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Morphology Study of Aluminium Deposition from Room Temperature Ionic Liquids (RTIL)

A Thesis

Submitted to the College of Science/Al-Nahrain University as a partial fulfillment of the requirements for the Degree of Master of Science in Chemistry

By:

Noor Laith Dawood

B.Sc. Chemistry / College Science / Al-Nahrain University

Supervised by:

Dr. Hadi M. A. Abood

(Assist. Prof.)

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بسم الله الرحمن الرحيم

۞ اقْرَأْ بِاسْمِ رَبِّكَ الَّذِي خَلَقَ ﴿١﴾ خَلَقَ
الْإِنْسَانَ مِنْ عَلَقٍ ﴿٢﴾ اقْرَأْ وَرَبُّكَ الْأَكْرَمُ
﴿٣﴾ الَّذِي عَلَّمَ بِالْقَلَمِ ﴿٤﴾ عَلَّمَ الْإِنْسَانَ
مَا لَمْ يَعْلَمْ ﴿٥﴾ ۞

صدق الله العظيم

سوره العلق

من الآية ١–٥

الإهداء

بسم الله الرحمن الرحيم
(قل 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..
إلى من بلغ الرسالة وأدى الأمانة .. ونصح الأمة .. إلى نبي الرحمة ونور العالمين
سيدنا محمد صلى الله عليه واله وصحبه وسلم

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

إلى من كلله الله بالهيبة والوقار .. إلى من علمني العطاء بدون انتظار .. إلى من أحمل أسمه بكل افتخار .. أرجو من الله أن يمد في عمرك لترى ثماراً قد حان قطافها بعد طول انتظار
وستبقى كلماتك نجوم أهتدي بها اليوم وفي الغد وإلى الأبد
(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)

بكل الحب
إلى عزي وسندي في الدنيا... إلى رفيق دربي ونور حياتي... إلى من سار معي نحو الحلم..
خطوة بخطوة.. بذرناه معاً.. وحصدناه معاً.. وسنبقى معاً بإذن الله ..جزاك الله خيراً وحفظك الله لنا
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Noor Laith Dawood

2016

Supervisor Certification

I certify that this thesis entitled " Morphology Study of Aluminium Deposition from Room Temperature Ionic Liquids (RTIL)" was prepared by "Noor Laith Dawood" under my supervision at the College of Science/Al-Nahrain University as partial fulfillment of the requirements for the Degree of Master of Science in Chemistry.

Signature:
Name: **Dr. Hadi Mohammed Ali Abood**
Scientific Degree: **Assistant Professor**
Date: \ \ 2016

In view of the available recommendation, I forward this **thesis** for debate by the examining committee.

Signature:
Name: **Dr. Nasreen Raheem Jber**
Scientific Degree: **Assistant Professor**
Title: **Head of Chemistry Department**
Date: \ \ 2016

Committee Certification

We, the examining committee certify that we read this **thesis** entitled "**Morphology Study of Aluminium Deposition from Room Temperature Ionic Liquids (RTIL)**" and examined the student " **Noor Laith Dawood**" in its contents and that in our opinion, it is accepted for the Degree of Master of Science in Chemistry.

Signature:
Name: **Falaha H. Musa**
Scientific Degree: Professor
Date: / /2016
(Chairman)

Signature:
Name: **Rashed T. Rasheed**
Scientific Degree: Assistant Professor
Date: \ \ 2016
(Member)

Signature:
Name: **Taghried A. Salman**
Scientific Degree: Assistant Professor
Date: \ \ 2016
(Member)

Signature:
Name: **Hadi M. A. Abood**
Scientific Degree: Assist. Prof. Dr.
Date: / /2016
(Member/**Supervised)**

I, hereby certify upon the decision of the examining committee.

Signature:

Name: **Dr. Hadi M. A. Abood**

Scientific Degree: Assistant Professor

Title: Dean of the College of Science

Date: / / 2016

Summary

Aluminium metal processing is only feasible at high temperature like extraction by electrochemical process from its ores at high temperature. Such process are not feasible in aqueous liquids due to production of hydrogen (-0.8V) much prior to aluminium electroreduction (-1.65V). Other solvents such as organic and ionic liquids have their setbacks for many practical, economic and environmental reasons.

Protective coating of metals by aluminium thin layer is an important for preventing substrate metals from corrosion or for decorative purposes.

Electrodeposition of aluminium on copper substrate from aluminium chloride / urea ionic liquid ($AlCl_3$:Urea) as electrolyte was successfully conducted at variable conditions. Protected by a layer of Decane on the top of the liquid under statistic air. The deposit microstructure was monitored by changing temperature, mole ratio, potential and deposition time. The surface morphology of deposited aluminium was investigated by visual microscope, Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and Energy Dispersive X-ray analysis (EDAX).

The effect of changing parameters on the morphology and microstructure of deposited aluminium was systematically studied. Results showed that by increasing temperature, the current density was increased linearly as a function of temperature and the visual appearance of deposited aluminium was changed with increasing temperature from silvery white at 20 ^{0}C to darker gray at 60 ^{0}C.

The deposit microstructure was changed with increasing temperature and the percentage of deposited aluminium increased with increasing

temperature (20 to 50) ^{0}C from 55 At. % to 91 At. %, while at 60 ^{0}C the percentage of deposited aluminium dropped from 91 At.% at 50 ^{0}C to 82 At. % at 60 ^{0}C.

Mole ratio of ionic liquid was also found to effect the deposit microstructure and the percentage of deposited aluminium which increased with increasing concentration of $AlCl_3$ in electrolyte. In the same manner, current density was increased with increasing mole ratio.

Increasing deposition time with fixed potential and mole ratio of ionic liquid have only increasing the percentage of deposited aluminium.

Using different electrodeposition potential at same mole ratio of ionic liquid resulted in changing the morphology and deposited microstructure aluminium coatings with an increase in current density with increasing cell potential.

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Abbreviations

Abbreviations	Name
ILs	Ionic Liquids
RTILs	Room temperature ionic liquids
$AlCl_3$	Aluminium chloride
$[BMIM]PF_6$	1-butyl-3-methylimidazolium hexafluorophosphate
$[BMIM]BF_4$	1-butyl-3-methylimidazolium tetraflouroborate
[EMIM]Cl	1-Ethyl-3-methylimidazolium chloride
$[EtNH_3][NO_3]$	Ethyl ammonium nitrate
AFM	Atomic force microscopy
EDAX	Energy dispersive X-ray analysis
SEM	Scanning electron microscopy
BF_4^-	Tetraflouroborate anion
PF_6^-	Hexaflourophosphate anion

RSO_3H	**Sulfonic acid**
$C_5H_{14}ClNO$	**Choline Chloride**
$[R_4N][OH]$	**Tetraalkyl ammonium hydroxide**
Tf_2N	**bis(trifluoromethylsulfonyl)imide**

Notations

Symbols	Name	Units
Cp	**Centipoise**	**10^{-3} Pa.s**
Ra	**Roughness**	**nm**
At. %	**Atom percent**	

Chapter 1

Introduction
and
Literatures
Review

Chapter One

Introduction

1.1 General Definition of Ionic liquids

Ionic liquids are mixtures of organic and inorganic salts that have a melting points below 100 ^{0}C. These liquids have large non-symmetric cations substituted with different bulky groups to weaken this ionic interactions, so it prevents packing of the cations/anions in to crystal lattice and (low lattice energy) and hence low melting points, Figure (1-1). Some ionic liquids are liquids at room temperature called (Room Temperature Ionic Liquids), while others are liquids below room temperature called (deep eutectic solvent)[1]. They have many fascinating properties which make them of fundamental interest to all chemists, due to both thermodynamics and kinetics of reactions carried out in ionic liquids which are different to those in conventional solvents. Thus the chemistry is different and unpredictable at the current state of knowledge[2].

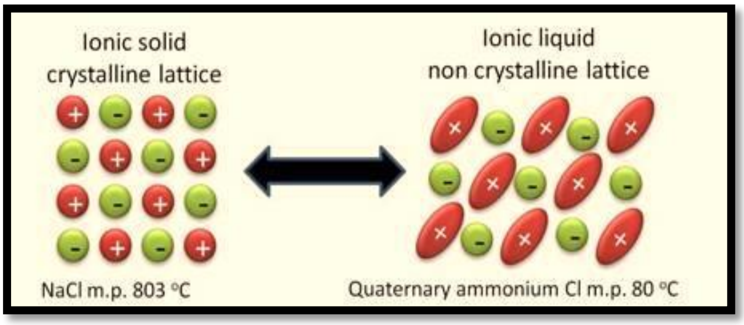


Figure (1-1): The non-crystalline lattice of ionic liquid and the crystalline lattice of ionic solid.

Ionic liquids are interesting for chemist because they are good solvents for both organic and inorganic compounds and can also be made to be immiscible with many organic solvents[1].

Traditional organic solvents like diethyl ether, toluene or methanol are linked to their application as their boiling point, but ionic liquids do not experience this issue. Their vapor pressure is negligible under most reaction conditions utilized[3,4].

As ionic liquids made up of at least two components which can be varied (anion and cation), the solvents can be designed as needed [2]. Besides, their potential as green solvents due to absence of volatility they pulled a lot of interest as they have been successfully employed in various technical processes[5]. Yet apparently the most outstanding quality after all is their modularity to which they owe their name 'designer solvent'. The nature of the anion and the cation determine the chemical and physical properties of the ionic liquid. As a result of the existing dependence of properties on the nature of the constituent ions, it is possible to achieve specific properties by choosing the right combination of cation and anion. Using this tailoring process, functional groups can be added to the structure to provide a better performance of the RTIL when chemical reaction or specific affinity and selectivity are required [6].

The discovery date of the "first" ionic liquid is disputed. Ethanol ammonium nitrate (m.p. 52-55 ^{0}C) was accounted for in 1888 by Gabriel and Weiner [7], while the early history of room temperature ionic liquid began in 1914 when the first room temperature ionic liquid was studied by Walden[8]. He reported the physical properties of ethyl ammonium nitrate, which has a melting point of 12^{0}C and formed by the reaction of ethylamine with concentrated nitric acid.

About two decades later in 1934[9] before the next ionic liquid was presented to the public in a patent in which it was claimed that certain organic salts have the ability to dissolve cellulose and alter its reactivity. later, in 1951[10] this ionic liquid was followed by chloroaluminate base ionic liquids, but interest did not develop until the discovery of binary ionic liquids were made from mixtures of aluminum(III) chloride and N-alkylpyridinium chloride[11] or 1,3-dialkylimidazolium chloride[12]. Alkylpyridinium (RPy+) chloroaluminate based ionic liquids were first reported in the early 1950 [13].

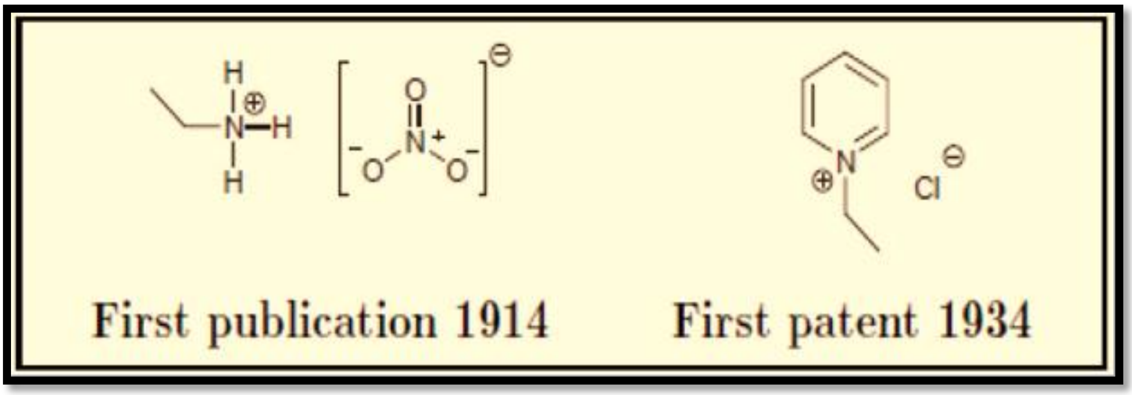


Figure (1-2): First reported ionic liquids. [9]

In 1975 the Osteryoung [11] group and Gilbert co-workers [14] reported the physical properties of pyridinium-based chloroaluminate ionic liquid, an ionic liquid that hoped to be applicable in batteries, especially by the United States air force. This hope had to be relinquished due to the easy reducibility of the pyridinium moiety, a real constraint for application in batteries. The chemical behavior of acidic chloroaluminate(III) ionic liquids (where $X(AlCl_3) > 0.50$) is that of a powerful Lewis acid. As may be expected, it promotes reactions that are conventionally promoted by aluminum(III) chloride, without suffering the disadvantage of the low solubility of aluminum(III) chloride in many solvents. It is well known that chloroaluminate (III) ionic liquids are outstandingly powerful solvents.

The stable room temperature ionic liquids (RTILs) 1-n-butyl-3-methylimidazolium tetrafluoroborate $[BMIM]BF_4$, hexafluorophosphate $[BMIM]PF_6$ and their analogues has begun in the middle of the 1990s a renaissance of the rich chemistry of molten salts and continued to prosper. 1,3-Dialkylimidazolium cations associated with relatively weak coordinating anions such as tetrafluoroborate, hexafluorophosphate and trifluoromethane sulfonate which are compounds with unique physical-chemical properties such as they are liquids over a large range of temperatures (down to -80 ^{0}C), possess high thermal and chemical stability, large electrochemical window (up to 7V), high density, relatively low viscosity and negligible vapor pressure **[15]**. Another important property that changes with structure is the miscibility of water in these ionic liquids. For example, 1-alkyl-3-methylimidazolium tetrafluoroborate salts are miscible with water at 25 ^{0}C, where the alkyl chain length is less than 6, they formed a separate phase when mixed with water if the alkyl chain $\geq$ 6 carbon atoms **[2]**.

$[EMIM]BF_4$ was prepared via metathesis of [EMIM]I with $Ag[BF_4]$ in methanol in 1992 **[16]**. This salt has a melting point of 12 ^{0}C and may be prepared significantly more cheaply using $[NH_4]BF_4$ in acetone **[17]**. This ease of preparation together with its relative moisture stability and its immiscibility with a number of organic solvents cause to increasing utilization in biphasic catalysis. The preparation of $[EMIM]PF_6$ instantly took after, it was prepared by reaction of [EMIM]Cl with HPF_6**[18]**, its melting point is 60 ^{0}C, which makes it slightly less attractive than the BF_4^- salt, in the event that room temperature working is desired.

Therefore, ionic liquids based on more hydrophobic anions such as tri-fluoromethanesulfonate $CF_3SO_3^-$, bis-(trifluoromethanesulfonyl) imide $(CF_3SO_2)_2N^-$, tris(trifluoromethylsulfonyl) methide $(CF_3SO_2)_3C^-$and many others have been developed. These ionic liquids have received a broad consideration not only because of their low reactivity with water, but also because of their large electrochemical windows. Usually these ionic liquids can be well dried the water contents below 1 ppm under vacuum at temperatures between 100 and 150 ^{0}C [19].

Most recently new ionic liquids based on aluminum chloride when it combined with either urea or acetamide or trimethyl urea were prepared by Abood and co-workers in 2011[20]. These ionic liquids are much stable than other chloroaluminate ionic liquids of i.e. imidazolium or pyridinium chloride, offering relatively cheaper, less sensitive, easily prepared ionic liquids with promising similar properties in at least its catalytic properties for organic reactions and aluminum coating on metal substrate .

A new class of air and moisture stable ionic liquids based on choline chloride was synthesized by Abbott and co-workers[21], a green chemistry of such ionic liquids were shown especially in the metal process such as metal winding coating, this process offered much safer conditions and good quality for the manufacture .

Diverse sorts of choline chloride based ionic liquids with metal chlorides (hydrated or anhydrous) were synthesized also, each could be utilized as a part of particularly for their constituent metal covering such as chrome, nickel, copper, zinc ….etc [22,23].

Advancement of chloroaluminate was not stopped at replacing the imidazolium or pyridinium by the less sensitive boron tetrafluoride or phosphate hexafluoride ions.

Abood [24a] was synthesized another sort of ionic liquid from alum sulfate instead of aluminium chloride for its ease of handling, cheaper, greener and availability of these compounds in variable industrial applications such as water purification. Alum of the type $AlNH_4(SO_4)_2.XH_2O$, $AlK(SO_4)_2.XH_2O$ and $Al(NO_3).9H_2O$/Urea[24b] with urea or acetamide offered room temperature ionic liquids with exceedingly air and moisture stable characterization. This is a green ionic liquid as it was expected to be used in variable process such as metal coating since it offers good media for some insoluble compounds in aqueous media to dissolve easily in this ionic liquid such as metal oxides or silver sulfate.

Ionic liquids come in two primary classifications, namely simple salts (made of a single anion and cation) and binary ionic liquids (salts where an equilibrium is involved). For example, $[EtNH_3]NO_3$ is a simple salt whereas mixtures of aluminum(III) chloride and 1,3-dialkylimidazolium chlorides (a binary ionic liquid system) contain several different ionic species, and their properties depend upon the mole fractions of the aluminum(III) chloride and 1,3-dialkylimidazolium chloride present. Examples of ionic liquids consisting of simple salts are given in Figure (1-3).

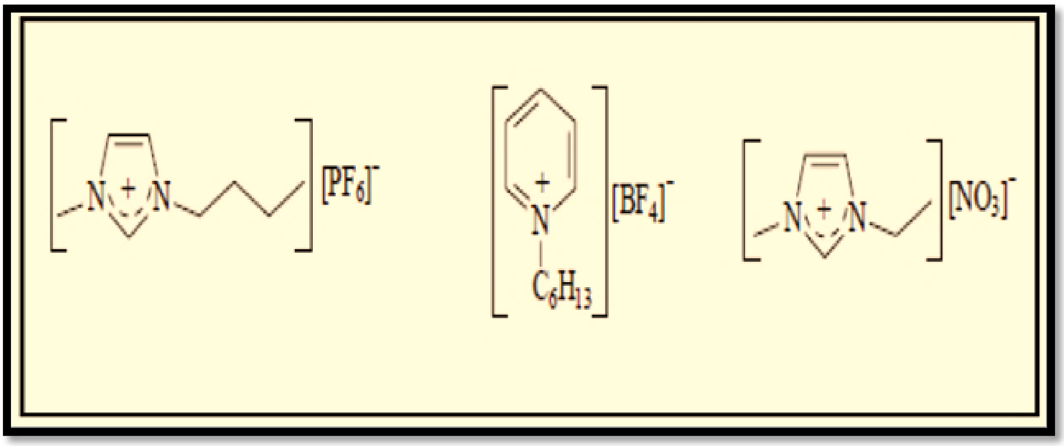


Figure (1-3) : Examples of simple room-temperature ionic liquids[6].

There are numerous approaches to prepare different types of ionic liquids such as[25]:

1- Metathesis reactions: are great competitors for the preparing of new ionic liquids for the first time. Nonetheless, they can leave the ionic liquids contaminated with a small amount of halide ions that may react with solute materials.

$$[EMIM]I + Ag[BF_4] \longrightarrow [EMIM][BF_4] + AgI \quad \text{at } 12^0C$$

2- Acid-base neutralization reaction: tetraalkylammonium sulfonates have been prepared by mixing equimolar amounts of the sulfonic acid and tetraalkylammonium hydroxide, the excess water was removed in vacuum.

$$RSO_3H + [R_4N][OH] \longrightarrow [R_4N][RSO_3] + H_2O$$

3- Direct combination of salts: direct combination of a halide salt with a metal halide such as:

$$AlCl_3 + [EMIM]Cl \longrightarrow [EMIM]^+ + AlCl_4^- \text{ (basic part)}$$

When a large amount of $AlCl_3$ was added, it gave $[Al_2Cl_7]^-$ this considered (acidic part), and the addition of excess from $AlCl_3$ gave $[Al_3Cl_{10}]^-$, this reaction must done in dry and high purity conditions.

4- Eutectic method: Another method for ionic liquid preparation:

$$C_5H_{14}ClNO + CO(NH_2)_2 \longrightarrow [C_5H_{14}ClNO][CO(NH_2)_2]$$

The imidazolium-based ionic liquids can be derived from a corresponding common precursor, the 1-alkyl-3-methylimidazolium halide, in general the chloride. This precursor is prepared by alkylation of methylimidazole. The alkylation is carried out in an autoclave, at 6 atmosphere of nitrogen and 90^0C without addition of solvent, if the chloroalkane is gaseous at room temperature (e.g. chloroethane), higher homologues can be prepared under atmospheric pressure.

This precursor is then either used in a metathetic reaction, where the 1-alkyl-3-methylimidazolium halide is reacted with a Group 1 metal salts, in particular a sodium salt, or a silver salt of the desired anion, or in an acid-base neutralization reaction[26]. This reaction is stoichiometric and therefore, equimolar amounts of waste MX or HX are produced. This could be circumvented by the direct alkylation of 1-methylimidazole with alkyltrifluoromethanesulfonate or alkyl bis(trifluoromethanesulfonyl) amide, for example [27].

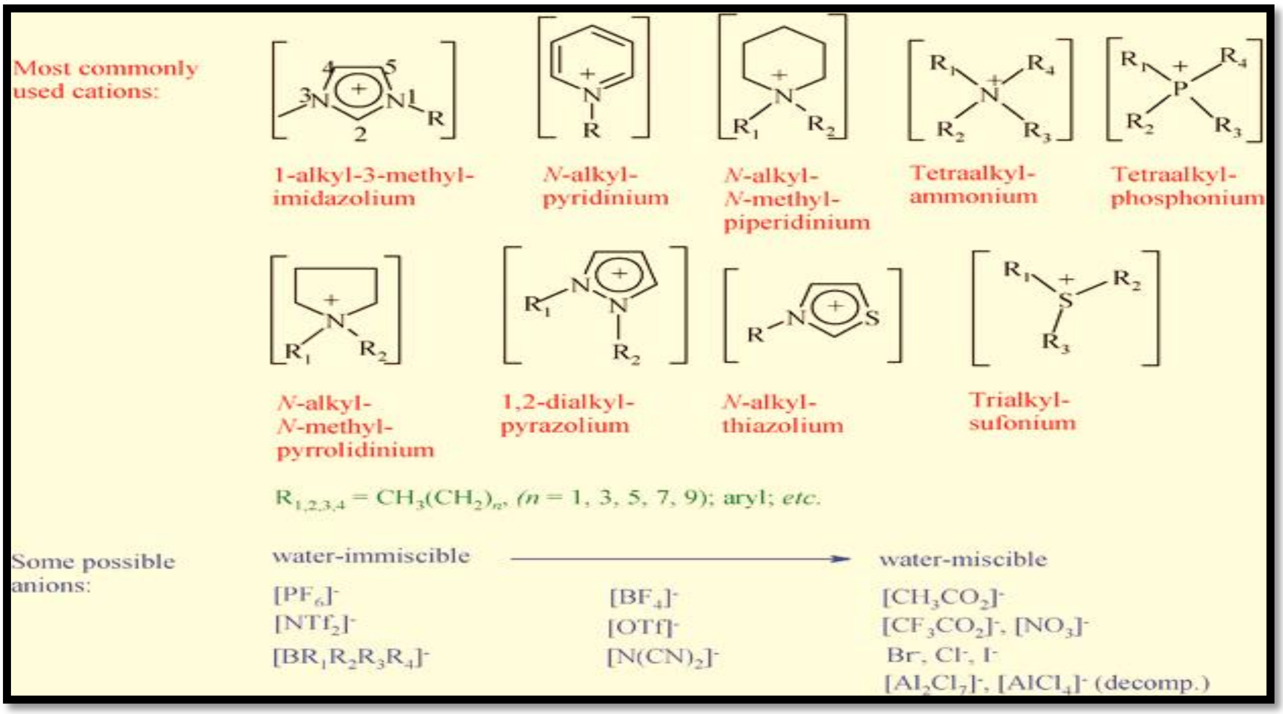


Figure (1-4): The building blocks of ionic liquids.

1.2 Physico-Chemical Properties of Ionic Liquids

1. **Melting Point:** Ionic liquids have melting points below 100 ºC and the greater part of them are liquid at room temperature. The increase in anion size leads to a decrease in melting point, for example, the melting point of $[C_2MIm]^+$ type ionic liquid with different anions such as $[BF_4]^-$ and $[Tf_2N]^-$ are 15 ^oC and -3 ^oC, respectively. Cations size and symmetry have a critical effect on the melting point of ionic liquids. Large cations and increased asymmetric substitution results in a melting point reduction[28].

2. **Density**: Ionic liquids are denser than water with values ranging from 1 to 1.6 g cm^{-3}, the increase in the length of the alkyl chain in the cation lead to decrease in densities. For example, the density in ionic liquids composed of substituted imidazolium cation and $CF_3SO_3^-$ anions decrease from 1.39 g/ml for $[C_2MIm]^+$ to 1.33 g/ml for $[C_2EIm]^+$, 1.29 g/ml for $[C_4MIm]^+$ and 1.27 g/ml for $[C_4EIm]^+$. The densities of ionic liquids are additionally influenced by the identity of anions[29,30].

3. **Viscosity:** In general, ionic liquids are more viscous than molecular solvents and their viscosities are ranging from 10 mPa s to about 500 mPa s at room temperature[29,30]. The viscosity of ionic liquids is determined by Van der Waals (VDW)[31] forces and hydrogen bonding. Electrostatic forces may also play an essential part. Alkyl chain lengthening in the cation leads to an increase in viscosity. This is due to stronger Van der Waals forces between cations leading to an increase in the energy required for molecular motion. Also, the ability of anions to form hydrogen bonding has a pronounced effect on viscosity[32].

4. **Conductivity**: Ionic liquids have sensibly great ionic conductivities compared with those of organic solvents/electrolyte systems (up to 10 mS cm^{-1}) **[33]**. However, their conductivities are usually lower than those of concentrated aqueous electrolytes at room temperature . Based on the fact that ionic liquids are composed solely of ions, it would be expected that ionic liquids have high conductivities. This is not the case since the conductivity of any solution depends not only on the number of charge carriers, but also on their mobility. The extensive constituent ions of ionic liquids reduce the ion mobility which thus leads to lower conductivities. Beside, ion pair formation and/or ion aggregation lead to reduced conductivity. The conductivity of ionic liquids of higher viscosity exhibit lower conductivity. Increasing the temperature increases conductivity and lowers viscosity**[33]**.

5. **Electrochemical window:** The electrochemical window is an essential property and plays a key role in using ionic liquids as solvents for the electrodeposition of metals and semiconductors. The electrochemical window is the electrochemical potential range over which the electrolyte is neither reduced nor oxidized at an electrode. This value determines the electrochemical stability of solvents. The electrochemical potential window is mainly dependent on the resistance of the cation to reduction and the resistance of the anion to oxidation. As known in aqueous solution, the electro-deposition of elements and compounds is constrained by the low electrochemical window of water (about 1.2 V). Actuality, ionic liquids have fundamentally larger electrochemical windows, e.g. 4.15 V for $[BMIM]BF_6$ at a platinum electrode, 4.10 V for [BMIM]BF4 and 5.5 V for $[BMP]Tf_2N$ at a glassy carbon electrode. For electrochemical application, the potential window of the electrolyte solution is one of the most essential properties. The potential window is

administered not only by the chemical structure of the materials used, but also by the electrode materials, sweep rate of the potential, temperature, atmosphere, solvent and impurities. The use of an alternate reference electrode to determine cathodic and anodic limits of an ionic liquid makes the circumstance even more complicated [34].

6. **Thermal stability:** Ionic liquids can be thermally stable up to temperatures of 450 C^0. The thermal stability of ionic liquids is limited by the strength of their heteroatom-carbon and their heteroatom-hydrogen bonds, respectively[28].

7. Low nucleophilicity and capability of providing weakly coordinating or non-coordinating environment[28].

8. **Color:** Ionic liquids are known to be colorless such as $[BMIM]^+$ cation and a variety of anions such as PF_6^-, BF_4^-, $CF_3CO_2^-$ and $(CF_3SO_2)_2N^-$, despite the fact they are not 100% pure. The color of less pure ionic liquids mostly ranges from yellow to orange. The formation of the color has been credited to the use of raw materials with color or by more heating during the synthesis of imidazolium salt[35,36].

9. **Hygroscopicity:** Viscosity estimations illustrate that ionic liquids become less viscous with increasing the water content. Hence, the water content has an influence on the viscosity of ionic liquids. Hydrolysis problems can also happen. Most of the ionic liquids have amazingly low vapor pressure, which allows removing water by simple heating under vacuum[35].

10. **Hydrophopicity:** The degree of polarity can be shifted by changing the length of the alkyl chain . The anion chemistry has a large impact on the properties of ILs, however, little variation in properties might be

expected between the same cation salts, so the actual differences can be significantly dramatically, for example, $[BMIM]PF_6^-$ is immiscible with water, whereas $[BMIM]BF_4^-$ is water soluble[35].

1.3 Some applications of ionic liquids[37-39]

1- Homogeneous and heterogeneous catalyst

Ionic liquids apparently are both homogeneous and heterogeneous catalysts. This is because some selected ionic liquids can be immiscible with the reactants and products, but dissolve the catalysts. This has the advantages of a solid for immobilizing the catalyst, with the advantages of a liquid for allowing the catalyst to move freely.

