl^- ions in solution promote local and generalized corrosion on Mg metal as reported in several researches [8,13,17], it was reveal that these ions have no effect on Mg metal due to the fact that they were restricted when present in ionic liquid. On the contrary, a protective thin film was formed on Mg surface by using these ionic liquids.

There are three different possible mechanisms proposed for the IL-Mg interaction of the conversion coatings: physical adsorption, chemical interaction, and electrochemical interaction [111] also, they were explained as stated in ref [112]:

1. Anion adsorption onto the metal (or metal oxide) surface followed by an electrostatic interaction with the cation to ensure charge neutrality, resulting in the formation of a double layer on the substrate.
2. Chemical interaction of the anion with the metal ions formed from surface corrosion in the IL solvent.
3. Electrochemical breakdown of the anion and/or cation to form new chemical species which interacts with the surface via chemical adsorption or the formation of insoluble surface films with Mg^{+2} or other metallic ion species.

In this work, the most appropriate mechanism applied for films formation was the breakdown of the anion and/or cation to form new chemical species that electrochemically interaction with Mg metal surface leading to highly adhesive film formed onto metal surface, which was accelerated by the highly electronegativity of Mg metals.

In addition, it was noticed that neutral aggressive gases have been evolution during the reaction between the pure Mg metal and the three ionic liquids and a white product has been participate. Therefore, the proposed chemical equation for the thin film forming by the interaction of those ionic liquids and Mg metal was thought to be as the suggested empirical equations:

- The proposed equation for the interaction between hydrate ammonium alum/urea IL and Mg metal:

$$Mg + NH_4Al(SO_4)_2.12H_2O/NH_2CONH_2 \longrightarrow MgAl_2O_4 \text{ or } Al_2O_3 + H_2\uparrow$$
$$SO_2\uparrow + N_2\uparrow + MgSO_4$$

- The proposed equation for the interaction between hydrate aluminum nitrate/urea IL and Mg metal:

$$Mg + Al(NO_3)_3.9H_2O/NH_2CONH_2 \longrightarrow Al_2O_3 + Mg(NO_3)_2 + H_2\uparrow + N_2\uparrow + CO_2\uparrow$$

While the proposed equation for the reaction of pure Mg metal with aluminum chloride/urea IL:

$$Mg + AlCl_3/\ NH_2CONH_2 \longrightarrow MgAl_2O_4 \text{ or } Al_2O_3 + MgCl_2 + H_2\uparrow + Cl_2\uparrow + N_2\uparrow$$

3.1.3 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^- ion thus three-compartment cell containing 3.5% NaCl solution have been used which, the coated Mg metal with $1cm^2$ exposure area was used as working electrode, platinum electrode and saturated calomel electrode used as counter and reference electrodes respectively. The corrosion resistance properties have been detected by polarization curves shown in **Figure (3-10)**. The Open circuits potential, corrosion potential (Ecorr) and corrosion current density (icorr) of the conversion coatings obtained from these curves were presented in **Table (3-5)**.

The pure Mg **(curve a)** showed a very negative potential of below -1.6V (vs. SCE) indicating its extremely active nature. The corrosion resistance of

The pure Mg **(curve a)** showed a very negative potential of below -1.6V (vs. SCE) indicating its extremely active nature. The corrosion resistance of pure Mg metal was improved by the conversion coating established from the three ionic liquids; hydrate ammonium alum/urea IL, hydrate aluminum nitrate/urea IL and aluminum chloride/urea IL. These treatments 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 **Figure (3-10)**, and the values in **Table (3-5)**, it was observed that the Mg metal sample treated with aluminum chloride/urea IL **(curve d)** showed highly corrosion resistant by shifting the potential to more noble values and extremely decreasing the corrosion current, which disclosed to the value indicated from Al metal sample. comparing to that of the pure Mg metal, the i_{corr} value of the Mg metal sample treated with aluminum chloride/urea IL sample is **(24)** times greater while the values of i_{corr} for Mg sample treated with hydrate ammonium alum/urea and hydrate aluminum nitrate/urea ILs is **(12)** times and **(7)** times respectively. Even though, it was reported that an ionic liquid containing no metal salt applied to a reactive metallic substrate may result in forming of a corrosion-resistant thin film that complexation with the underlying substrate [112].

Additionally, these results revealed that the immersion of pure Mg metal in these ionic liquids provide a significant ennoblement of the surface comparing with previously studies in other ionic liquids and aqueous solutions. In a non-ideal comparison between reported results of magnesium alloys [110,129] and the present results of pure magnesium metal and although the alloy has corrosion resistance more than pure Mg metal, the present results showed a noticeable low current density than the treated alloy by variable conversion coating solution. For example, chemical conversion coatings (stannate solution, cerium oxide, chromate and galvanic black anodizing) of magnesium alloy (AZ31B) was tested for corrosion ability in higher salt concentration of 5% NaCl [129]. The published results showed that the treatment of AZ31B Mg alloy with Galvanic black anodizing gave the best corrosion resistance by reducing the corrosion current to **4.8 μA/cm²**. Even though, this result was higher than current density value resulted by the treatment of pure Mg metal with aluminum chloride/urea IL.

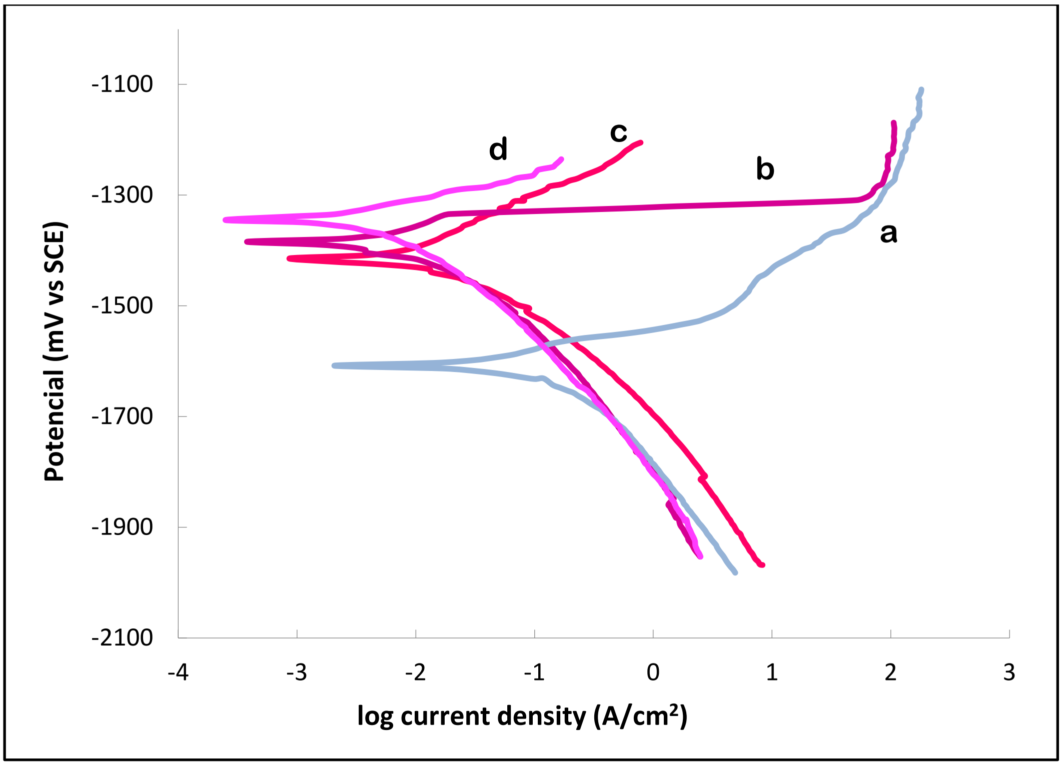


Figure (3-10): Polarization curves in 3.5% NaCl of (a) bare Mg, (b) treated with ammonium alum/urea IL (c) treated with aluminum nitrate/urea IL (d) treated with aluminum chloride/urea IL

Table 3-5: Polarization data of the conversion coatings on Mg metal in 3.5% NaCl solution

