Surface Modification of Metals by Means of an Ultrasound Irradiation Technique in Liquid Media

by

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A thesis submitted in conformity with the requirements for the degree of Master of Applied Science

Materials Science and Engineering
University of Toronto

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2014

Abstract

Ultrasound irradiation has recently received considerable attention due to its abilities in nanoparticle synthesis and also in modifying surfaces and depositing nanoparticles on a surface. Such a sonochemical method facilitates the deposition of nanoparticles on various substrates in a one-step process. The aim of this work is to use the ultrasound irradiation technique to deposit silver particles on the surface of metals in particular copper as a model system. By controlling the concentration of silver ions in the solution, reaction temperature and sonication time a homogeneous coating of silver particles formed on the surface of copper.

However, the electrochemical studies of the silver deposited copper sample compared to a pure copper, showed an increase in corrosion rate after the treatment. Electrochemical measurements were used to quantify the roughening of the copper substrate. Electrochemistry also enabled the mass transfer enhancement due to sonication to be quantified.
Acknowledgments

I would like to express my appreciation to Professor Roger C. Newman, my research supervisor, for his around the clock guidance, enthusiastic encouragement and enlightening directives along the way. My completion of this project could not have been accomplished without the support provided by him.

I would also like to thank Dr. Ali Torabi for his constructive recommendations on this project. I am particularly grateful for the assistance of Dr. Anatolie Carcea and Dr. Dorota Artymowicz.

My genuine thanks are extended to my mother Mrs. Simin Dehghani for all her encouragements and her generous support.

Finally, to my caring and supportive husband, Mr. Mehdi Pahlavan; this journey would not have been possible without him.
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1 Introduction

Sonochemical irradiation has recently attracted major attention due to its ability to facilitate unique chemical and physical conditions. The phenomenon responsible for sonochemistry is acoustic cavitation; the formation, growth and collapse of a cavitational bubble in the liquid medium. Upon the collapse of a bubble, several unusual reaction conditions will be created: high temperature of around 5000 K, high pressure of about 1000 atmosphere, high velocity microjets and powerful shock waves. The resulting impact of the generation of high temperatures and pressures on the sonolysis of the solvent, have been lately used to produce different nanoparticles; upon the water sonolysis, highly reactive radicals such as H• and OH• will be produced. These are believed to be responsible for the nanoparticle synthesis. On the other hand, the effect of microjets and shockwaves induced by the bubble collapse has been used to obtain deposits as synthesized nanoparticles on different materials.

In the current study, copper hydride and silver nanoparticles were separately produced by ultrasonic irradiation of copper sulfate and silver nitrate solutions. But since, the primary focus of this work was on surface modification, more investigation was performed on deposition-assisted aspect of ultrasound irradiation. For that reason, an attempt was made to deposit silver particles on the surface of pure copper, as a model system, by the aid of ultrasound irradiation of silver nitrate solution. It has been decades that researchers have used sonochemistry to produce silver nanoparticles utilizing silver nitrate (AgNO₃) as the initial precursor. Ultrasound irradiation technique has been further employed to deposit silver nano particles on substrates; mostly non-metallic materials such as polymers, textiles and glass. However, only a few studies have been conducted on sonochemical silver deposition on the surface of metals such as stainless steel.

Silver particles deposited on the surface of copper were simultaneously synthesized by two methods;

1) Displacement reaction, in which silver ions from the solution will replace copper from the surface and will be reduced on the surface;
2) Ultrasound irradiation method, in which silver particles will be produced by the effect of acoustic cavitation.

The homogeneity and uniformity of the coating layer was investigated under variable reaction conditions such as reaction temperature, ion concentration and sonication time. One aspect of this investigation was to find the optimum reaction conditions in order to develop a homogeneous deposition layer. But the more important goal was to investigate the surface electrochemistry changes of copper in silver nitrate solution during and after the sonication: mass transfer phenomenon, limiting current density, open circuit potential and corrosion resistance.

A brief background and literature review is presented in the second chapter of this work. In chapter three, the experimental details are provided; subsequently results are discussed in chapter four. Finally in chapter five, conclusions are drawn and future research is recommended.
2 Background and Literature Review

2.1 Introduction to ultrasound

Ultrasound is a sound with a pitch of above 20 kHz which can be extended up to 20 MHz which is above human hearing [1, 2]. Depending on the application, the ultrasound could be divided into two major categories: 1- Low intensity, High frequency ultrasound (above 5 MHz) or Diagnostic Ultrasound. This is used in medical scanning, imaging, non-destructive analysis and non-invasive testing of materials [1, 3, 4]; 2- High intensity ultrasound (20 kHz - 2 MHz) or Power Ultrasound which is used in liquid mixing, de-agglomeration and emulsifying [2, 4].

2.1.1 Application of power ultrasound

Power ultrasound is applied in two ways: 1- Through direct transmission of mechanical energy: in which the vibration transmit onto the surface of a material from the transducer; welding, metal forming, chemical extraction, cleaning and machining. 2- Through indirect transmission of energy by acoustic cavitation [2].

2.1.2 Acoustic cavitation

When high-power ultrasound passes through a liquid, propagation of high-pressure (compression) and low-pressure cycles (rarefaction) of ultrasound is changed, resulting in altering the state of that liquid [1, 4]. In a liquid medium irradiated with high intensity ultrasound, the acoustic waves during the expansion cycle create vacuum cavities (bubbles). By decreasing the pressure surrounding the bubble in the rarefaction cycle, the bubble volume will increase. The opposite happens in the compression cycle, the bubble volume will decrease by increasing the pressure [5]. These bubbles absorb ultrasonic energy while growing [4][6]. When they reach their critical size which is determined by the ultrasound frequency and the liquid nature (usually 5-20 µm), they collapse intensively during a compression cycle and release a considerable amount of stored energy [4, 6, 7, 8]. This phenomenon (the creation, growth, and collapse of a bubble that is formed in the liquid) is known as “acoustic cavitation” (Figure 1).
In aqueous systems, each cavitation collapse generates a localized high temperature of around 5000 K and high pressure of 1000 atm, with cooling rates of above $10^{10}$ K/s, and strong shock waves in the area surrounding the bubble [7].

**Figure 1** The process of acoustic cavitation (formation, growth, and collapse of cavitation bubble)

### 2.1.2.1 Homogeneous liquid phase reactions

When there is no solid material in the liquid medium, reaction will be homogeneous, which means the area of the collapsing bubbles will be divided to two critical regions (Figure 2): 1- Inside the bubble which is a “localized hot spot”, with temperature of above 5000 K and pressure of about 1000 atm leading to chemical reactions. 2- the wave shocks formed from the collapse, in the immediate surroundings of the collapsing bubble, will induce shear forces in the bulk medium [2].
2.1.2.2 Heterogeneous solid/liquid phase reactions

2.1.2.2.1 Solid/liquid interface

Figure 3 shows the dynamic change of the collapsing bubble near a solid surface. On the surface of a substrate, the cavitation collapse creates localized high temperature and pressure, as well as shockwaves and powerful microjets of liquid towards the surface at very high speeds (200 m/s)[3, 9]. These microjets and shockwaves can cause erosion and plastic deformation on the attacked surface producing pits [9].

This effect of ultrasound close to/on the surface of a substrate can be used for surface cleaning, surface activation, destruction of boundary layer and improving the heat and mass transfer [3].

2.1.2.2.2 Solid/liquid slurry reactions

In presence of micrometer-sized solid powders floating in the liquid medium, the shockwaves and turbulent flow generated by collapsing of bubbles can cause collision, effective melting at the point of collision and bonding of the powder particles together (Figure 4) [9, 10].
Figure 4 SEM image of bonded Zn powders by interparticle collision induced by ultrasound irradiation. Adopted from reference [10].

2.2 Sonochemistry

The use of high intensity ultrasound to attain chemical alteration is known as Sonochemistry [11]. Figure 5 shows a usual laboratory-scale sonochemical device. A high-intensity ultrasonic titanium horn is connected to a transducer. The transducer converts electrical energy coming from a generator to mechanical energy in form of ultrasound vibration. Ultrasound irradiation apparatus also contains an ultrasound bath with gas inlet/outlet branches. In order to control the temperature of the ultrasound bath, usually double walled vessels are used [12].
2.2.1 Sonochemical production of nanostructured materials

Nano-sized materials, due to their exceptional properties, have been in the focus of research in recent years. There are several fabrication methods to produce nanostructured materials: mechanical, chemical, hydrothermal, sol-gel, chemical deposition in vacuum, pyrolysis, combustion, chemical precipitation, etc. [13]. Nanostructured materials with narrow size distributions and high surface areas can also be produced by a sonochemistry method [12]. Compared with the other conventional techniques, ultrasound can more easily control the particle size just by adjusting the critical parameters such as, irradiation time, reaction temperature and the initial concentration of the precursor [14]. It is worth to mention that ultrasound irradiation method is a green, cheap and one step process to synthesize the nanoparticles; no polluting wastes are produced; eliminating high costs of chemical waste recycling. The products which are the nanoparticles floating in water can easily be collected [12].
Sonochemistry is a simple and energy-saving process, which can be described as hot-spot theory [15]. Based on this theory, acoustic cavitation is the main phenomenon accountable for sonochemistry [16]. Two accountable regions for sonochemical activities are: the inside of the cavitation bubble with the temperature around 2300-5100 K, and the interface between the bubble and the liquid where the temperature is about 1900 K [17]. This interface region where is called “hot shell” has a 200 nm thicknesses and only lasts for 2 µs. Solutes in the hot shell may experience thermally activated reactions [18].

In an aqueous system including volatile precursors, cavitation bubbles enclose precursor vapor. Upon the collapse of the bubble, very high temperature over 5000 K is obtained which can break down the solute molecules into extremely reactive radical species. These radicals are extremely reductant and oxidant. As per their reaction with nearby molecules and ions in the system, new materials can be chemically synthesized [9].

In the case of having water as solvent, the sonolysis products are H• and OH•. They can form water by recombination, or can produce H₂O₂ and H₂. In presence of O₂, HO₂• can also be formed. These strong oxidizing and reducing radicals are believed to be in charge of sonochemical reductions [12]. H• radicals act as reducing species, attach to the metal ions dissolved in the solution and reduce them to metal particles.

\[
\text{H}_2\text{O} \rightarrow \text{H}• + \text{OH}•
\]

\[
\text{Ag(I), Au(III), Pt(II), Pd(II) + 1H}• \text{ (reducing radical)} \rightarrow \text{Ag(0), Au(0), Pt(0), Pd(0)}
\]

It has been estimated that 80% of the active radicals will recombine to produce H₂, H₂O₂, H₂O and HO₂• (Figure 6).

\[
\text{H}• + \text{H}• \rightarrow \text{H}_2
\]

\[
\text{H}• + \text{OH}• \rightarrow \text{H}_2\text{O}
\]

\[
\text{OH}• + \text{OH}• \rightarrow \text{H}_2\text{O}_2
\]

\[
\text{H}• + \text{O}_2 \rightarrow \text{HO}_2•
\]
Therefore, to prevent these primary radicals from recombination and also to produce a secondary reductant radical, some types of alcohol could be added (Figure 7).