2- Biological reactions media

Because of enzymes are stable in ionic liquids, this opens the possibility for ionic liquids to be used in biological reactions, such as the synthesis of pharmaceuticals.

3- Treatment of high-level nuclear waste

The ionizing radiation does not affected in ionic liquids, so they could even be used to treat high-level nuclear waste.

4- Removing of metal ions

Several new ionic liquids have been designed and synthesized to remove cadmium and mercury from contaminated water. When these water-insoluble ionic liquids come in contact with contaminated water, they snatch the metal ions out of water and sequester them in the ionic liquid.

5- Purification of gases

Ionic liquids can selectively dissolve and remove gases and could be used for air purification on submarines and spaceships.

6- Synthesis of coordination complex

The reports of directed synthesis of coordination complexes in ionic liquids are oxo-exchange chemistry, exposure of chloroaluminate ionic liquid to water leads to formation of aluminum oxo- and hydroxo-containing species.

7- Synthesis of organometallic compounds

The imidazolium-based ionic liquids being utilized to prepare metal imidazolylidene complexes and some other compounds·

8- Electrochemical applications

RTILs can provide high opportunities for overcoming the limitations encountered in traditional chemical processes, particularly in electrochemistry. The wide electrochemical window, nonvolatile, noncombustible, and heat resistance nature of RTILs is observed for applications in electrodeposition, batteries, fuel cells, electrosynthesis, electrocatalysis, and electrochemical bio sensing.

1.4 Electrodeposition

The terms of electrodeposition and electroplating are often used interchangeably. As a matter of fact, "electroplating" can be considered to occur by the process of electrodeposition. The electrodeposition is the process of delivering a metallic deposition on a surface by the activity of electric current. The deposition of a metal on the surface of substrate is achieved by converting the substrate to anion to be coated and immersing it into the solution of the metallic salt. The positive charges carried by the metallic ions are thus attracted to the negatively charged substrate, they give electrons to diminish the positive charge ions to metallic form. Electrodeposition is essential for a variety of industries like electronics, optics, sensors, automotive and aerospace. The conventional solutions, such as water, suffer from , the draw back that it has a relatively small potential window, hence the deposition of metals with high negative reduction potentials is hindered by oxygen and hydrogen being produced. RTILs are superior media for the electrodeposition of metals and semiconductors, and have an exceptional potential to revolutionize electroplating. The use of ionic liquids heralds not only the ability to electrodeposit metals that have hitherto been impossible to reduce in aqueous solutions, but also the capability to engineer the redox chemistry and control metal nucleation characteristics[40].

1.4.1 Electrodeposition of semiconductors

Semiconductors are widely utilized in many fields, e.g. in electronic devices and solar cells[33]. Ionic liquids were used successfully to get semiconductors, which cannot be obtained from aqueous solutions because of hydrogen evolution, which sets in before semiconductor electrodeposition. Endres et al[41-43]. reported that the elemental semiconductor germanium can be electrodeposited in 1-butyl-3-methylimidazolium hexaflurophosphate ionic liquid that was saturated with germanium bromide ($GeBr_4$) or germanium chloride ($GeCl_4$), and they stated that the reduction of elemental germanium from Ge(IV) halides occurs via Ge(II) species. As germanium, silicon cannot be obtained from aqueous media. Zein El Abedin et al. [44] had reported that nanocrystalline silicon of 50-150 nm diameter can be electrodeposited in the room temperature ionic liquid 1-butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl) amide.

Ionic liquids are not only utilized to get elemental semiconductors, but they can be also employed to get compound semiconductors like indium antimonide (InSb)[45] and cadmium telluride (CdTe)[46] by electrodeposition in 1-ethyl-3-methylimidazoliumchloride / tetrafluroborate ionic liquid. These two compound semiconductors are relevance in electronics and solar cells industries.

1.4.2 Electrodeposition of metals and alloys

Room temperature ionic liquids can be utilized as solvents for the electrodeposition of metals and alloys, for example, Katayama and co-workers [47] have reported that the room temperature ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM]BF_4) is applicable as an alternative electroplating bath for silver. This ionic liquid is prevalent to the chloroaluminate systems since the electrodeposition of silver can be performed without the risk of aluminium co-deposition. Also, the electrochemical deposition of silver was investigated at a glassy carbon electrode in hydrophobic 1-n-butyl-3-methylimidazolium hexafluorophosphate [BMIM]PF_6 and hydrophilic 1-n-butyl-3-methylimidazolium tetrafluoroborate [BMIM]BF_4 ionic liquids[48]. Tai et al. [49] studied the electrodeposition of Pd–Ag alloys from the basic [EMIM]Cl-BF_4 ionic liquid in solutions containing Pd(II) and Ag(I) in a temperature range from 35 to 120 ^{0}C. Scanning electron micrographs of the coatings indicated that the Pd–Ag alloys were nodular and become more compact upon increasing the temperature up to 120 ^{0}C. It was moreover expressed that copper can be coated in a mixture of 1-ethyl-3-methyl imidazolium tetrafluoroborate [EMIM]BF_4 and [EMIM]Cl and the deposits obtained are red brown in appearance with good adhesion[50]. Chen et al.[51] reported that copper and copper-zinc alloys can be electrodeposited on tungsten and nickel electrodes in a Lewis acidic 50-50 mol % $ZnCl_2$–[EMIm]Cl molten salt containing Cu (I). The copper content in the Cu-Zn alloys increases as the Cu (I) concentration in the plating bath and/or the deposition temperature increases and decreases as the deposition overpotential increases. Cadmium also can be electrodeposited in basic 1-ethyl-3 methylimidazolium chloride / tetrafluoroborate[52].

Electrodeposition of palladium–indium alloys is of interest because the incorporation of indium into palladium provides higher microhardness and wear resistance than pure palladium without yielding the low contact resistance of the palladium[53]. Thus, the Pd–In coatings can be used as replacement for pure gold. The electrodeposition of Pd–In in aqueous baths are also available nowadays [54]. The general difficulties associated with the electrodeposition of Pd-In from aqueous baths are the significant difference between the deposition potentials of palladium and indium, the low hydrogen overvoltage and the large hydrogen solubility in the Pd metal. Therefore, trials have been made to reduce these problems, one approach is to replace the aqueous bath with aprotic solvents. The Pd-In coatings were electrodeposited successfully in the [EMIm]Cl-BF_4 ionic liquids and the obtained deposits are compact and smooth [55].

The electrodeposition of Zn and its alloys is possible in the Lewis acidic $ZnCl_2$–[EMIM]Cl ionic liquid. It was shown that ionic liquid (when the molar percentage of $ZnCl_2$ is higher than 33 mol%) was potentially valuable for the electrodeposition of zinc and zinc containing alloys[56]. Huang and Sun had shown that Pt–Zn alloy[57], iron and Zn–Fe alloy[58], tin and Sn–Zn alloy[59] can be electrodeposited in Lewis acidic $ZnCl_2$–[EMIM]Cl ionic liquid. Moreover, Zinc can be coated from Lewis basic 1-ethyl-3-methylimidazolium bromide – zinc bromide molten salts with and without dihydric alcohols (ethylene glycol, 1,2-propandiol, 1,2 butanediol) at 120 ^{0}C [60].

The study of nanoparticles of catalytically active material has attracted grown interest in recent years because of the important role of nanoparticles in catalysis. Platinium film/nanoparticle is of particular interest, as it is known to be one of the most important catalysts for many chemical reactions, for example, production of hydrogen from methane, conversion of automobile exhaust gas, and especially oxygen reduction and methanol oxidation in a fuel cell[61]. Ping et. al.[62] reported that platinum can be electrodeposited in [BMIM]BF_4 and [BMIM]PF_6 ionic liquids at glassy carbon electrodes, and the electrocatalysis effect of nanostructured platinum films obtained in these ionic liquids on the methanol electro oxidation was also investigated. The obtained platinum deposits were uniform, shiny and fairly dense and the separate spherical nanoclusters were less than 100 nm, obviously different from those of far more than 100 nm prepared in $HClO_4$ aqueous solution. Based on the observed size of platinum nanoclusters, it was reasonable that the catalytic performance and usage efficiency of the platinum film prepared in [BMIM]BF_4 and [BMIM]PF_6 would be much higher than that prepared in $HClO_4$ aqueous solution. Nanostructures possess unique properties due to size and interface effects and hence find many applications in electronics, catalysis, and material science[63]. Therefore many attempts have been done to make nanostructured materials.

Electrodeposition is considered as a versatile method to prepare metal nanostructures, as it allows the precise control over grain size by adjusting the electrochemical parameters such as over potential, current density and the bath composition.

Abbott et. al.[64] studied the electrodeposition of aluminum and aluminum/platinum alloys from $AlCl_3$/benzyltrimethylammonium chloride ionic liquid.

Abbott et. al. [65] have reported the synthesis and characterization of new moisture stable, Lewis acidic ionic liquids/deep eutectic solvents made from metal chlorides and quaternary ammonium salts, which are commercially available. They have shown that mixtures of choline (2-hydroxyethyltrimethylammonium) chloride $(H_3C)_3NC_2H_4OH)Cl$ and MCl_2 (M = Zn, Sn) gave conducting and viscous liquids at or around room temperature. These liquids are easy to prepare, they are water and air insensitive and their low costs make their use in large-scale applications likely. Furthermore, they have reported[66] that a dark green, viscous liquid can be formed by mixing choline chloride with chromium (III) chloride hexahydrate and the physical properties of this liquid are characteristic of an ionic liquid. The eutectic composition is found to be 1:2 choline chloride/chromium chloride, from this ionic liquid, chromium black can be electrodeposited efficiently to yield a crack-free deposit. Addition of LiCl to the choline chloride/$CrCl_3$-$6H_2O$ mixture was found to allow the deposition of nanocrystalline black chromium films[67].

1.5 Electrodeposition of aluminium

Aluminum is the most abundant metal and the third most abundant element in the earth's crust, after silicon and oxygen. It makes up about 8% by weight of the earth’s crust. Aluminum is very reactive chemically to occur naturally as a free metal. alternatively, it is found combined in over 270 different minerals. The main raw of aluminum is bauxite, a mixture of hydrated aluminum oxide ($Al_2O_3.xH_2O$) and hydrated iron oxide $Fe_2O_3.xH_2O$. Cryolite (Na_3AlF_6) is another mineral critical in the generation of aluminum metal. However, cryolite is not used as an ore and thus aluminium is not extracted from it. Metallic aluminum was first prepared by

Hans Oersted, a Danish chemist, in 1825. He obtained the metal by heating dry aluminum chloride with potassium metal.

$$AlCl_3 + 3K \longrightarrow Al + 3KCl$$

Robert Bunsen prepared aluminum metal in the 1850 by passing an electric current though molten sodium aluminum chloride. However, because both electricity and potassium metal were quite expensive, aluminum remained a chemical lab compound and of an interest until after the invention of the mechanical electrical generator. In 1886, Charles Martin Hall of Oberlin, Ohio, and Paul Héroult of France, they were both 22 years old at the time, autonomously discovered and patented the process in which aluminum oxide is dissolved in molten cryolite and decomposed electrolytically**[68]**. With Hall-Héroult process, this method is still the main industrial method for primary aluminum production. The first step in the commercial aluminum production is the separation of aluminum oxide from the iron oxide in the bauxite. This is accomplished by dissolving the aluminum oxide in a concentrated sodium hydroxide solution, aluminum ions form dissoluble complex ion with hydroxide ions, but iron ions do not.

$$Al_2O_3.xH_2O_{(S)} + 2OH^-_{(aq)} \longrightarrow 2Al(OH)^-_{4\,(aq)} + {}_{(x-3)}\,H_2O_{(l)}$$

After filteration the insoluble iron oxide from the solution, $Al(OH)_3$ is precipitated from the solution by adding acid to reduce the pH to about 6. After that the precipitate is heated to produce dry Al_2O_3 (alumina).

$$2Al(OH)_{3\,(S)} \longrightarrow Al_2O_{3(s)} + 3H_2O_{(g)}$$

In the Hall-Héroult process Figure (1-5), aluminum metal is obtained by electrolytic reduction of alumina. Pure alumina melts at higher than 2000 ^{0}C. To produce an electrolyte at lower temperature, alumina is dissolved in molten cryolite at 1000 ^{0}C. The electrolyte is put in an iron vat, lined with graphite. The vat works as the cathode and the carbon anodes are inserted into the electrolyte from the top. The oxygen produced at the anodes interacts with them, forming carbon monoxide and carbon dioxide. Therefore, the anodes are consumed and need to be replaced occasionally. Molten aluminum metal is produced at the cathode, and it sinks to the bottom of the vat. The principal cell reactions are:

$$\text{cathode: } 4Al^{+3} + 12\ e^{-} \longrightarrow 4\ Al_{(l)}$$

$$\text{anode: } 6\ O^{-2} \longrightarrow 3\ O_{2\ (g)} + 12\ e^{-}$$

$$\text{net: } 4Al^{+3} + 6\ O^{-2} \longrightarrow 4\ Al_{(l)} + 3O_2\uparrow_{(g)}$$

In stages, a plug is uprooted from the vat and the molten aluminum is drained. The heat needed to keep the mixture molten is equipped by resistive heating of the electrolyte by the current passing through the cell. Typical cells use a potential of 4 to 5 volts and a current of 300,000 amperes.

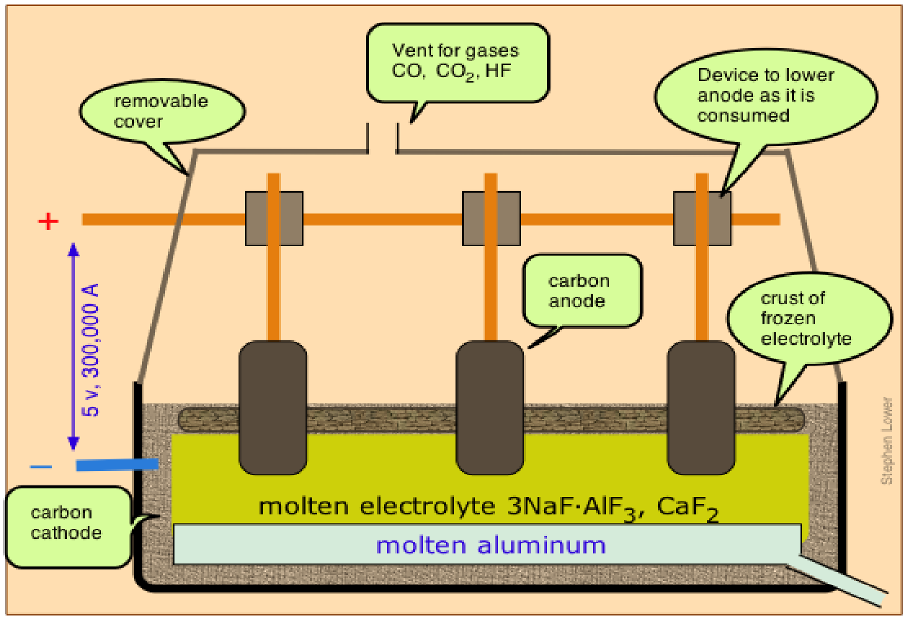


Figure (1-5): The Hall-Héroult process.

Aluminum is a silvery-white metal with numerous valuable properties. It is light (density 2.70 g/cm^3), nontoxic, with an electrical conductivity 60% that of copper and a much lower density, it is utilized extensively for electrical transmission lines. Pure aluminum is soft and brittle, but can be strengthened by alloying with small amounts of copper, magnesium, and silicon. Based on its chemical reactivity, aluminum should not be very useful at all. Its standard reduction potential is -1.67 volts, indicating that it is a very good reducing agent. It is far more active than iron, which has a reduction potential of -0.44 volt. Aluminum obviously better than iron, because the product of its corrosion, Al_2O_3 , adheres strongly to the metal's surface, protecting it from further reaction. This is quite different from the behavior of iron. Rust flakes off the surface of iron, exposing the surface to further corrosion, as shown in Figure (1-6). The protective oxide coating on aluminum is frequently enhanced by the process of anodization. Aluminum metal is made the anode in an electrolytic cell, where aluminum metal is oxidized, and its protective oxide coating is thickened. The oxide coating on aluminum renders it impenetrable to most acids. However, any chemicals that form a strong complex with aluminum ions, e.g. OH^- and Cl^- ions, will react with the oxide coating. Therefore, aluminum will dissolve in hydrochloric acid and sodium hydroxide solutions.

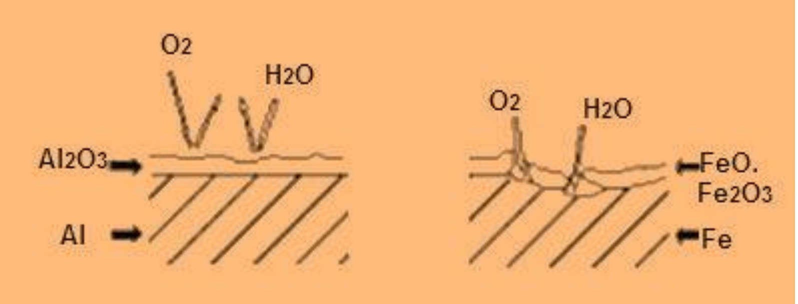


Figure (1-6): Difference between Al_2O_3 and $FeO.Fe_2O_3$ protective layer.

Currently, there are several methods available for aluminium plating such as hot dipping [69,70], thermal spraying [71], sputter deposition [72,73], vapor deposition [74,75] and electrodeposition [76,77] ,but all of these methods except electrodeposition are expensive, performed at elevated temperatures which may damage the specimens, low dissolving capability of Al salts, high volatility, flammability and not suitable to get a thin aluminium films. However, it was reported that electrodeposition was employed successfully to get a thin aluminium film with higher purity and lower porosity. The coating has a good corrosion resistance and the thermal stress can be avoided since electroplating process can be carried out below 180^0C[76].

Aluminium cannot be electrodeposited from an aqueous solution because of its reactivity (E^o = -1.67 V *vs.* normal hydrogen electrode NHE). The electrodeposition process would be restricted by hydrogen evolution at the cathode surface, consequently, aluminium can only be electrodeposited from non-aqueous aprotic electrolytes such as molten salts and organic solvents. Many of these electrolytes are sensitive to air and moisture so that the electrodeposition process must be carried out in inert atmosphere such as argon or nitrogen gas.

There are some requirements for aluminium electrodeposition before introducing the different baths used for electrodeposition of aluminium:

a) The electrolyte should consist of a solvent acting as a slight Lewis base and a solute acting as a Lewis acid so that mutual coordination and dissolution of the solute can take place.

b) The solute that is used as an Al source should exhibit a high solubility in the solvent. A stable complex must be formed in the plating solution.

c) For some applications, it is desirable that the composition of the bath remains constant during the operation. This implies that the electrode process has to be chemically reversible. This permits the long-term operation of the bath without a change in the electrodeposition characteristics.

d) The medium must exhibit reducing and water-consuming properties.

Additionally a potentially suitable solvent for the preparation of Al-electrodeposition baths must comply with the following criteria[78]**:-**

i) The solvent must be electrochemically stable in order to permit the reduction of an Al (III) compound without electrolysis of the solvent. This requires that the standard potential that characterizes the electrochemical equilibrium between metallic aluminium and the aluminium complex in solution lies within the existence regime of the solvent.

ii) The electrode reaction has to be kinetically feasible (low overpotential) and mass-transport phenomena have to favour a controllable surface morphology. The free energy of the co-ordination complex of the solvent and aluminium solute, e.g. aluminium halide, should be sufficiently low to ensure a good solubility of the salt.

iii) The dissociated Al complex ion must release Al at a less negative potential than that of possible electrode reactions involving the solvent.

1.6 Aluminium electrodeposition baths

1.6.1 Electrodeposition of Aluminium from organic solvents

The first attempt to electrodeposit aluminium from organic solvents was made by Plotnikov [79]. He used solutions of aluminium bromide and Alkali bromide in benzene, toluene and xylene. Till now, there are three classes of organic solvents, which have been successfully used for aluminium electrodeposition[80].

1.6.1.1 Etheric solvents or hydride baths

In these baths the etheric solvents, such as diethyl ether (Et_2O) and tetrahydrofuran (THF), $AlCl_3$ and LiH or $LiAlH_4$ are combined together to form solutions containing the electroactive species from which aluminium can be electrodeposited. These resulting solutions are called hydride baths and they are classified into two baths, NBS (National Bureau of Standards) and THF baths.

i) National Bureau of Standards (NBS) baths

Brenner and co-workers[81,82] at the NBS succeeded to electrodeposited aluminium in an industrial scale by using solution made by dissolving aluminium chloride ($AlCl_3$) and lithium hydride (LiH) in diethylether (Et_2O). Later, lithium hydride was replaced by lithium aluminium hydride ($LiAlH_4$), which can be dissolved in diethylether more easily[83]. The addition of $LiAlH_4$ increased the bath lifetime. The obtained cathodic current efficiency at current densities 2-5 A dm^{-2} and ambient temperatures was 90%. The anodic current efficiency was 100% but the anodically dissolved aluminium could not be deposited onto the cathode, therefore the aluminium content of the bath decreased during the electroplating process and $AlCl_3$ must be added from time to time to increase the bath lifetime. NBS electrolyte was used on a pilot plant scale at General Electric by Schmidt and coworkers[84,85] who electroformed parabolic mirrors. The cathode current densities were 1.5 - 10 A dm^{-2}. Both the micro and the macro throwing powers were reported to be excellent. Adherent aluminium coatings of 300 μm in thickness were deposited on various aluminium alloys, titanium alloys and copper alloys as well as steel in NBS baths[86]. The application of the NBS bath to Electro-Optical Systems[87] was similar to the application at General Electric, namely the electroforming of solar mirrors. Withers and Abrams[88] electroformed composites containing boron filaments. To strengthen the aluminium deposit they added magnesium solution to the NBS bath, probably as ethylmagnesium bromide. By using bare Al anodes, Clay et al.[89] succeeded in determining the optimum conditions such as agitation, low current densities (up to 2 A dm^{-2}) and somewhat higher temperature (40 ^{0}C) to prolong lifetime of the bath. Under these circumstances the anodic current efficiency was found to be 100 %.

Levinskas and coworkers[90] studied the relation between the geometry of the cell and the pre-treatment of the cathode surface on the one hand and the optimum current density on the other hand. They also studied the influence of additives such as diethylamine, butylamine and piperidine on the deposit and bath quality[91].

The NBS bath[92] had several drawbacks such as flammability, limited lifetime, variation of the composition and low anodic current efficiency, hydrogen embrittlement due to excessive hydrogen evolution. Nevertheless the process has been a commercial reality for a long time, and has also been adopted by NASA[93].

ii) The tetrahydrofuran (THF) baths

The use of THF alone or THF in combination with benzene instead of diethyl ether has been suggested by Ishibashi and Yoshio[94]. It was not only less flammable and less volatile, it also showed better anode dissolution and therefore a longer bath lifetime. The composition of the bath was roughly 60 vol.% THF, 40 vol.% benzene with 0.7-1.3 mol/L $AlC1_3$ and $LiA1H_4$. Excellent deposits were obtained with an $AlC1_3$:$LiA1H_4$ molar ratio of 3:1. Other hydrocarbons were tried in addition to benzene, such as 1,2-dichloroethane and toluene, in these cases the deposit on the cathode was obtained but a white precipitate was observed on the anode. An unsuccessful endeavor was made to improve the operation of the NBS electrolyte by adding some aromatic hydrocarbons[95].

The THF electrolyte has been utilized by the Nisshin Steel Co. in Japan for the continuous aluminium coating of steel wires and strips used, for example, in integrated circuits[96]. Also, It has been used for the electroplating of carbon fibers[97]. Graef studied the mechanism of aluminium electrodeposition from solutions of $AlCl_3$ and $LiAlH_4$ in THF[98]. In 2000[99,100], Lefebvre and Conway reported in two papers that aluminium can be electrodeposited from plating baths of varying ratios of $AlCl_3$ and $LiAlH_4$ dissolved in THF. They studied the kinetics, mechanisms, nucleation and surface morphologies in the process of electrocrystallization of aluminium on smooth gold and glassy-carbon substrates.

1.6.1.2 Aromatic hydrocarbons baths

These electrolytes are known as bromide baths because $AlBr_3$ is the aluminium-containing compound. The aromatic hydrocarbons used are usually benzene, toluene, xylene and their mixtures and derivatives.

i) $AlBr_3$ + MBr as the electroactive components

Attempts were done to increase the conductivity of $AlBr_3$ solutions by the addition of quaternary ammonium or pyridinium salts such as ethylpyridinium bromide[101], ethylenepyridinium dichloride and ethylenepyridinium dibromide[102]. The best deposits were obtained with quaternary pyridinium or dimethylaniline salts in toluene. The anionic species was assumed to be $Al_2Br_7^{-}$ on the basis of conductivity measurements. These electrolytes are complicated to operate and the results are rather poor. In small amounts, the quaternary salts can improve the brightness of the deposit but higher concentrations lead to the incorporation of the quaternary salt into the deposit and thus to a decrease in its purity and corrosion resistance.

ii) $AlBr_3$ +HBr as the electroactive components

This mix has been utilized by Capuano and Davenport[103-105]. The electrolyte consisted of 36-45 vol.% $A1Br_3$ in a 1:1 mixture of ethylbenzene or diethyl benzene and toluene. The electrolyte was prepared using an inert gas saturated with water vapor and passed through the solution prior to dissolution of the $AlBr_3$, and this led to the formation of HBr. The solution thus prepared must be carefully protected against moisture and oxygen by an inert atmosphere. The presence of HBr in the solution ensures the required specific conductivity of 3-4 mS cm^{-1}. The coated surfaces were copper and steel and the anode was pure aluminium. Although Davenport and Capuano regard their electrolyte as highly suitable for application, no industrial use is known as yet.

iii) Organoaluminium compounds as the electroactive components

The bath is based on the compounds: $(C_2H_5)_4NCl$ / $2Al(C_2H_5)_3$, NaF / $2Al(C_2H_5)_3$ and $NaF/2Al(C_2H_5)_3/3.3C_7H_8$. The solvent is toluene. The composition of the bath and the influence of additives on the brightness of the deposit have been studied by Dötzer and coworkers [106,107]. Electrolytes with organoaluminium compounds are used by SIGAL (Siemens- Galvano- aluminium) in discontinuous operation for manufacturing reflectors as well as light and heat radiators. In principle the electrolytic cell is put in a double-walled chamber filled with inert gas to prevent the influence of air and moisture on the electrodeposition process.

1.6.1.3 Electrodeposition of aluminium from dimethylsulfone ($DMSO_2$)

With various of attractive features such as: high conductivity, good thermal stability, ability to dissolve numerous metallic cations, dimethylsulfone ($DMSO_2$) has been considered a promising organic solvent for rechargeable cells[108]. Recent investigations [109,110] have shown that aluminium can be reversibly plated and stripped in a mixture (2:1 mole ratio) of $AlCl_3$: LiCl dissolved in $DMSO_2$ while no aluminium plating was observed in that of a 1:1 mole ratio. SEM observations [109] showed that smooth and continuous aluminium deposits could be obtained from the $DMSO_2$ baths by potential step technique. A Raman study[111] revealed:

a) $AlCl_4^-$ ion was always the main Al (III) species even in a melt without LiCl.

b) $Al_2Cl_7^-$ was never found even in the more acidic baths, i.e. with $AlCl_3$/LiCl mole ratio greater than one.

c) A coordination complex, $Al[(CH_3)_2SO_2]_3^{3+}$ was formed in the acidic melts between $DMSO_2$ and Al (III). This complex was responsible for aluminium deposition on tungsten electrode from $AlCl_3$/LiCl/$DMSO_2$ bath through the following reactions **[109]**:

$$Al[(CH_3)_2SO_2]_3^{3+} + 3e^- \longrightarrow Al + 3(CH_3)_2\,SO_2$$

No aluminium plating process occurred in a mixture (2:1 mole ratio) of $AlCl_3$: LiCl, indicating that as a Lewis base, $DMSO_2$ was weaker than Cl^- but stronger than $AlCl_4^-$, leading to the following equilibrium for $DMSO_2$-based electrolytes:

$$AlCl_3 + Cl^- \longrightarrow AlCl_4^-$$

$$4\,AlCl_3 + 3(CH_3)_2SO_2 \longrightarrow Al[(CH_3)_2SO_2]_3^{3+} + 3AlCl_4^-$$

Unfortunately, All the organic solvent baths have many disadvantages such as they are flammable, volatile, hygroscopic and consequently relatively complicated to handle. For example, from the disadvantages of organoaluminium baths, their self-ignition in air and their vigorous reaction with water.

To avoid the disadvantages of organic solvent baths, the investigation of new nonaqueous electrolytic systems for the electrodeposition of aluminium has continued. Of them, ambient temperature chloroaluminate molten salts such as $AlCl_3$-NaCl and related lower melting chloroaluminates based on quaternary ammonium chloride salts (ionic liquids) such as N-butylpyridinium chloride (N-BPC) and 1- ethyl-3-methylimidazolium chloride [EMIM]Cl. These ambient temperature molten salts have received more attention as the most promising aluminium plating baths for industrial applications.