Samples	OCP, V	Ecorr, V (SCE)	Icorr, μA/cm^2
Bare Mg	-1.66	-1.59	44.51
Treated with $NH_4Al(SO_4)_2.12H_2O$/urea IL	-1.55	-1.38	3.82
Treated with $Al(NO_3)_3.9H_2O$/urea IL	-1.57	-1.41	6.48
Treated with $AlCl_3$/urea IL	-1.27	-1.34	1.80
Pure Al	-0.698	-0.659	1.44

3.2 Electrodeposition of aluminum on conversion coated magnesium metal in aluminum chloride/urea IL

In this investigation, the conversion coatings have been tested as corrosion protective layers on pure Mg metal surface and as pre-treatment process for additional aluminum coating layer. The plating process enables a dense and thick aluminum film to be uniformly coated on the magnesium and its alloy using an ionic liquid as an electrolyte, which Aluminum chloride-based ILs have been widely used for the electrodeposition of Al and its alloys. The adhesion strength between the Al coating and the Mg substrate is an important issue. Moreover, it is difficult to realize that Al would be directly electroplated on the Mg metal surface. This might be arise due to the fact that magnesium and its alloys are extremely easy to be oxidized under the existence of oxygen thus a porous oxides film is formed on the surface which would hinder the Al plating. In addition, a replacement reaction would occur between the plating electrolyte and the Mg metal substrate, which its products will harm the Al-plating process [123]. On the other hand, it was reported that a compact intermediate layer deposited on the magnesium alloy surface thought to be beneficial to the electroplating of Al to obtain a highly adhesive electrodeposited Al layer [123]. In such publication, the surface activation and zinc-immersion belong to the traditional surface treatments used for AZ31Mg alloys. In another studies [128], a surface layer of magnesium fluoride (MgF_2), which was formed by immersion the Mg alloy substrate in a bath containing an alkali metal fluoride or hydrofluoric acid in sufficient concentrations represented as a chemical etching preparation for magnesium alloy.

In this work, it was found that the room temperature aluminum chloride/urea ionic liquid would have the ability to electrodeposit of aluminum on previous conversion coated Mg metal substrates, which were acted as initial preparation for Al deposit on pure Mg metal as surface layer to promote plating.

Al metal was successfully electrodeposited in aluminum chloride/urea IL by using a constant voltage of -0.6V at room temperature on conversion coated Mg metal samples, which initially treated with hydrate ammonium alum/urea or hydrate aluminum nitrate/urea ILs.

Aluminum chloride/urea IL was relatively stable towards air, easy to prepare, less water sensitive and easy to handle enabling the electrodeposition process to be successfully conducted on closed atmosphere with no requirement for farther precaution.

In an exemplary embodiment, the plating process including surface pre-treatment of the magnesium metal and a surface post-treatment of the aluminum coated magnesium surface to remove residual traces of ionic liquids.

3.2.1 The treatment process

The pure magnesium metal surface undergoes various treatments to yield a clean surface character suitable for a subsequent electroplating operation and for control of nucleation and adhesion. The pre-treatment process for preparation of Mg metal surface has been discussed in **(section 3.3)**, which was followed by the conversion coating process via immersion in hydrate ammonium alum/urea and hydrate aluminum nitrate/urea ILs.

The exemplary anodic Electrocleaning was used for final cleaning in which the metal surface is actually being dissolved as well as cleaned. The reverse etching process is performed to etch the prior coated Mg metal surface and remove any magnesium oxide (MgO) layers that will inhibit good adhesion of the aluminum metal on the surface of the substrate. As well as to remove any other foreign contaminants including other surface oxide layers and metallic smuts. This process was carried out by applying a positive potential of 1V for 1 min to Mg specimen.

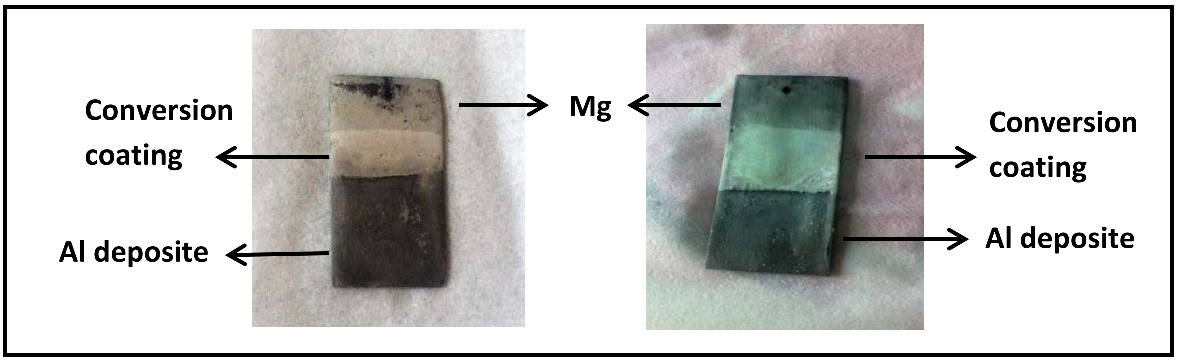
The electrodeposition process have been carried out by applying a constant voltage of -0.6 for 4hr at room temperature in closed atmosphere.

A conversion coated Mg electrode was used as cathode and aluminum mesh as anode, Aluminum chloride/urea ionic liquid with mole ration of 1.2:1 as electrolytic bath.

The final treatment utilized the surface post-treatment process. It was conducted after the electrodeposition process to terminate any remaining surface reactions that might be continued and to stabilize the aluminum coated on Mg metal surface. Finally, a good final coating layer could be obtained. In this investigation, the post-treatment process includes rinsing with dichloromethane then with propanol, which was discussed in **section (3-2)**. These solvents found to dissolve all remainder ionic liquid also acted as stabilizer agents.

3.2.2 Electrodeposition characterizations

Al was successfully deposited on both prior conversion coated Mg samples as shown in **Figure (3-11)**, which were gray compact and rather rough metallic coating.



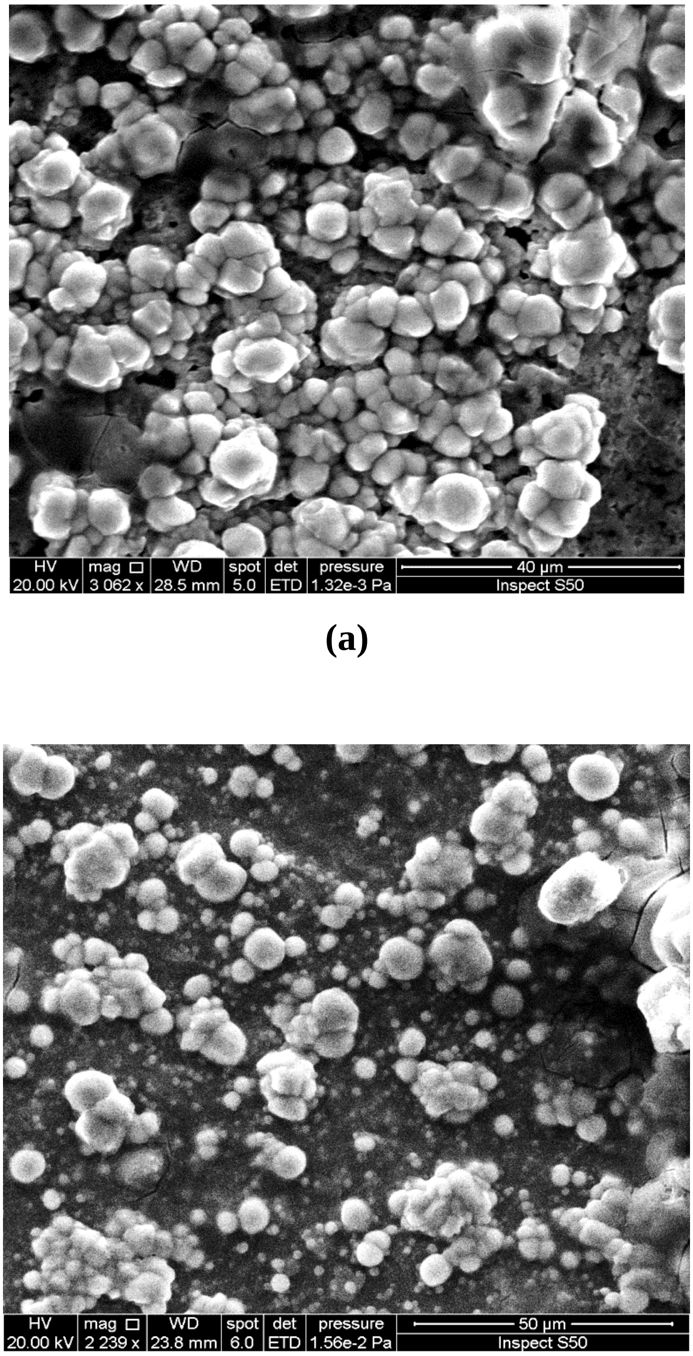
(a) (b)

Figure (3-11): Photographs of Al-deposit on conversion coated Mg samples pre-treated with (a) ammonium alum/urea IL (b) aluminum nitrate/urea IL

The surface morphologies of both electrodeposited magnesium metal samples have been examined by Scanning Electron Microscope (SEM), as shown in **Figure (3-12)**.