Figure 6 Formation and recombination of hydrogen and hydroxyl radicals.

Figure 7 Formation and recombination of hydrogen, hydroxyl radicals in presence of alcohol.
Equations below present the formation of the reducing radical ($R\cdot$) via ultrasound irradiation and scavenging action of hydrogen and hydroxyl radicals towards the hydrogen of the additive [19].

\[
RH \rightarrow R\cdot \text{(reducing radical)} + H\cdot
\]

\[
OH\cdot \text{ or } H\cdot + RH \rightarrow R\cdot \text{(reducing radical)} + H_2O \text{ or } H_2
\]

Ag(I), Au(III), Pt(II), Pd(II) + 1R\cdot \text{(reducing radical)} \rightarrow Ag(0), Au(0), Pt(0), Pd(0) + R' + H^+

In work done by Takatani et al. [14] surfactants such as sodium dodecyl sulfate (SDS) and PEG-MS which is a polyethylene glycol compound have been used to produce bimetallic nanoparticles of Au/Pd and Au/Pt.

Darroudi et al. [1] produced silver nanoparticles by ultrasound irradiation of silver nitrate solution in presence of gelatin [20]. Polyvinyl alcohol (PVA) in addition to copper nitrate and sodium hydroxide solution as a starting precursor was used by Wongpisutpaisan et al. to produce copper oxide nanoparticles using sonochemical approach.

In a very recent study by Hasin et al. [21] on sonochemical synthesis of CuH, methanol has been added to the copper sulfate solution in order to promote the rate of production of CuH. They reported that the methanol vapor goes into the cavitation bubble and scavenges the OH\cdot radicals. At very high temperature inside the bubble, the thermal reforming of methanol vapor will create secondary hydrogen radicals (or molecules) therefore the rate of reduction will accelerate significantly. In this current study also CuH was produced by sonicating copper sulfate solution, but instead of methanol, ethanol was added to the reaction solution.

2.2.1.1 Sonochemical synthesis of single-metal nanoparticles

It has been reported that ultrasound irradiation of aqueous solutions containing metal salts produces metal nanoparticles which compared to nanoparticles synthesized by other conventional methods have smaller particle size, greater surface area, and narrower size distribution [22].

Y. Nagata and coworkers [19] using high intensity ultrasound fabricated fine gold particles with an average size of 10 nm, using NaAuCl$_4$ as the main precursor. They observed that in presence
of some organic additives such as water-soluble polymers, aliphatic alcohols and ketone, the rate of synthesis of gold particles was increased. They also claimed that the radicals formed from thermal reaction of these additives inside the bubble as well as in the interfacial region of bubble and the bulk solution, are more responsible for the gold reduction than the hydrogen and hydroxyl radicals formed inside the bubble.

In another work done by A. Nemamcha et al. [22], palladium nanoparticles with a mean size of 3 nm were synthesized from an ultrasonically irradiated palladium nitrate solution in presence of ethylene glycol and poly (vinylpyrrolidone) (PVP). They showed that by increasing the Pd(II)/PVP molar ratio, the particle size increases and the number of the particles decreases consequently.

Dhas and coworkers [23] prepared metallic copper nanoparticles by sonochemical synthesis. A slurry of copper hydrazine carboxylate (CHC) precursor was exposed to ultrasound irradiation for 3 h. The synthesized Cu nanoparticles were partially oxidized to Cu$_2$O due to the generation of H$_2$O$_2$ in the solution. They also used an argon/hydrogen atmosphere to yield the reduction rate (the hydrogen can scavenge the hydroxyl radical). They believed that the H• radicals formed from sonolysis of water under irradiation, reduce Cu$^{2+}$ to Cu$^{0}$.

### 2.2.1.2 Sonochemical synthesis of alloy or compound nanoparticles

The advantage of using an ultrasound irradiation method to produce alloy nanoparticles to other conventional methods is that it does not need high temperatures during the reactions.

Silver iodide (AgI) nanoparticles were prepared ultrasonically by reaction between AgNO$_3$ and KI in a study by Abbasi and Morsali. [24] They investigated and changed the different parameters such as effect of stirring, temperature and sonicating time to optimize the conditions for the best nanostructured growth and morphology. They found that by increasing the sonication time the particle size will increase. Stirring of the solution has the same effect on the particle size.

J. Kim et al [25] produced Pd-Sn nanoparticles with particle size of about 3-5 nm, by using an ultrasound irradiation method. In their synthetic approach, they used a solution of (NH$_4$)$_2$PdCl$_4$ and SnCl$_2$ as primary precursors. Ethanol and citric acid were used as reducing agent and
stabilizing agent, respectively. They showed that the particle size and the distribution of Pd-Sn nanoparticles are controlled by the amount of ethanol and stabilizer as well as the initial metal ion concentration.

Recently Radziuk and coworkers [26] have fabricated silver/gold-alloy nanoparticles from preformed gold and silver nanoparticles using high intensity ultrasound. In their synthetic route, a solution of preformed gold nanoparticles, by citrate reduction of chloroauric acid in water, and silver nanoparticles, after reduction of silver nitrate by sodium borohydride, were irradiated ultrasonically in presence of surface-active species to produce gold/silver-alloy nanoparticles. The reduction of silver nanoparticles on the layer of gold particles by H• radicals and also the fusion of silver particles at the edge of gold nanoparticles during the sonication, are two theoretical reasons for the formation of the gold/silver-alloy nanoparticles.

In another work by Radziuk et al. [26] silver-gold nanoparticles were produced ultrasonically by using a slurry solution of citrate-reduced gold nanoparticles and silver nitrate. SDS, 2-propanol and ethylene glycol were added to the solution separately in three different reduction experiments. Depending on the type of used surface active additive, different shaped silver-gold nanostructures were formed.

2.2.2 Sonochemical deposition of nanoparticles on a solid surface

The utilization of ultrasound irradiation has been further developed for surface modification and depositing the nanoparticles on the surface of a substrate. The sonochemical method facilitates the deposition of nanoparticles on various substrates in a one-step process [27]. As described above, the phenomenon responsible for ultrasound irradiation is acoustic cavitation; involving the formation, growth and collapse of microbubbles in a liquid medium. The collapse at solid surfaces creates high pressure and temperature as well as shockwaves and microjets of liquid towards the surface. These high velocity microjets throw the nuclei of produced nanoparticles at the surface and as a consequence, strong adhesion of nanoparticles to the surface may be achieved [28]. In addition, the simultaneous formed shockwaves with energy higher than microjets, can promote the deposition on the substrate [29].

V. Pol et al. [30] ultrasonically deposited gold nanoparticles with an average size of 5 nm on silica submicrospheres using chloroauric acid (HAuCl₄) as the main precursor. They claimed
that the formation of the gold nanoparticles occurs at the outside of the collapsing bubble at the interfacial region, in which the temperature required to rupture the Si-O-Si bonds will be met. They used liquid ammonia in drops during sonication to activate silica surface to produce reactive silanol groups and achieve a better coating. Based on their work, the gold nanoparticles thrown at the silica surface react with free reactive silanols to form Au-O-Si bonds. They suggested that an optimization of initial gold concentration is needed to achieve a homogeneous deposition layer.

Silica nanoparticles were deposited on the surface of titanium plates via ultrasound irradiation technique in a study done by Kaş and coworkers [31]. The authors claimed that they overcame the adhesion problem of the nanoparticles to hard substrates such as titanium by creating a chemical contact between the substrate and the deposited silica nanoparticles. They carried out two different experiments: in the first one, a solution of water as solvent, ammonia and tetraethyl orthosilicate (TEOS) with different water/TEOS ratio, temperature, and pH and sonication time was sonicated; no homogeneous coating was formed on the surface. In the second experiment, the surface of the titanium plates were activated by sitting in piranha solution (70% sulfuric acid and 30% hydrogen peroxide) for 30 min resulting in surface oxidation and also active hydroxyl groups creation on the surface where the silica particles can attach covalently. Silica nanoparticles were synthesized ultrasonically in ethanol or acetone used as solvent and deposited onto a piranha activated surface with the high intensity ultrasound. The piranha treatment was found to be essential to obtain homogenous and thicker coatings since with no surface activation treatment, non-uniform coatings were achieved.

In a report by Z. Zhong et al. [32], amorphous submicrospherical alumina was coated by molybdenum oxide using molybdenum hexacarbonyl as the precursor. In a different deposition work by Belova and colleagues [33], a slurry of Au colloid solution and TiO₂ particles was ultrasonically irradiated for different sonication times to produce Au-TiO₂ nanocomposites with small particle size, narrow pore-size distribution and large surface area. The authors showed that the insertion of the Au nanoparticles into the TiO₂ was highly dependent on the time and amplitude of ultrasonic treatment.
2.2.3 Ultrasound-assisted electrodeposition

It has been demonstrated that ultrasound irradiation can improve the quality of an electrodeposited layer, increase its adhesion to the substrate, enhance its hardness and brightness and reduce its porosity and internal stress. Walker and Walker reported the ultrasound frequency and intensity as two important experimental parameters that can affect the quality of the deposits. They claimed that the smaller grain size obtained under the effect of sonication can be responsible for hardness improvement of electrodeposits. However, the hardness was shown to be reduced by increasing frequency. In terms of internal stresses, it was presented that microdistortion induced by cavitation on the surface, pH changes during the ultrasound and the smaller grain size are associated with the reduction of internal stresses [34, 35].

Hyde and Compton [36] also studied the influence of ultrasound on electrodeposition of metals. They specifically investigated the relationship between concentration of the solution and the effect of ultrasound. They found out that, a system with low concentration (which is under diffusion control), under the effect of ultrasound will be changed to charge transfer controlled system. This can be attributed to the increase of mass transfer coefficient due to ultrasonic agitation during the electrodeposition.

In another study done by Kobayashi [37], the effect of ultrasound on both electroless and electrolytic nickel deposition was studied. They observed an improvement on diffusion rate of Ni\(^{2+}\) ions and also deposition rate in an electroless nickel deposition process under the effect of ultrasound. And for electrolytic nickel deposition process, a more oriented crystal structure, an increase in exchange current density was reported.