1.6.2 Electrodeposition of aluminium from chloroaluminate molten salts

Electrodeposition of aluminium in molten salts would have many advantages. The low working temperature (120 ^{0}C and higher) compared with the hot plating process suppresses the formation of brittle intermetallic compounds in the under layer. The higher electrical conductivity of the electrolyte (by 1 to 2 orders) makes it possible to carry out the electrolysis at higher current densities. There is less toxicity and no danger of explosion and control of the thickness of the Al layer make it potentially attractive for wider application**[19]**.

Aluminium can be electrodeposited in molten salts (chloroaluminate molten salts), mainly chlorides, where Al can be deposited either by using a soluble aluminium anode or the electrochemical decomposition of the electroactive species, $Al_2Cl_7^-$, which formed in the Lewis acidic molten $AlCl_3$: Alkali metal chloride mixture of 2:1 mole ratio. The electrochemical reduction of the electroactive species occurs by the following reaction**[112]**:

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

The first paper on the electrolytic aluminium deposition from a molten $AlCl_3$-NaCl mixture was published at the mid of nineteenth century**[113]**.

Bromides as well as chlorides have been tested as possible electrolytes for the deposition of Al layers[114,115].

The drawbacks of the $AlCl_3$-NaCl molten salt are its high $AlCl_3$ vapor pressure, which may result in explosions at elevated temperatures and the fact that the melt is very corrosive.

1.6.3 Electrodeposition of aluminium in ionic liquids

Popular examples of ionic liquids include the chloroaluminates, which are prepared by mixing anhydrous $AlCl_3$ with a suitable organic halide. This kind of ionic liquids can be considered as the first generation of ionic liquids. Furthermore, it is the simplest system from which aluminium can be easily electrodeposited. As the molar ratio of this mixture changes, the melt can be classified as basic, neutral or acidic in the sense of Lewis acidity. In the neutral 1:1 melt Al is present almost entirely as $AlCl_4^-$ ions, whereas in the 2:l melt it is present as $Al_2Cl_7^-$. In melts having a molar ratio between 1:l and 2:1, both $Al_2Cl_7^-$ and $AlCl_4^-$ ions will be present. The acid-base properties of the melt at ambient temperature may be described by the following equilibrium equation[116].

$$2\,AlCl_4^- \longleftrightarrow Al_2Cl_7^- + Cl^-$$

with an equilibrium constant $K = 3.8 \times 20^{-13}$ at 30 ^{0}C. In acidic melts, in which the electroactive $Al_2Cl_7^-$ ions are the only reducible species from which aluminium can be electrodeposited according to the following reaction:

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

In presence of excess of $AlCl_3$, the following reaction is virtually complete:

$$AlCl_4^- + AlCl_3 \longrightarrow Al_2Cl_7^-$$

A lot of work has been done using chloroaluminate ionic liquids to obtain high quality aluminium deposits by other researchers. For example, aluminium chloride / 1-ethyl-3- methylimidazolium chloride and aluminium chloride / N-butylpyridinium chloride have been widely used in electrodeposition of aluminium and its alloys[117].

1.6.3.1 Electrodeposition of aluminium in aluminium chloride / imidazolium based ionic liquids.

Hussey and co-workers carried intensive studies on the electrodeposition of aluminium and aluminium alloys in $AlCl_3$ / [EMIM]Cl ionic liquid. They succeeded to electrodeposit transition metal-aluminium alloys such as Al-Mo[118], Al-Ti[119], Al-Zr[120], Ag-Al[121], and ternary Al-Mo-Mn alloys[122]. These alloys are technologically important because of their corrosion resistance, especially pitting corrosion, and in some cases, their interesting magnetic properties. The $AlCl_3$ / [EMIM]Cl ionic liquid is especially attractive for the electrodeposition of aluminium and its alloys because it has a very low melting point over a wide range of compositions, high intrinsic electrical conductivity at room temperature and a low vapor pressure.

Jiang et al[123]. have studied the electrodeposition, electrochemical nucleation and surface morphology of aluminium on both tungsten and aluminium electrodes from 2:1 molar ratio $AlCl_3$ \ [EMIM]Cl ionic liquid. The electrodeposits obtained on both tungsten and aluminium electrodes were dense, continuous and well adherent.

The $AlCl_3$ / [EMIM]Cl ionic liquid was used to electroplate mild steel by well adherent and highly resisted to scratches aluminium coatings[124]. However, the quality of the deposit can be greatly improved by utilizing pulse plating techniques[125,126] or by addition of some organic solvents such as benzene and methyl t-butyl ether[126] that improve the deposit surface morphology. It is possible that the organic molecules play the role of brighteners.

Endres et al[127]. reported that nanocrystalline aluminium can be made electrochemically in Lewis acidic ionic liquids based on $AlCl_3$ and [EMIM]Cl under galvanostatic conditions by addition of nicotinic acid.

Lai[128] have electrodeposited aluminium in room temperature $AlCl_3$ /[EMIM]Cl ionic liquid on glassy carbon, platinum and tungsten. Moreover, he has studied the mechanism of the electrodeposition and dissolution processes in this ionic liquid and found that the aluminium deposition process at the above-mentioned substrates is preceded by a nucleation step and is kinetically complicated. The deposition of Al was found to be unstable and subject to a slow corrosion process. This is due to impurities and organic cation present in the liquid.

1.6.3.2 Electrodeposition of aluminium in ($AlCl_3$ / N-BPC) system.

The aluminium chloride / N-butylpyridinium chloride ($AlCl_3$ / N-BPC) system is liquid at ambient temperatures over a wide composition range (molar ratio from 0.75:1 to 2:1 $AlCl_3$ / N-BPC) [129].

Researchers used different electrodes such as glassy carbon, tungsten [130] and platinum [131] to investigate the mechanism of aluminium deposition and dissolution reactions in $AlCl_3$ / N-BPC melts at ambient temperature. The results showed that the electrodeposition of aluminium from this liquid at glassy carbon and tungsten electrodes is kinetically complicated and the corrosion rate of aluminium is linearly proportional to the acidity of the melt at 40 ^{0}C. Besides impurities, the major reason for the corrosion of the deposited aluminium in that melt was also found to be due to the organic butylpyridinium cation (BuPy+) while at platinum electrodes, the results indicated that the aluminium deposition reaction is a quasi-reversible process and there is an evidence for formation of Pt-Al alloy in the initial stages of aluminium deposition[131].

In 1980, Robinson and Osteryoung [132] studied the electrodeposition and stripping processes of aluminium in $AlCl_3$ / N-BPC melts with and without benzene at tungsten, platinum and glassy carbon electrodes. Yang [133] studed the electrodeposition of aluminium from an acidic liquid of this system by using DC constant current and pulse current methods at 30 ^{0}C. The quality of deposited aluminium layer was improved by applying pulse current, the particle size decreased and the adhesion became much better.

Abood and co-workers [20] had investigate that the addition of simple amide (urea or acetamid) to anhydrous $AlCl_3$ causes the formation of a liquid of the form $[AlCl_2.nAmide]^+$ $AlCl_4^-$, the materials thus produced is liquid over a wide temperature range, this liquid is relatively insensitive to water and has the properties of ionic liquid. This prepared liquid is shown to be a suitable medium for acetylation of ferrocene and the electrodeposition of aluminium and demonstrated that quaternary ammonium cations are not always needed to form ionic liquids.

The ionic liquid $AlCl_3$/urea was found to be yellow colored net, deep red color in benzene and of dark green color in toluene[134].

The reaction that occur to produce the aluminium based ionic liquid is:

$$2AlCl_3 + nAmide \longrightarrow [AlCl_2.nAmide]^+ + AlCl_4^-$$

This ionic liquid can be easily handled by adding a layer of hydrophobic liquid on its surface, such as decane. Relatively thick, good adherent coating of aluminium can be obtained by using this ionic liquid [135].

1.7 Parameters effect on surface morphology of Al coatings

It is necessary to explore optimum experimental conditions of aluminium coatings on substrate for industrial application. Consequently, the effect of the main experimental parameters includs:

1.7.1 Temperature

Temperature has a significant impact on the surface morphology of aluminium coatings, so it is necessary to find the optimum temperature that is suitable for metal electrodeposition.

Zheng and co-workers [136] highlighted on the study of the effect of different temperatures on surface morphology of Al coatings. By using 2:1 $AlCl_3$/[AMIM]Cl ionic liquid, smooth, bright, dense deposits were obtained in the range of temperature from 40 to 80 ^{0}C , while the deposits turned dark and poorly adherent at temperature higher than 80 ^{0}C, particularly at 100 ^{0}C. The SEM micrographs shows the deposits produced at 40, 60 and 80 ^{0}C all display homogeneous and dense with spherical particles. By contrast, a relatively rough and incompact surface with large clusters of platy shaped crystals is observed at 100 ^{0}C. A higher temperature up to 80 ^{0}C display a nonuniform distribution of current density and high deposition rate is prone to promote the dendritic growth, which often leads to rough coatings [136].

1.7.2 Current density

Appropriate current density is probably the key to the Al coatings. It has a significant influence on the deposit brightness, thickness distribution, current efficiency and microstructure of electrodeposits.

Zhang and co-workers[137] studied the effect of different current density on the microstructure of Al deposits. They use current density from 8 to 26 mA/cm^2 in 2:1 $AlCl_3$/[BMIM]Cl ionic liquid at 45 ^{0}C. The result showed that the deposits are dense, homogeneous, adherent. Actually, the deposits formed at 14-24 mA/cm^2 were completely bright, smooth, dense, smaller crystallites and thus the optimum current densities were determined to be in this range. Relatively rough surface with large cluster of particles was observed at 26 mA/cm^2. The current efficiency slightly decreased with increase in the current density. As the current density increases, the total charge passed through the cell increases, hence the theoretical amount of deposits also increases. However, the actual weight deposited does not follow a similar trend as that of current density due to the current loss (polarization effects) involved in electrolysis process. Therefore, lower current efficiencies can be attributed to the above phenomena. It should be noted that higher current densities > 26 mA/cm^2 resulted in darker grey deposits with dendritic growth and poor adherence[137]. Jiang and co-workers [138] had investigated the morphology of Al coatings on tungsten and aluminium electrodes from 2:1 molar ratio $AlCl_3$/[EMIM]Cl ionic liquid. They proved that the deposits obtained at lower current densities are quite dense and well adherent to the Al substrates and those obtained at higher current density have dendritic growth with relatively poor adherence. The ionic liquids also became less chemically stable when the electrodeposition was performed at higher current densities. However, the morphology of aluminium deposits was relatively independent on current density at constant temperature, as we say the current density affected morphology of aluminium deposit as a function of temperature [138].

1.7.3 Deposition time

In general, time has a significant influents on the thickness of deposits and effected on the structured and the aggregation of particles and their compaction[139].

To understand the relationship between electrodeposition time and the nominal thickness, Zhang and co-workers [137] had investigated the deposition time from 10 to 60 minutes for 2:1 $AlCl_3$ /[BMIM]Cl at 318k and found that the nominal thickness increased with increasing the deposition time and the grain size increased also.

1.7.4 Molar ratio

The molar ratio of the salts from which ionic liquids are prepared is an important parameter that influences the reactions taking place at the electrodeposition. For example, when the molar ratio of $AlCl_3$ to[BMIM]Cl is 1:1, Al is present almost entirely as $AlCl_4^-$ ions which cannot be reduced, when the molar ratio of $AlCl_3$ to [BMIM]Cl is greater than 1 (Lewis acid), the $AlCl_4^-$ tends to further complex with $AlCl_3$ forming Al_2Cl_7 which is the only reducible aluminium species [140]. Kamavaram and co-workers[141] , highlighted on the study of the effect of molar ratio on surface morphology of aluminium deposit by using different mole ratios of $AlCl_3$ with [BMIM]Cl. It can be seen that with increase in $AlCl_3$ content in the electrolyte, the current density was increased and the amount of deposited aluminium also increased, and the clustering of particles can be seen at higher $AlCl_3$ content.

1.7.5 Diluents

Many groups of researchers had studied the effect of additives on the morphology of aluminium deposits[142-144]. Hussey et al. had investigated the Lewis acidic $AlCl_3$/[EMIM]Cl ionic liquid [>50 mol % $AlCl_3$] and found that aluminium could be electroplated from the neat liquid, but the quality of the electrodeposit is greatly enhanced by adding benzene as a co solvent [144].

Abbott and co-workers[145] studied the addition of 18% toluene to $AlCl_3$/[BMIM]Cl ionic liquid which caused an increase in the charge associated with both the deposition and stripping processes which showed that mass transport may have an effect on metal growth rates. The addition of toluene decreased metal concentration and viscosity. Hence, diluents could have two effects: first they will cause a decrease in solution viscosity and metal concentration; second is the change in speciation.

1.7.6 Water content

The influences of water content was studied in the BMP-TFSI melts containing aluminum chloride hexahydrate. With adding the hydrate, a new reduction wave appeared in cyclic voltammograms at the potential range more positive that for the aluminum deposition. As the concentration of water increased, the peak current density of this cathodic peak became higher. The peak current for the aluminum deposition became lower with the water content. These results indicated that water in the melt prevented the electrodeposition of aluminum, while, the aluminum could be deposit from BMP-TFSI melt under an argon atmosphere[146].

1.8 Techniques of topographic and morphology study

1.8.1 Atomic Force Microscopy (AFM)

AFM used to measure the topography for the surface of the sample by producing a 3D image at magnifications over one million times giving much more topographical information than optical microscopes. It works by scanning an extremely fine probe on the end of a cantilever across the surface of material. The AFM tip gently touches the surface and records the small force between the probe and the surface, Figure (1-7).[147-149]

There is a renewed interest in the study of surface roughness. Nanda and co-workers 1998[150] investigated the relationship between roughness and thickness of the surface of sample and found that roughness depends on the thickness of the surface. As the thickness of a sample increases, the roughness increases.

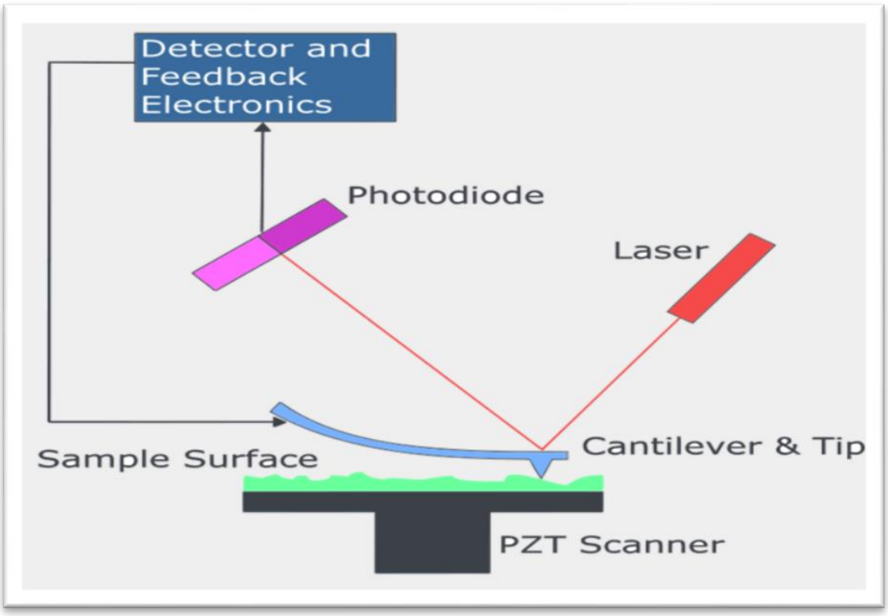


Figure (1-7): Block diagram of atomic force microscope using beam deflection detection.

1.8.2 Scanning Electron Microscopy (SEM)

SEM used instead of optical microscopes for micro- and nanoscale. Electron microscopes used electrons instead of photons, because electrons have a much shorter wavelength than photons and so allow observing matter with atomic resolution. Signals produced by SEM result from interactions of the electron beam with atoms at or near the surface of the sample, include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light (cathodoluminescence), specimen current and transmitted electrons as shown in Figure (1-8).

By detection of secondary electron, SEM can produce vivid images of a sample surface (secondary electron image SEI), with superior resolution about 1 to 5 nm. Due to the relative narrower electron beam, SEM has a much greater depth of field than TEM, thus yielding a characteristic three-dimensional appearance useful for investigating the surface of objects which have a complicated topography.

Characteristic X-rays are emitted as the electron beam removes an inner shell electron from the sample, causing a higher energy electron to fill the shell and release energy. These X-rays can be used to identify and quantitatively determine the elements in samples[151].

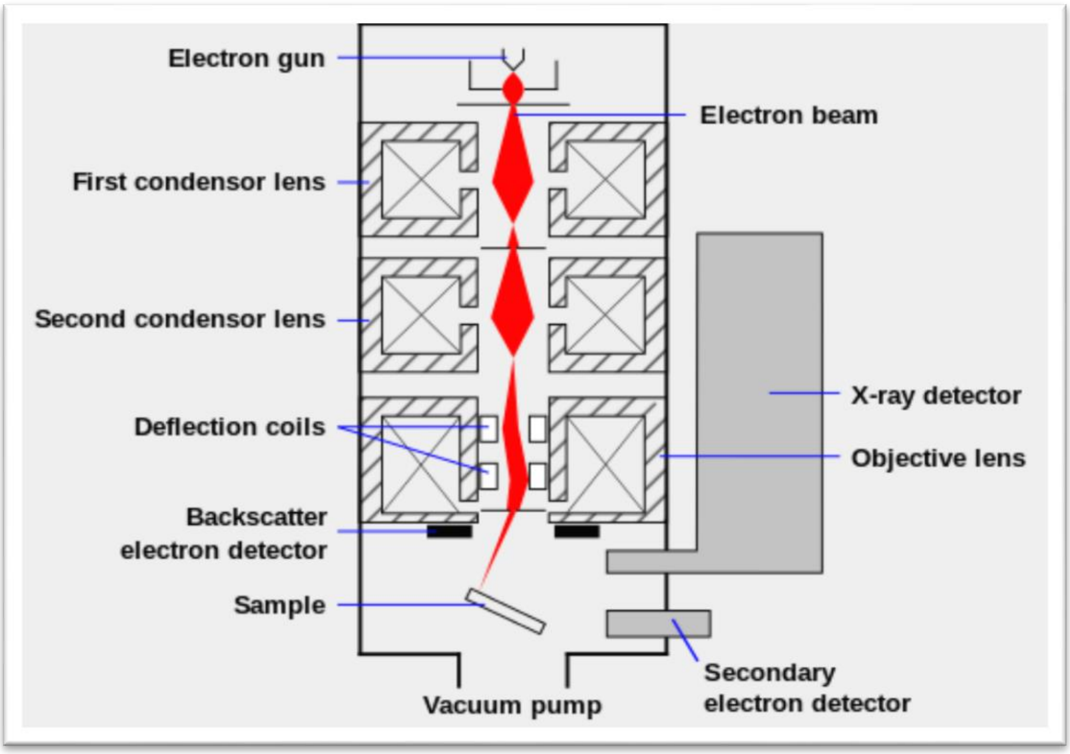


Figure (1-8): Schematic of an SEM illustrates the stages of signal production.

1.9 Aim of The Present Work.

1. Preparation of $AlCl_3$/Urea room temperature ionic liquid which does not need an organic cation.

2. Electrolytic deposition of aluminium metal on copper from $AlCl_3$/Urea ionic liquid.

3. Investigating the effect of changing parameters such as, temperature, mole ratio, potential and deposition time on the morphology of the expected deposited aluminium on copper substrate with the aid of Scanning Electron Microscopy, Atomic Force Microscopy , Energy dispersive x-ray analysis EDAX.

Chapter 2

Experimental Part

Chapter two

Experimental part

2.1 Chemicals.

All chemicals were used with the most available purity without further purification. Table (2-1) shows the reagents, their purities and suppliers.

Table (2-1): ***The chemicals used in this work with their purities and suppliers.***

No.	Chemical compounds	Formula	Purity %	Company
1	Anhydrous aluminum chloride	$AlCl_3$	99.5	BDH
2	Acetone	CH_3COCH_3	99.5	Thomas Baker
3	Decane	$CH_3(CH_2)_8CH_3$	99.5	Fluka
4	Paraffin oil	C_nH_{2n+2}		
5	Propan-1-ol	$CH_3CH_2CH_2OH$	99.5	BDH
6	Toluene	$C_6H_5CH_3$	99.5	BDH
7	Urea	NH_2CONH_2	99.5	Thomas Baker
8	Sodium Hydroxide	NaOH	99	BDH
9	Hydrochloric acid	HCl	37	BDH

2.2 Practical Methods.

2.2.1. Preparation of Aluminum chloride- Urea ionic Liquids:

Anhydrous aluminium chloride and urea were utilized to prepare the chloroaluminate ionic liquids in different mole ratios which are within 2:1 to 1:1 mole ratios to insure the formation of the ionic liquids[135].

Two procedures were used to prepare the ionic liquid:

1- First method consist of mixing the salts in presence of an inert organic solvent like toluene. This was carried out by weighting a proper amount of the salts, each one separately and a volume of toluene to make the right volume percentage with ionic liquid. Aluminium chloride was added to a reaction tube containing toluene. Then the weighted urea was added incrementally to the reaction tube, when color changed from color less to green color and the consuming of aluminum chloride and urea indicating the reaction of urea with aluminum chloride forming ionic liquid. This was continued until no further urea or aluminum chloride was left in the reaction tube.

2- Second method was made inside a schlenk tube under nitrogen gas using a glove box as shown in Figure (2-2). A small portion of aluminium chloride (pre-weighted) was introduced inside the reaction tube and then a little amount of uncrushed urea was added and stirred with a glass road. When ionic liquid was formed then additional portions were added until both salts were consumed. Un immediate elevation in temperature was noticed when salts reacted which was reported to be 75 ^{0}C [20]. The liquid was left to cool to room temperature producing clear, yellow colored and free flowing liquid. A layer of decane can be added on the top of the liquid to protect the top layer from air.

Figure (2-1): The glove box under nitrogen gas.

After that the ionic liquids produced from both procedures were kept in a sealed tube and wrapped by para film for experiments.

2.2.2. Pre-treatment of cathode and anode.

In electroplating experiments, a cathode copper metal sheet of ($60mm^x10mm^x1mm$) with an immersed part of 20mm length in ionic liquid, and an anode of aluminium mesh with (30mm diameter) were used. The cathode was rubbed with sand paper followed by rinsing with deionised water, then plunged into 0.5% HCl, rinsed with deionized water then immersed in 0.5% NaOH, rinsed with deionized water and acetone sequentially. The anode was abraded with iron brush followed by rinsing with deionized water, dipped it into 0.5% HCl, deionized water, 0.5% NaOH, deionized water and finally rinsed with acetone.

2.2.3. Post-treatment of specimens

The specimen when removed from the ionic liquid was directly treated by dipping it in toluene until all ionic liquid was removed and then rinsed with n-propanol, acetone respectively and finally dried and stored for further analyses.

2.3 Instruments.

2.3.1. Scanning Electron Microscope (SEM)

The surface morphology of specimens of aluminium coatings on copper surfaces was investigated by using a high-resolution field emission scanning electron microscopy (INSPECT S50). The measurements were carried out in the laboratories of department of physics /college of science /Al-Nahrain university.

2.3.2. Energy dispersive X-ray analysis (EDAX)

The (X Flash 6110) Bruker EDX was used in conjunction with SEM. This was used to determine the composition of samples surface. This was carried out in the laboratories of department of physics / college of science / Al-Nahrain university.

2.3.3. Atomic force microscopy (AFM)

The surface topography of samples was analyzed by atomic force microscopy (AFM) (AA2000, Angstrom Advanced Inc.) contact mode. These were carried out in the laboratories of department of chemistry / college of science / Al-Nahrain university.

2.3.4 Microscope

The (OLYMPUS BX 51-P POLARIZING MICROSCOPE) was used for visual observation. This was carried out in laboratories of department of engineering mechanics / college of science / Al-Nahrain university.

2.4 The Electrochemical cell deposition process.

The (Thurlby 15V-4A, England) power supply was used to control the current and the potential of electrodeposition process as shown in Figure (2-2).

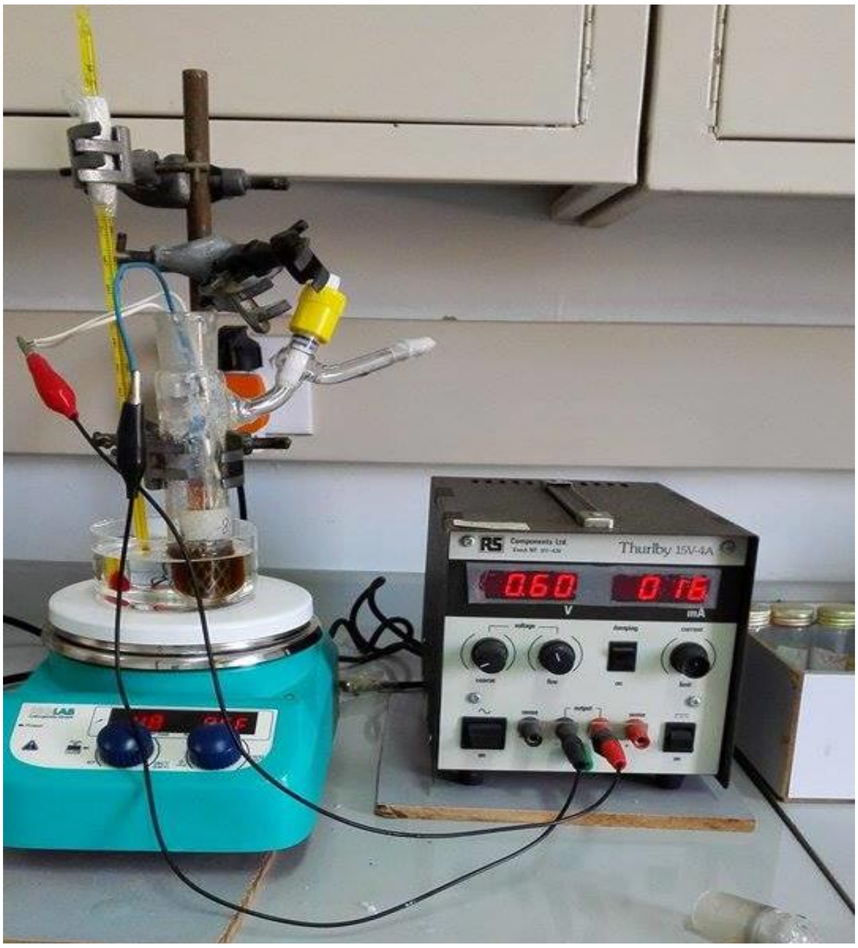


Figure (2-2): Electrochemical cell used for Al electrodeposition.

Chapter 3

Results & Discussion

Chapter Three

Results &Discussion

3.1 Preparation of Aluminum Chloride-Urea Ionic Liquid.

Aluminium chloride-Urea ionic liquid was prepared in this work by two methods:

The first was by slowly mixing aluminium chloride with urea in a schlenk tube under nitrogen gas to form portions of ionic liquid with different mole ratios. The addition of urea to aluminium chloride caused the formation of a yellow liquid which reported to contain the cationic species $[AlCl_2.n\ Urea]^+$ and the anionic species $AlCl_4^-$ as illustrated in the following equation [20]:

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

The aluminium chloride and urea were found to reacted immediately due to the strong Lewis acid nature of aluminium chloride with the Urea as Lewis base. They reacted exothermically without external heating and the mixture was hot which reach a temperature around 75 ^{0}C [20]. The liquid, at the end of preparation, was left to cool gradually to room temperature producing transparent, yellow colored, free flowing liquid as shown in Figure (3-1).

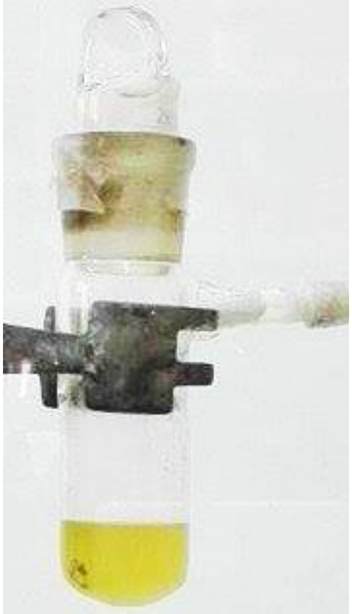


Figure (3-1): Optical photograph of $AlCl_3$/urea neat ionic liquid.

The produced ionic liquid was found to be relatively insensitive to air when compared with other chloroaluminate ionic liquid such as $AlCl_3$:Imidazolium salts or pyridinium [145] that immediately reacted when exposed to air. The prepared liquid has a density of 1.4 g cm^{-3} with a conductivity of 0.804 ms cm^{-1}, viscosity of 60 cp at 25 ^{0}C and a glass transition temperature around -63 ^{0}C and thermally stable up to 100 ^{0}C [20]. Although the liquid is less sensitive to air, it was covered with a layer of Decane to prevent it from direct contact reaction with air [135]. This ionic liquid was shown to be a suitable medium for electrodeposition of aluminium and demonstrated that quaternary ammonium cations are not always needed to form ionic liquid[20].