The both deposited layers on Mg samples were rather rough while the Al deposition on Mg substrate treated with hydrate ammonium alum/urea IL **Figure (3-12a)** appeared to be quit dense and has a bulky spherical grains structure and was uniformly covered the entire Mg alloy substrate. Otherwise, the Al deposition was less compact with bulky spherical grain when Mg metal sample was treated with hydrate aluminum nitrate/urea IL **Figure (3-12b)**.

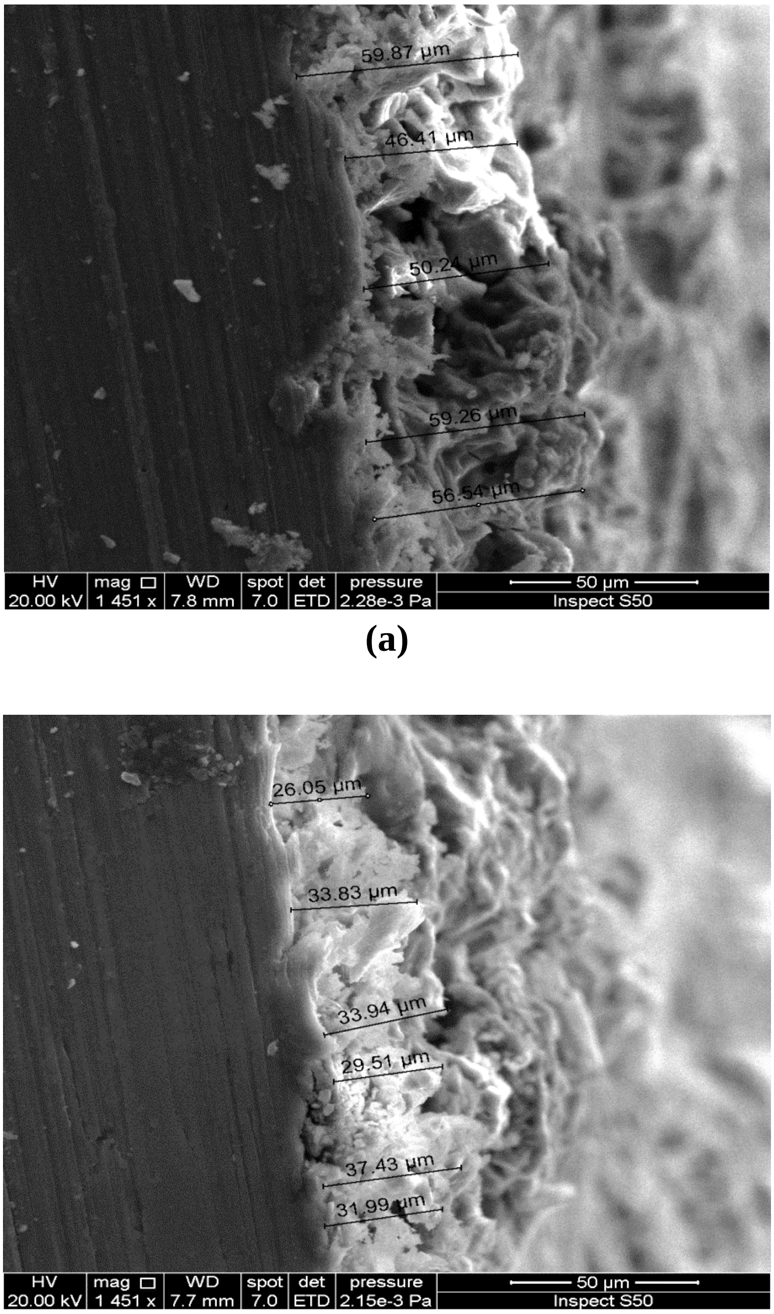
The cross-sectional SEM images of electrodeposited magnesium metal samples **Figure (3-13)** have indicated that a uniform and continuous Al layer was adhered on the magnesium substrate. As observed in this figures **Figure (3-13 a and b)**, the thickness of the deposited layer was approximately between **(30-50) µm**, in which the coating layer formed on Mg metal prior treated with hydrate ammonium alum/urea IL, have the highest value. Additionally, the results showed that both coating layers were incorporated to the previous conversion coating presented on Mg metal surface and have a peel like structure.



(a)

(b)

Figure (3-12): SEM images of Al-deposit on conversion coated Mg samples pre-treated with (a) ammonium alum/urea IL, (b) aluminum nitrate/urea IL



(a)

(b)

Figure (3-13): Cross-sectional SEM images of Al-deposit on conversion coated Mg samples pre-treated with (a) ammonium alum/urea IL, (b) aluminum nitrate/urea IL

The chemical compositions of both deposition layers were inspected with EDXA and the results revealed an identical spectrum shown in **Figure (3-14)** and **Figure (3-15)**. The analytical data revealed that the deposited layer obtained on Mg metal sample pre-treated with hydrate ammonium alum/urea IL was composted of pure Al in a high percentage with no other element could be recognized **Figure (3-14)**. Furthermore, no residual salts were detected on the sample surface **Table (3-6)**. Whilst, a small percentage of O, C elements and (Mg and Al oxide) in addition to Al metal were appeared on the Mg metal sample treated with hydrate aluminum nitrate/urea IL deposition layer, **Figure (3-15)** and the weight percentage of all elements and compounds were tabulated in **Table (3-7)**. In addition, the results of EDXA have indicated that the coating layer formed on Mg metal surface by the treatment with hydrate aluminum nitrate/urea IL was composted of MgO and Al_2O_3 mixed oxides as exhibited in **Table (3-7)**. It was thought that this small fraction of O and C and the oxide compounds were detected are related to the conversion coating layer which previously formed on the Mg metal surface. This is an indication to the non-continuous and non-compacting coating deposit on the Mg substrate treated with hydrate aluminum nitrate/urea IL.

These results are consistence with the results indicated from the X-ray diffraction analysis. It was exhibited that in the first deposited layers of Al metal was the only element observed on the Mg metal surface as shown in **Figure (3-16a)**. In which the second deposition layer was $(MgAl)(AlMg)O_4$ complex as well as the Al metal, **Figure (3-16b)**.