2.3 Effective parameters in sonochemistry in a heterogeneous solid/liquid system

Important parameters such as temperature, initial concentration of the precursor solution, content of ethanol, effective distance between the sonicator tip and the substrate, amplitude and sonication time will affect the amount, size, shape and contribution of the particles as well as the quality and density of the nanoparticle deposition layer on the substrate.
2.3.1 The effect of temperature

It has been known that temperature plays an important role in the bubble nucleation process. As the temperature increases, in an ultrasound irradiation approach, the rate of nucleation will increase resulting in significant enhancement of the nanoparticles production rate. Higher temperature, apart from the facilitating the nucleation process, increases the vapor pressure and decreases the surface energy. Therefore, for the nucleation in presence of a solid surface (heterogeneous nucleation), an increase in temperature accelerates the effect of liquid microjets towards the surface causing more surface attack. [38]. In terms of particle size, an increase in temperature creates an increase in the mean particle size [27].

2.3.2 The effect of initial concentration of metal ions in the precursor solution

Both the size of particles and the coverage density of the deposited layer on the surface of a substrate are dependent on the concentration of the metal ions in the solution. By increasing the concentration of the initial salt precursor solution, the particle size will increase. lower the concentrations of the precursor solution results in smaller size, as well as a less dense deposition layer [29]. This is in agreement with the results reported by Avila-Alfar o et al. [27].

2.3.3 The effect of ethanol content

In the ultrasound irradiation nanoparticle synthetic approach, for increasing the particle production rate, usually a source of secondary reducing radicals such as different types of alcohol (e.g. propanol or ethanol) will be added to the salt precursor solutions. Moreover, the particle size is highly dependent on the concentration and type of the alcohol [39].

Kim et al. [25] investigated the effect of ethanol on the formation of Pd-Sn nanoparticles. They observed that with no alcohol added to the solution, a small amount of Pd-Sn particles were produced, but in the presence of 50% ethanol, high amount of nanoparticles were produced.

Caruso and coworkers [18] significantly enhanced the production rate of platinum by adding aliphatic alcohols to PtCl₂⁻ precursor solution. Their explanation for this increase is that the interfacially adsorption of alcohol to the cavitation bubble in the irradiated solution will scavenge the primary radicals from recombination. Therefore, more radicals will be available to
reduce Pt from the solution, and also the alcohol will produce a secondary reducing radical which increases the reduction rate.

2.3.4 The effect of sample–probe distance: The distance between the sonicator tip and the substrate surface

It has been shown that shortening the distance from the sonicator tip to the surface of the substrate will increase the amount of deposited nanoparticles on the surface and will narrow the size distribution of the nanoparticles. In the deposition of nanoparticles on the surface of a substrate by sonochemical method, in longer sample-probe distance, the nanoparticles will be thrown to the surface with less speed and kinetic energy. Therefore, their adherence to the substrate surface will be weaker and they could be washed off the surface easily [29]. In addition, based on some studies done on the effect of ultrasound on the surface roughness, it has been shown that there is a decrease in roughness uniformity for sample-probe distance shorter and higher than the optimal distance (which is different for the different metallic materials and could be achieved by trial and error) [40].

2.3.5 The effect of amplitude

The ultrasound amplitude determines the velocity and acceleration of the particles [31]. The acoustic amplitude has a significant impact on the maximum bubble size reached during the rarefaction phase and both the resulting collapse intensity and the time required for bubble to collapse will be affected consequently [41]. The larger the amplitude is, the collapse of the cavitation bubble on the solid surface will be more destructive and the surface damage will increase dramatically [4]. In terms of ultrasound-driven deposition, some studies show an increase in thickness of the coating layer by increasing the ultrasound amplitude [31].

2.3.6 The effect of sonication time

In case of nanoparticle synthesis by ultrasound irradiation approach, the longer the time for which the solution is exposed to the radiation results in larger amount of produced nanoparticles. However, the longer sonication time does not produce a significant variation in the average particle size [27]. Moreover, in the ultrasound-assisted deposition process, the
longer sonication time leads to a significant increase in surface roughness and less uniformity of the deposited nanoparticle layer on the surface of the substrate [40].

2.3.7 The effect of ultrasound frequency

By increasing the frequency, on one hand, number of the cavitation bubbles will increase, therefore, the higher amounts of free radicals will be expected to be formed. But on the other hand, at very high frequencies, the amount of free active radicals decreases due to there not being enough time for the evaporation of water and the reducing agent molecules to happen during the expansion cycle of the bubbles.

Okitsu et al. [42] investigated the effect of variations of ultrasound frequencies on the reduction rate and the particle size. To identify the optimum frequency in the sonochemical reduction of gold nanoparticles, they ultrasonically irradiated 0.2 mM HAuCl₄ at frequencies in the range of 20-1062 kHz. They found that, at frequency of 213 kHz, the rate of the gold reduction was the highest with formed smallest particle size.

2.3.8 The effect of irradiation atmosphere

Usually the nanoparticles reduction rate is strongly dependent on the irradiation atmosphere. In other words, the gas environment which is used in the sonication process affects the amount of produced hydroxyl radicals and H₂O₂ and H₂. Nagata et al. [19] produced gold nanoparticles in an environment with and without oxygen. They found that the rate of reduction of gold nanoparticles, in presence of oxygen, decreased significantly. They assumed that the oxygen scavenged the hydrogen radicals formed from water sonolysis process and the reducing radicals produced from additive reducing agents will also be scavenged. As a consequence, the rate of gold nanoparticle reduction will be reduced.

\[ \text{H}^\bullet + \text{O}_2 \rightarrow \text{HO}_2^\bullet \text{ and } \text{R}^\bullet + \text{O}_2 \rightarrow \text{ROO}^\bullet \]

2.3.9 The effect of deaerating time

Oxygen radicals will be formed due to thermal decomposition if sonolysis occurs in presence of oxygen [43]. It has been suggested that the oxygen radicals in an irradiated solution are generated mostly by decomposition of O₂ rather than decomposition of water molecules [44]. In
the presence of oxygen, the hydrogen and hydroxyl radicals produced from sonolysis of water will react with oxygen atoms and form HO$_2^\bullet$ radicals which are strong oxidants [45]. Therefore the deaerating time before sonication process plays an important role in the quality of the produced nanoparticles. The longer the deaeration time is, the lower the oxidation rate of the nanoparticles will be.

2.3.10 The effect of type of deaerating gas

The gas environment which is used in a sonication process affects the amount of produced hydroxyl radicals and H$_2$O$_2$ and H$_2$ consequently. Lavigne et al [45]. In recent work have shown that gas solubility and thermal conductivity will influence the amount of produced OH• radicals, in which will lead to an enhancement in the passive current density values of a stainless steel plate. Moreover, the dissolved gases (nitrogen, argon or oxygen) in the sodium sulfate solution will undergo degradation under the high temperatures and pressures induced by cavitation and as a result may affect the chemical reactions.

2.4 The surface modification induced by ultrasound

The irradiation induced by high intensity ultrasound in liquid medium can provide cavitation bubbles. These bubbles collapse on or near a solid surface immersed in an irradiated solution generating shockwaves and high velocity microjets towards the surface of the substrate. Therefore, the solid surface will deteriorate and undergo plastic deformation. Some material will be removed from the surface under the effect of microjets and shockwaves induced by the collapsing of the bubble. This phenomenon is called cavitation erosion [35].

2.4.1 Surface roughness

Ultrasonic surface treatment can be an effective method to homogeneously roughen metallic surfaces and obtain a vast range of surface qualities.

An extensive study was published by Chiu et al. [46] who investigated the effect of sonication on surface roughness of different materials: AISI 316L stainless steel, commercially pure titanium, and brass (30 wt. % Zn) in deionized water at the distance of 0.5 mM from the sonicator horn tip. They defined three stages for roughness evaluation in which the roughness
increases in the initial stage (stage I) when the erosion begins and a negligible amount of material is removed from the surface. In transition stage (stage II), by increasing the erosion, the roughness decreases. Finally in the steady-state stage (stage III), the material removal tends to occur at a constant rate, and due to a self-regulating process, the roughness remains unchanged.

2.5 The effect of ultrasound irradiation on electrochemical behavior of metallic materials

Ultrasound irradiation apart from its chemical impact on the liquid medium (e.g. water sonolysis), can cause microscopic mechanical effects on the surface of an immersed substrate due to collapse of the cavitation bubbles and the effect of induced shockwaves and microjets [40, 47]. Ultrasonic radiation can change the interfacial reactions mechanism, modifies the surface properties, chemistry and reactivity [48], increases the mass transport in the solid-liquid interface [40], enhances the hardness of metals produced through ultrasound-assisted electrodeposition [49], and for the metal substrates; it can affect the behavior of the metal (if the metal is passive, the passivity breakdown will be promoted under the effect of ultrasound) [50]. All these changes made by ultrasonic radiation, especially the higher mass transport of solution, influence the electrochemical/corrosion processes.

2.5.1 Corrosion performance

De Morais and Brett [51, 52] investigated the effect of ultrasound on the corrosion behavior of aluminum and high speed steel electrodes in chloride solution (KCl with various concentrations of 0.01 to 1 M). It was reported that, in the case of aluminum, the passive layer on the surface of aluminum was removed by the effect of the cavitation phenomenon and deep pits were formed and in consequence, corrosion rate increased. As for high speed steel, the passive film formed on the surface of steel was not as strong as the one on Al, then pitting occurred even before the start of sonication. However, the pitting and the corrosion rate were increased under the effect of sonication.

Doche et al. [50] have studied the electrochemical behavior of zinc in 20 kHz sonicated NaOH solution. The passive film, formed on the surface of zinc in the passivating 1M NaOH electrolyte, was observed to be very resistant to the sonication. However, under the mechanical
effect of cavitation collapse, partial parts of the passivation layer were broken down. Besides, no corrosion rate increases were reported.

The effect of ultrasound on corrosion behavior of a 304L stainless steel has been investigated by Whillock and Harvey. [41] Based on their results, corrosion rate of 304L stainless steel in 2 M nitric acid solution increases when the frequency and acoustic power increase and the sample-probe distance decreases. The increase of corrosion rate due to increase of the acoustic power and frequency is attributed to the cavitation intensity. The higher the power is, the more intensive the bubble collapse will be. Hence, the surface damage and corrosion rate will increase. They further found that, by decreasing the sample-probe distance, the surface pressure and stress will increase exponentially resulting in production of microjets with higher velocity towards the surface.

2.5.2 Mass transfer, diffusion layer and limiting current density

When a liquid is exposed to high intensity-low frequency ultrasound, besides the cavitation phenomenon, microstreams and turbulent flows are generated [53, 54] resulting in an improvement in mass transport and a reduction in thickness of diffusion layer [55, 10]. As a consequence, the limiting current density will increase dramatically. Lavigne et al [45] suggest that the increase of current density is attributed to an increase of the oxygen reduction by increasing the agitation of the irradiated solution, and possibly to the reduction of oxidant OH• and HO2• radicals.