A second method was used to prepare the same aluminium chloride / urea ionic liquid in the diluent, such as toluene. A different mole ratios of the salts (from 1:1 to 2:1) and different volume ratios of toluene (20, 25, 30, 35, 40, 50, 60, 70, 75V%) were prepared and the 2:1 mole ratio ($AlCl_3$/Urea) diluted with 35v% toluene and 1.6:1 mole ratio $AlCl_3$ / Urea also diluted with 35v% toluene were used in this work for electrodeposition of aluminium. Toluene as a diluent did not react with /or dissolve aluminium chloride or urea [152]**.** This made the preparation of the aluminum chloride / urea ionic liquid safer, since toluene would work as a protector for the unreacted salt and as a diluent to the ionic liquid because aluminium chloride and its ionic liquids known to be sensitive to air moisture or water. This method afford toluene as a reaction medium and it helped to disperse the heat that released from the exothermic reaction usually evolved from direct mixing of the reactant, thereby preventing the ionic liquid from overheating. This would also prevent the formation of hot spots area which could burn some of ionic liquid and there by forming impurities by undesirable decomposition reaction.

It is worthy to know that this type of preparation is not necessarily successful with other reactant or other medium as a protective layer to the medium on the surface of reactant particles that could prevent the reactant to commence a reaction. This could occur if the medium is viscous enough to make a protective layer on the surface of the reactant particles preventing the contact needed to commence the reaction within the time limit needed for such reaction particularly when a solid-solid reaction is to be carried out.

Toluene interacted with the ionic liquid indicated by changing it from faint yellow to dark green color as shown in Figure (3-2). The color change to green of ionic liquid in presence of toluene was studied by UV-Visible recently[152] and related to a coordination interaction between aluminium cation and the lone pair of the benzene ring of toluene. This is therefore expected to give different color change if ionic liquid is prepared in different diluent, particularly if the solvent provide a lone pair to interact with aluminium cations and the absorption is within the visible region.

Figure (3-2): Optical photograph for ionic liquid 2:1 mole ratio diluted with 35v% of toluene.

3.2 Pretreatment of the cathode.

Pretreatment of copper substrate is a common procedure to obtain a successful coating. Copper is fast to be oxidized under the existence of oxygen and moisture. It form a type of rust known as copper oxide. So the pretreatment is very important to reduce impurities and oxide from the surface as shown in the experimental part. An electrochemical pretreatment is important in order to strengthen the adherent of Al on the surface of cathode [153] as was observed in this work by reverse polarization at -1V for 2 minutes. This protocol was found to reduce the impurities from the surface of cathode which dissolved in the ionic liquid with a very thin layer of copper. Hence, the surface of cathode became clean and ready for electrodeposition process with expected good adherence of coated metal on the surface.

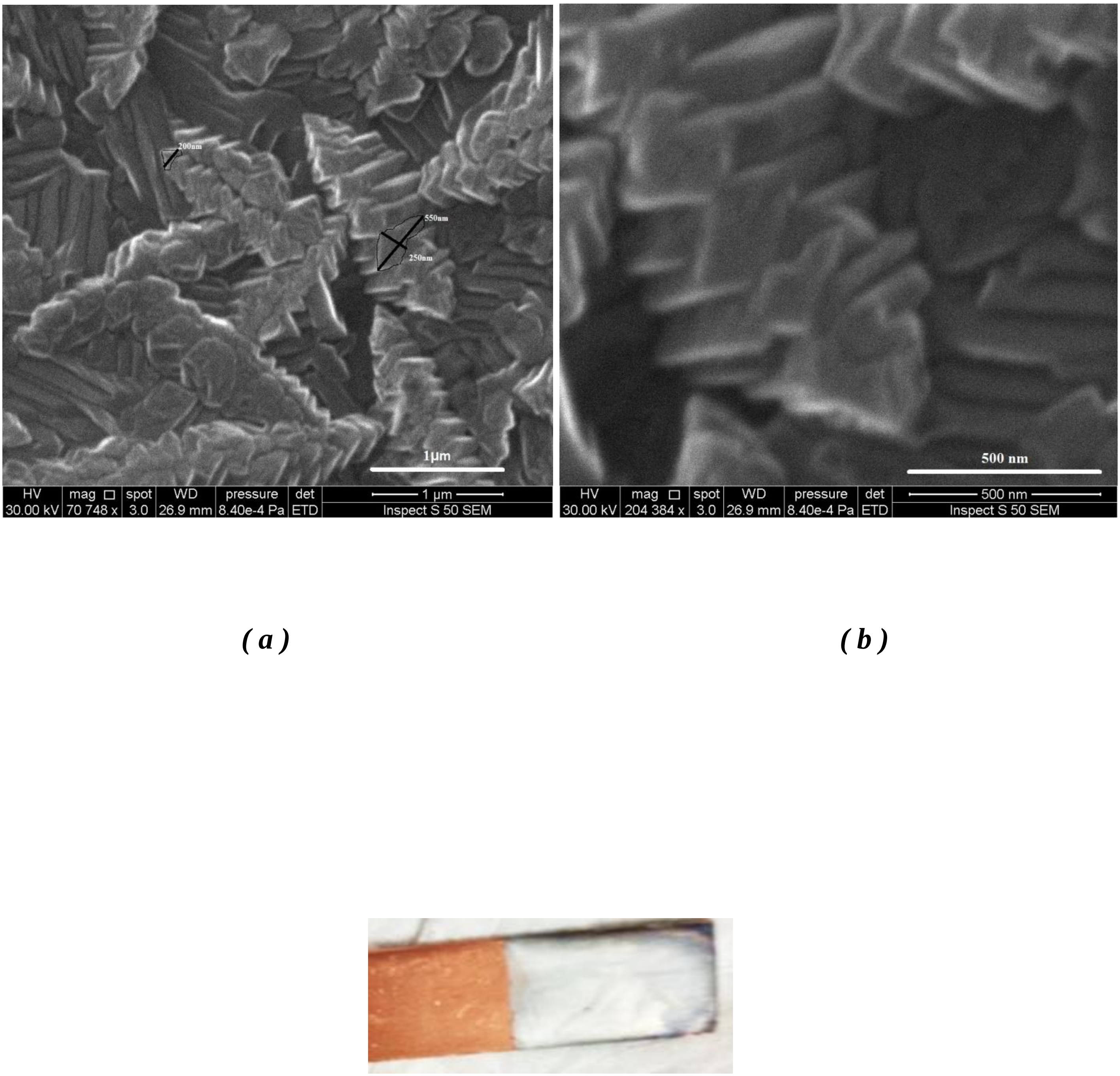
3.3 The effect of electrolyte mole ratio on the morphology of deposited aluminium.

Ionic liquids of the mole ratios 1.6:1 and 2:1 $AlCl_3$:Urea were used for electrodeposition of aluminium metal on copper substrate. Both ratios were diluted with 35v% toluene to insure fast mobility and expected better coating[140] as free movement of ions could influence the rate of deposition. The electrodeposition were conducted at a potential of -0.6V for 2 hours at 25 ^{0}C. The appearance of coated aluminium on the cathode was silvery white from both mole ratios as shown in the corresponding optical photograph of the samples in Figure 3-3(c) and Figure 3-4(c). The electrodeposited layer of aluminium from both experiments were well adhered to copper with smooth texture.

Current densities were found to follow the aluminium chloride concentration in ionic liquid as it was found to be 6.6 mA/cm^2 in 1.6:1 mole ratio, while it increased to 10 mA/cm^2 in 2:1 mole ratio due to the increase in the reducible aluminium cation concentration in the electrolyte [140]. It was reported that on increasing the concentration, the cathodic polarization decreases due to the decrease in the thickness of the diffusion layer at the cathode. An increase in the concentration of ions at the cathode favors growth of the existing layer of the deposit and hence, resulting in the formation of larger amount of coated aluminium [140].

Scanning Electron Microscopy of coated aluminium samples from both mole ratios of ionic liquids is presented in Figure (3-3) and (3-4) at different magnifications.

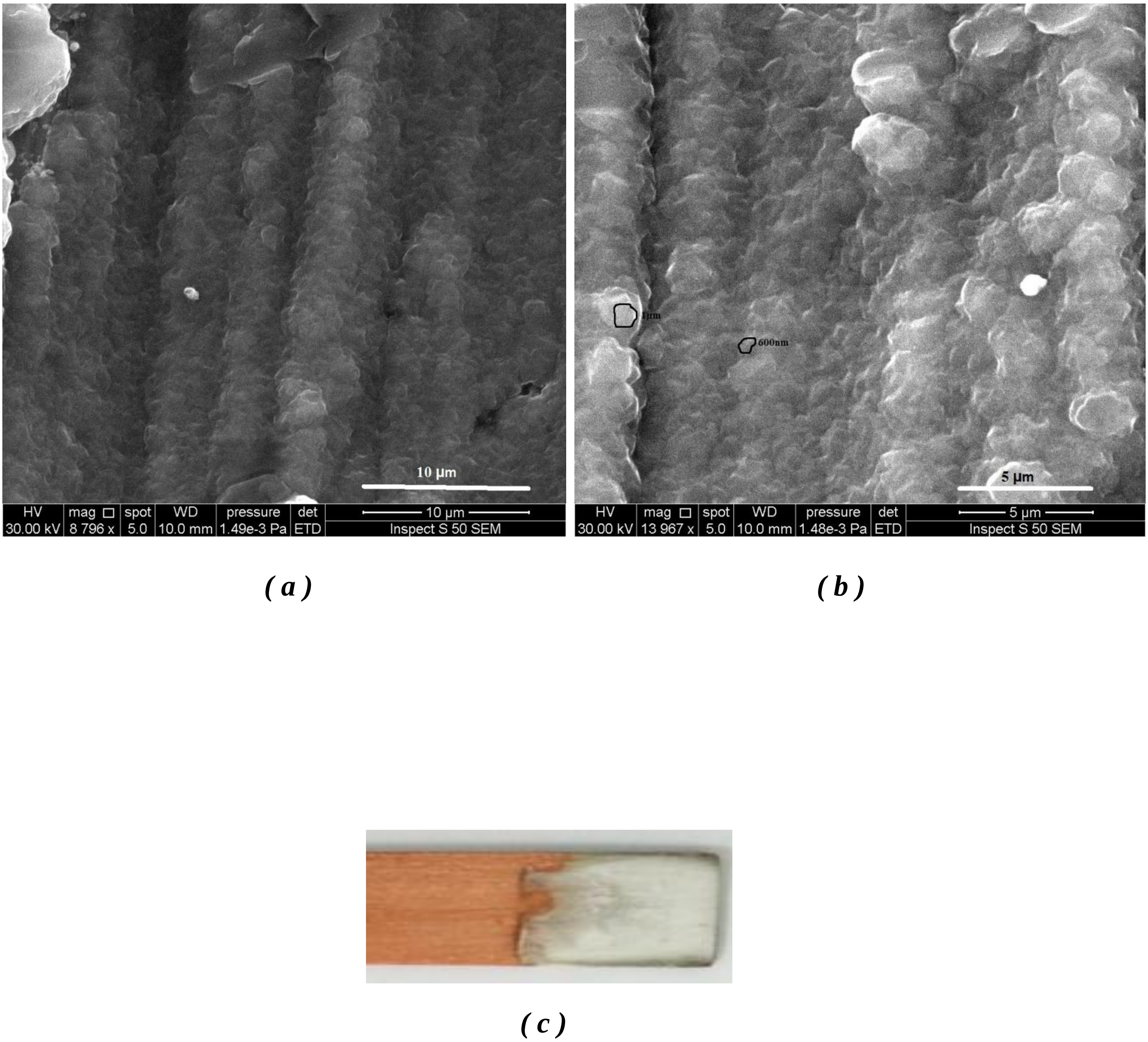
Deposited aluminium particles took the form of a leaf dendritic shape with particle size ranged between 200nm-550nm deposited from the 2:1 mole ratio, Figure (3-3). However, a relatively larger particle size of aluminium with 600nm-1000nm were obtained with an oval shape arranged in chips lines, Figure (3-4). these differences might be related to the concentration effect of ionic liquid probably influence the polarization at the double layer of the cathode.



(a) *(b)*

(c)

Figure (3-3): SEM images of aluminium deposited from 2 AlCl$_3$: 1Urea diluted with 35v% of toluene at - 0.6V, 2 hours at room temperature and under statistic air, (a) Magnified at 70748x, (b) Magnified at 204384x, (c) The corresponding optical photograph of the deposited aluminium on copper substrate.



(a) *(b)*

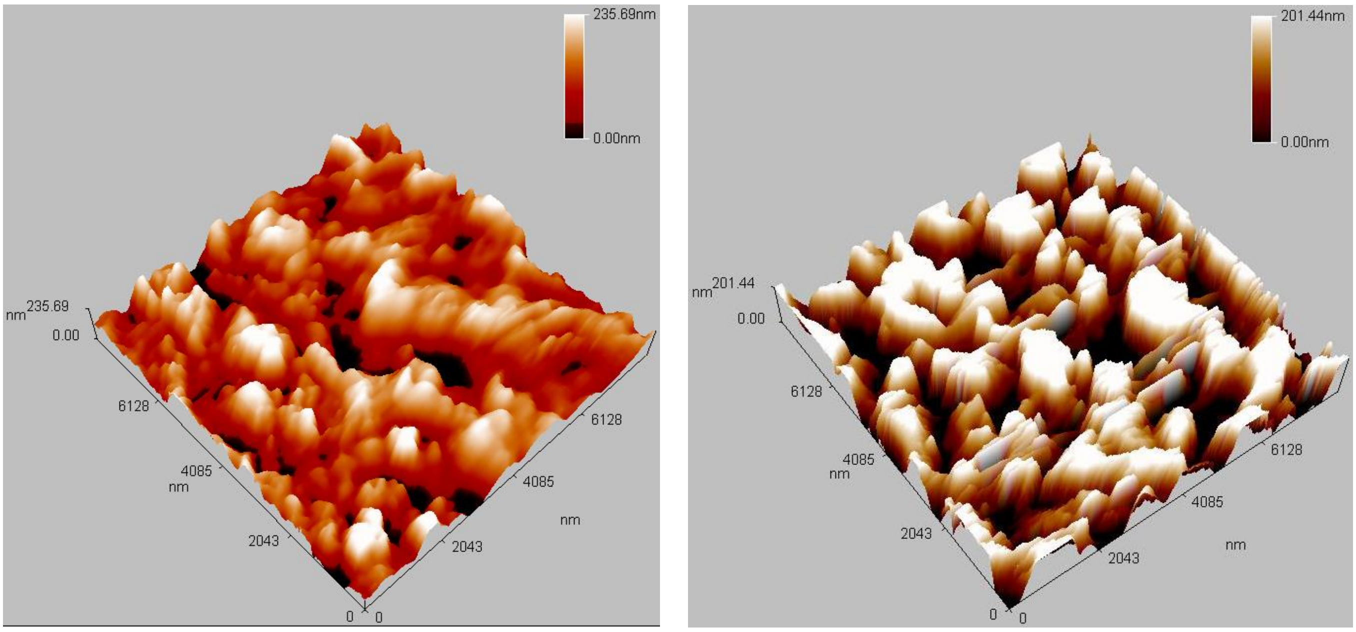
(c)

Figure (3-4): SEM images of aluminium deposited from 1.6$AlCl_3$: 1Urea diluted with 35v% of toluene, at - 0.6V, 2 hours at room temperature and under statistic air, (a) Magnified at 8796x, (b) Magnified at 13967x and (c) The corresponding optical photograph of the deposited aluminium on copper substrate.

AFM images and data of the coated aluminium samples are presented in Figure (3-5) and Table (3-1) respectively. The average height and roughness of coated aluminium crystals have a higher value in 1.6:1 mole ratio than in 2:1 mole ratio ionic liquids. It can also be noted that the increase in current density from 6.6 mA/cm^2 to 10.0 mA/cm^2 for both mole ratio associated with an increase in the amount of electrodeposited aluminium as indicated in the increased percentage of Al from (72.2 At. %) in 1.6:1 mole ratio to (95 At. %) in the 2:1 mole ratio. This follows a normal increase in the rate of reaction with increasing concentration of present aluminium cations that are available in higher concentration in the larger ionic liquid mole ratio (2:1).

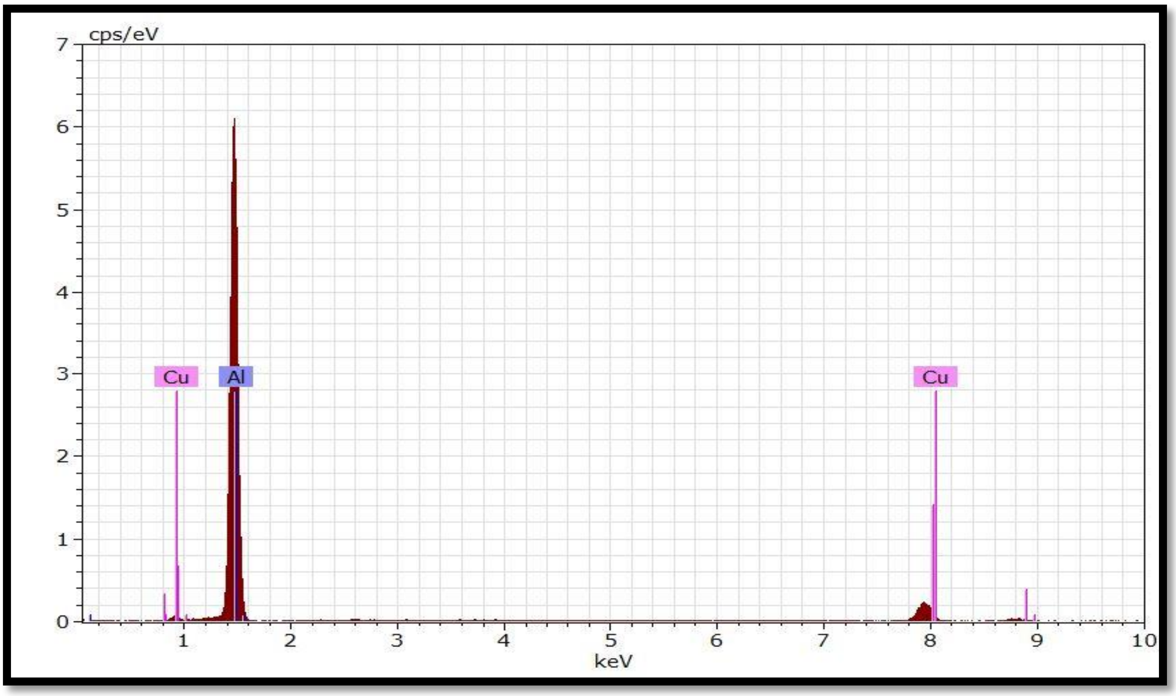
From EDAX spectra Figures 3-6 (a) and (b) revealed that there is consensus between the results of deposited aluminium percentage and the EDAX spectra, the peak of copper metal from 2:1 mole ratio is smaller compared with the peak from 1.6:1 mole ratio, this agree with the large percentage of deposited aluminium from 2:1 mole ratio (95 At. %) compared with (72.2 At. %) from 1.6:1 mole ratio.

This normal increase in deposited aluminium and increasing current densities with increasing aluminium mole ratio were also reported in $AlCl_3$/[BMIM]Cl ionic liquid [141] .

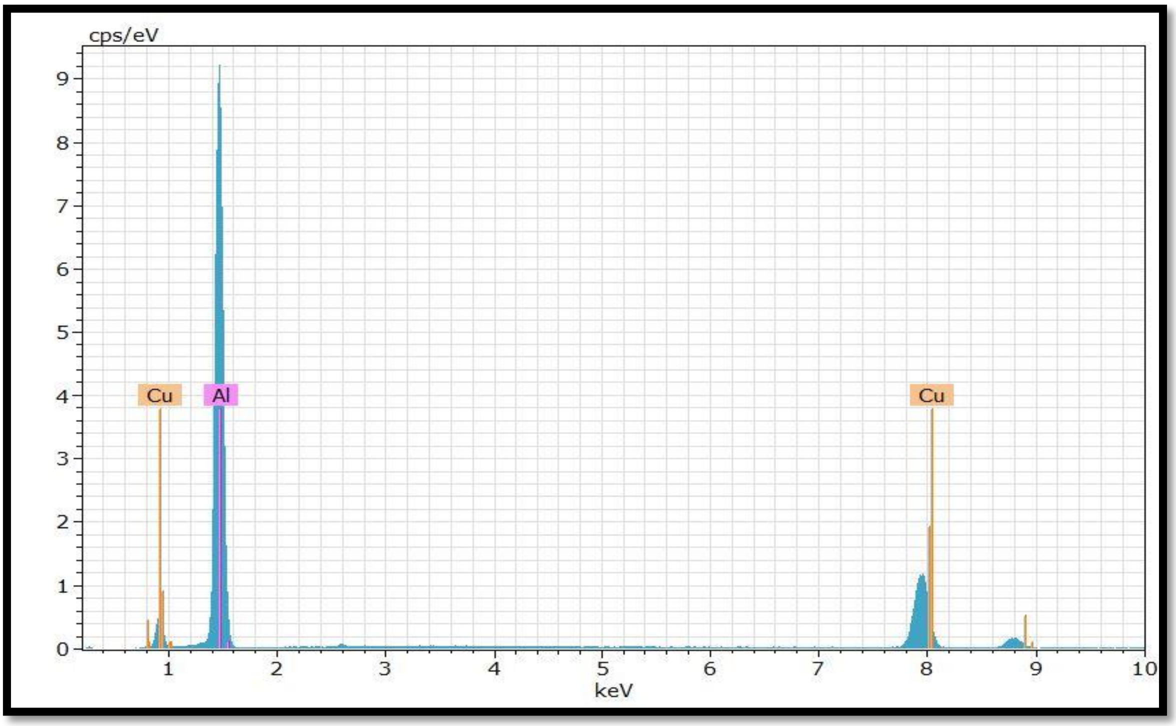


(a) 2:1 mole ratio ***(b) 1.6:1 mole ratio***

Figure (3-5): AFM images (contact mode)of aluminium deposited (a) from 2:1 mole ratio $AlCl_3$:Uere ionic liquid,(b) from 1.6:1 $AlCl_3$:Urea ionic liquid, both diluted with 35v% of toluene, at - 0.6V, 2 hours at room temperature and under statistic **air.**



(a)



(b)

Figure (3-6): EDAX spectra of deposited aluminium (a) from 2:1 mole ratio $AlCl_3$:Uere ionic liquid,(b) from 1.6:1 $AlCl_3$:Urea ionic liquid.

Table (3-1): Grain number, roughness, average size, average height, % of Al coating and particle size of electrodeposited aluminium at different mole ratio $AlCl_3$/Urea ionic liquid diluted with 35v% of toluene, E=-o.6V and 2 hours at room temperature under statistic air.

No.	**Mole ratio**	**Total grain**	**Roughness (Ra) [nm]**	**Avg. size[nm^2]**	**Avg. Height [nm]**	**% of Al from EDAX**	**Particle size [nm]**
1	2:1mole ratio diluted with 35v% of toluene	224	46	147806	69	95	200-250
2	1.6:1 diluted with 35v% of toluene	223	62	145975	80	72.2	600-1000

3.4 Effect of temperature on the morphology of deposited aluminium.

Temperature is reported to have an impact on the surface morphology of aluminium coatings from chloroaluminate ionic liquid [136], so it was useful to study the temperature effect on electrodeposition of aluminium in this ionic liquid.

The effect of a temperature range from (20 - 60) ^{0}C on surface morphology of copper cathode was investigated using 1.3:1 mole ratio $AlCl_3$/Urea net ionic liquid covered with Decane. All experiments were carried out for 1.5 hour at -0.6V under statistic air. Figure (3-7) shows the variation in current density obtained as a function of temperature, which increases with increasing temperature.

The current densities obtained from these experiments were lower than 14-24 mA/cm^2 reported by Zhang and co-workers **[137]** to give a bright appearance of electrodeposited aluminium from 2:1 $AlCl_3$/[BMIM]Cl ionic liquid. The differences might be related to different viscosities of both ionic liquids [compare 60 cp for $AlCl_3$/Urea with 19 cp for $AlCl_3$/[BMIM]Cl ionic liquid]. Temperatures would influence physical properties of the electrolyte, such as conductivity. Electrical conductivity increases with increasing the temperature due to lowering the viscosity of the electrolyte and hence the mobility of the ions increases which would cause an increase in rate of reaction**[136]**.

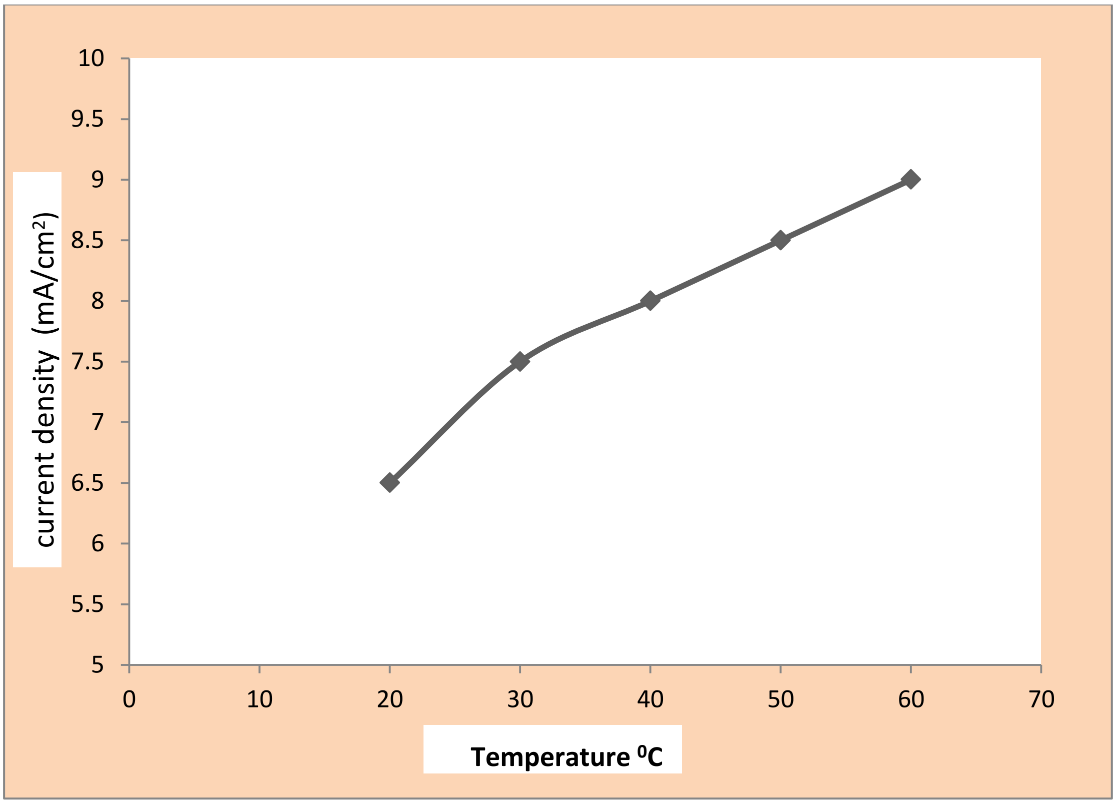


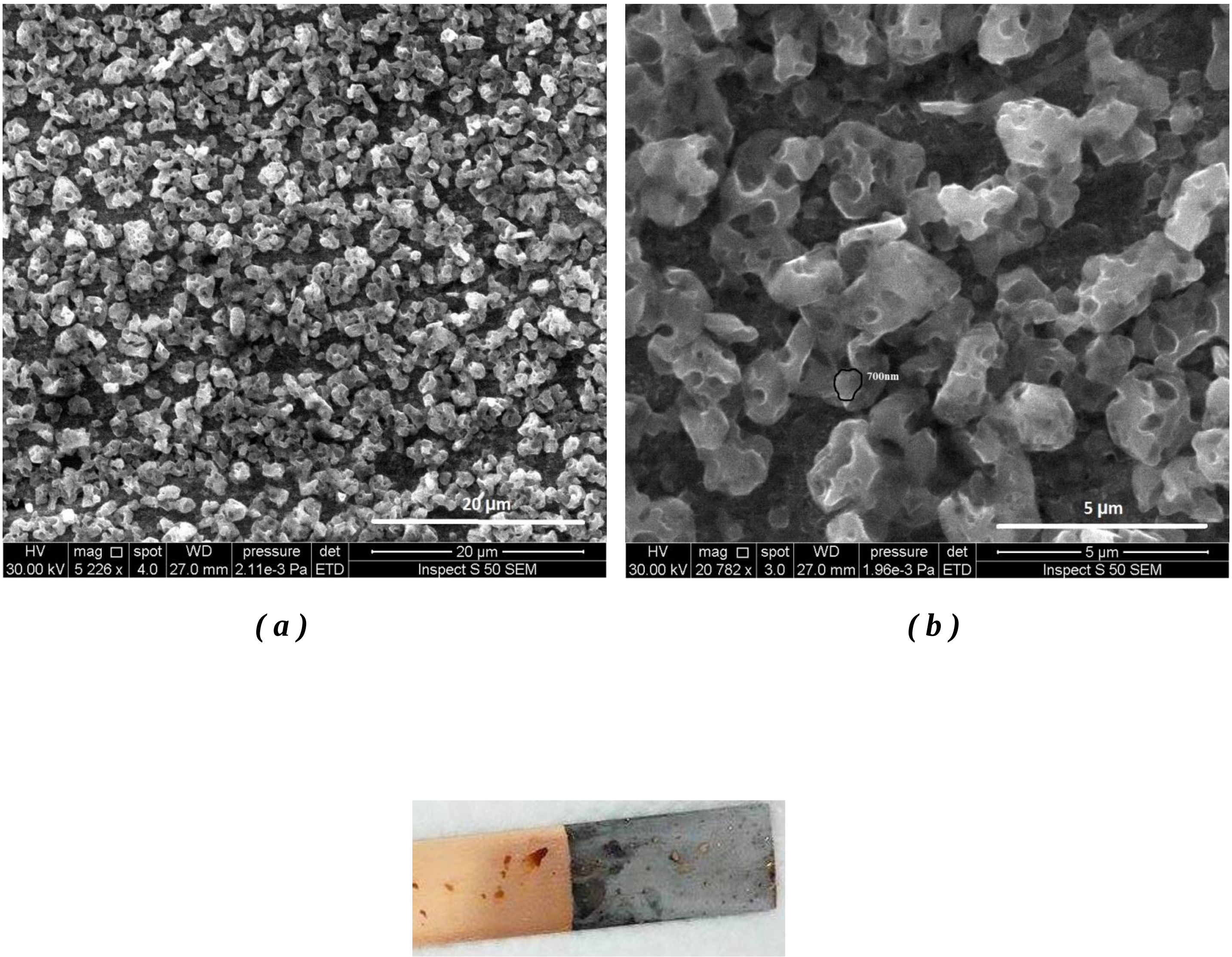
Figure (3-7): Relation between temperature and current density of aluminium deposited from 1.3:1 mole ratio $AlCl_3$:Urea ionic liquid for 1.5 hour, at -0.6V and different temperature under statistic air.