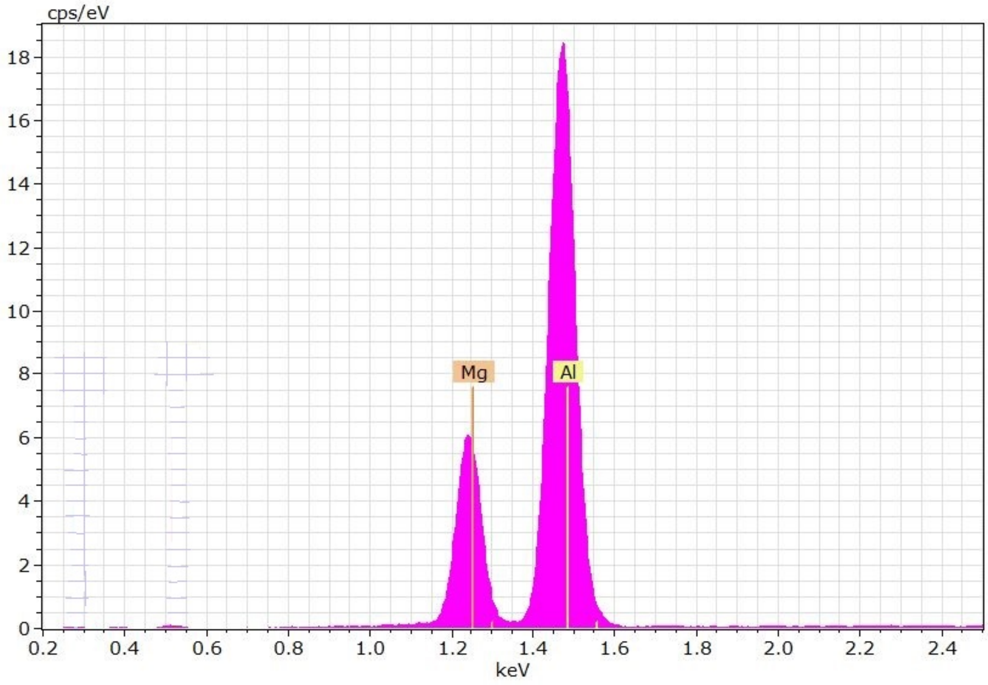
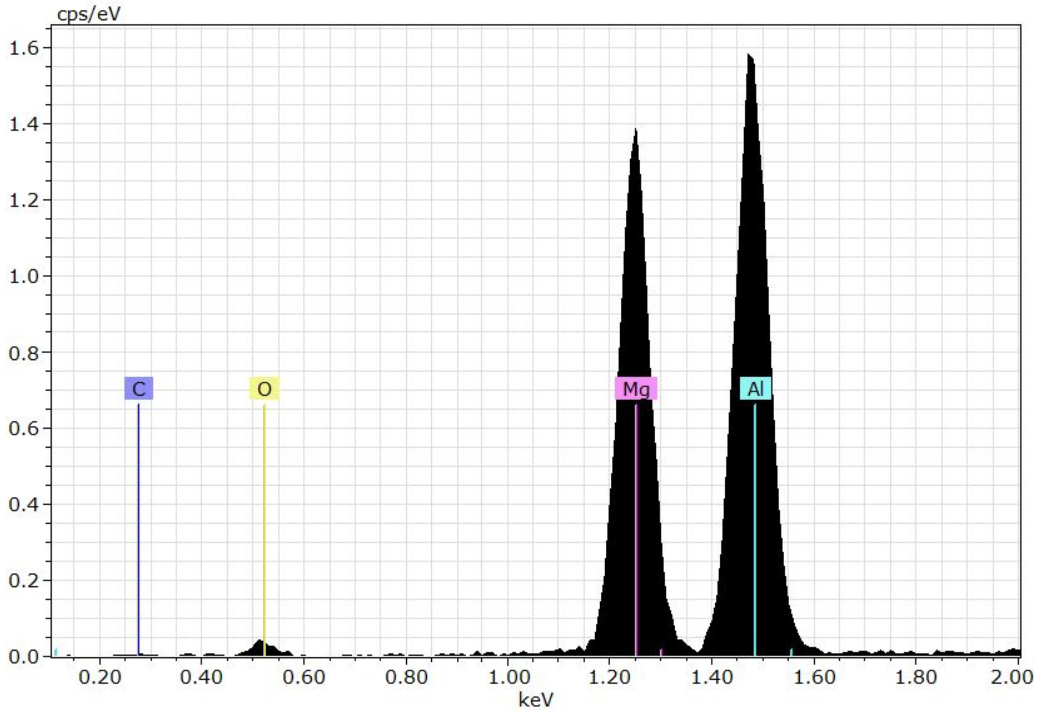


Figure (3-14): EDXA spectrum of Al-deposit on conversion coated Mg sample pre-treated with ammonium alum/urea IL

Table (3-6): wt. % of elements consist the deposition layer on conversion coated Mg sample pre-treated with ammonium alum/urea IL

Element	[wt.%]	[norm. wt.%]	[norm. at.%]
Aluminum	120.0059	70.8623	71.345
Magnesium	53.3112	30.6674	27.1174



(b)

Figure (3-15): EDXA spectrum of Al-deposit on conversion coated Mg sample pre-treated with aluminum nitrate/urea IL

Table (3-7): wt. % of elements and suggested compounds consist the deposition layer on conversion coated Mg sample pre-treated with aluminum nitrate/urea IL

Element	[wt.%]	[norm. wt.%]	[norm. at.%]	Compound	[wt.%]	[norm. wt.%]
Aluminum	51.8355	30.5983	23.0101	Al_2O_3	97.9413	57.8144
Magnesium	43.0960	25.4394	21.2373	MgO	71.4651	42.1856
Oxygen	74.4749	43.9622	55.7525		-4E-09	-2.3E-09

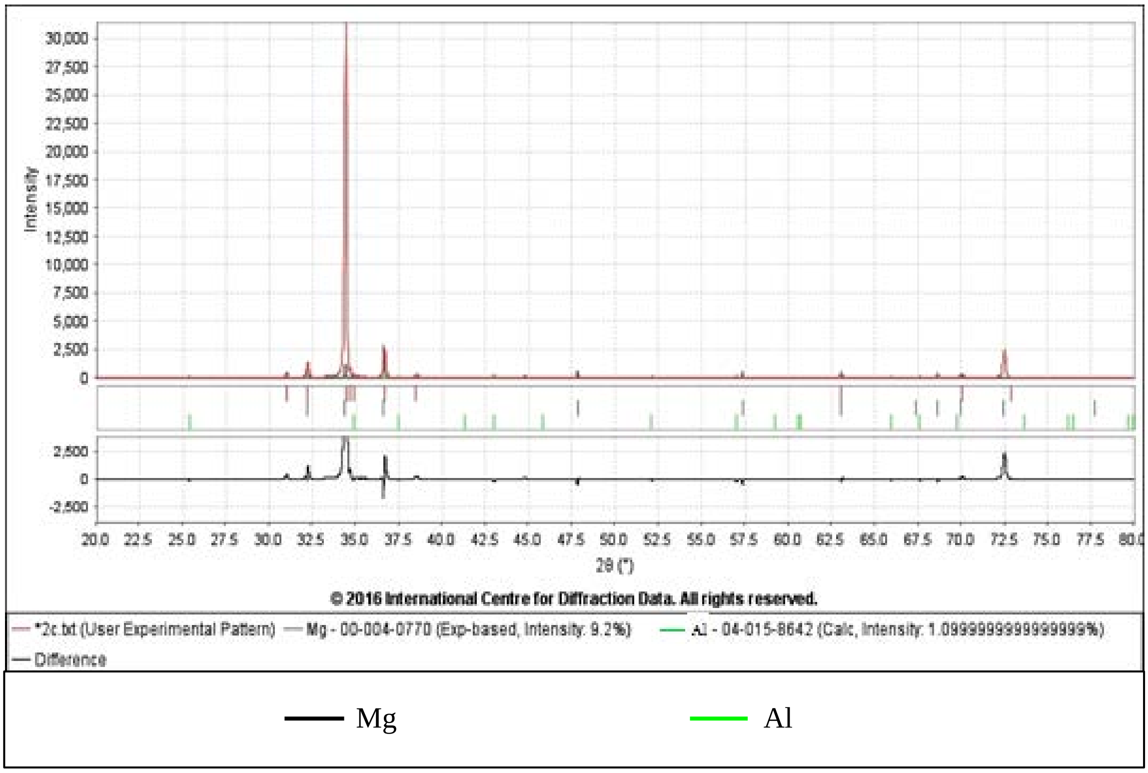


Figure (3-16a): XRD spectra of Al-deposit on conversion coated Mg samples pre-treated with ammonium alum/urea IL