2.5.3 Open circuit potential

The measurement of the oxidizing power of the solution is usually described as the electrode potential [56]. Open circuit potential (OCP) can be defined as the electrode potential when there is no current applied to the electrochemical cell. OCP is usually measured as a potential difference between a working electrode and a reference electrode [57].

Lavigne et al. [45] investigated the effect of ultrasound on OCP evolution of a 316L stainless steel. They measured OCP of a sonicated stainless steel plate in different concentration of Na2SO4 solution under the flow of argon. Under the effect of ultrasound, hydrogen peroxide and hydrogen will be produced upon water sonolysis which affect the thickness of diffusion layer
and limiting current density and the value of OCP. Based on their results, by increasing the concentration of the irradiated solution, OCP of the sample shifts to more positive values indicating that \( \text{H}_2\text{O}_2 \) is more dominant.

2.6 Synthesis and deposition of silver

2.6.1 Sonochemical synthesis of silver nanoparticles

Silver nanoparticles with applications in nanotechnology, medicine, catalysis, and biomaterials have some unique properties which are strongly dependent on the particle size such as optical, electrical, chemical, and catalytic properties.

Recently in a study done by Zhu et al. [58] silver nanorods with lengths of 4–7 µm and mean diameters of about 100 nm have been synthesized by ultrasonic irradiation of aqueous solution of silver nitrate, methenamine (HMTA) and poly (vinyl pyrrolidone) (PVP). It was discovered that the morphology of silver nanorods is strongly dependent on the concentration of PVP, the irradiation time and the reaction temperature.

In another study by He and colleagues [59], the sonochemical formation mechanism of silver nanoparticles in neutral and alkaline aqueous solution was examined. They indicated that in neutral solution, the total cell reaction potential is negative (anodic reaction: \( \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2} \text{O}_2 + 2e^\cdot (E^\circ_1 = +0.4010 \text{ V}) \), cathodic reaction: \( 2\text{Ag}^+ + 2e \rightarrow 2\text{Ag} (E^\circ_\text{R} = +0.7994 \text{ V}) \) which means the reaction cannot happen on its own. But under high temperature and pressure induced by cavitational bubble collapse, the cell reaction is accessible. It was shown that in an alkaline aqueous solution (a mixture of AgNO\(_3\), NaOH and diluted ammonia), the silver nanoparticle production rate was higher than the neutral solutions. Figure 8 shows the Ag nanoparticles formation under alkaline conditions; Ag\(_2\)O was produced by decomposition of AgOH and was hydrolyzed into Ag(OH)\(_x\) complexes again, then by accepting released electron from OH\(^-\) or OH\(^\cdot\), Ag\(^0\) was formed.
2.6.2 Deposition of silver nanoparticles on different substrates

Silver nanoparticles have been simultaneously reduced and deposited on different substrates including a stainless steel plate, silica microspheres, acrylonitrile–butadiene–styrene (ABS), polystyrene spheres (PS) and a glass slide.

A stainless steel plate was coated with silver nanoparticles in work reported by M. Soloviev and coworkers [29]. A solution of silver nitrate, water, ethylene glycol was the initial precursor solution. A solution of 25% aqueous ammonia was added to the slurry solution in order to get the maximum amount of silver nanoparticles. Aqueous ammonia by producing the OH$^{-}$ ions yields the formation of transitional silver(I) oxide (Ag$_2$O), which will be converted to metallic silver immediately, and also, by forming the [Ag(NH$_3$)$_2$]$^+$ complex prevents the agglomeration and fast growth of silver nuclei. In this work, the effect of the distance of the sonicator tip from the substrate is emphasized. By sonicating a stainless steel plate in 17-50 mM AgNO$_3$ solution with a distance of 2 cm away from the sonicator tip, aggregates of 100-200 nm was detected (no fully dense homogeneous coverage was achieved). But by reducing the sample-probe distance to 1 cm, better quality coverage with almost no aggregates was formed.

Pol et al. and Askari et al. [60] with the aid of power ultrasound deposited silver nanoparticles on silica submicrospheres to produce silver-silica nanocomposites [63, 64]. In the report by Pol and his coworkers, a mixed slurry solution of silica microspheres, silver nitrate and ammonia was sonicated for 90 min under an atmosphere of argon and hydrogen (95:5). It was shown by carrying out some control experiments that sonochemical reduction of silver nanoparticles occurs in the interfacial region (hot shell). In this report unlike the previous one, a uniform deposition layer of silver nanoparticles on the surface of silica submicrospheres were produced.
And also a 4h deaeration time was highlighted to remove the oxygen completely and prevent the conversion of metallic silver particles to silver oxide.

The surface of acrylonitrile–butadiene–styrene (ABS) as a substrate was silver coated by sonochemical method in work done by Avila-Alfaro et al. [27]. A solution of silver nitrate (AgNO₃), ethylene glycol, water and PVP (stabilizer) was chosen as the initial precursor solution. Similar to the previous reports, a 24 vol. % ammonia aqueous solution was added to the solution. The effect of temperature, sonication time and concentration of Ag⁺ ions in the solution on the amount of the deposited silver nanoparticles and also the quality of the coating layer was the focus of this research. It has been reported that, by increasing the concentration of silver nitrate in the solution, sonication time and temperature, the silver content increased to almost 100%, however, the particle size was observed to be independent to the sonication time. Additionally it was detected that, the silver was not chemically but rather physically linked to the surface of ABS.

V. Pol and coworkers [62] also used ultrasound irradiation method to deposit metallic nanoparticles of Au, Ag, Pd, and Pt on polystyrene spheres (PS) particles employing AgNO₃, Pd(NO₃)₂ and H₂PtCl₆ as the main precursors. The liquid microjets and shockwaves resulting from the collapse of the cavitation bubbles near the surface of PS push the nanoparticles towards the surface. Interparticle collision between PS surface and produced nanoparticles and sintering of those nanoparticles to the PS surface occur when the nanoparticles hit the surface resulting in the bonding of the Au, Ag, Pt, and Pd nanoparticles to the surface and finally in the coating of the spheres. Their proposed sonochemical mechanism is based on chemical interactions between the particles.

In another work published by N. Perkas et al. [28], a glass slide was coated by silver nanoparticles using a sonochemical method. Perkas and co-workers used silver nitrate as the precursor solution and a water-soluble polymer, poly vinyl alcohol (PVA) and poly(vinylpyrrollidone) (PVP) as the stabilizing agents to avoid silver nanoparticles agglomeration. The throwing of the small silver nanoparticles at the glass substrate by the effect of microjets induced by bubble collapse and their adhesion to the surface was the first step in the silver deposition on the glass. In the subsequent steps silver nuclei were deposited on the existing layer, resulting in layer by layer growth and crystallization during the reaction.
Subsequently, a close-packed crystalline silver film slowly formed on the surface of the glass substrate. They claimed that they found the diffusion of the silver particles with a size of up to 60 nm into the surface of glass slide. They also investigated the effect of initial precursor, reaction temperature and sonication time on the homogeneity of the deposited silver layer.

2.6.3 Deposition of silver particles on copper substrate by means of displacement reaction and ultrasonic irradiation

2.6.3.1 Introduction to metal displacement reduction reaction

Metal displacement reduction reaction can be described as a replacement of atoms of a more electropositive metal soaked in a solution by a more noble metal from the solution [39]. An example of such a reaction can be displacement of copper atoms by silver from silver nitrate solution. Figure 9 shows an illustration of the displacement reaction process in copper-silver system.

![Figure 9 Copper atoms replacement by silver ions (displacement reaction). Adopted from reference [63].](image)

Displacement reaction can be considered as a type of corrosion in which the oxidation and dissolution of less noble metal as one half anodic cell reaction balances reduction and deposition of more noble metal from the solution as the other half cell reaction (cathodic reaction) [63]. The equation for copper-silver displacement reaction will be:

\[ 2 \text{Ag}^+ + \text{Cu} \rightarrow 2 \text{Ag} + \text{Cu}^{2+} \]
The silver-involved replacement reaction can principally be extended to any less active metal with redox potential lower than that of the Ag\(^+\)/Ag pair [64]. The metal activity series (redox potential series) is given in Table 1.

Table 1 Metal activity series

![Metal activity series](image)

Furthermore, displacement reaction between a metal and a solution (sometimes referred to as galvanic replacement reaction) can be used to produce nanostructured materials [65]. Liu and Sen [66] have recently synthesized 1-D silver nanostructures by displacement reaction process. Based on their report, when a copper substrate is placed in AgNO\(_3\) aqueous solution, initial deposited silver seeds grow preferentially from the tips of cathodic silver seeds.

The growth mechanism of silver is illustrated in Figure 10.

![Growth mechanism of silver nanobelts](image)

Figure 10 Growth mechanism of silver nanobelts from 500 nm copper nanoparticle in 5 mM AgNO\(_3\) in 5 min. Adopted from reference [66].
They have claimed that the type of silver nanostructure (nanobelt, nanodisk, dendrite and nanoparticle) varies depending on the concentration of the initial AgNO\(_3\) solution and the size of copper substrates. Figure 11 is a scheme of various silver nanostructures proposed by Liu and Sen for different AgNO\(_3\) concentration and copper particle size.

Figure 11 Different formed Ag nanostructures based on the concentration of AgNO\(_3\) and the substrate particle size proposed by Liu and Sen [66].

Therefore based on the theory published by Liu and Sen, although the theory is for copper nano/micoparticles, it could be extended to bulk copper (>5\(\mu\)m)). In AgNO\(_3\) aqueous solution with concentration more than 5 mM, the silver particles grown on the surface of the bulk copper will have dendritic structure. By increasing the concentration of AgNO\(_3\), the structure still remains dendritic but its size grows bigger. The higher concentration leads to higher reduction and deposition rate of silver particles on the tips of already existed Ag seeds, then, dendritic structure will be formed owing to this fast growth (Figure 12) [66].
2.6.3.2 Nanomaterials synthesis by means of ultrasound-assisted metal displacement

Zeng and coworkers [39] introduced a novel synthetic approach called sonomechanical-assisted metal displacement reduction to produce gold and platinum nanoparticles. Au and Pt nanoparticles with 6-10 nm sizes and narrow size distributions were produced through the displacement reduction of precursor salts of HAuCl₄ by Cu foils and H₂PtCl₆ by Fe foils. A low intensity high frequency ultrasound device (laboratory cleaner) was used to dislodge the nanoparticles from the foils. In this method, ultrasound was not directly engaged to reduce the metal salts. However, the physical effect of ultrasound (the shockwaves, liquid microjets and shear forces induced on the collapse of cavitation bubbles) was preferentially employed.