The shape of particles and appearance of deposited aluminium on the surface of copper cathode were found to be non-identical and affected by changing temperature.

The shape of particles is sand like at 20 ^{0}C, Figure (3-8), while at 30 ^{0}C the shape was flak, Figure (3-9), both were compact and smooth metallic coating and well adhered to copper substrate.

However aluminium changed its shape to less compact coating of needles and flaks at 40 ^{0}C, Figure (3-10), while a net of needles was formed at 50 ^{0}C, Figure (3-11) and a sponge with needles at 60 ^{0}C, Figure (3-12). All are smooth coating and well adhered to copper. The latter was characterized with holes surrounded by metallic aluminium coating.

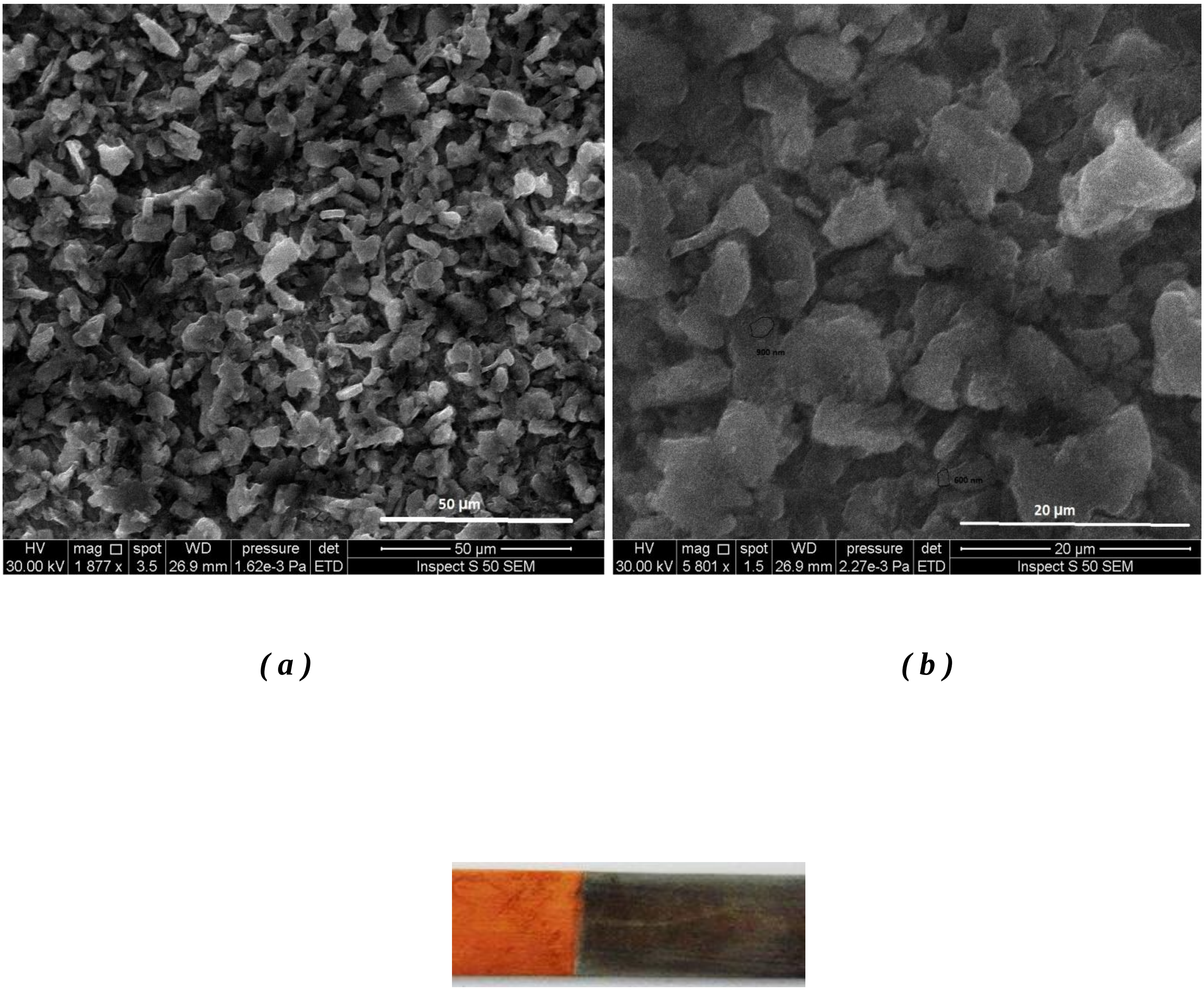
From the corresponding optical photograph of deposited aluminium on the copper cathode at different temperatures, it was found that the appearance of coated aluminium was silvery white at 20 ^{0}C , silvery at 30 ^{0}C, silvery gray at 40 ^{0}C, gray at 50 ^{0}C and was darker gray at 60 ^{0}C. This was associated with changes in the shape of particles and hence changed in the reflection of light. The more hole spaces between the particles made scattering of the light and thereby reducing the reflection of light and the appearance of deposited aluminium becomes more darker as shown in samples at 40, 50 and 60 ^{0}C with less dense and dull appearance. In contrast, more dense and less hole spaces between the particles made the appearance of deposited aluminium more brighter as in samples at 20 and 30 ^{0}C.



(a) *(b)*

(c)

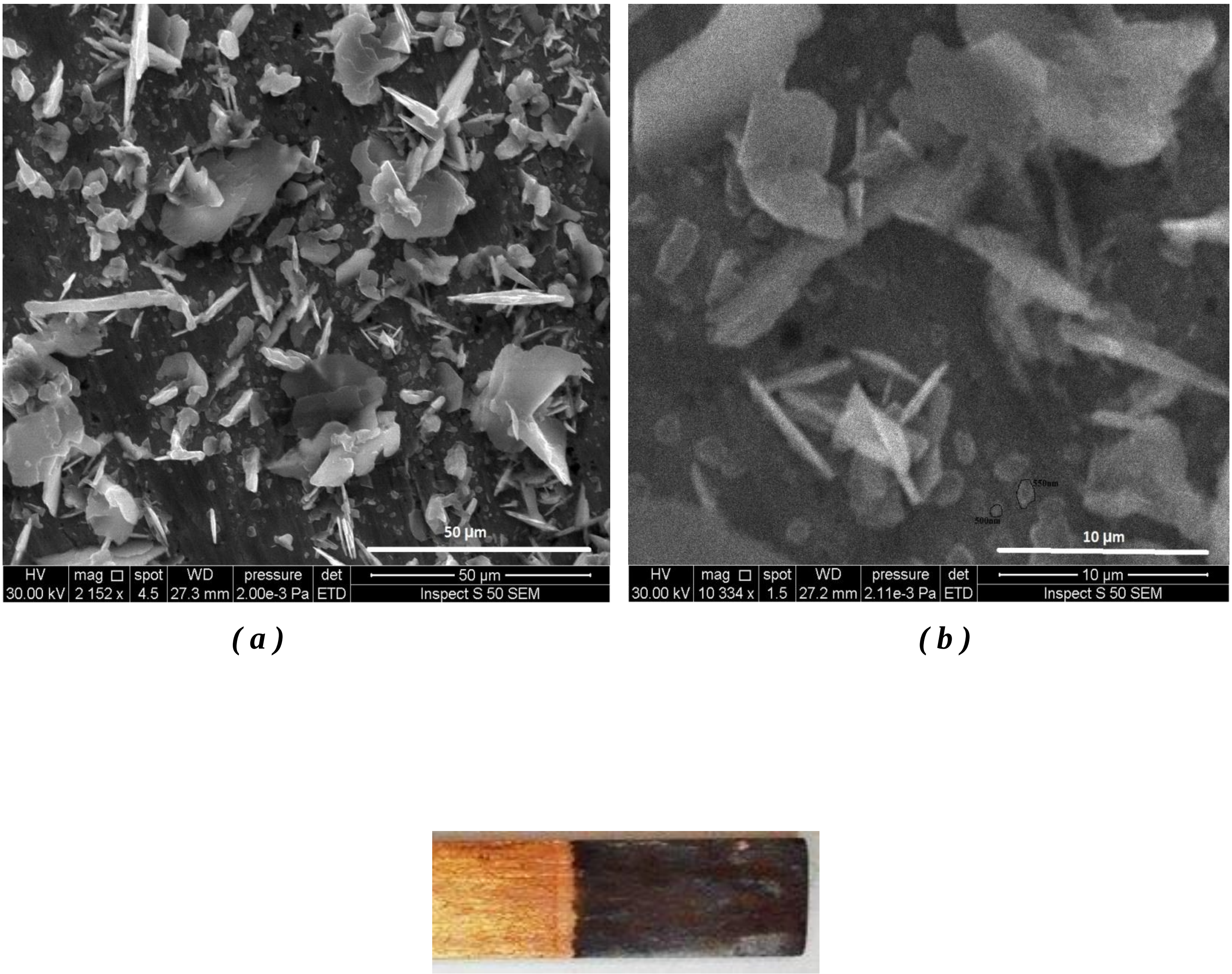
Figure (3-8): SEM images of aluminium deposited from 1.3:1 mole ratio $AlCl_3$:Urea ionic liquid at 1.5 hour, -0.6V, 20 ^{0}C and under statistic air, (a) Magnified at 5226x, (b) Magnified at 20782x and (c) The corresponding optical photograph of the deposited aluminium on copper substrate.



(a) *(b)*

(c)

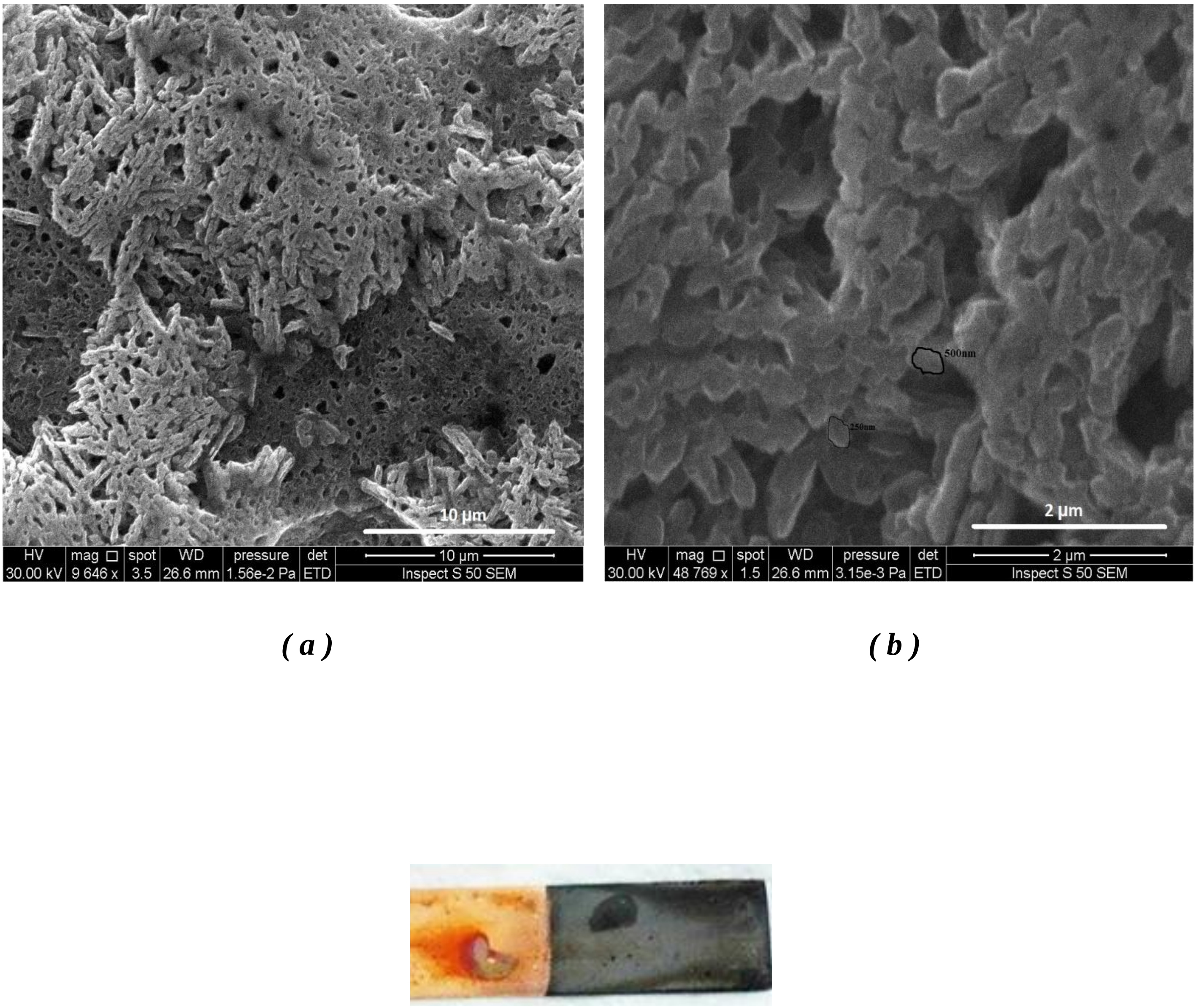
Figure (3-9): SEM images of aluminium deposited from 1.3:1 mole ratio $AlCl_3$:Urea ionic liquid at 1.5 hour, -0.6V, 30 ^{0}C and under statistic air, (a) Magnified at 1877x, (b) Magnified at 5801x and (c) The corresponding optical photograph of the deposited aluminium on copper substrate.



(a) ***(b)***

(c)

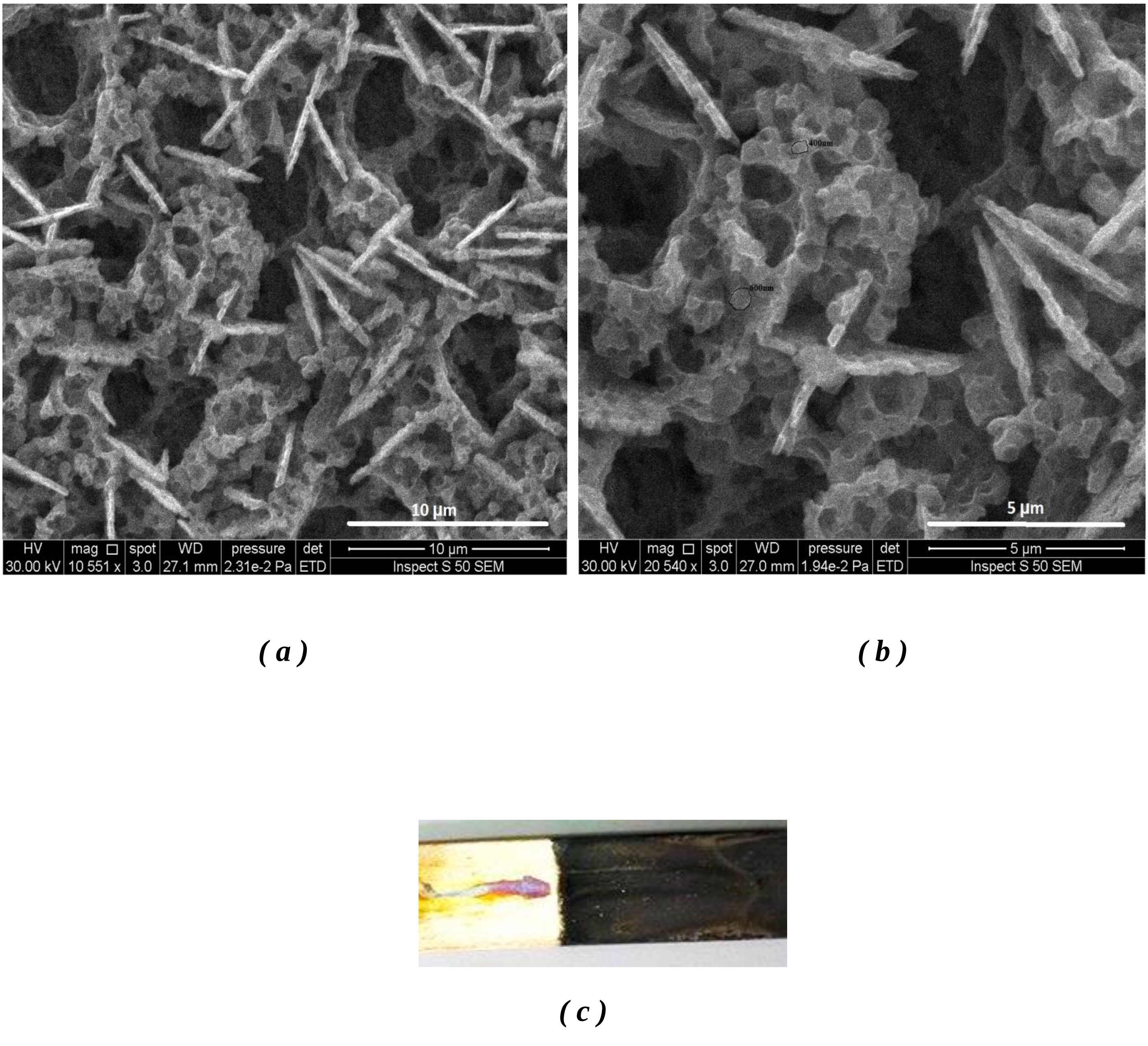
Figure (3-10): SEM images of aluminium deposited from 1.3:1 mole ratio $AlCl_3$:Urea ionic liquid at 1.5 hour, -0.6V, 40 ^{0}C and under statistic air, (a) Magnified at 2152x, (b) Magnified at 10334x and (c) The corresponding optical photograph of the deposited aluminium on copper substrate.



(a) ***(b)***

(c)

Figure (3-11): SEM images of aluminium deposited from 1.3:1 mole ratio $AlCl_3$:Urea ionic liquid at 1.5 hour, -0.6V, 50 ^{0}C and under statistic air, (a) Magnified at 9646x, (b) Magnified at 48769x and (c) The corresponding optical photograph of the deposited aluminium on copper substrate.



(a) ***(b)***

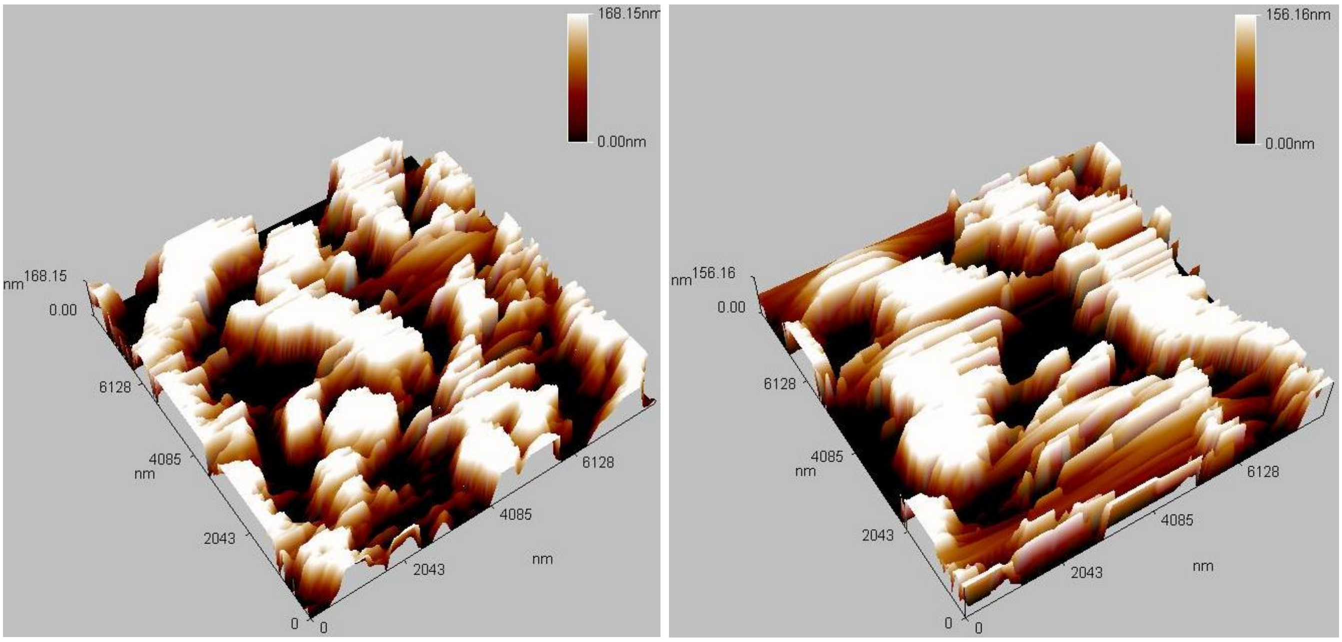
(c)

Figure (3-12): SEM images of aluminium deposited from 1.3:1 mole ratio $AlCl_3$:Urea ionic liquid at 1.5 hour, -0.6V, 60 ^{0}C and under statistic air, (a) Magnified at 10551x, (b) Magnified at 20540x and (c) The corresponding optical photograph of the deposited aluminium on copper substrate.

AFM images and data are presented in Figure (3-13) and Table (3-2) respectively. The data were inconsistent with temperature (total grain and roughness) except the average height of the coated particles increased gradually with temperature (20 to 50 ^{0}C) from 123 nm to 139 nm respectively, but showed a jump from 139 nm at 50 ^{0}C to 152 nm at 60 ^{0}C.

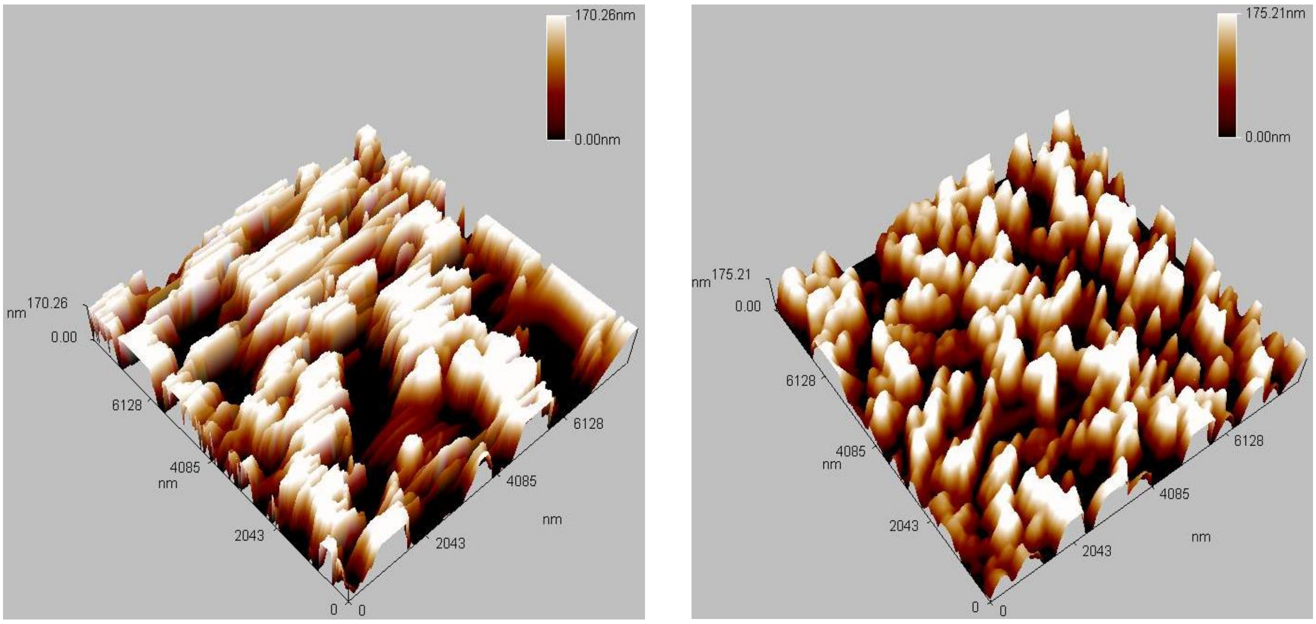
The amount of aluminium adhered coating on copper increased from (20 to 50) ^{0}C as shown in Table (3-2) from (55 At. % at 20 ^{0}C to 91 At. % at 50 ^{0}C), but at 60 ^{0}C when the percentage of aluminium dropped from (91 At.% at 50 ^{0}C to 82 At.% at 60 ^{0}C).

The size of particles ranged from (600-900 nm) at 20 ^{0}C, (500-700 nm) at 30 ^{0}C , (450-650 nm) at 40 ^{0}C, (250-500 nm) at 50 ^{0}C and (400-600 nm) at 60 ^{0}C.

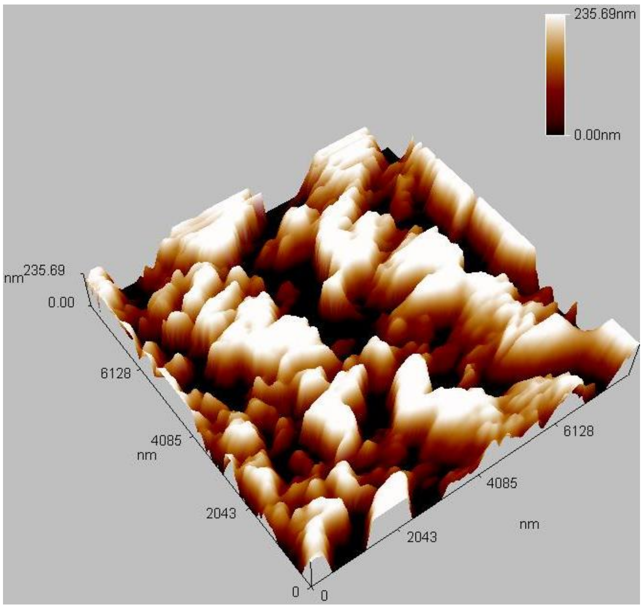


(a) 20 ^{0}C

(b) 30 ^{0}C



(c) 40 ^{0}C *(d) 50 ^{0}C*



(e) 60 ^{0}C

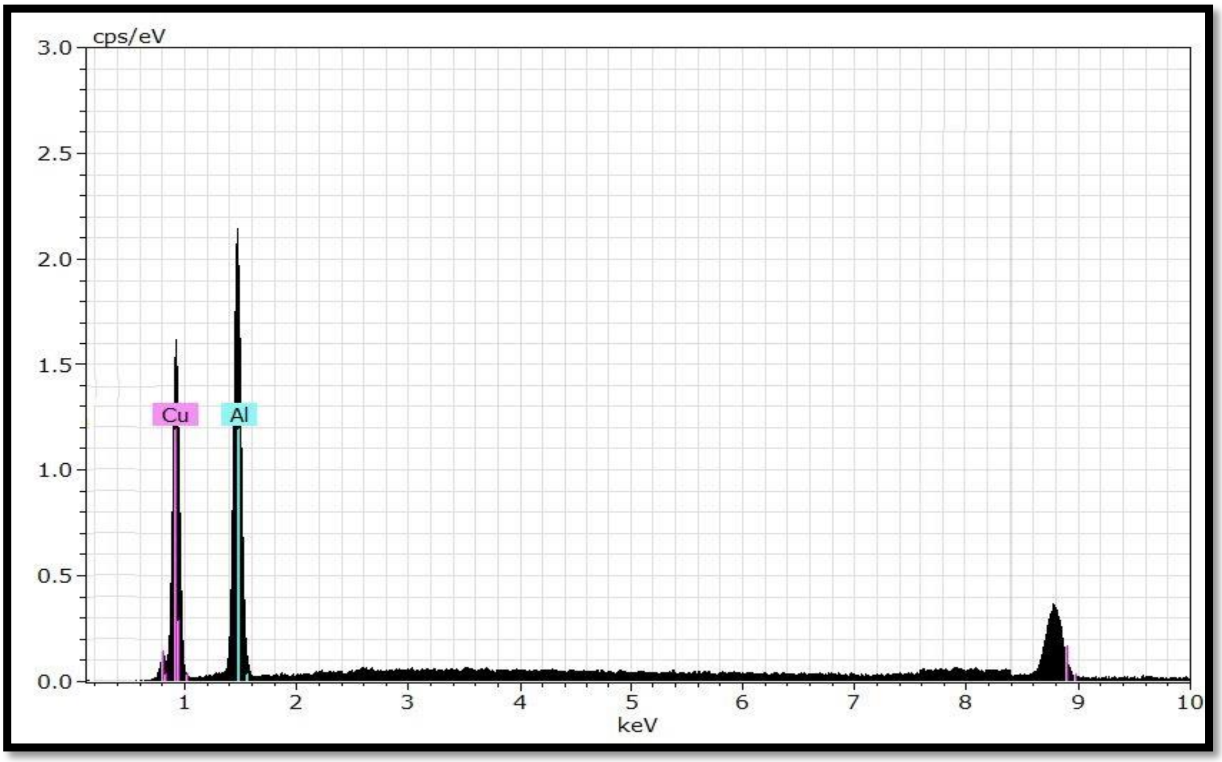
Figure (3-13): AFM images (contact mode) of the deposited aluminium obtained from 1.3:1 mole ratio $AlCl_3$:Urea ionic liquid for 1.5 hour, -0.6V and different temperature, (a)20 ^{0}C, (b) 30 ^{0}C, (c) 40 ^{0}C, (d) 50 ^{0}C and (e) 60 ^{0}C under statistic air.