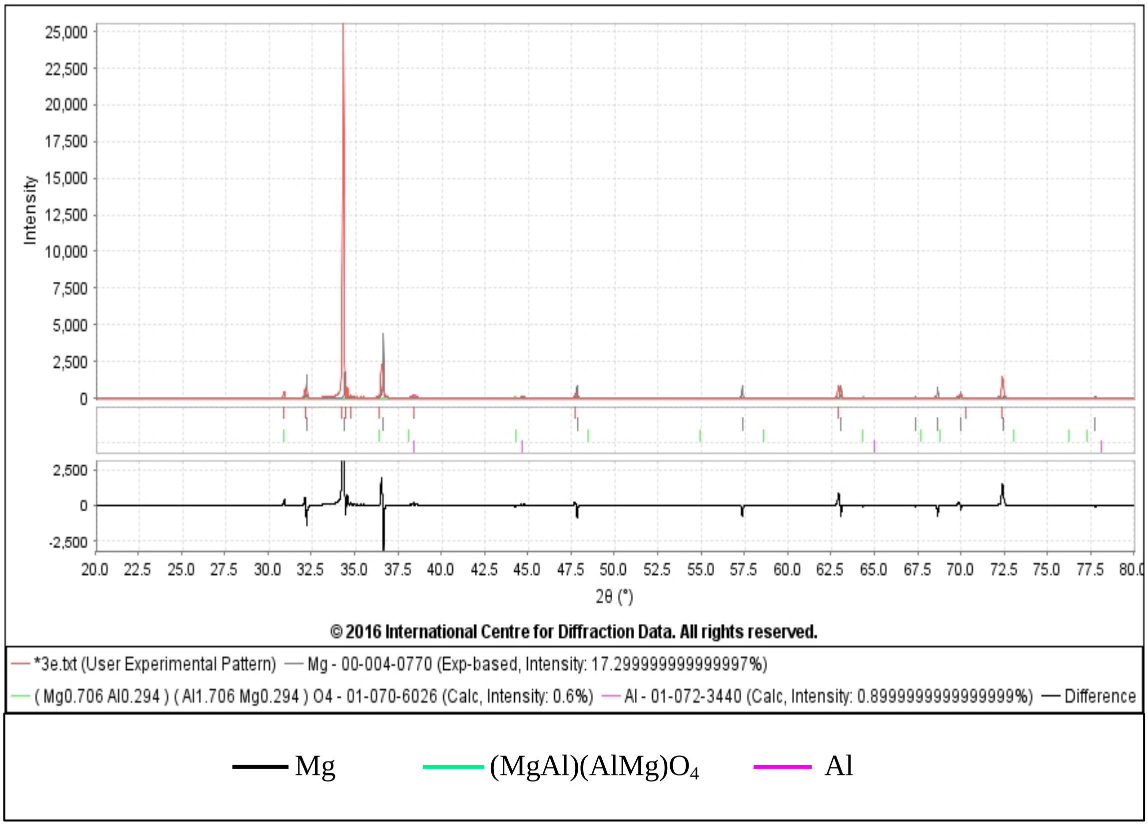


Figure (3-16b): XRD spectra of Al-deposit on conversion coated Mg samples pre-treated with aluminum nitrate/urea IL

3.2.3 Corrosion test

A comparative study was performance to indicate the effect of Al deposit layers obtained on both pre-conversion coated samples with the corrosion behavior of pure Mg metal. The equipment and the conditions of the corrosion test have been discussed in **section 3.1.3**.

The corrosion behavior of the uncoated and Al-coated Mg metal in 3.5 wt% NaCl aqueous solution have been evaluated by galvanostatic polarization experiments. The corrosion resistance characteristic was detected by polarization curves shown in **Figure (3-17)**. The Open circuits potential, corrosion potential (E_{corr}) and corrosion current density (i_{corr}) of the conversion coatings obtained from these curves are tabulated in **Table (3-8)**.

As shown in **Table (3-8)**, the polarization data were clearly shifted toward the noble tend due to the protective Al layer which was successfully obtained on the Mg metal surface and indicates that the Al coating led to an improvement in its corrosion resistance. Otherwise, the deposited sample, which was prior treated with aluminum nitrate/urea IL showed poorer corrosion resistance. This lower protective performance was thought to be due to its loose and sporadic structure, as appeared in SEM examination previously shown in **Figure (3-12b)**. The anodic passivation behavior was found in the Al deposited sample pre-treated with ammonium alum/urea IL **(curve b)**, in which the polarization curve was characterized by a passive region that have followed by a passivation breakdown. Furthermore, the formation of an alumina (Al_2O_3) protective layer on the surface of the deposited Al contributed to the passivity phenomenon [81].

However, the Al- deposited on both pre-conversion coated Pure Mg metal showed poor corrosion resistance comparing with the results observed from conversion coatings on pure Mg alone, **section 3.1.3 Table (3-5)**. The high porosity of the both coated layers thought to decrease the corrosion resistance of the treated specimens as seen in **Figures (3-12) and (3-13)**.

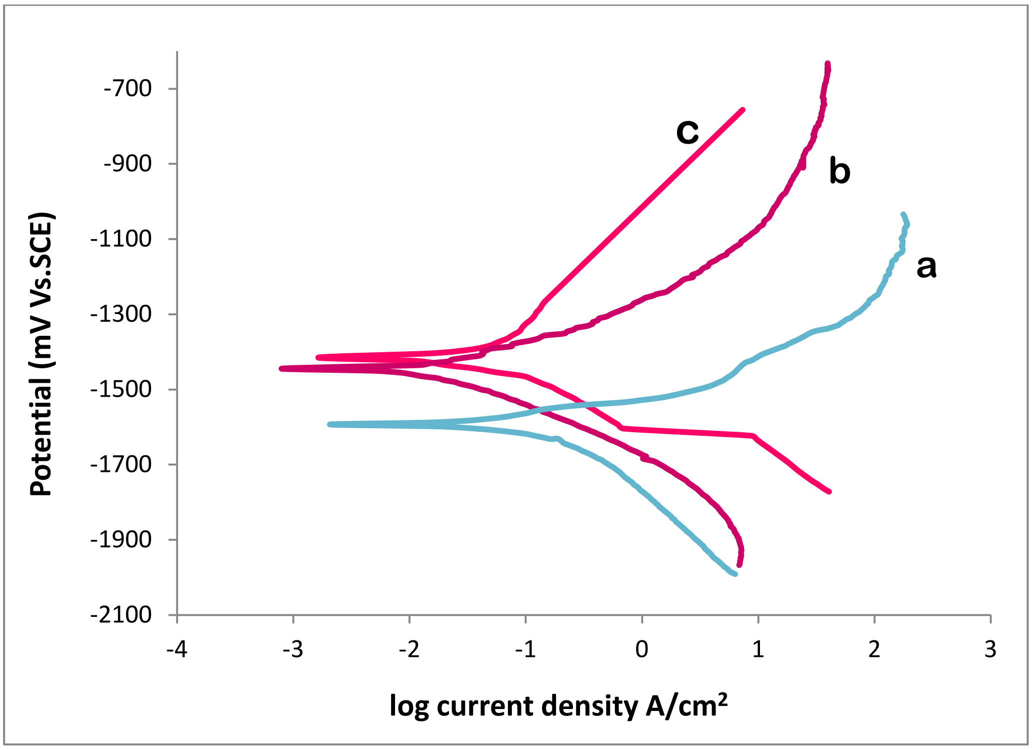


Figure (3-17): Polarization curves in 3.5% NaCl of (a) bare Mg (b) Al-deposit on conversion coated Mg samples pre-treated with ammonium alum/urea IL, (c) Al-deposit on conversion coated Mg samples pre-treated with aluminum nitrate/urea IL

Table 3-8: Polarization data of Al-deposit on the conversion coated Mg metal samples in 3.5% NaCl solution

Samples	OCP, V	Ecorr, V (SCE)	Icorr, μA/cm^2
Bare Mg	-1.66	-1.59	44.51
Al-deposit on pre-treated with $NH_4Al(SO_4)_2.12H_2O$/urea IL	-1.51	-1.41	5.62
Al-deposit on pre-treated with $Al(NO_3)_3.9H_2O$/urea IL	-1.53	-1.44	7.21
Pure Al	-0.698	-0.659	1.44

3.3 Electrodeposition of aluminum on uncoated magnesium metal in aluminum chloride/urea IL

Electrodeposition of Al on bare magnesium metal in aluminum chloride/urea ionic liquid has been revealed. It was found that Al metal was successfully deposited on pure Mg metal without any further intermediate layer.