In work done by Mancier et al. [67], copper core-silver shell nanopowders were produced by ultrasound-assisted electrochemistry followed by a displacement reaction. The copper suspension was first created by means of pulsed sonoelectrolysis, and then poured in silver oxide solution for displacement reaction process. The copper core-silver shell nanopowders were formed by substitution of copper atoms from the surface of powders by silver ions from the solution.
3 Experimental Details

3.1 Ultrasound irradiation assisted reduction studies

3.1.1 Materials

For the sonochemical reduction/production part of the present work, different salt solutions were exposed to ultrasound irradiation; including copper sulfate (CuSO₄) and silver nitrate (AgNO₃). CuSO₄ was supplied by EMD and AgNO₃ was purchased from Alfa Aesar.

3.1.2 Solution preparation and experimental setup

A solution made up of 100 ml solution of 20 mM of each salt listed above, 65 ml of deionized water and 35 ml of ethanol, was introduced to a 250 ml ultrasound bath. The ultrasound bath was purged with argon before and during experiments. Argon purge was applied for 20 min before sonication, in order to remove oxygen from the reaction solution. The solution was irradiated with a high intensity ultrasonic horn for 3 h at room temperature to examine the nanoparticle formation. The irradiation was done with amplitude of 120 µm which is the maximum device amplitude.

The ultrasound vessel was attached to a water-cooling bath to maintain the container temperature at 25 °C. To avoid ethanol evaporation during argon purging, argon gas was bubbled through a sealed container of ethanol; the gas was then discharged to the sonication solution (Figure 15).

The produced nanopowders were washed with sprayed water and ethanol, filtered using paper filters, kept in a desiccator and took for analysis by XRD.

3.1.3 Operating procedure

3.1.3.1 Principles of operation

The ultrasonic machine has a generator that converts the alternating current (AC) power to a 20 kHz signal which in turn, enables the piezoelectric transducer to drive a mechanical vibrator. This phenomenon occurs because of the characteristics of the piezoelectric crystals inside the converter. The generated vibration is amplified and is transmitted outwards toward the horn tip,
creating a longitudinally expansions and rarefactions. The distance that the tip travels depends on the amplitude which configured as manual setting. When the amplitude is increased the sonication intensity will also increase. The rapid vibration of the tip of the horn in the liquid sets off cavitation. The cavitation generates energy in the surrounding area in the liquid solution. The size of the probe (diameter of the tip) essentially ordains the intensity of sonication. The smaller the size, the higher is the intensity within a small and focused area. The larger the size, the larger volume of sonication is produced at a lower intensity.

Figure 13 Q500 sonicator including a standard ½” diameter probe with replaceable tip, convertor, converter cable and a generator.

The unit of measurement of sonication is in watts. Furthermore, amplitude is a measurement of the probe (horn) distance travelled. As the movement of the horn becomes harder in the solution, more power is delivered to maintain amplitude. For instance, 5 watts of power is required to operate a ½” probe at 100% amplitude, in air. The amplitude of Q500 probe is almost 120 µm. The same probe in water will require 90 watts to operate at the same amplitude. The intensity of sonication ultimately depends on the concentration and strength of the cavitation not the amount of power delivered. Cavitation intensity is directly impacted by the
amplitude. The importance of maintaining accurate amplitude is paramount in deriving optimal results.

3.2 Ultrasound irradiation assisted deposition studies

3.2.1 Materials

For most of sonochemical experiments present in this study; copper slugs, silver nitrate and ethanol were used as the substrate, precursor for silver deposition and reducing agent, respectively. The copper slugs (cut from a copper rod with a diameter of 6.35 mM and purity of 99.5%) were purchased from Alfa Aesar. Silver nitrate (AgNO₃) was also obtained from Alfa Aesar and used without any further purification.

3.2.2 Sample preparation and treatment

The copper slugs were annealed at 800 °C for 20 min and then quenched in cold water. In order to remove oxidation from the surface of the slugs, they were kept in a 3M nitric acid solution for 2 minutes and then washed with deionized water and ethanol. For being able to conduct further electrochemistry tests on the final products of the experiment, the samples had to be built in such way that an electrical connection could be made to the sample after running each leg of the experiment. To achieve this, a connection was made by gluing a steel needle to the bottom surface of the sample (Figure 14). Conductive silver epoxy glue was used in order to get the best connection. The slugs, afterwards, were embedded in epoxy.

Figure 14 A vertical cross section illustration of the copper sample prepared for ultrasound bath.
The mounted samples were mechanically polished with silicon carbide grit paper (320 grit) and diamond suspension (9 μm, 6 μm, 3 μm), and alumina suspension (0.05 μm). After polishing, the samples were washed with deionized water, ultrasonically cleaned in water-ethanol solution for 5 minutes, and air dried.

### 3.2.3 Experimental Setup

In a typical experiment, a mounted copper slug was placed in a home-made frame in order to guarantee the steadiness of the sample (Figure 16). The sample was secured in the sonicator vessel at a distance of 1 cm from the ultrasonic titanium horn. The reaction temperature was controlled by a water cooling bath. A solution made up of 100 ml solution of 20 mM AgNO₃, 65ml of deionized water and 35 ml of ethanol, was introduced to a 250 ml sonication bath. The concentration of AgNO₃ was varied in order to get a more uniform coating. The bath was purged with argon before and during experiments. Argon purge was applied for 20 min before sonication, in order to remove oxygen from the reaction solution. The same solution was irradiated with a high intensity ultrasonic horn. The irradiation was done with an amplitude of 84 μm (which is 70% of the maximum device amplitude), concurrently applying a consistent flow of argon. The deaeration duration was chosen to be 20 min based on Figure 52; the OCP measurement curve of samples sonicated versus different concentration of AgNO₃. As can be realized from Figure 52, deaeration time of 1200 s, is a safe starting point at which the surface does not experience severe corrosion by displacement reaction.

To avoid ethanol evaporation during argon purging, argon gas was released into a sealed container of ethanol; the gas was then discharged to the sonication solution. To capture disposed ethanol from the solution, a gas outlet tube was run from the solution into a container of industrial oil (Figure 15).
Figure 16 Sample placement in the home-made frame in an ultrasound under ultrasonic irradiation.

After sonication, the silver deposited copper sample was removed from the solution and was washed with deionized water and ethanol. To take any possible unbound silver particles away from the surface, the coated samples were rubbed gently by a wet cotton ball.
The effects of different concentrations of the precursor, reaction temperature and sonication time on the homogeneity of the deposited layer were investigated in order to prepare the best reaction conditions for depositing silver particles on the copper slugs.

3.3 Electrochemical studies

3.3.1 Materials and sample preparation

For all the electrochemical experiments (except for the open circuit potential (OCP) measurement experiments), a three-electrode setup consisting of a counter electrode (CE), a reference electrode (RE) and a working electrode (WE) was used. For OCP measurement experiments, two electrodes (working and reference) were used. A copper slug, a silver slug and silver deposited copper slugs were separately embedded on a basic epoxy housing that was hand-made in the lab. The samples also embodied a steel needle, stretching from below the slug to the outside of the epoxy housing. The needle was glued to the bottom of the slug with a silver-glue to ensure sufficient conductivity (Figure 17). To make the adequate conductivity, a plastic coated copper wire was tied to the needle and sealed with lacquer (Microshield). After the lacquer dried, the connection was secured by shielding it with a glass tube using epoxy glue. The tube was used to prevent solution and air to come to contact with the copper sample. This sample preparation procedure was applied for all the electrochemical experiments. The experimental setup is shown in Figure 18. For all the experiments, a junction was used for the reference electrode to avoid its destruction by microstreaming induced by ultrasound.

![Figure 17](image.png) A cross section illustration of the copper sample prepared for electrochemical tests.
Different reference electrodes were utilized according to the type of electrolyte employed in the different electrochemical techniques. In an alkaline environment with pH of 10 (0.1M sodium borate) a mercury/mercury oxide reference electrode (Hg/HgO) was used. In regular silver nitrate solution with pH of 7-7.5, a silver wire (surface area of 50 mm$^2$ with purity of 99.9% supplied by Alpha Aesar) was chosen as a reference electrode. But before use, its stability was measured against mercury sulfate electrode (MSE) in 5 mM AgNO$_3$ using a portable voltammetry device. In order to monitor the stability of the silver wire, it was kept in the solution overnight (12 h). For the solution of 0.1 M sodium sulfate and 0.1 M sodium bisulfate with pH of 2, mercury sulfate electrode (MSE) was employed as a reference electrode. All the reference electrodes were obtained from Koslow Scientific Company, USA. A graphite rod (purity of 99.9%) was placed in the sonication vessel as the counter electrode.

The OCP, potentiodynamic polarization curve and cyclic polarization curve measurements were carried out, utilizing a certified Gamry600 potentiostat. The Gamry600 potentiostat device was controlled by Gamry Framework™ software.

Figure 18 Typical setup for electrochemical tests.
3.4 Characterization and analytical techniques

3.4.1 Environmental scanning electron microscopy (ESEM)

A FEI QUANTA FEG 250 environmental scanning electron microscope (ESEM) was used to observe the surface morphology and structure of the deposited silver particles. It was also used for imaging of the samples before and after sonication. An aluminum stub holder was used to clamp the samples. The scanning electron microscope was operated at 10 kV and with a 10 mM working distance. The ESEM was equipped with an EDAX Apollo XL-SDD detector.

3.4.2 Energy-dispersive x-ray spectroscopy (EDX)

Energy-Dispersive X-ray Spectroscopy (EDX) was utilized to confirm the silver distribution of the surface of samples sonicated and also to confirm the silver deposition. An EDAX Apollo XL-SDD Energy-Dispersive X-ray Spectrometry (EDX) detector attached to the ESEM, and EDAX software was used for all chemical composition analysis. Point analysis was run with an accelerating voltage of 10 kV with a 30 second count time.

3.4.3 X-ray diffraction (XRD)

X-ray Diffraction (XRD) was used to confirm whether the produced particles were metallic silver or silver oxide. A Philips diffractometer, model PW 1830 with X-PERT system software was employed for this matter. A rectangular aluminum-glass composite sample holder (2cm×1cm×0.2cm) was filled with the filtered powder sample. The X-rays were generated from Cu-Kα radiation (λ= 1.54 Å) with nickel filter. Bragg's angle (2θ) range of 10-50° and a scan speed of 2 second per step with a step-size of 0.02° were used. The ICDD Powder Diffraction File (1998) database was made available to obtain h, k and L values. The Philips diffractometer was operated at 40 kV and 40 mA. The structural pattern was recorded and analyzed with X-PERT HighScore™ software.