Table (3-2): Grain number, roughness, average size, average height, % of Al coating and particle size of deposited aluminium obtained from 1.3:1 mole ratio $AlCl_3$:Urea ionic liquid for 1.5 hour, -0.6V at different temperature and under statistic air.

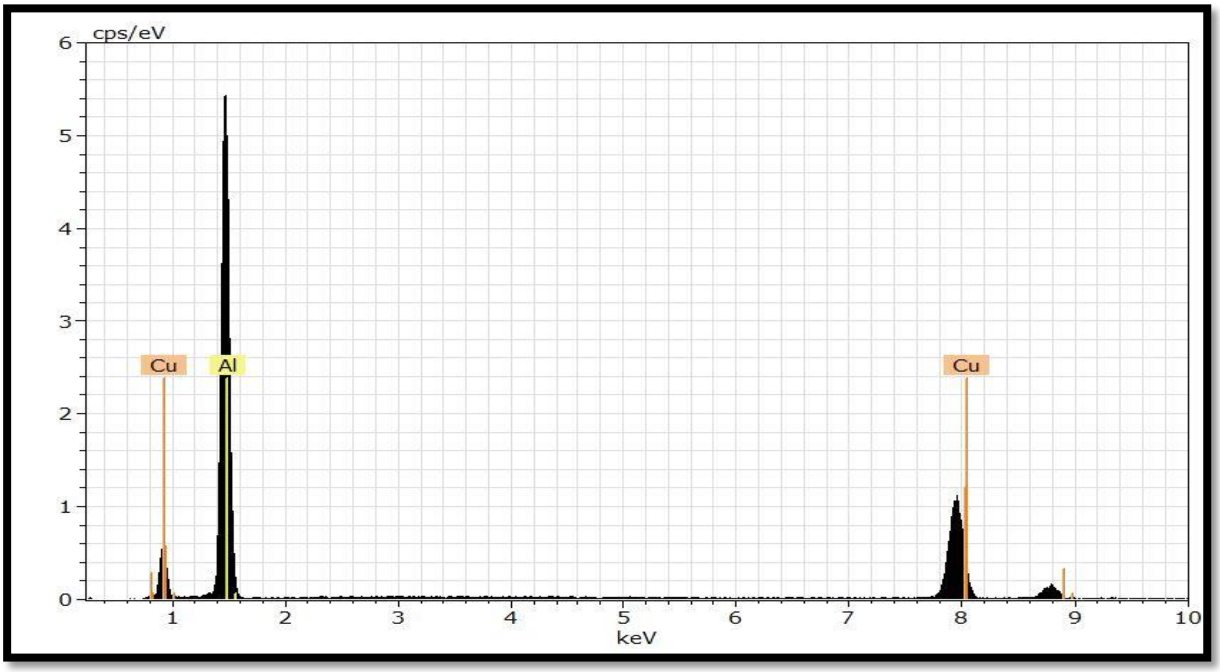
No.	**Temperature ^0C**	**Total grain**	**Roughness (Ra) [nm]**	**Avg. size[nm^2]**	**Avg. Height [nm]**	**% of Al from EDAX**	**Particle size [nm]**
1	20	276	67	150883	123	55	600-900
2	30	224	56	183420	121	76.1	500-700
3	40	256	57.1	147806	133	80.1	450-650
4	50	259	74	213961	139	91	250-500
5	60	160	76.2	310630	152	82	400-600

EDAX spectra in Fig. 3.14(a), (b), (c), (d) and (e) shows the correspondence between the results of the percentage of deposited aluminium and the peak from EDAX, we observed that when the temperature increase the peak for copper metal begins to decline.

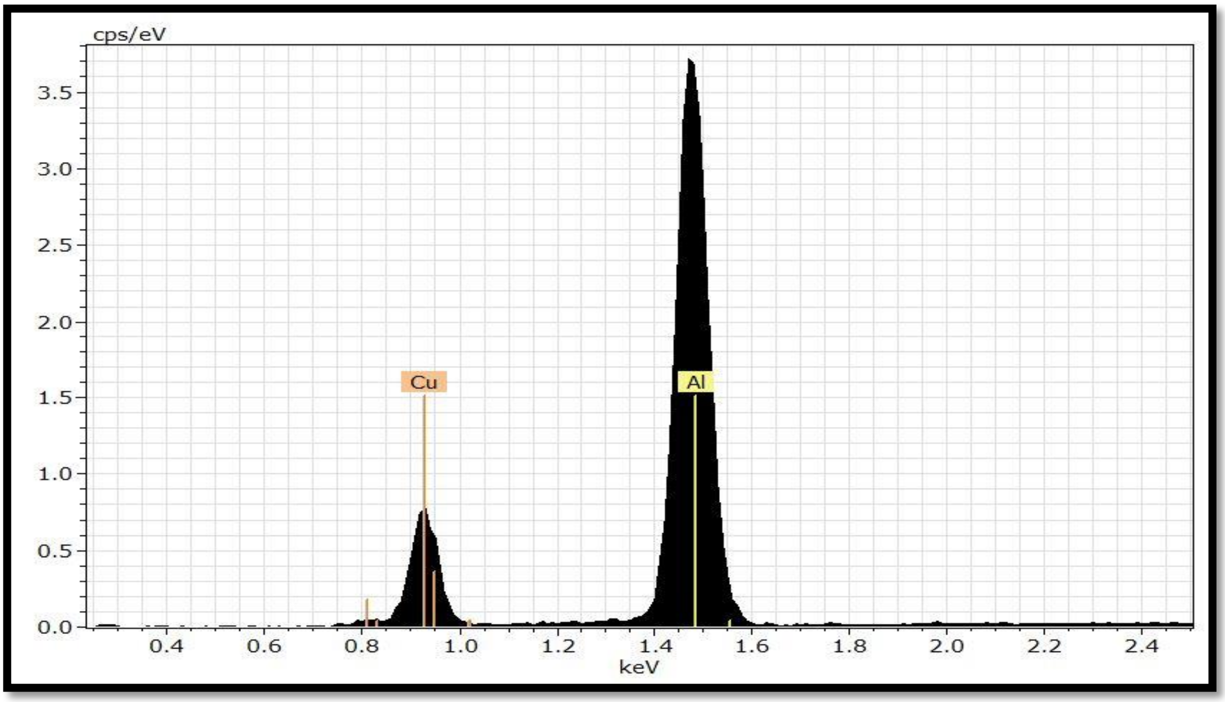
This results is consistent with the percentage of deposited aluminium with increased temperature. Sample at 60 ^{0}C showed the drop in deposited aluminium percentage to 82 At.% compared with 91 At.% at 50 ^{0}C as stated earlier.



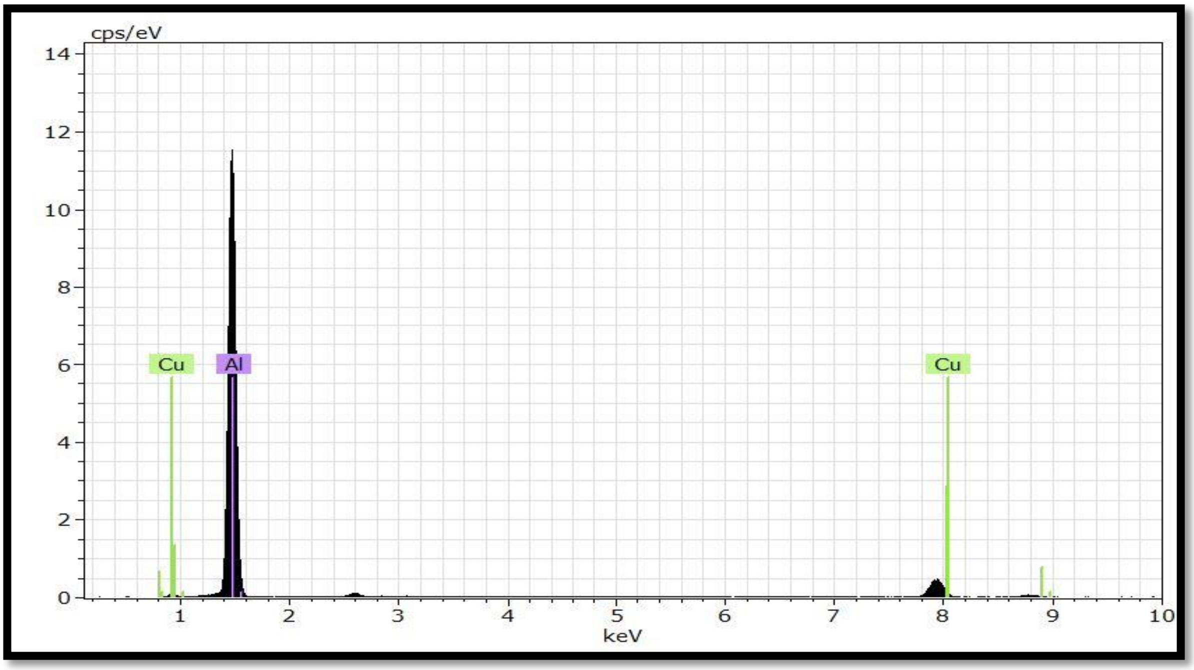
(a) at 20 ^{0}C



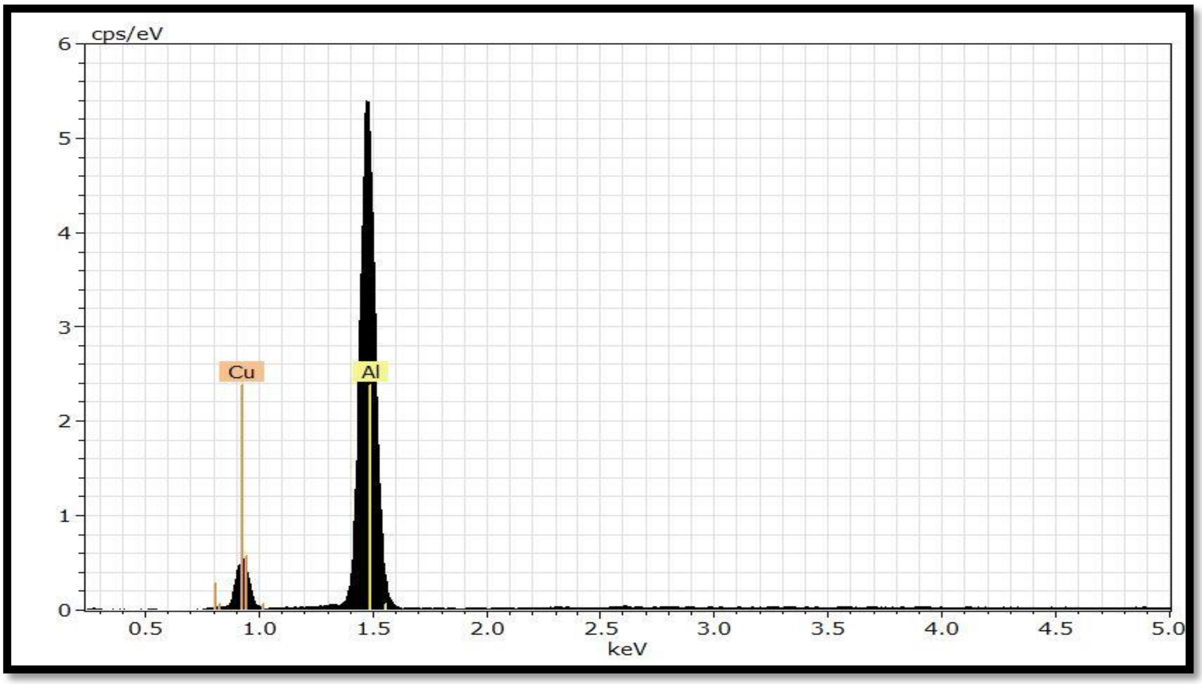
(b) at 30 ^{0}C



(c) at 40 ^{0}C



(d) at 50 ^{0}C



(e) at 60 ^{0}C

Figure (3-14): EDAX spectra of deposited aluminium from 1.3:1 mole ratio $AlCl_3$:Urea ionic liquid for 1.5 hour, at -0.6V and different temperature, (a)20 ^{0}C, (b) 30 ^{0}C, (c) 40 ^{0}C, (d) 50 ^{0}C and (e) 60 ^{0}C under statistic air.

In comparison with reported electrodeposited aluminium from different ionic liquid of $AlCl_3$/[AMIM]Cl at different temperatures[136], it was found that the darker appearance also appeared in presence work with increasing temperature. Yet it was reported at higher temperature in above reported ionic liquid (i.e. > 80 ^{0}C) while it appeared at around 60 ^{0}C in present work. Both obtained aluminium shared a good adherent to substrate with smooth coating. However, the shapes in presence work varied with temperature while in the other ionic liquid it said to have an incompact spherical shape up to 80 ^{0}C and only changed to cluster of platy shape crystals at 100 ^{0}C said to be due probably to the non-uniform distribution of current density. The latter was not observed in this work as the current density was homogenously increased linearly with temperature, Figure (3-7).

3.5 The effect of time on the morphology of deposited aluminium.

Long coating time was expected to influence the thickness of deposited metal and effected the aggregation of particles and their compaction[139]. The effect of deposition time of aluminium ranging from 1 to 3 hours was investigated from 1.3:1 mole ratio of $AlCl_3$:Urea net ionic liquid covered with decan at -0.6V and 25 ^{0}C under statistic air.

Figure (3-15) shows the SEM images for the deposited aluminium at 1 hour, Figure (3-16) at two hours and Figure (3-17) at three hours.

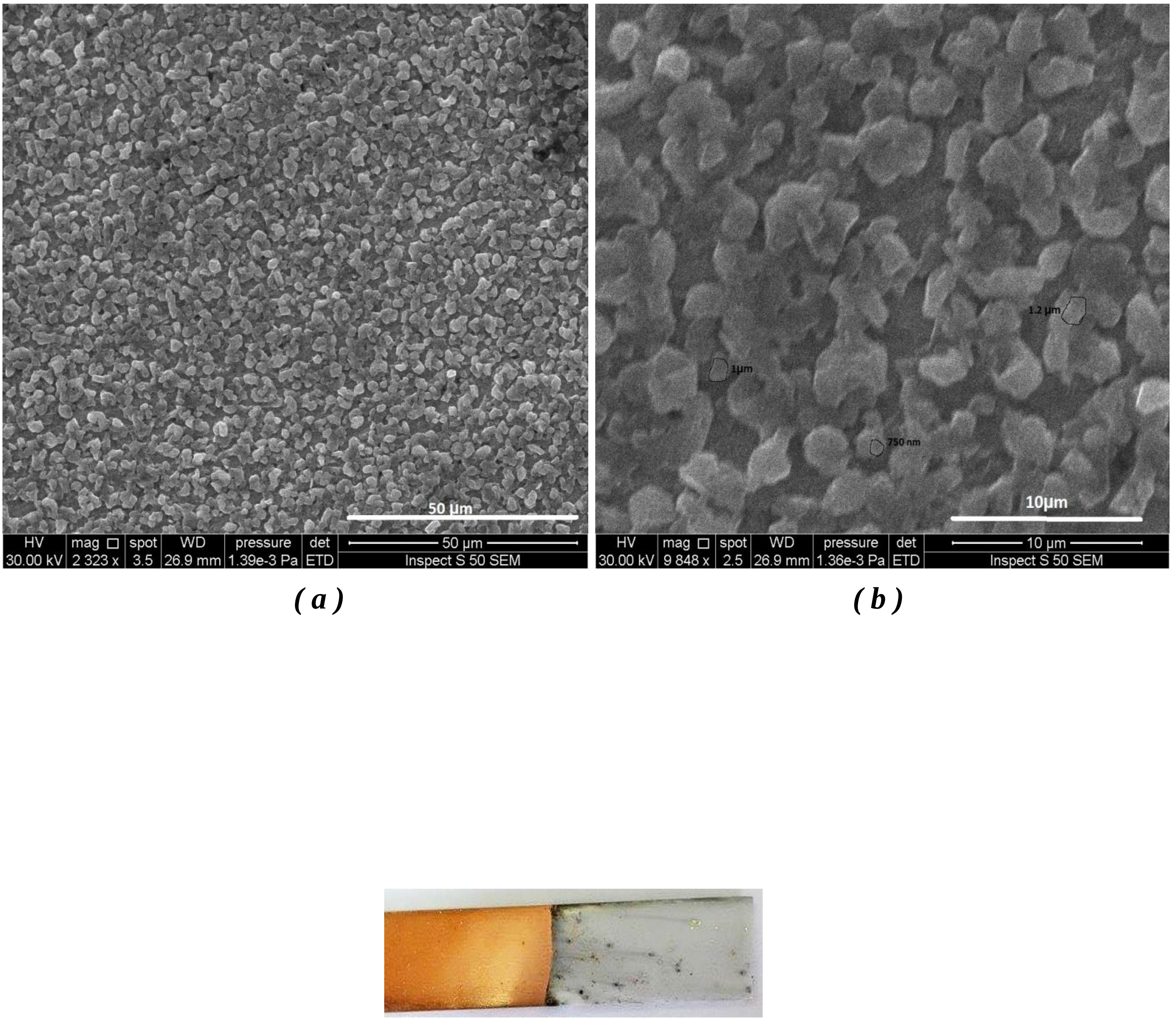
The current density was found to be simillar (6.5 mA/cm^2) during the three experiments with time as the potential and temperature was constant.

It was found that the appearance of coated aluminium was silvery white as shown in the corresponding optical photograph of the sample in Figure (3-15)(c), (3-16)(c) and (3-17)(c) respectively, with bright, dense and homogeneous deposits.

AFM image presented in Figure (3-18) show the accumulation and the building up of particles that increased with increasing the deposition time.

EDAX spectra in Figure (3-19) shows the correspondence between the results of the percentage of deposited aluminium and the peak from EDAX, we observed that the percentage of deposited aluminium in 1 and 2 hours was relatively convergent 64.93 At% and 68.16 At. % respectively, while in 3 hours the percentage increased to 76.86 At.% and this results are consistent to the EDAX peak. In 1 and 2 hours the peak for copper metal was relatively similar and it was decreased in 3 hours, so this is consistent with the percentage of deposited aluminium.

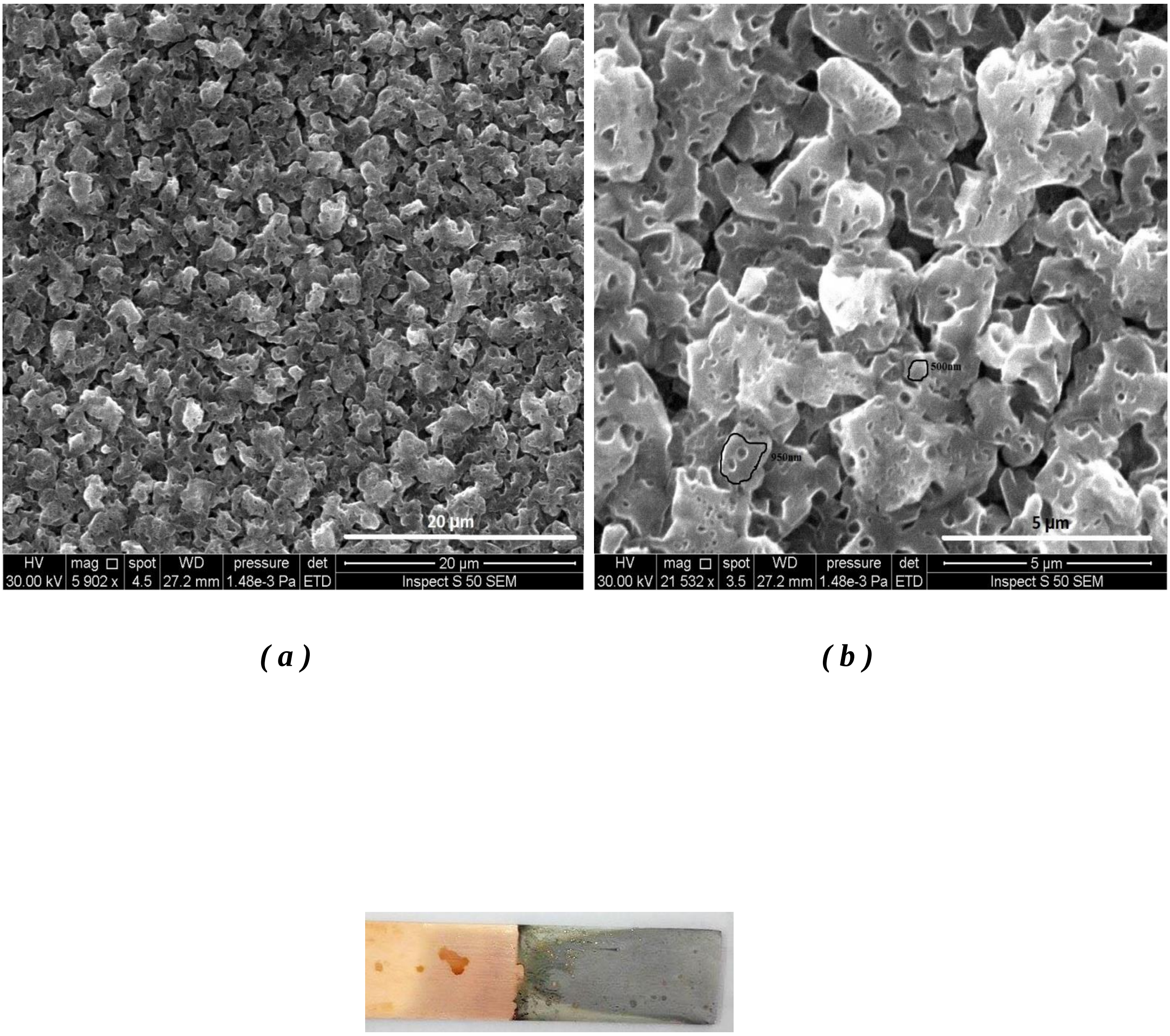
Table (3-3) shows the total grain, roughness, average size, average height, percentage of Al coating and particle size of deposited aluminium obtained from 1.3:1 mole ratio $AlCl_3$:Urea neat ionic liquid, -0.6V, 25 ^{0}C and under statistic air that all increased with time, except the average size which decrease with time.



(a) *(b)*

(c)

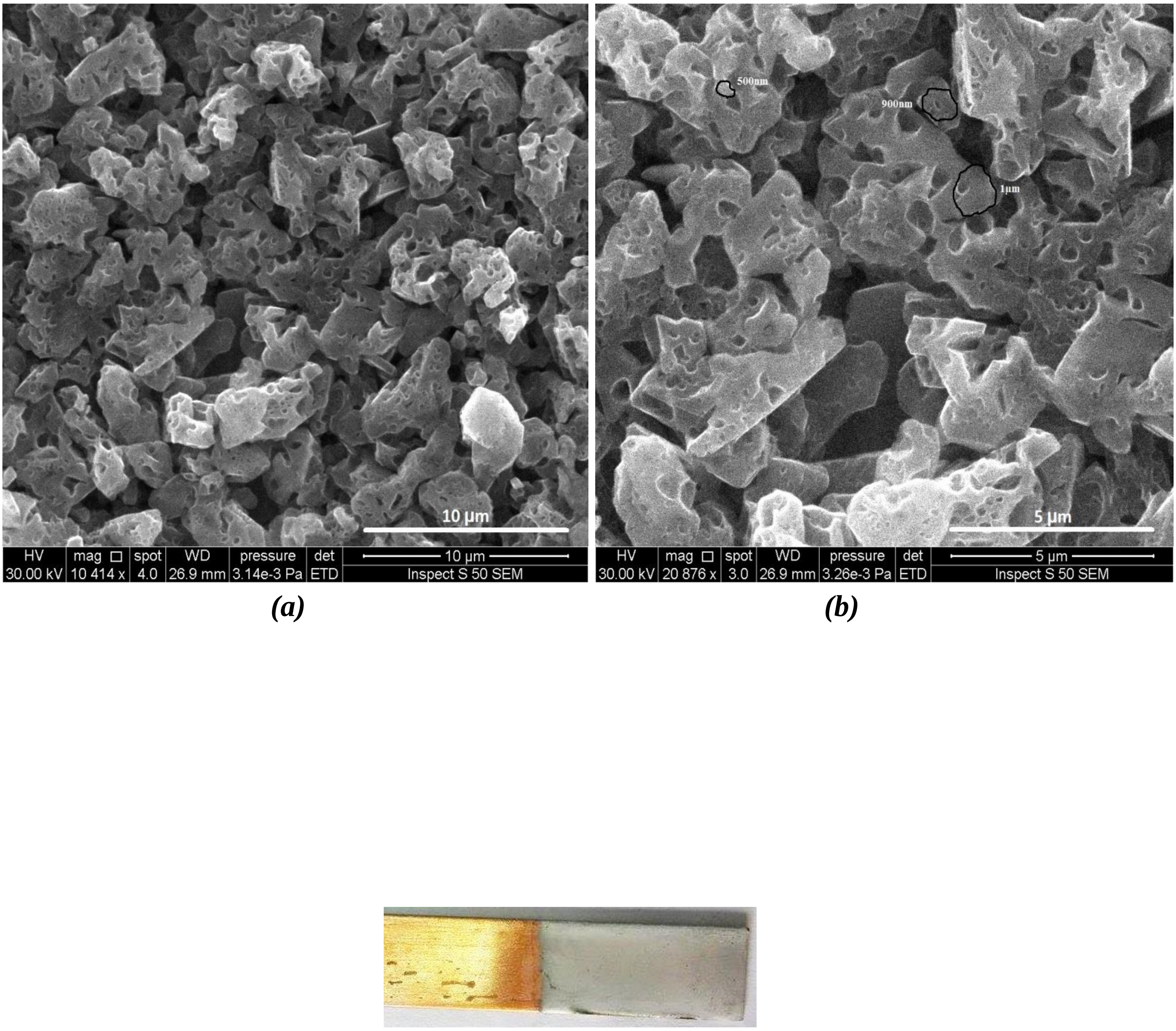
Figure (3-15): SEM images of deposited aluminium from 1.3:1 mole ratio $AlCl_3$:Urea ionic liquid, -0.6V, 1hour, at room temperature 25 ^{0}C and under statistic air, (a) magnified at 2323x, (b) magnified at 9848x and (c) the corresponding optical photograph of the deposited aluminium on copper substrate.