A silver-gray and rather smooth adhesive layer **Figure (3-18)** was yield by applying a constant current of -0.6V for 4h. Aluminum chloride/urea IL utilized as electrolytic bath where the cathode of bare Mg metal and the anode of Al mesh have been immersed.

The pure magnesium metal surface was previously prepared for electrodeposition process and after Al-deposition has accomplished the post-treatment process was performed as mentioned in practical part. These treatments were required to obtain a clean smooth Al-coating on the surface of pure Mg metal as had discussed in **section 3.2.1**.

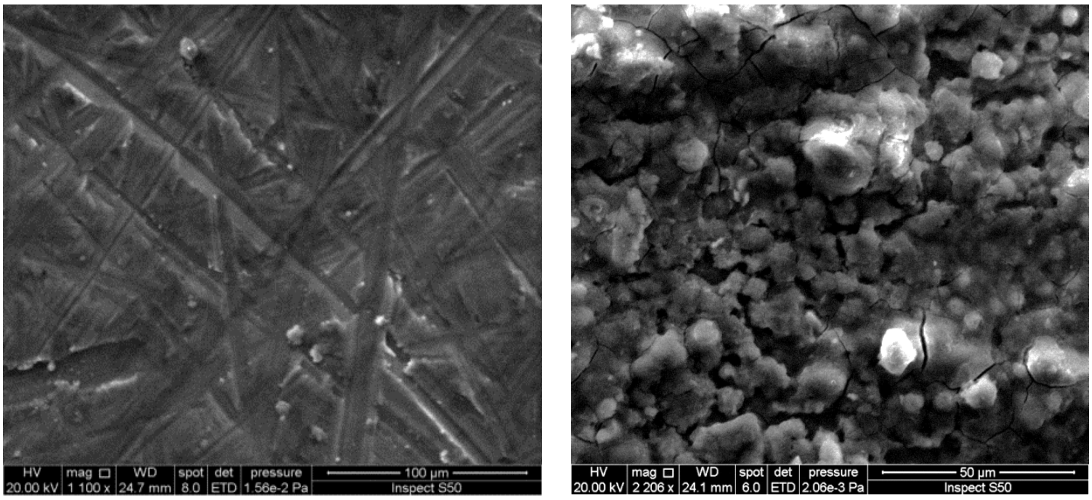
Figure (3-18): Photograph of Al-deposit on pure Mg sample in aluminum chloride/urea IL

3.3.1 Electrodeposition characterizations

The surface morphologies of the uncoated and Al-coated pure Mg metal were examined by SEM, which exhibited in **Figure (3-19 a, and b).** As displayed in these SEM images, The Al-deposition has a bulk grain structure with nodulous-like form with many fine pores and several small cracks could be found within the deposit whose structure. **Figure (3-20)** shows a typical cross-sectional SEM micrograph of the Al-coated Mg metal surface. A uniform and continuous Al layer adhered on the substrate and a good deposition quality. Additionally, as observed in this figure, the thickness of the deposited layer was approximately 40µm.

The chemical composition of the deposition layer formed on pure magnesium surface was examined by EDXA. **Figure (3-21)** shown the EDXA spectra, in which observed that the deposited layer was only of Al metal. While the XRD result exhibited an Al oxide in addition to Al metal are presented as shown in **Figure (3-22)**.

From these results, it was indicated that Al metal has successfully deposited on pure Mg metal surface with fine reasonable coating.



(a) **(b)**

Figure (3-19): SEM images of (a) bare Mg metal (b) Al deposited on pure Mg metal

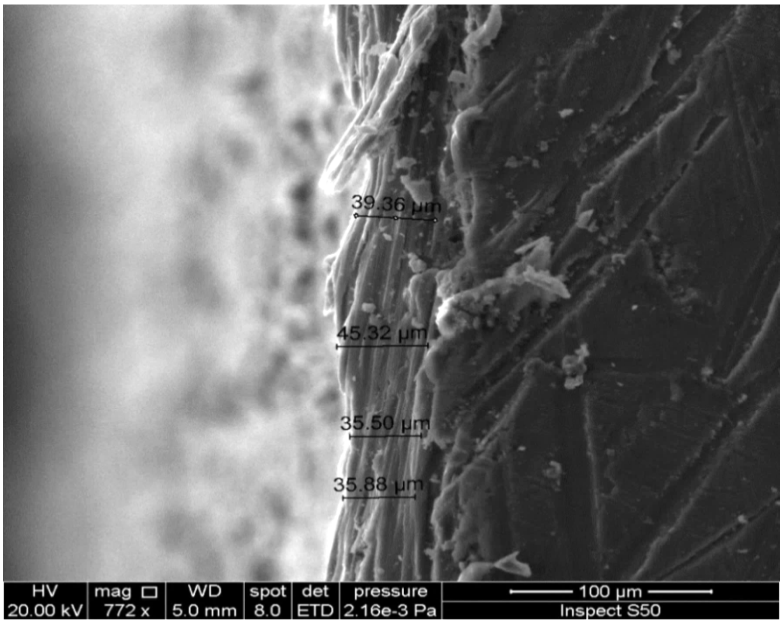


Figure (3-20): Cross-sectional SEM image of Al-deposit on pure Mg metal

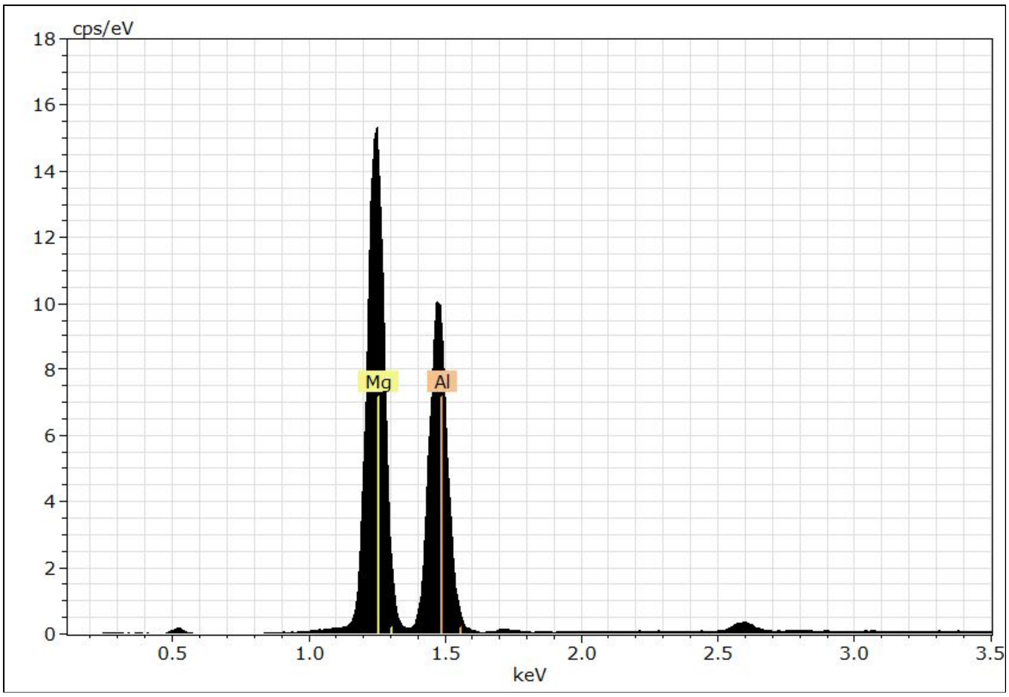


Figure (3-21): EDXA spectra of Al-deposit on pure Mg metal

Table (3-9): wt. % of elements consist the deposition layer

Element	[wt.%]	[norm. wt.%]	[norm. at.%]
Aluminum	46.0559	57.11749	52.8255
Magnesium	34.5775	42.8822	47.1743