3.4.4 Cross-section analysis

The cross-section analysis was done to measure the thickness of the silver coating. Due to the porous nature of the silver coating deposited on the surface of copper, the Ni electroplating was exploited in a home-made Watts solution. The Watts solution was made of nickel sulfate, nickel
chloride, boric acid and deionized water. The electrodeposition cell contained a graphite rod as a counter electrode, silver/silver chloride (Ag/AgCl) as a reference electrode and a silver coated copper as a working electrode. A magnetic stirrer was used to stir the Watts solution and the solution was heated before and during the treatment. Based on our previous experiments, the temperature of 50 °C was chosen as an optimum reaction temperature to obtain the best surface plating. The galvanostatic measurement curve was carried out at 10 mA for 300 s. After Ni electroplating, the sample was cut in half vertically. Then the sample was polished to 3µm. The EDX analysis was conducted on the cross-section using a JEOL JSM6610-Lv scanning electron microscope, supplemented by an Oxford/SDD EDS detector with an accelerating voltage of 10 kV.
4 Results and Discussion

4.1 Nanoparticle synthesis by means of ultrasound irradiation

4.1.1 Irradiation of CuSO$_4$

By irradiation of 20 mM CuSO$_4$ in 65 ml deionized water and 35 ml ethanol, for 3h at room temperature some powder was produced, which was identified as copper hydride (CuH) by x-ray diffraction analysis. The XRD pattern of the produced powders by ultrasound irradiation of CuSO$_4$ is shown in Figure 19.

![XRD pattern of CuH](image)

Figure 19 The XRD pattern of the produced powder by ultrasound irradiation of CuSO$_4$ for 3 h at room temperature. The peaks are assigned to CuH.

The Cu$^{2+}$ ions in the solution will react with hydrogen radicals produced by acoustic cavitation to form Cu$^+$. Then, the Cu$^+$ ions will be combined to produce Cu$^0$ and Cu$^{2+}$. Cu$^0$ will react with H$^+$ and CuH will be formed.

\[
H_2O \rightarrow H^+ + OH^-
\]

\[
Cu^{2+} + H^+ \rightarrow Cu^+ + H^+
\]
4.1.2 Irradiation of AgNO₃

By irradiation of 20 mM AgNO₃ in 65 ml deionized water and 35 ml ethanol for 3 h at room temperature some powder was produced which was characterized by x-ray diffraction analysis as elemental silver (Figure 20).

Figure 20 XRD pattern of the produced powder by ultrasound irradiation of AgNO₃ for 3 h at room temperature. The peaks are assigned to elemental silver.

The silver nanoparticles were produced by 3 h ultrasonic irradiation of silver nitrate solution. After 2 h of the irradiation, the solution color started changing as the confirmation of silver nanoparticles production.

The silver ions dissolved in the solution will react with hydrogen radicals to produce zero-valent metal and finally produce silver nanoparticles.

\[
\text{Ag}^+ + \text{H}^* \rightarrow \text{Ag}^0 + \text{H}^+
\]

\[
n\text{Ag}^0 \rightarrow \text{Ag}_n
\]
4.2 Ultrasound assisted deposition of nanoparticles on a solid surface

Ultrasound has been recently known to be a useful and green tool for fabrication and modification of some practical materials [68]. Acoustic cavitation; the formation, growth and impulsive collapse of cavitation bubbles in a liquid medium, is responsible for chemical and physical changes induced by ultrasound irradiation [10]. During the ultrasound irradiation of a liquid medium (which usually contains metal salt) in presence of a solid surface, besides the formation of hot spots, shockwaves and high velocity microjets will be generated by the collapse of cavitation bubbles. These microjets throw the as-synthesized nanoparticles to the surface. Therefore kinetic energy of the solution motion will convert into heat and upon the high temperature and also the speed of thrown nanoparticles, the particles will adhere to the surface strongly [72, 73]. Several researchers have used this resulting impact to deposit different silver nanoparticles on the surface of different substrates [27, 28, 29, 65, 63, 74].

4.2.1 Deposition of silver particles on copper samples by means of simultaneous effect of displacement reaction and ultrasound irradiation

For the copper-silver system (copper as a substrate) besides the effect of ultrasound, the effect of displacement reaction should also be considered. In displacement reaction of copper in silver nitrate solution, a more noble metal (in this case silver) is replaced by copper which is less noble [63]. The silver dendrites will form on the surface of copper right after the sample is placed in silver nitrate solution.

The related equation will be \( \text{Cu} + 2\text{Ag}^+ \rightarrow \text{Cu}^{2+} + 2\text{Ag} \)

Therefore, under the effect of ultrasound, two kinds of silver particles will be produced; one by means of ultrasound irradiation method in the bulk solution and the other by means of displacement reaction on the surface of copper.

Under the effect of sonication, the shockwaves induced by ultrasound, dislodge the Ag seeds propagated on the surface of copper from the surface, or break the Ag dendrites formed on copper into smaller size particles [39]. Then microjets generated by the bubble collapse push these dislodged particles and also the ultrasonically produced particles towards the surface and cause a strong adhesion to the surface of the substrate. Perkas et al. and Avila-Alfaro et al.
applied this impact of high intensity ultrasound to deposit silver nanoparticles on a glass slide and an ABS sheet, respectively.

The first set of experiments was done using a 30 mM AgNO₃ aqueous solution in 100ml of mixed of water and ethanol (65 ml deionized water and 35 ml ethanol). The percentage of the deionized water and ethanol was fixed for all the experiments while the reaction temperature, the amount of initial concentration of AgNO₃ and sonication time were experimental variables. The reaction temperature was selected to be 25 °C and 50 °C to test the effect of temperature on the morphology of the deposited particles. The sample-probe distance of 1cm was chosen based on previous works [27, 28], and ultrasonic amplitude of 70% (84 µm) was chosen based on trial and error experiments done by the current researcher.

In order to make sure the produced particles were elemental silver, XRD analysis was done on the filtered and dried powder. The XRD peaks for the produced particles in Figure 21 are assigned to silver.

![Figure 21 XRD pattern of produced silver particles on the surface of copper by means of simultaneous effect of displacement reaction and ultrasound irradiation.](image)

Figure 21 XRD pattern of produced silver particles on the surface of copper by means of simultaneous effect of displacement reaction and ultrasound irradiation.
To analyze the homogeneity and continuity of the deposited silver particles on copper substrates, the ESEM images were obtained. Figure 22 shows the ESEM image of copper sonicated in 30 mM AgNO$_3$ aqueous solution at room temperature which was treated for 60 min.

Due to high concentration of silver nitrate in the initial solution, the silver displacement formation happens immediately after placing the sample in the solution. During the argon purging, depending on the reaction temperature and concentration of AgNO$_3$, type and particle size of copper substrate, the Ag particles grow differently in shape and size. For bulk copper, silver deposition may be hydrodynamically controlled, producing dendrites.

![Figure 22 ESEM image of copper sonicated in 30 mM AgNO$_3$ at 25 °C for 60 min.](image)

The initial hypothesis is that as sonication continues, two kinds of particles hit the surface of the substrate under the influence of high velocity microjets induced by cavitation bubble collapse: 1- the broken dendrites and the dislodged silver seeds (displacement reaction products) [39] 2-
the reduced silver particles from bulk AgNO₃ solution by means of ultrasound irradiation method [6, 7, 20, 62]. As a consequence, a strong adhesion will be made between the surface and attacking silver particles (Figure 22). After 10 min of sonication, the color of the reaction solution started changing to a light brown color which confirms the formation of the silver particles in the solution.

As it can be seen in Figure 22 and also in Figure 23 (a), at room temperature, some of the deposited silver particles with micron size dimensions have a polyhedral structure while others with nano size dimensions have irregular shape. This confirms the production of two kinds of silver particles by means of displacement reaction and ultrasound irradiation, although further confirmation is required.

![Image](image.png)

Figure 23 a) Higher magnification image of a copper sample sonicated in 30 mM AgNO₃ at 25 °C for 60 min, b) EDX result of spot 1.

In a higher magnification image of the same sample (Figure 23), the surface corrosion is clearly distinguishable. The chemical composition of the damaged surface and also the randomly deposited particles are determined by EDX analysis (Figure 23 (b)). This could be a combined effect of displacement reaction which is considered to be a type of corrosion [65] and particle
erosion [72]. Those spots of the surface that undergo the displacement nucleation of silver seeds are morphologically more vulnerable to the erosion corrosion induced by cavitation bubble collapse and the collided silver particles. The displacement reaction will be accelerated by hydrodynamics resulting from the ultrasound. Moreover, the existence of deep pits is a confirmation of the particle erosion on the surface of the substrate. However, the depth of pits is a function of produced particle size; by increasing the particle size, a bigger surface area will be influenced by the repeated particle bombardment resulting in higher surface erosion corrosion. In addition to the particle size impact, the intensity of the cavitation bubble collapse has also the same influence on surface erosion. The more intensive the collapse occurs near or on the surface of copper, the more aggressive the damage will be [4, 41].

Hence, depending on the initial concentration of the precursor, reaction temperature, and sonication time, quality of the adherent layer is different [31, 63].

The experimental conditions are summarized in Table 2.
Table 2 Summary of the treated samples and the surface coverage conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration of AgNO$_3$</th>
<th>Sonication time</th>
<th>T</th>
<th>Surface coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu 53</td>
<td>30 mM</td>
<td>60 min</td>
<td>25 °C</td>
<td>discontinuous, silvery shiny</td>
</tr>
<tr>
<td>Cu 54</td>
<td>20 mM</td>
<td>60 min</td>
<td>50 °C</td>
<td>continuous porous, dark matte gray</td>
</tr>
<tr>
<td>Cu 55</td>
<td>20 mM</td>
<td>60 min</td>
<td>25 °C</td>
<td>discontinuous, silvery shiny</td>
</tr>
<tr>
<td>Cu 60</td>
<td>20 mM</td>
<td>30 min</td>
<td>25 °C</td>
<td>discontinuous, silvery shiny</td>
</tr>
<tr>
<td>Cu 61</td>
<td>20 mM</td>
<td>30 min</td>
<td>50 °C</td>
<td>continuous porous, light matte gray</td>
</tr>
<tr>
<td>Cu 63</td>
<td>20 mM</td>
<td>0</td>
<td>25 °C</td>
<td>formation of silver dendrites on the surface</td>
</tr>
<tr>
<td>Cu 64</td>
<td>20 mM</td>
<td>0</td>
<td>50 °C</td>
<td>formation of silver dendrites on the surface</td>
</tr>
<tr>
<td>Cu 66</td>
<td>0</td>
<td>30 min</td>
<td>25 °C</td>
<td>no changes on the surface</td>
</tr>
<tr>
<td>Cu 65</td>
<td>0</td>
<td>30 min</td>
<td>50 °C</td>
<td>no changes on the surface</td>
</tr>
<tr>
<td>Cu 70</td>
<td>5 mM</td>
<td>30 min</td>
<td>50 °C</td>
<td>continuous porous, very light matte gray</td>
</tr>
</tbody>
</table>

4.2.2 Sonication of copper in water and ethanol solution in presence of already made Ag dendrites

Figure 24 shows the ESEM images of copper sonicated for 60 min at room temperature in silver nitrate, water and ethanol solution in presence of preformed Ag dendrites. After the sonication, the copper surface was covered with silver particles, but the coverage was removed easily by a cotton wipe due to its weak adhesion.
Figure 24 The effect of preformed Ag dendrites; ESEM images of the surface of a copper sample sonicated in 20 mM AgNO₃ for 60 min at 25 °C.