(a) *(b)*

(c)

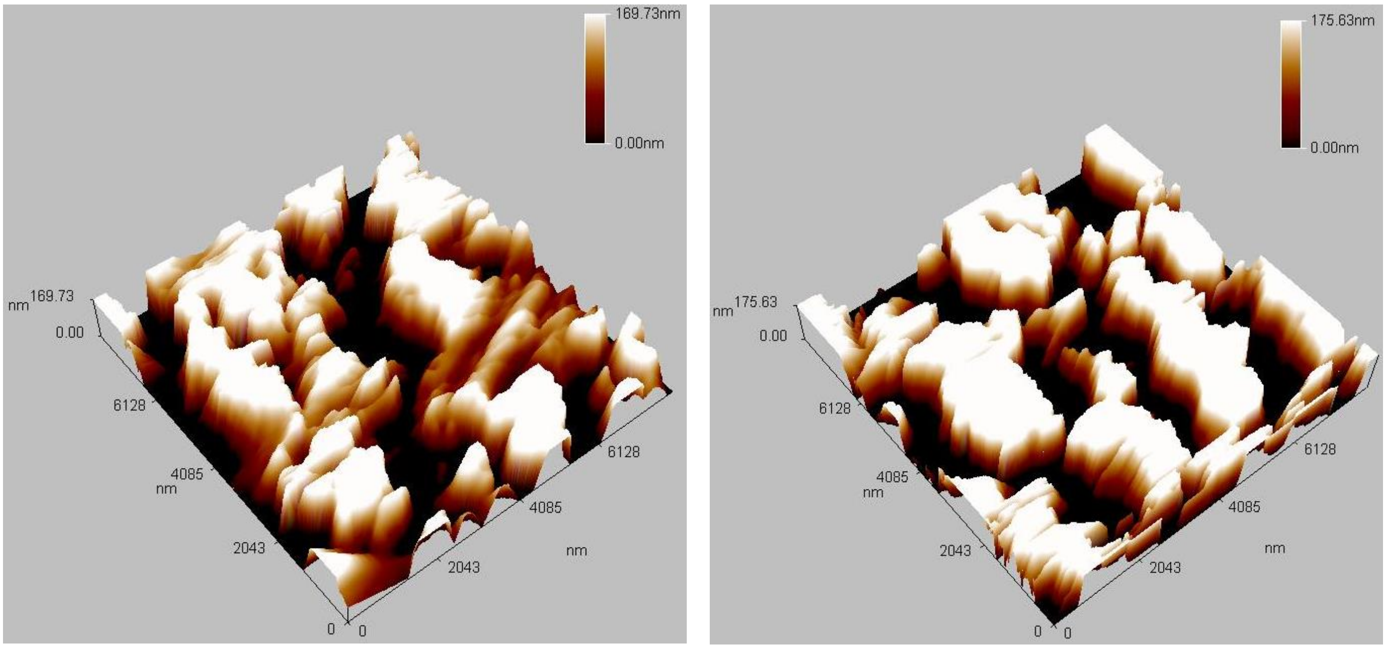
Figure (3-16): SEM images of deposited aluminium from 1.3:1 mole ratio $AlCl_3$:Urea ionic liquid, -0.6V, 2hours, at room temperature 25 ^{0}C and under statistic air, (a) magnified at 5902x, (b) magnified at 21532x and (c) the corresponding optical photograph of the deposited aluminium on copper substrate.



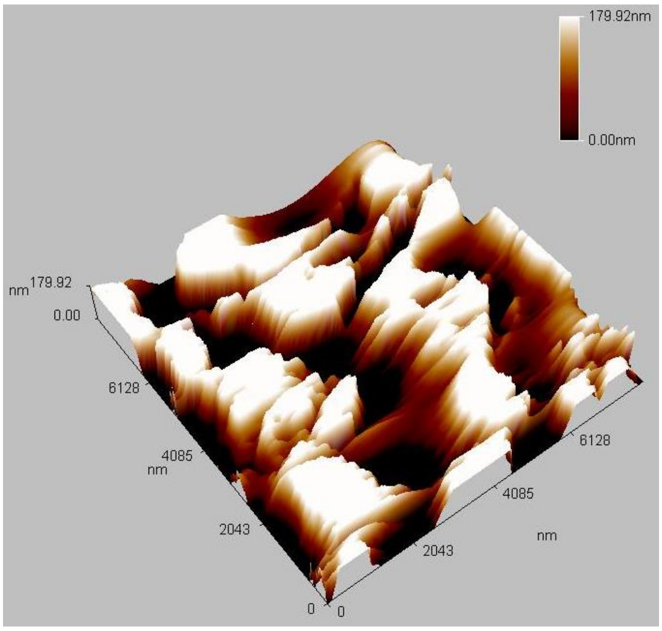
(a) *(b)*

(c)

Figure (3-17): SEM images of deposited aluminium from 1.3:1 mole ratio $AlCl_3$:Urea ionic liquid, -0.6V, 3 hours, at room temperature 25 ^{0}C and under statistic air, (a) magnified at 10414x, (b) magnified at 20876x and (c) the corresponding optical photograph of the deposited aluminium on copper substrate.

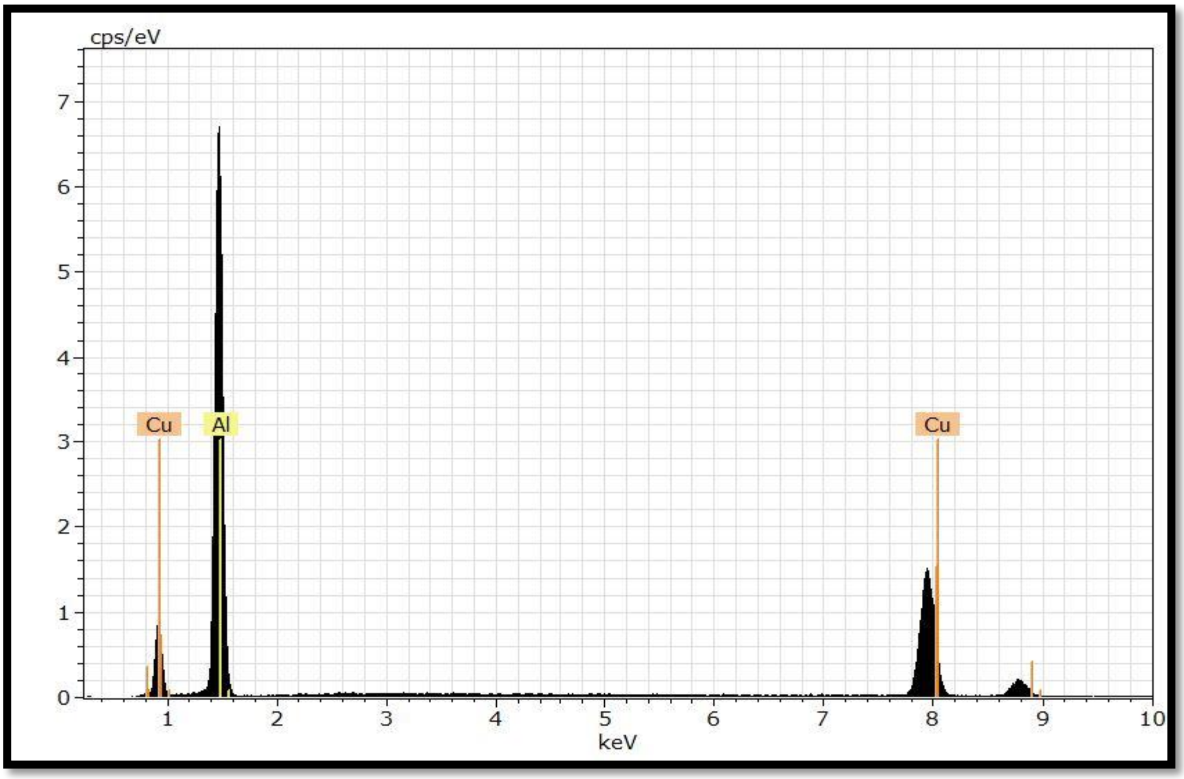


(a) 1 hour *(b) 2 hours*

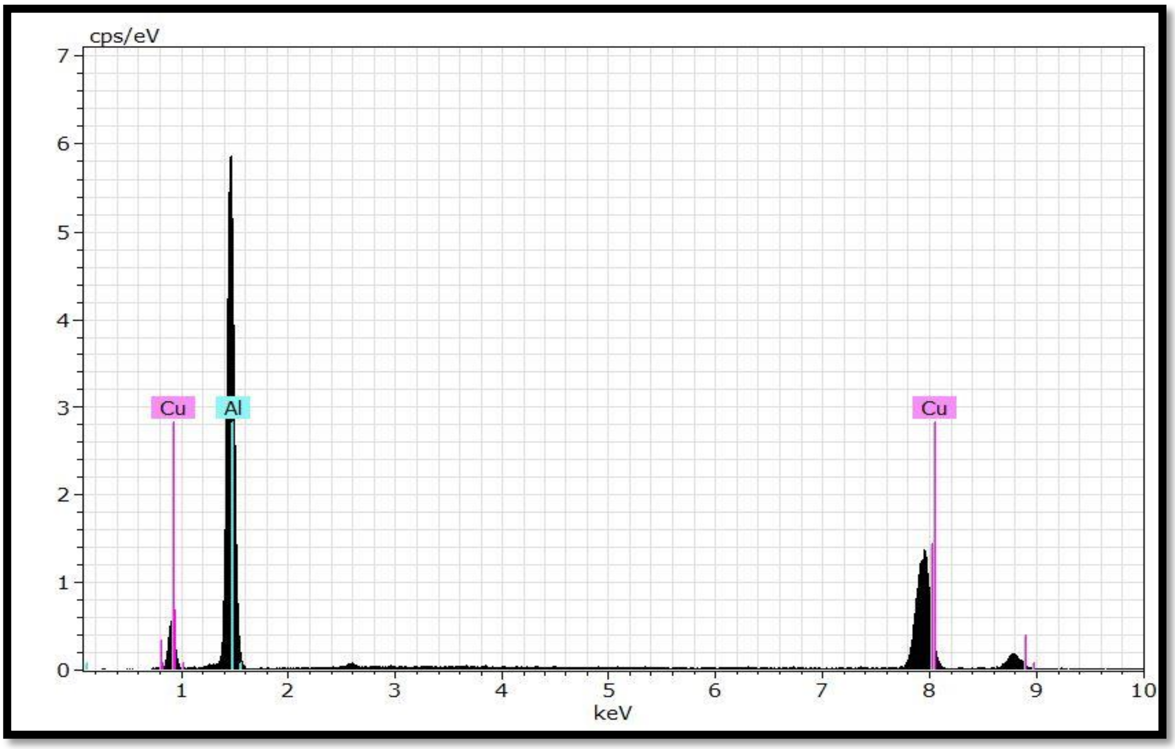


(c) 3 hours

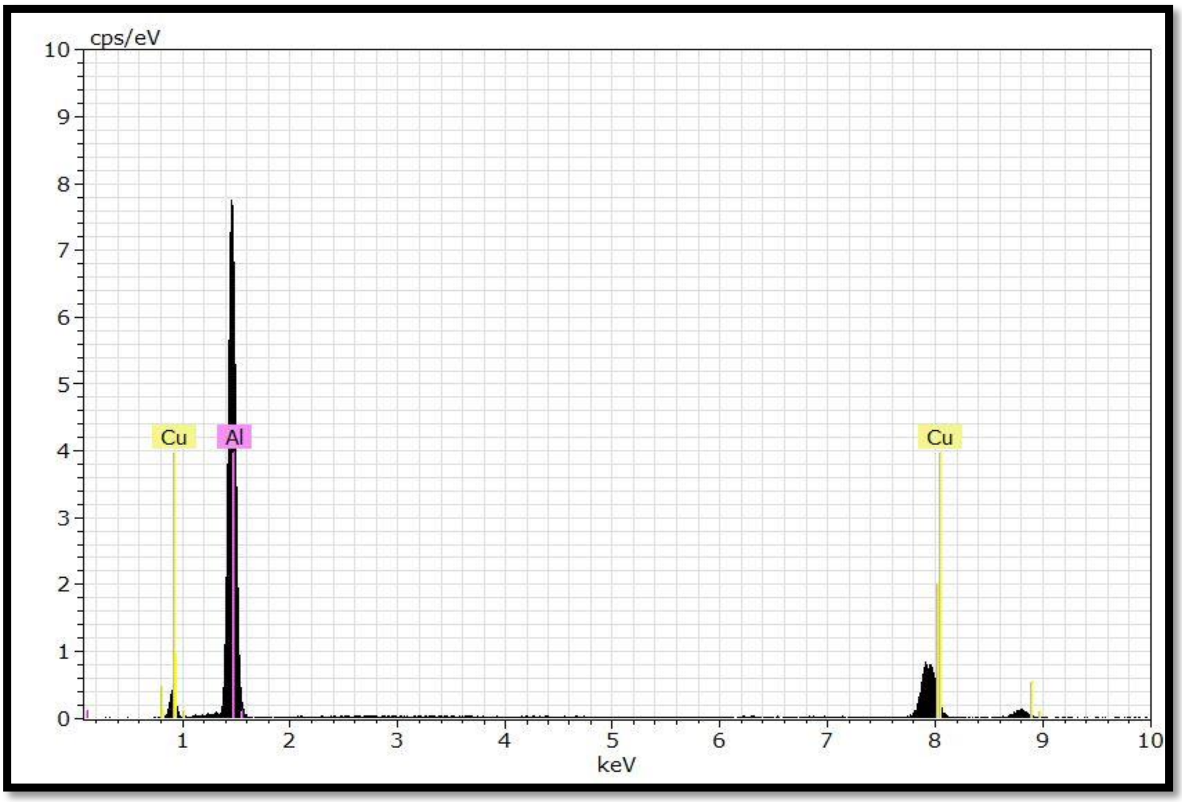
Figure (3-18): AFM images (contact mode) of the deposited aluminium obtained from 1.3:1 mole ratio $AlCl_3$:Urea ionic liquid, -0.6V, at room temperature and different deposition time (a)1hr, (b)2hrs and (c)3hrs under statistic air.



(a) 1 hour



(b) 2 hours



(c) 3 hours

Figure (3-19): EDAX spectra of deposited aluminium from 1.3:1 mole ratio $AlCl_3$:Urea ionic liquid, at room temperature, -0.6V, and different deposition time, (a)1hr, (b)2hrs and (c)3hrs under statistic air.

Table (3-3): Grain number, roughness, average size, average height, % of Al coating and particle size of deposited aluminium obtained from 1.3:1 mole ratio $AlCl_3$:Urea ionic liquid, -0.6V, at room temperature 25 ^{0}C, using different deposition time and under statistic air.

No.	Time	Total grain	Roughness (Ra) [nm]	Avg. size[nm^2]	Avg. Height [nm]	% of Al from EDAX	Particle size [nm]
1	1	85	62	420210	128	64.93	750-1200
2	2	113	67	414175	129	68.16	500-950
3	3	123	75	408693	137	76.86	500-1000

It was observed that the shape of particles was relatively similar and did not changed with increasing the deposition time, while the percentage of deposited aluminium and the number of particles was increased. This is in a good agreement with other workers who reported the increase in deposition thickness with time [137].

The shape of particles was comparable to the shape of particles at 20 ^{0}C which is sand like, Figure (3-8), this is due to the temperatures which were relatively close (20 ^{0}C and 25 ^{0}C) and they are classified under room temperature, so it was noticed that the temperature have an impact on the shape of particles, particularly on the roughness of the surface and an increase on the average height of the coating.

3.6 Effect of the potential on the deposited aluminium morphology.

The effect of cell potential on current density of the electrodeposition process of aluminium was obtained in the range of (-0.6V to -1V) at temperature of 35 ^{0}C from 1.3:1 $AlCl_3$/Urea net ionic liquid covered with Decane under statistic air. Figure (3-20) shows the variation of current density with cell voltage. The current density was also found to increase linearly with increasing potential expected leading to increase the rate of reduction of aluminium at the cathode. This increase in current densities is similar to that obtained at increasing the temperature from 20 to 60 ^{0}C in the same ionic liquid, Figure (3-7).

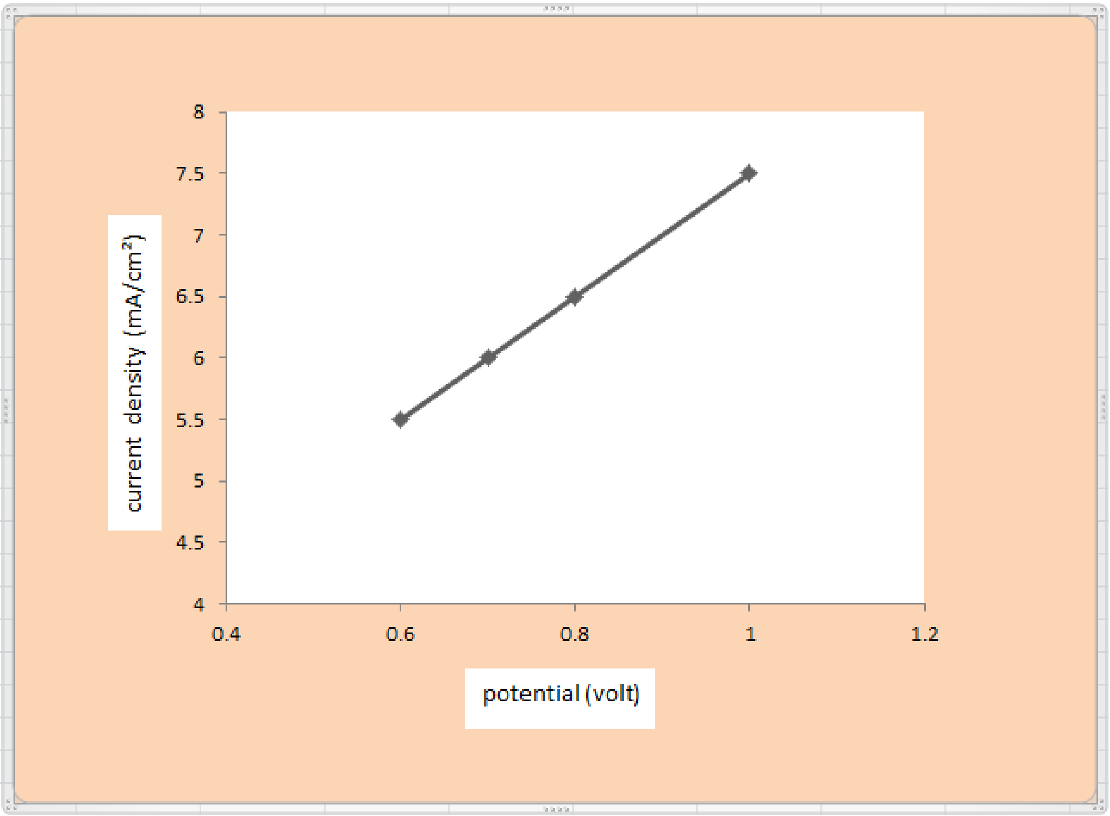


Figure (3-20): Relation between potential and current density of deposited aluminium from 1.3:1 mole ratio $AlCl_3$:Urea ionic liquid from different potential, 35 ^{0}C and 2 hours under statistic air.

At -0.6V and -0.7V The shape of particles were homogeneous in stars shape with two layers. The first layer crystals were small while the second layer crystals were larger. This different in size may be due to the different in substrate. The first layer adherent on the copper substrate, while the second was adherent on the first layer of electrodeposited aluminium which adherent on the copper cathode as shown in Figure (3-21) and Figure (3-22) respectively.

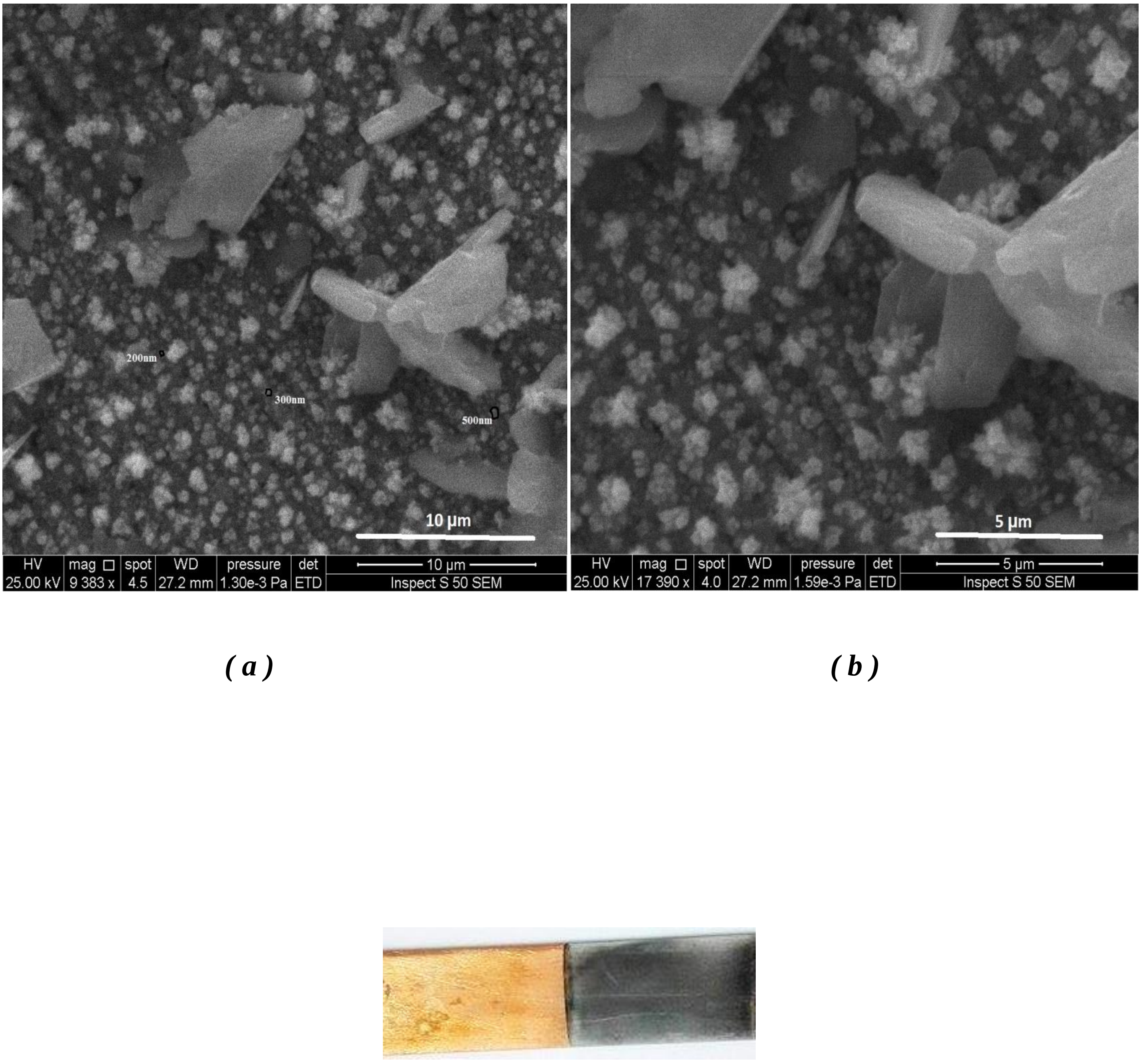
At -0.8V the particles compacted together with prism shape as shown in Fig. (3.23).

At -1V the shape of compacted particles like needles and they arranged in random orientation. Some are vertical and other are horizontally built on each other's as shown in Figure (3-24).

The appearance of coated aluminium in all experiments with changing potential was silvery gray as shown in the corresponding optical photographs of the deposited aluminium on copper substrate Figure 3-21 (c), Figure 3-22(c), Figure 3-23(c) and Figure 3-24(c) respectively. It was revealed that the appearance of coated aluminium did not changed with increasing potential as in the case of changing temperatures. The appearance was relatively similar to the appearance of deposited aluminium for the sample at 40 ^{0}C, Figure 3-10 (c).

AFM images and data are presented in Figure 3-25(a), (b), (c) and (d) and Table (3-4) respectively. It can be revealed the difference in the accumulation of particles for samples at different potential.

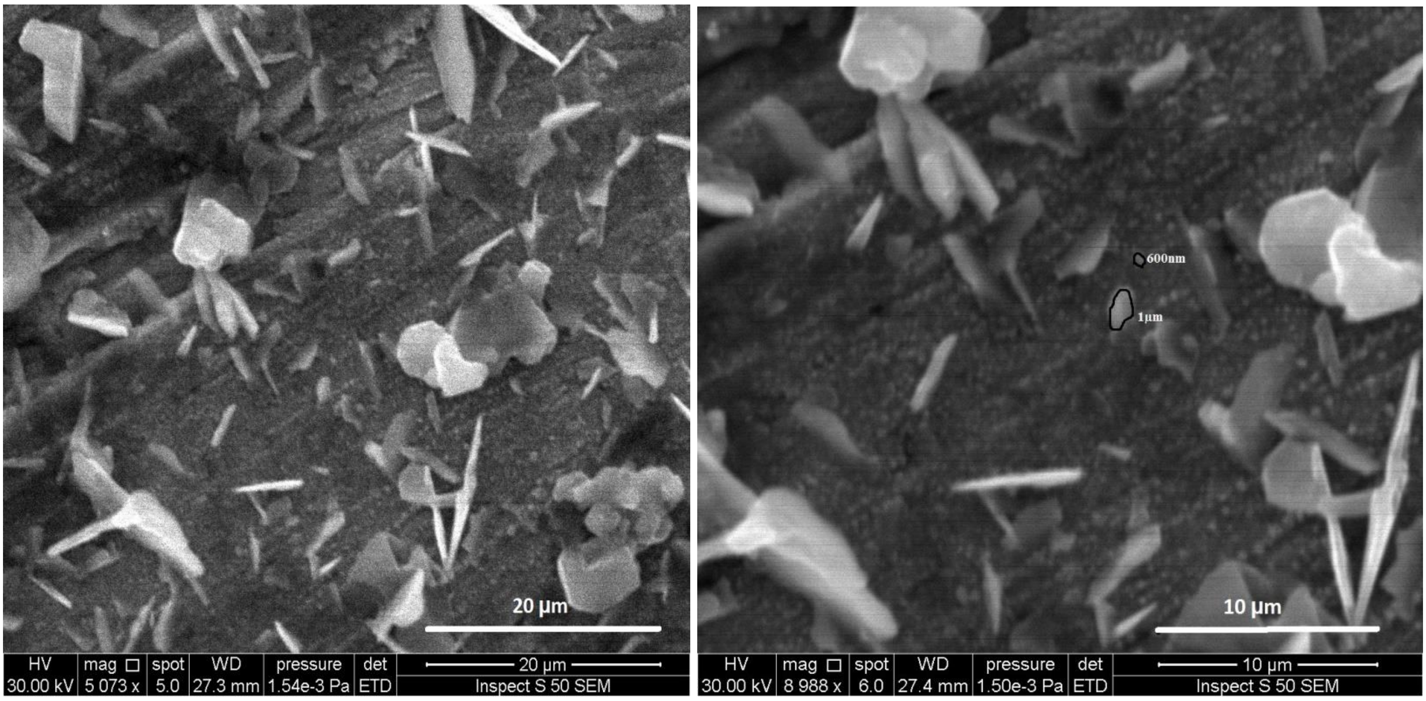
EDAX spectra for deposited aluminium at different cell potential was shown in Figure 3-26(a), (b), (c) and (d).



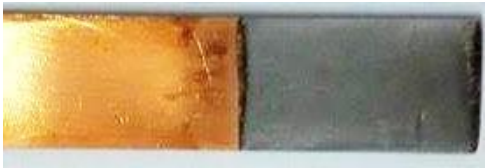
(a) *(b)*

(c)

Figure (3-21): SEM images of deposited aluminium from 1.3:1 mole ratio $AlCl_3$:Urea ionic liquid, 2hours, 35 ^{0}C, -0.6V and under statistic air, (a) magnified at 9383x, (b) magnified at 17390x and (c) the corresponding optical photograph of the deposited aluminium on copper substrate.