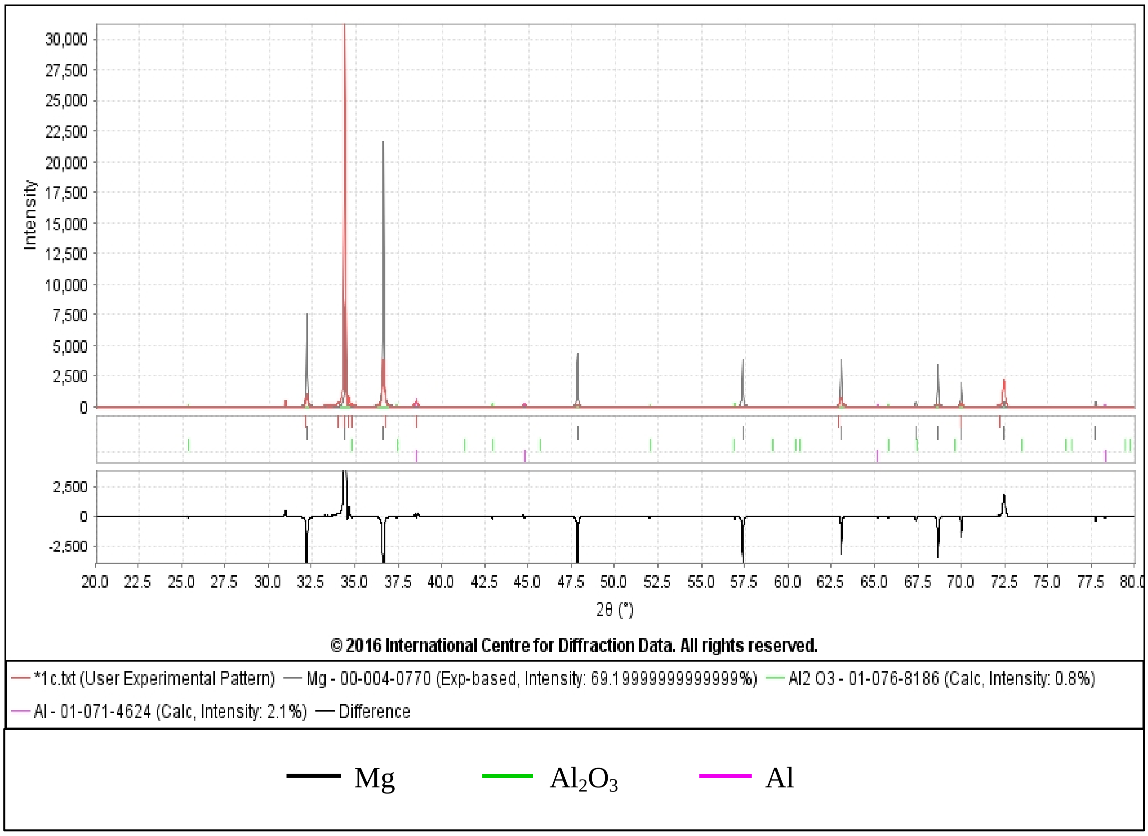


Figure (3-22): XRD spectrum of Al-deposit on pure Mg metal

3.3.2 Corrosion test

The uncoated and Al coated on Mg metal samples were measured in a 3.5% NaCl aqueous solution by potentiodynamic polarization curves as exhibited in **Figure (3-23)**. The data in **Table (3-10)** clearly seen that the electrodeposition of Al could significantly improve the corrosion-resistance of pure Mg metal by reducing the corrosion current as well as altering the corrosion potential to less negative values.

On the other hand, matching these results with results observed in **section 3.2.3** would disclosed that the electrodeposited Al layers can effectively prevent both pre-coated and uncoated Mg metal substrates from rapid corrosion, as demonstrated in **Figure (3-24)**. However, it was indicated that the polarization curve observed from the deposition of Al metal on bare magnesium metal could more effectively protect the Mg substrate **(curve d)**. The Open circuits potential, corrosion potential (Ecorr) and corrosion current density (i_{corr}) of Al-deposited on bare and pre-coated Mg metal samples obtained from these curves are tabulated in **Table (3-11)**.

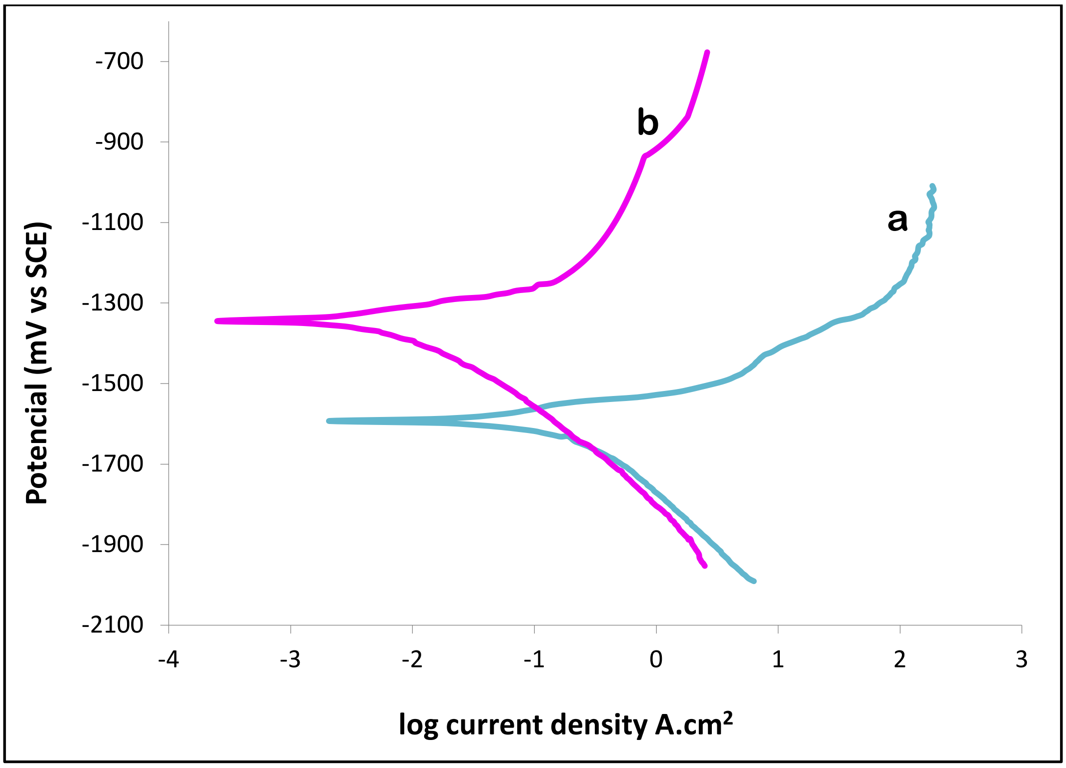


Figure (3-23): Polarization curve in 3.5% NaCl solution of (a) bare Mg (b) Al deposited on pure Mg metal

Table 3-10: Polarization data of Al deposited on pure Mg metal in 3.5% NaCl solution

Samples	OCP, V	Ecorr, V (SCE)	Icorr, μA/cm^2
Bare Mg	-1.66	-1.59	44.51
Al deposit on pure Mg metal	-1.48	-1.35	2.41