4.3 Effect of different reaction conditions

4.3.1 The effect of temperature

4.3.1.1 The effect of reaction temperature on surface of copper in silver nitrate solution without the effect of sonication

To investigate the effect of displacement reaction of copper substrate in silver nitrate solution, two samples of Cu-63 and Cu-64 were kept in a 20 mM AgNO₃ for 60 min at two temperatures of 25 °C and 50 °C. The solution was also argon purged during that time. The silver dendrites were formed right after the sample was merged in AgNO₃ aqueous solution. However, the amount of produced silver dendrites was different at two temperatures. The silver dendrites with
very weak adhesion to the surface were removed from the surface by spray water. The surface was gently rubbed by a wet cotton ball to remove all the loose particles from the surface. The SEM images and EDX results are discussed below.

- **SEM results**

The SEM images of samples Cu-63 and Cu-64 are shown in Figure 25.

![A: Cu-63: Temperature of 25 °C](image)

![B: Cu-64: Temperature of 50 °C](image)
Figure 25 The effect of displacement reaction; ESEM images of the surface of the copper samples kept in 20 mM AgNO₃ for 60 min with no sonication effect at A) room temperature, B) 50 °C.

As can be observed in the above images, the surface of both samples is corroded by displacement reaction effect. The silver ions from the solution will be reduced to metallic silver and replace the copper atoms on the surface. These silver seeds are not strongly attached to the surface and will be taken off the surface easily. Based on the reaction temperature, the intensity of the surface damage varies. At 25 °C after 60 min in 20 mM AgNO₃, the surface looks corroded but still the original surface can be identified. The surface has been oxidized a little bit (the EDX results confirm the presence of oxygen on the surface). While, at 50 °C, the sample has been undergone severe structure damage (oxidation). The amount of oxygen, detected by
EDX detector in this sample compared to the sample treated at 25 °C, is much higher which displays a higher oxidation rate.

- EDX results

After silver dendrites were removed from the surface of the two samples of Cu-63 and Cu-64, EDX analysis was done. The results are given in Figure 26 and Figure 27.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Net Int.</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>9.29</td>
<td>29.03</td>
<td>22.94</td>
<td>11.31</td>
</tr>
<tr>
<td>CuL</td>
<td>89.48</td>
<td>70.4</td>
<td>144.87</td>
<td>4.03</td>
</tr>
<tr>
<td>AgL</td>
<td>1.23</td>
<td>0.57</td>
<td>0.98</td>
<td>69.12</td>
</tr>
</tbody>
</table>
Figure 26 a) ESEM image of the surface of the copper sample kept in 20 mM AgNO₃ for 60 min at room temperature; EDX spectra and the table of chemical composition of b) spot 1 and c) spot 2.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Net Int.</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>1.18</td>
<td>4.56</td>
<td>3.5</td>
<td>27.43</td>
</tr>
<tr>
<td>CuL</td>
<td>97.53</td>
<td>94.7</td>
<td>204.8</td>
<td>3.38</td>
</tr>
<tr>
<td>AgL</td>
<td>1.28</td>
<td>0.73</td>
<td>1.27</td>
<td>66.32</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Net Int.</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>3.4</td>
<td>12.32</td>
<td>0.77</td>
<td>51.3</td>
</tr>
<tr>
<td>CuL</td>
<td>9.02</td>
<td>12.9</td>
<td>3.45</td>
<td>13.69</td>
</tr>
<tr>
<td>AgL</td>
<td>88.81</td>
<td>74.79</td>
<td>29.93</td>
<td>14.28</td>
</tr>
</tbody>
</table>
Figure 27 a) ESEM image of the surface of the copper sample kept in 20 mM AgNO$_3$ for 60 min at 50 °C; EDX spectra and the table of chemical composition of b) spot 1 and c) spot 2.

The EDX results revealed a small amount of oxygen on the surface of the treated sample at room temperature while a considerable amount of oxygen was detected on the copper surface of the treated sample at 50 °C, which indicates a higher oxidation rate of copper at a higher temperature. By increasing the temperature from 25 °C to 50 °C, it is assumed that the copper substrate will be more affected. Therefore, if any oxidation occurs during the treatment, it is believed to be from the oxidation of copper. Assuming that the pH of the silver nitrate is neutral, based on the Pourbaix diagram for Cu, it does not have much solubility at pH 7. So it is not immediately apparent that there should be a high corrosion rate. The copper may passivate by CuO, locally, which could explain the uneven nature of the corrosion and pit-like features (and the observed oxygen). On the other hand, under ultrasound, even 1 micromolar solubility of Cu$^{2+}$ can drive a considerable uniform corrosion rate.

4.3.1.2 The effect of reaction temperature on the surface of copper sonicated in water-ethanol solution without effect of displacement reaction

A SEM image of the surface of untreated copper is shown in Figure 28.
The effect of sonication on copper substrate in water-ethanol mixture without AgNO$_3$ at two temperatures of 25 °C and 50 °C is illustrated in Figure 29. The mixture was argon purged for 20 min in presence of the samples then the samples (Cu-65 and Cu-66) were sonicated for 60 min.

A: Cu-65: Temperature of 25°C

B: Cu-66: Temperature of 50°C
Figure 29 The effect of ultrasound irradiation; ESEM images of the surface of the copper samples sonicated in water-ethanol mixture without AgNO$_3$ for 60 min at A) room temperature, B) 50 °C.

Based on Figure 29, the high intensity ultrasound on the surface of the copper substrate in absence of silver nitrate has made minor pitting at surface irregularities. These physical impacts made by the effect of microjets on the surface of copper sonicated in water-ethanol mixture, compared to the ones made in silver nitrate solution, are negligible. Therefore, ultrasound by itself could not cause such severe modifications as seen in Figure 22.

4.3.1.3 The effect of reaction temperature on copper sonicated in silver nitrate solution; the simultaneous effect of displacement reaction and ultrasound irradiation

The effect of reaction temperature was studied with two samples Cu-54 and Cu-55. These samples were sonicated in 100 ml of 20 mM AgNO$_3$ aqueous solution (65 ml deionized water and 35 ml ethanol) with amplitude of 70% for 60 min at 25 °C and 50 °C.

- Discussion on SEM images

To analyze the effect of reaction conditions especially the temperature on the homogeneity and continuity of the deposited silver particles on copper substrates, the ESEM images were obtained. The images presented in Figure 30 (A) indicate a discontinuous deposition of silver
particles on the surface of the sample, while by increasing the temperature to 50 °C (Figure 30 (B)); there is less discontinuity.

A: Cu-55: Temperature of 25 °C

B: Cu-54: Temperature of 50 °C
Figure 30 The effect of simultaneous effect of displacement reaction and ultrasound irradiation; ESEM images of the surface of the copper samples sonicated in 20 mM AgNO₃ for 60 min at A) room temperature, B) 50 °C.

By increasing the temperature, the morphology and the amount of deposited silver particles on the surface of copper were altered. The deposited polyhedral particles disappeared; instead, a coarse, non-uniform porous layer of silver (Figure 31) was developed on the surface of copper.

In addition to the morphology change, the shininess of the deposited layer was also eliminated at a higher temperature. The deposited layer at 50 °C had a matte light gray due to surface micro-roughness made upon the oxidation of the surface of copper during the treatment. The oxidation process is highly dependent on the reaction temperature. The oxidation rate of copper will increase upon the rise of temperature [73, 74]. But as described in a previous subchapter, where the effect of temperature on copper substrate in silver nitrate with no sonication effect
was discussed (4.3.1.1), at 50 °C, the copper substrate experiences more oxidation than silver. In fact, as will be proven later in electrochemical studies chapter, only copper will undergo oxidation due to the formation of a galvanic couple between copper and silver.

Figure 32 presents ESEM images of two samples - Cu-64 which was sonicated in 20 mM AgNO$_3$ for 30 min at room temperature and Cu-60, which was not sonicated. The comparison illustrates that the partially changed surface morphology on the sample sonicated at 25 °C is the same as the entirely modified surface structure of the untreated sample at 50 °C which had undergone displacement reaction.

Figure 32 a) and b) ESEM image of a copper sample sonicated in 20 mM AgNO$_3$ for 30 min at room temperature; c) displacement reaction modified sample in 20 mM AgNO$_3$ for 60 min at 50 °C without the effect of ultrasound.

Although this structure change has been seen to occur at 50 °C not at 25 °C, it is believed that the “hot spot” theory [15] is not unrelated to this matter. The localized high temperature
generated by cavitation bubble collapse on the surface and also the silver particles collision with the surface which converts the kinetic energy into heat, will provide the localized high temperature and severe corroding conditions, therefore, at the point of collision the surface will experience oxidation.

- **Discussion on EDX results**

EDX analysis was carried out on the surface of both samples (sonicated in 20 mM AgNO₃ for 60 min at room temperature and 50 °C) to clarify the chemical composition of the deposited layer. Although the analysis was run at 10 kV, due to the thickness of the coating which is examined to be approximately 2 µm, the electron beam may penetrate to the bulk substrate. Then, the signals from the surface detected by EDX detector may not be as reliable as the cross-section results.

Figure 33 and Figure 34 show the ESEM images and EDX results of two samples of Cu-54 and Cu-55; the copper samples sonicated in 20 mM AgNO₃ for 60 min at 50 °C and room temperature, respectively.
Figure 33 Copper sonicated in 20 mM AgNO₃ at 50 °C for 60 min. a) ESEM image of the structure of deposited particles. b) EDX spectra and the chemical composition table of the full area.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Net Int.</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>4.87</td>
<td>21.19</td>
<td>3.24</td>
<td>27.66</td>
</tr>
<tr>
<td>Cu L</td>
<td>38.56</td>
<td>42.28</td>
<td>23.99</td>
<td>11.13</td>
</tr>
<tr>
<td>Ag L</td>
<td>56.57</td>
<td>36.53</td>
<td>25.58</td>
<td>10.02</td>
</tr>
</tbody>
</table>
Figure 34 Copper sonicated in 20 mM AgNO₃ at 25 °C for 60 min. a) ESEM image of the deposited silver particles. EDX spectra and the chemical composition table of b) spot 1, c) spot 2.

The EDX analysis of silver particles deposited on the surface of copper at 50 °C indicates the presence of Cu, Ag and O. The detected oxygen is from the oxidized copper substrate.