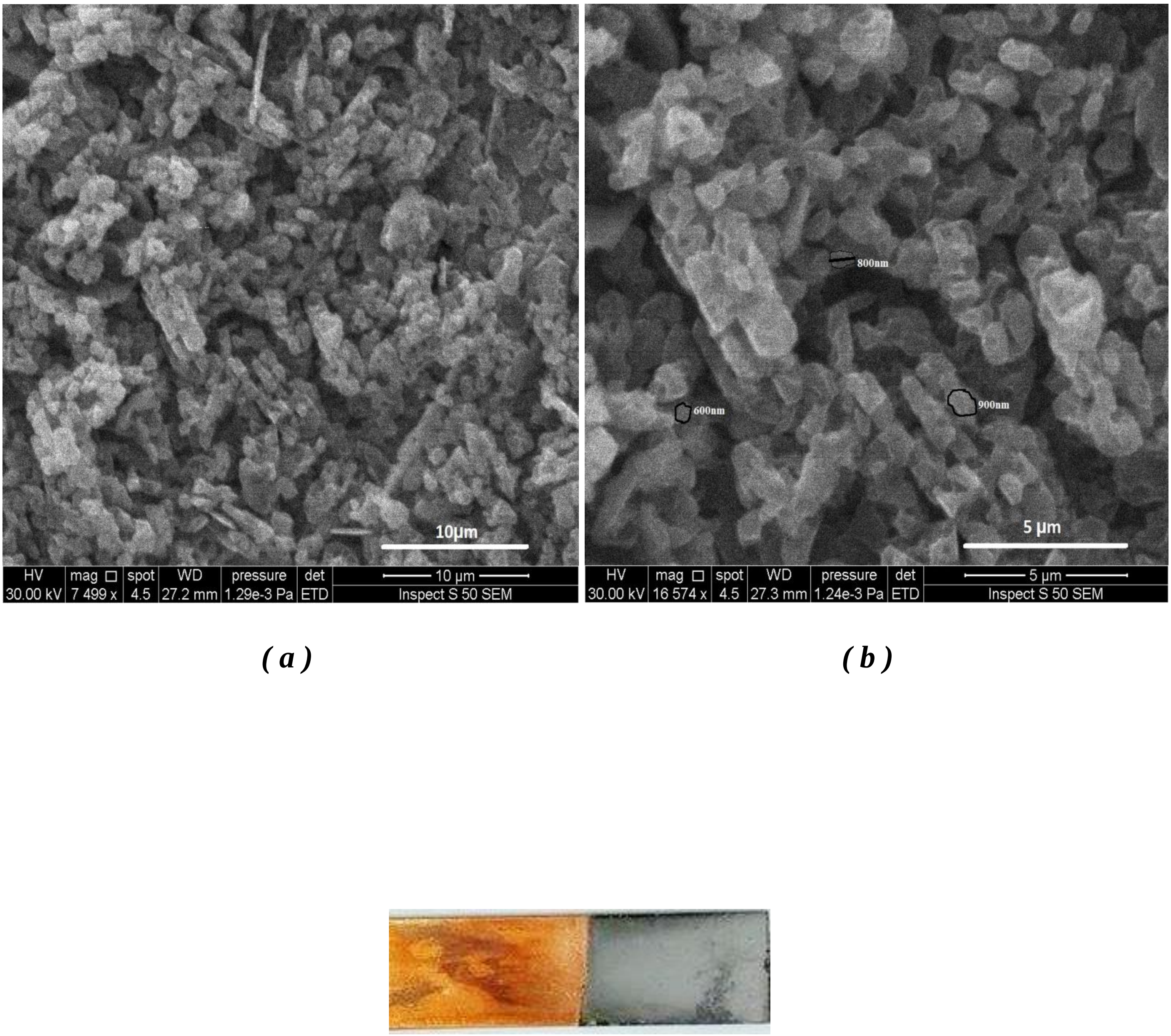


(a) *(b)*



(c)

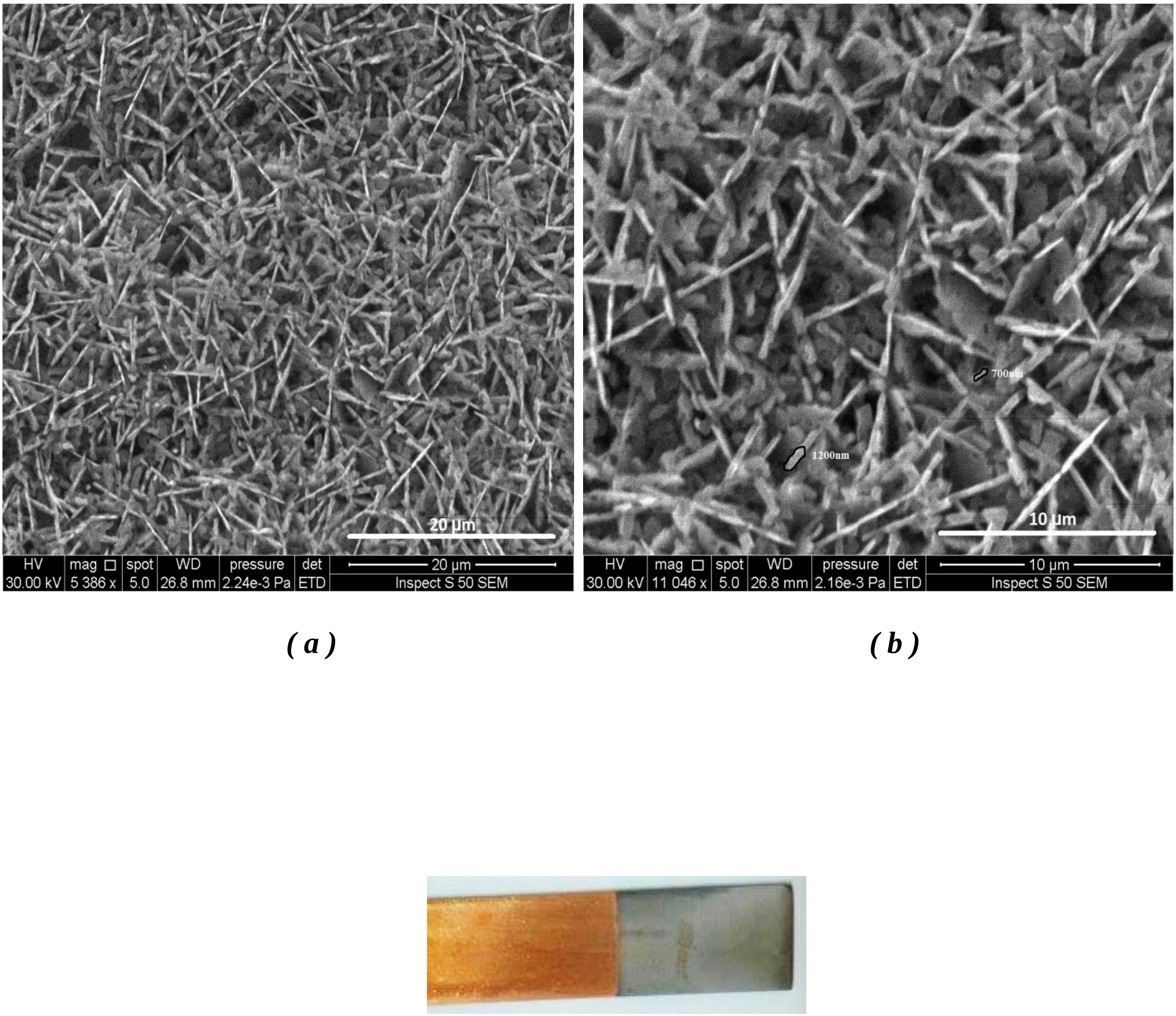
Figure (3-22): SEM images of deposited aluminium from 1.3:1 mole ratio $AlCl_3$:Urea ionic liquid, 2hours, 35 ^{0}C, -0.7V and under statistic air, (a) magnified at 5073x, (b) magnified at 8988x and (c) the corresponding optical photograph of the deposited aluminium on copper substrate.



(a) *(b)*

(c)

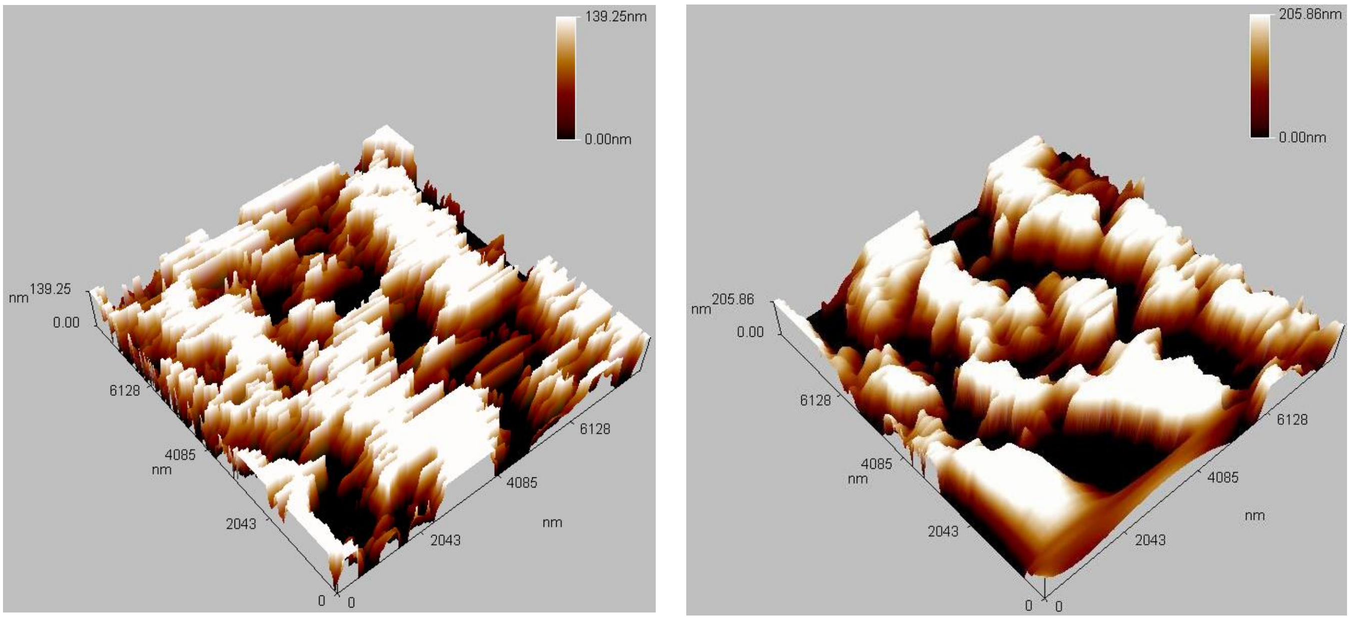
Figure (3-23): SEM images of deposited aluminium from 1.3:1 mole ratio $AlCl_3$:Urea ionic liquid, 2hours, 35 ^{0}C, -0.8V and under statistic air, (a) magnified at 7499x, (b) magnified at 16574x and (c) the corresponding optical photograph of the deposited aluminium on copper substrate.



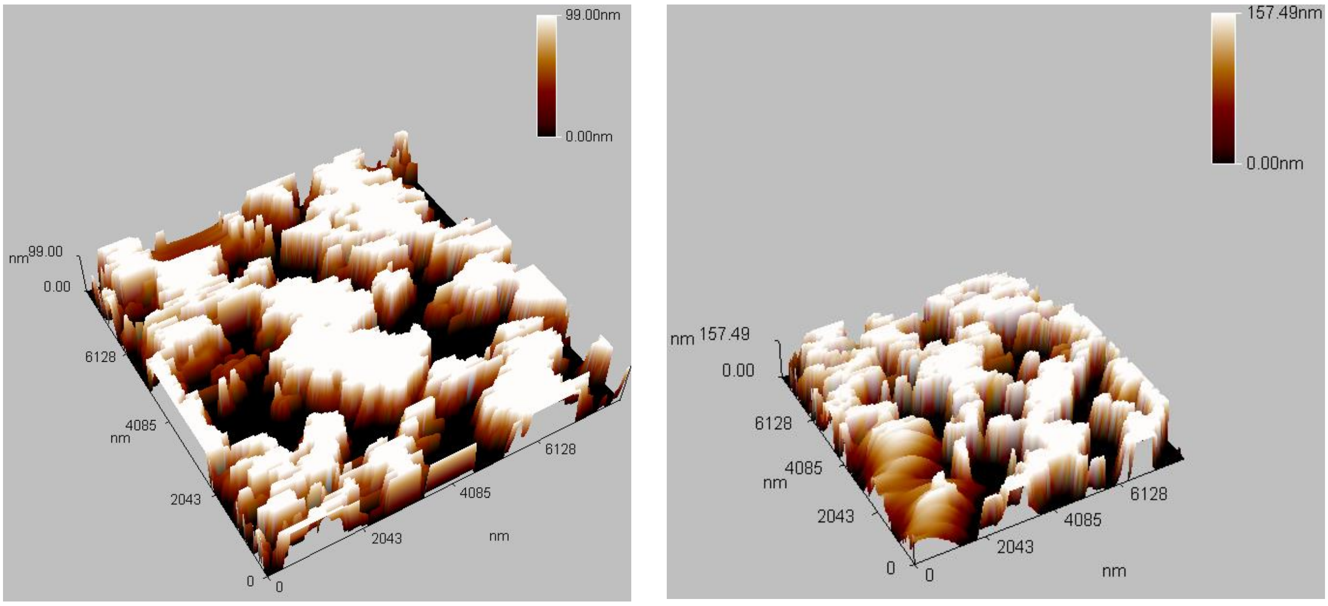
(a) ***(b)***

(c)

Figure (3-24): SEM images of deposited aluminium from 1.3:1 mole ratio $AlCl_3$:Urea ionic liquid, 2hours, 35 ^{0}C, -1V and under statistic air, (a) magnified at 5386x, (b) magnified at 11046x and (c) the corresponding optical photograph of the deposited aluminium on copper substrate.

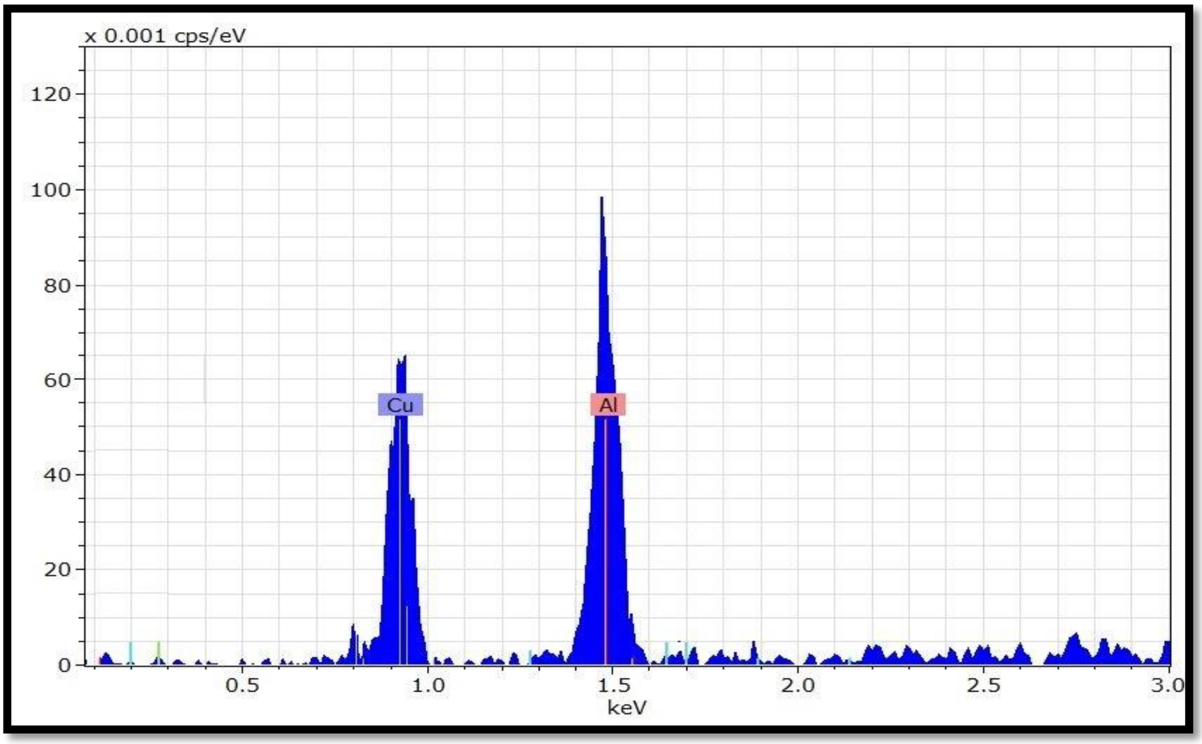


(a) -0.6V *(b) -0.7V*

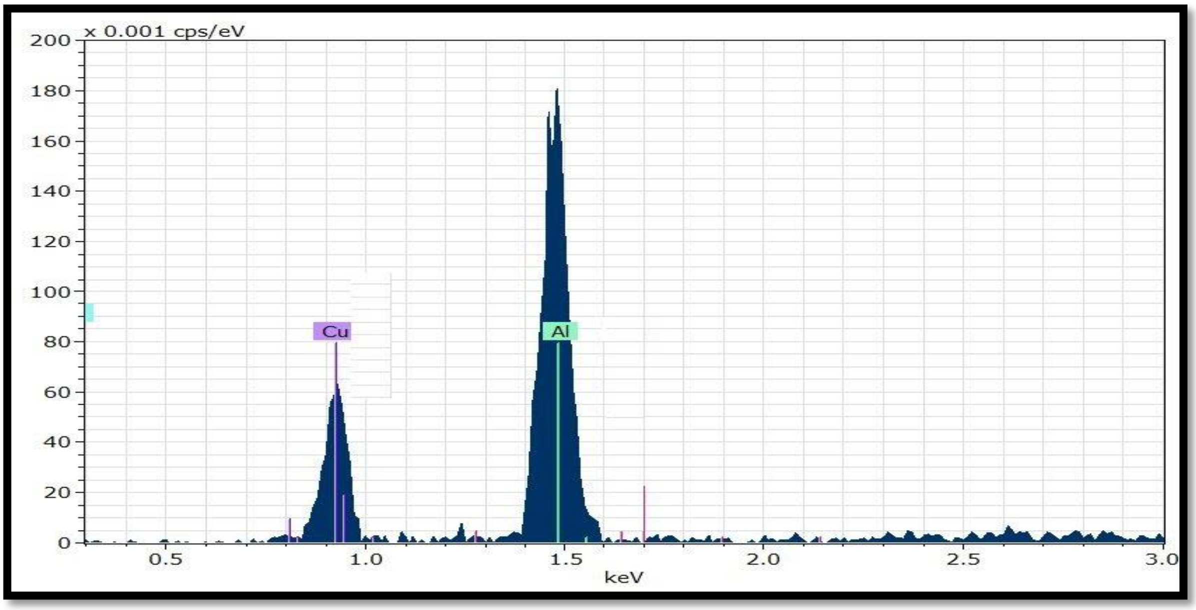


(c) -0.8V *(d) -1V*

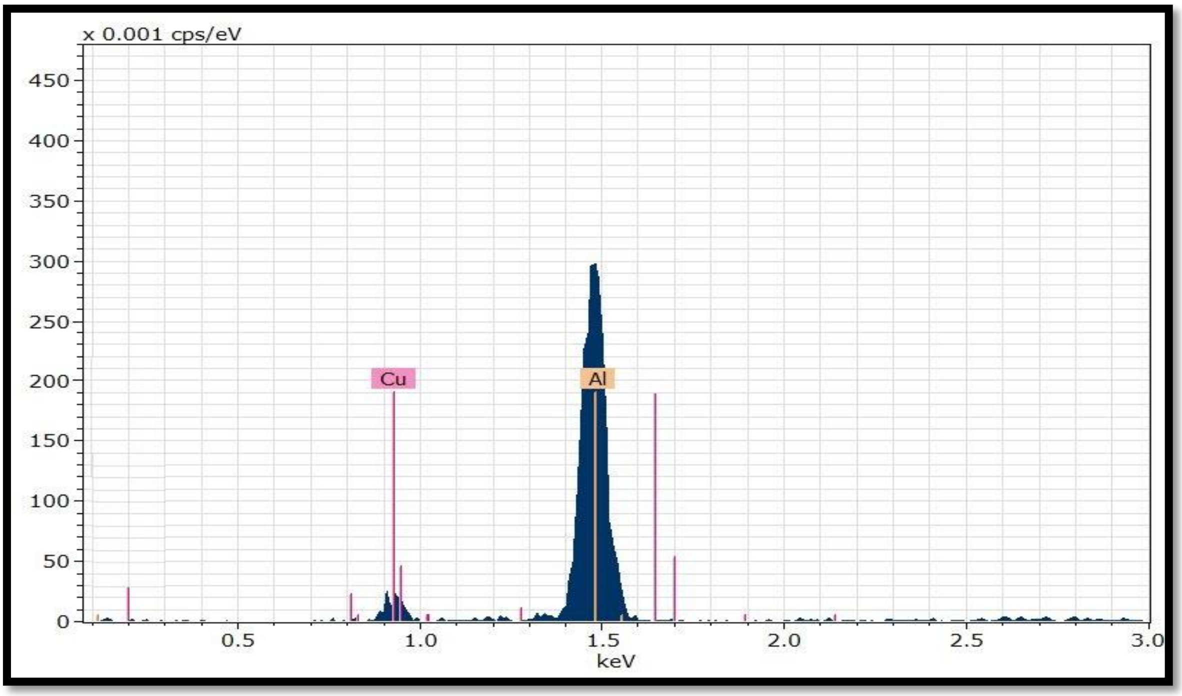
Figure (3-25) AFM images (contact mode) of the deposited aluminium obtained from 1.3:1 mole ratio $AlCl_3$:Urea ionic liquid using different deposition potential, (a)-0.6V, (b)-0.7V, (c)-0.8V and (d)-1V, 2hours, 35 ^{0}C and under statistic air.


x 0.001 cps/eV
120
100
80
60
40
20
0
Cu
Al
0.5
1.0
1.5
2.0
2.5
3.0
keV

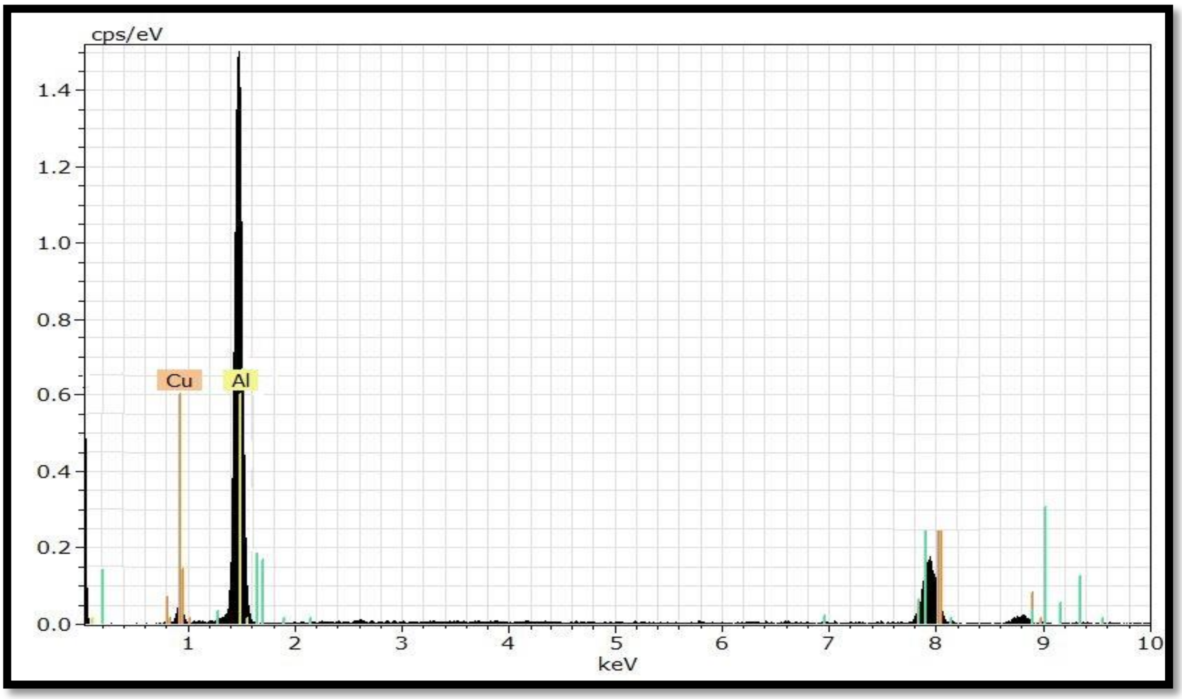
(a) -0.6V


x 0.001 cps/eV
200
180
160
140
120
100
80
60
40
20
0
Cu
Al
0.5
1.0
1.5
2.0
2.5
3.0
keV

(b) -0.7V



(C) -0.8 V



(d) -1 V

Figure (3-26): EDAX spectra of deposited aluminium from 1.3:1 mole ratio $AlCl_3$:Urea ionic liquid, 35 ^{0}C, 2 hours, using different deposition potential, (a)-0.6V, (b)-0.7V, (c)-0.8V and (d)-1V and under statistic air.

Table (3-4): Grain number, roughness, average size, average height, % of Al coating and particle size of deposited aluminium obtained from 1.3:1 mole ratio $AlCl_3$:Urea ionic liquid using different deposition potential, 2hours, 35 ^{0}C and under statistic air.

No.	Potential [volt]	Total grain	Roughness (Ra) [nm]	Avg. size[nm^2]	Avg. Height [nm]	% of Al from EDAX	Particle size [nm]
1	-0.6V	203	58	118166	100	61	200-600
2	-0.7V	136	41	313435	99	72	600-1000
3	-0.8V	116	40	106758	77	86.7	600-900
4	-1V	231	62	174695	108	88.2	700-1200

From Table (3-5) we can conclude a simple comparison between the samples. A very good value of Ra was measured for the roughness of Al coating ranging between 40 nm to max of 76 nm, Colum 8, Table (3-5). This value indicated a smoothness comparable to superfinishing of metal process and within the range of Fly cut or Ground aluminium **[154]** which have Ra values of less than 100 nm and better than milled aluminium which has Ra value of less than 1000 nm.

It can be seen that increasing the $AlCl_3$ mole ratio would influence the amount of coated aluminium on copper substrate (comparing samples of A1, A2 with D1) which conducted at 2:1, 1.6:1 and 1.3:1 mole ratio of

$AlCl_3$:Urea ionic liquid, although the latter sample was 10 ^{0}C higher than the previous samples. Lowering the temperature to 20 ^{0}C for sample B1 or increasing to 35 ^{0}C for sample D1 did not give a large difference in the amount of coated aluminium although the time for both samples were different too (1.5 and 2 hours respectively)

The average height was decreased with increasing mole ratio comparing A1, A2 and C1 of 69 nm, 80 nm and 128 nm respectively.

Also the average height increased with increasing temperature from (123nm to 152 nm) for B1 to B5 of 20 ^{0}C to 60 ^{0}C respectively. Yet, at (40 ^{0}C and 50 ^{0}C) this trend was not found in roughness value as similar value were obtained for B2 and B3 with 56 nm and 57.1 nm respectively.

The percentage of electrodeposited aluminium was found to increase with increasing temperature, time, potential and mole ratio of the aluminium chloride in ionic liquid. Although at 60 ^{0}C sample B5, showed a drop in deposited aluminium percentage of 82 At.% compared with B4 of 91 At.% deposited at 50 ^{0}C.

Good Ra values could be obtained from samples A1 and D3 with Ra values of 46 nm and 40 nm of average height of 69nm and 77nm respectively.

Comparing A1 with D3, increasing the potential from -0.6V to -0.8V and the temperature for 25 ^{0}C to 35 ^{0}C, did not give a higher % of aluminium when ionic liquid contain 2:1 $AlCl_3$:Urea than 1.3:1 mole ratio (comparing 95 At. % with 86.7At. %).

However, Ra was relatively smaller in D3 than in A1, (compare 40 nm with 46nm).

Table (3-5) : Grain number, roughness, average size, average height, % of Al coating and particle size of electrodeposited aluminium from $AlCl_3$/Urea ionic liquid at different conditions.

Samples	No.	Potential (volt)	Mole ratio	Temperature ^{0}C	Time (hour)	Total grain	Roughness [nm]	Avg. size [nm^2]	Avg. height [nm]	% of Al from EDAX	Particle Size [nm]
A	1	-0.6	2:1	25	2	224	46	147806	69	95	200-250
	2	〃	1.6:1	〃	〃	223	62	145975	80	72.2	600-1000
B	1	-0.6	1.3:1	20	1.5	276	67	150883	123	55	600-900
	2	〃	〃	30	〃	224	56	183420	121	76.1	500-700
	3	〃	〃	40	〃	256	57.1	147806	133	80.1	450-650
	4	〃	〃	50	〃	259	74	213961	139	91	250-500
	5	〃	〃	60	〃	160	76.2	310630	152	82	400-600
C	1	-0.6	1.3:1	25	1	85	62	420210	128	64.93	750-1200
	2	〃	〃	〃	2	113	67	414175	129	68.16	500-950
	3	〃	〃	〃	3	123	75	408693	137	76.86	500-1000
D	1	-0.6	1.3:1	35	2	203	58	118166	100	61	200-600
	2	-0.7	〃	〃	〃	136	41	313435	99	72	600-1000
	3	-0.8	〃	〃	〃	116	40	106758	77	86.7	600-900
	4	-1	〃	〃	〃	231	62	174695	108	88.2	700-1200

Conclusions:

1. The RTIL of aluminium chloride and urea have a stable properties towards air that differ from other ionic liquids based on quaternary ammonium cations or chloroaluminate ionic liquid. It was easy to prepare, less water sensitive and easy to handle by adding a layer of Decane on the top of the liquid as protective top layer from air, so the electrodeposition process was successfully conducted under statistic air.
2. The deposition of aluminium metal from $AlCl_3$/Urea ionic liquid is possible with and without diluent at different mole ratio of $AlCl_3$ 2, 1.6 and 1.3 to 1 mole urea. The deposition was found to be smooth, well adhered to copper cathode in all the studied conditions. The appearance of coated aluminium was metallic coating changed to dull appearance with increasing potential (> -0.8V) or temperature (> 60 ^{0}C).
3. The average height of coated particles was less than 139 nm with the highest value obtained for particles at 60 ^{0}C at -0.6V and 1.5 hours.
4. The Ra values are within the smooth mean of metal surfaces with Ra < 77 nm at -0.6 V and 60 ^{0}C, too. From other chloroaluminate ionic liquid, the deposition of aluminium could not be occur if the mole ratio of $AlCl_3$ < 2:1, while in the present ionic liquid a good adherent aluminium coating from 1.3:1 mole ratio of aluminium chloride/urea ionic liquid was obtained.
5. It could be concluded that aluminium chloride/urea ionic liquid is a promising RTIL to extract or refine aluminium at reasonable and controlled conditions.

Future work:

1- Due to the ease of obtaining electroplating of copper substrate, it could also be possible to study the effect of crystallographic properties of electroplating different substrate such as Ni, Fe, etc.…

2- The present results could also be studied further by X-ray diffraction to illustrate the nature of crystallographic layer at different conditions.

3- In addition, it might be possible to study the reduction of other metal from this ionic liquid as it offered a wide range of electrochemical window.

4- Furthermore, aluminium alloy co-deposition of other metals is a possible area of research in the present ionic liquid.

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