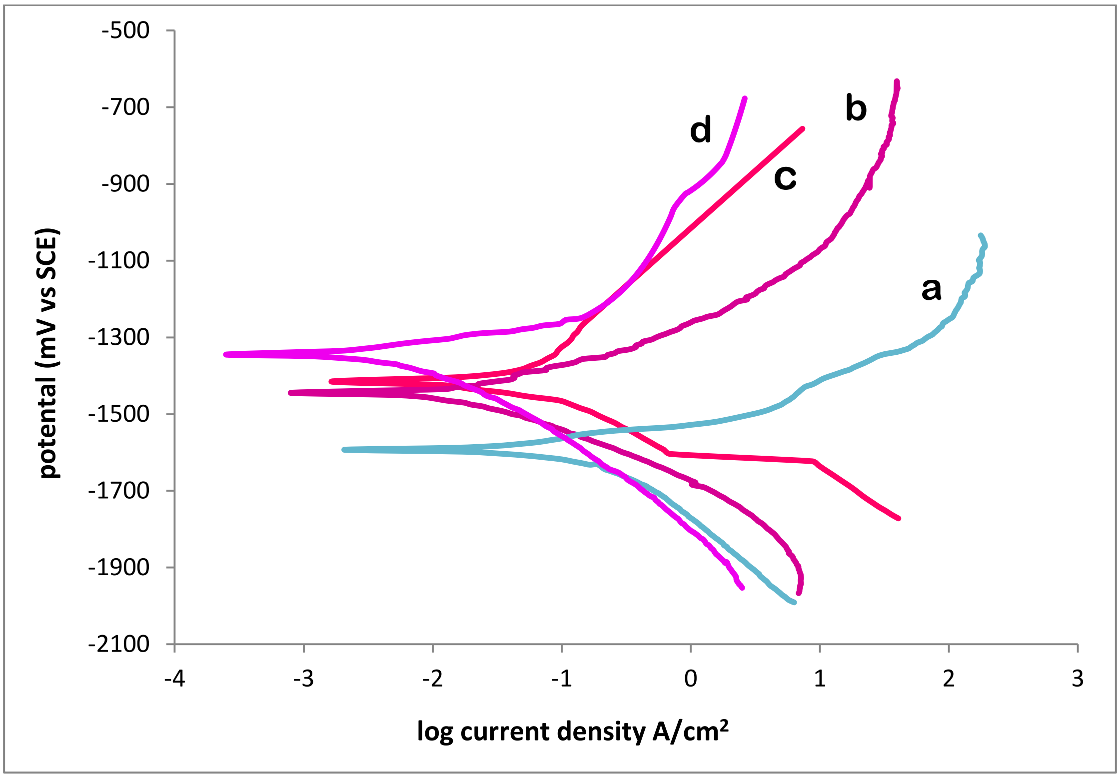


Figure (3-24): Polarization curve in 3.5% NaCl solution of (a) bare Mg (b) Al-deposit on conversion coated Mg samples pre-treated with ammonium alum/urea IL, (c) Al-deposit on conversion coated Mg samples pre-treated with aluminum nitrate/urea IL (d) Al deposited on pure Mg metal

Table 3-11: Polarization data of Al deposited on bare and pre-coated Mg metal in 3.5% NaCl solution

Samples	OCP, V	Ecorr, V (SCE)	Icorr, $\mu A/cm^2$
Bare Mg	-1.66	-1.59	44.51
Al deposit on pre-treated with NH4Al(SO4)2.12H2O/Urea IL	-1.51	-1.41	5.62
Al deposit on pre-treated with Al(NO3)3.9H2O/Urea IL	-1.53	-1.44	7.21
Al deposit on pure Mg metal	-1.48	-1.35	2.41
Pure Al	-0.698	-0.659	1.44

3.4 Conclusion:

1. Conversion coatings of pure magnesium metal were successfully obtained by the treatment with hydrate ammonium alum/urea, hydrate aluminum nitrate/urea and aluminum chloride/urea room temperature ionic liquids.
2. The completion of adhesive conversion coatings were achieved at room temperature with short time of 40 min.
3. The three conversion coatings were consisted of metals oxides of Mg and Al.
4. The conversion coating layers gave a good appearance of Mg metal and showed a good corrosion resistance.
5. Aluminum metal was successfully deposited on uncoated and on prior conversion coated magnesium metal in $AlCl_3$/urea ionic liquid.
6. Al-deposit layer on previous conversion coated Mg metal specimens showed poor corrosion resistant due to the high porosity appeared on both coated specimens.
7. Al-deposit layer showed a good corrosion protection for bare Mg metal without any further intermediate layer.

3.5 Future work:

1. Investigating reactivity of magnesium alloys in the ionic liquids of presented work.
2. Investigate the effect of temperature on the reactions of conversion coating or electrodeposition of aluminum metal.
3. Use different current densities for electroplating of aluminum on magnesium metal.

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اظهرت النتائج ان طبقات الطلاء التحولي الثلاثة التي تم الحصول عليها باستخدام ثلاثة سوائل ايونية مختلفة كانت موحدة ومتجانسة وغطت سطح معدن المغنيسيوم بأكمله وكذلك كانت الجسيمات وخشونة الطبقات ومتوسط الارتفاعات نانوية. وكذلك كانت الطبقات عالية الالتصاق مع سطح المعدن في حين أن متوسط السمك حوالي (٢-٥) مايكرومتر. أظهرت نتائج (EDXA) و(XRD) أن أوكسيد الألومنيوم وأكاسيد المعدنين المغنيسيوم والالمنيوم المختلطة ($MgAl_xO_x$) من المكونات الاساسية لطبقات الطلاء التحولي التي تم تشكيلها على سطح معدن المغنيسيوم. اما طبقات معدن الالمنيوم التي تم ترسيبها على سطح معدن المغنيسيوم الغير مطلي والمطلي سابقا بطبقات الطلاء التحولي المختلفة كانت ذات لون رمادي بسمك حوالي (٣٠-٥٠) مايكرومتر.

اظهرت نتائج دراسة التاكل ان مقاومة معدن المغنيسيوم قد تم تحسينها بعد انجاز نوعي الطلاء التحولي والترسيب الكهربائي للالمنيوم على سطح المعدن وذلك بتغيير جهد التاكل وتيار التاكل لمعدن المغنيسيوم النقي الى قيم اكثر ايجابية.

الخلاصة:

معدن المغنيسيوم عنصر فعال جداً ضعيف المقاومه للتاكل مما يحد كثيرا من استخداماته في الصناعة. واحدة من الطرق المهمة لحماية معدن المغنيسيوم وسبائكه من التاكل هي بعزل المعدن عن المحيط الخارجي باستخدام الطلاء الكيميائي لسطح المعدن. هناك عدة تقنيات للطلاء المستخدم تتضمن (الطلاء الكيميائي-الكهربائي ، الطلاء التحولي، الانودة، الطلاء المولد و عملية الطور البخاري).

في هذا العمل امكن تطبيق الطلاء التحولي والكهربائي على سطح معدن المغنيسيوم النقي باستخدام ثلاثة انواع من السوائل الايونية. تم استخدام ثلاثة سوائل ايونية هي: شب الامونيوم/اليوريا و نترات الالمنيوم/يوريا وكلوريد الالمنيوم/يوريا للحصول على طلاء تحولي وقائي على سطح معدن المغنيسيوم وذلك بواسطة غمر المعدن في هذه السوائل لمدة ٤٠ دقيقة في درجة حرارة الغرفة .

وتم ايضاً ترسيب معدن الالمنيوم على سطح معدن المغنيسيوم المطلي مسبقا والغير مطلي باستخدام طريقة الترسيب الكهربائي في السائل الايوني (كلوريد الالمنيوم/يوريا).

تم استخدام الطلاء التحولي في هذا العمل كطلاء وقائي وكذلك كطبقة اولية لترسيب معدن الالمنيوم.

تم التحقق من مظهر سطح معدن المغنيسيوم بعد انجاز عمليتي الطلاء (التحولي والكهربائي) بأستخدام المجهر الالكتروني (SEM) ومجهر القوه الذرية (AFM) اما التركيب الكيميائي لنوعي الطلاء فقد تم باستخدام تحليل طاقة الاشعة السينية المشتتة (EDAX) و حيود الاشعة السنية (XRD).

تم اختبار سلوك التاكل لمعدن المغنيسيوم بعد تطبيق الطلاء باستخدام جهاز الاستقطاب الكلفاني-الستاتيكي في المحلول المائي لملح كلوريد الصوديوم بتركيز 3.5% .

جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة النهرين
كلية العلوم
قسم الكيمياء

الطلاء المعدني الوقائي لمعدن المغنيسيوم باستخدام السوائل الايونية

رسالة

مقدمة إلى كلية العلوم /جامعة النهرين
كجزء من متطلبات نيل درجة الماجستير في علوم الكيمياء

من قِبَل
رشا حسين علوان
بكالوريوس ٢٠٠٧/ كلية العلوم / جامعة بغداد

إشراف
الاستاذ الدكتور
هادي محمد علي عبود

جمادى الثاني- ١٤٣٨ اذار - ٢٠١٧