4.3.2 The effect of concentration of silver nitrate solution

The effect of concentration on the surface modification of copper substrate inspected by naked eye is given in Table 3.
Table 3 The effect of concentration on the surface coating.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration of AgNO₃</th>
<th>Sonication time</th>
<th>T</th>
<th>Visual observation of surface conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-61</td>
<td>20 mM</td>
<td>30 min</td>
<td>50 ºC</td>
<td>Continuous, very rough silver coating surface</td>
</tr>
<tr>
<td>Cu-70</td>
<td>5 mM</td>
<td>30 min</td>
<td>50 ºC</td>
<td>Continuous, smoother silver coating surface compared to Cu-61</td>
</tr>
</tbody>
</table>

It is demonstrated in Figure 35 that the surface uniformity caused by Ag particles deposition for a constant temperature of 50 ºC, ultrasonic amplitude of 70% and sonication time of 30 min, is dependent on the initial concentration of the precursor. The ESEM images of copper samples sonicated in 20 mM and 5 mM of AgNO₃ for 30 min at 50 ºC are presented in Figure 35.

A: Cu-61: AgNO₃ Concentration of 30 mM

B: Cu-70: AgNO₃ Concentration of 5 mM

Figure 35 The effect of concentration on the surface modification; ESEM images of the surface of the copper samples sonicated for 30 min at 50 ºC in A) 20 mM AgNO₃ B) 5 mM AgNO₃.

The amount and growth pattern of silver particles produced by displacement reaction are functions of ion concentration of the precursor [66, 69]. An increase in the initial concentration of AgNO₃ in the solution on one hand, leads to an increase in amount of synthesized silver particles by displacement reaction and sonochemistry and also an increase of particle size of
produced silver particles. Upon starting sonication, higher amount of silver particles with larger particle size, floating in the solution will attack the surface intensively resulting in more non-uniform deposition of silver particles and appearance of more surface roughness.

4.3.3 The effect of sonication time

4.3.3.1 Visual observation by unaided eye

The effect of sonication time on quality of the surface coating was visually investigated on the samples with treatment duration of 180, 60, 30 and 10 min. In terms of surface homogeneity, the sample which was sonicated for 180 min was roughly pitted. Numerous wide and deep erosion pits were formed on the surface of sonicated sample by effect of high speed microjets. In addition to pitting, the surface color was dark gray which indicates the rate of oxidation of the copper substrate which increases by increasing the sonication duration.

By decreasing the sonication duration, the number and size of the erosion pits decreased and a more homogeneous and smoother surface coating was obtained. The surface color turned to lighter gray compared to the one with 180 min sonication time, which can be due to less oxidation during the treatment. However, not fully surface coating coverage was achieved by sonicating of a copper sample for 10 min.

4.3.3.2 ESEM aided observation

The comparison of the effect of sonication time on two samples, Cu-55 and Cu-60, in 20 mM AgNO₃ at room temperature for two durations of 60 and 30 min is given in Figure 36.
Figure 36 The effect of sonication time; ESEM images of the surface of the copper samples sonicated in 20 mM AgNO₃ at room temperature for A) 30 min B) 60 min.

On one hand, the high velocity microjets induced by cavitational bubble collapse near the surface of copper are believed to be responsible for the strong adhesion of thrown silver particles to the surface of copper. But on the other hand, upon the collapse of cavitation bubble near the surface of copper, intensive shockwaves will also be generated which may detach adherent particles. For that reason, by reducing the sonication time, the chance of surface damage will be reduced.
Figure 37 shows ESEM images of two samples of Cu-54 and Cu-61, copper sonicated in 20 mM AgNO₃ at 50 °C for 60 min and 30 min, respectively.

A: Cu-61: sonication time of 30min

B: Cu-54: sonication time of 60min

Figure 37 The effect of sonication time; ESEM images of surface of copper samples sonicated in 20 mM AgNO₃ at 50 °C for A) 30 min, B) 60 min.

As said before, the long sonication time increases the amount of deposited silver particles on the surface of a substrate in sonodeposition methods and also leads to formation of a non-uniform coating [40]. In Figure 43 (B), a rough silver coating was formed on the surface of the copper substrate after 60 min irradiation while the coating formed after 30 min irradiation had a finer structure.
4.4 Summary of improved reaction conditions

In order to get the best homogeneous silver coating on the surface of copper, the initial AgNO\textsubscript{3} concentration, the reaction temperature and the sonication time have been varied from 30 mM to 5mM, 25 °C to 50 °C and 180 min to 30 min, respectively.

In summary, by decreasing the initial Ag\textsuperscript{+} ion concentration of the initial precursor from 30 mM to 5mM, despite the fact that, the amount of silver particles produced by displacement reaction and sonochemistry on top surface of copper substrate was decreased, but the deposition of particles on the surface occurred more uniformly.

In terms of temperature, by increasing the temperature, the morphology of the silver coating was converted to a continuous and porous well-attached silver layer from discontinuous randomly deposited silver particles. However, the increase of temperature caused the surface of copper substrate to be oxidized. Hence, sonicating the sample at 50 °C for extended reaction duration will be more rapidly oxidized. As a result, a sonication time of 30 min seemed to be a suitable factor in order to achieve a homogeneous silver coating layer. At a less than 30 min duration, silver coverage was not spread out fully; in contrary at duration of more than 30 min a very rough and eroded coating was achieved. The ESEM images of the surface of copper sonicated in 5 mM AgNO\textsubscript{3} solution at 50 °C for 30min are shown in Figure 38; there was no evidence of the thick, rough and non-uniform silver deposition observed in Figure 31.
Figure 38. The sonication of copper with the optimized reaction conditions; ESEM images of the surface of copper sample sonicated in 5 mM AgNO₃ for 30 min at 50 °C.
The EDX analysis done on the surface of copper sonicated in 5 mM AgNO₃ solution at 50 °C for 30 min, run at 10 kV (Figure 39), detected approximately 64 wt% silver on the surface.

Figure 39 Copper sonicated in 5 mM AgNO₃ at 50 °C for 30 min. a) ESEM image. b) EDX spectra and the chemical composition table of the full area.

- Cross-section analysis

To observe the structure, detect the chemical composition of the deposited layer and find an approximate thickness of the coating, SEM imaging using backscattered electrons (BSE) and EDX analysis were done on cross-section of the coated sample (copper sonicated for 30 min in 5 mM AgNO₃ aqueous solution at 50 °C). In order to improve the bond between the deposited
silver coating to the substrate and also fill the pores (in case of having porous coating), the sample was Ni electroplated. The Ni plating was carried out in a home-made Watts solution for 3 min using a 10mA current density. The SEM image is provided in Figure 40 (a).

- EDX Point Analysis

The disconnection of the coating from the surface of the substrate is believed to occur during the epoxy curation. The structure difference between the substrate and the coating is shown in the given BSEM image (Figure 40 (a)). The coating has different morphology (brighter and darker areas). The brighter spots, based on the EDX spectra results presented in Figure 40, are silver. There is a strip seen on the top surface of the copper with a slightly lighter color than the color of the substrate which has been identified as Ni.
Figure 40 Copper sonicated in 5 mM AgNO₃ at 50 °C for 30 min. a) SEM image of the cross section of the sample. EDX spectra point analysis of b) spot 1, c) spot 2, d) spot 3 and e) spot 4.

The presence of Ni on top surface of the substrate as well as in the coating, confirms the porosity of the deposition layer. There are no peaks detected for the oxygen amongst the obtained EDX peaks. It is assumed that the pores have been filled by Ni and carbon during the nickel electroplating and carbon coating.

- **EDX line scan analysis**

EDX line scan analysis was conducted across the coating with a starting point within the substrate towards the coating. The results are given in Figure 41. Ni can be seen in both the coating as well as the top surface of the copper substrate which indicates its traveling route through the coating. Carbon comes from epoxy and the carbon coating.
Figure 41 Copper sonicated in 5 mM AgNO₃ at 50 °C for 30 min. a) SEM image of the cross section of the sample. b) EDX spectra line scan analysis across the coating with a start point at the substrate towards the coating.

Therefore the formed silver coating layer on copper by sonication for 30 min in 5 mM silver nitrate at 50 °C is porous and has a thickness of 2.5 µm.

4.5 Electrochemical studies

To better understand how ultrasound irradiation affects the surface of a copper substrate with and without the effect of displacement reaction, different types of electrochemical studies were carried out in suitable electrolytes. In all cases, a 99.9% pure graphite rod was used as a counter
electrode. Potentiodynamic scan, cyclic polarization scan and OCP measurement analysis were performed using a Gamry600 potentiostat.

4.5.1 The chemical composition estimation of the surface coating via an electrochemical approach

In order to estimate the relative amounts or surface areas of exposed silver and copper and also verify if any surface alloying has formed at the interface of coating and substrate, cyclic polarization scans were performed on untreated silver, untreated copper and a sample sonicated in 0.1 M sodium borate solution. The potential was controlled against a mercury/mercury oxide reference electrode. The purpose of this test was to oxidize the working electrode (Ag, Cu and Ag deposited Cu), in a controlled manner in a passivating solution that does not dissolve any metals, to see if any other features except the peaks for pure Cu and pure Ag will be formed in the graph of a copper sample sonicated in 20 mM AgNO₃ at 25 °C for 60 min (Figure 42). In that case, it would be concluded that surface alloying (some sort of Cu/Ag alloying) has taken place.
Figure 42 Cyclic polarization curves for three samples of a) pure Ag, b) pure Cu, c) copper sonicated in 20 mM AgNO₃ at room temperature for 60 min, and d) copper sonicated in 20 mM AgNO₃ at 50 °C for 60 min. The tests were done in sodium borate solution (pH = 10) with a forward and backwards scan rate of 0.5 mV/s.
The silver coated copper cyclic curves started at a potential of -200 mV versus Hg/HgO reference electrode with oxygen reduction as the cathodic reaction. The return potential started at +800 mV versus reference electrode and the cycle finished at +200 mV versus reference electrode.

The compared cyclic polarization curves of tree samples (pure Cu, pure Ag and sample sonicated in 20 mM AgNO₃ at 25 °C for 60 min) are presented in Figure 43.

Figure 43 Compared cyclic polarization curves of three samples (pure Cu, pure Ag and sample sonicated in 20 mM AgNO₃ at 25 °C for 60 min). The test was carried out in sodium borate solution (pH = 10) with a forward and reverse scan rate of 0.5 mV/s.

Figure 44 illustrates the compared cyclic polarization curves of pure Cu, pure Ag and sample sonicated in 20 mM AgNO₃ at 50 °C for 60 min.
Figure 44 Cyclic polarization curves of three samples (pure Cu, pure Ag and sample sonicated in 20 mM AgNO₃ at 50 °C for 60 min). The test was carried out in sodium borate solution (pH = 10) with a forward and reverse scan rate of 0.5 mV/s.

In Figure 44, there are no other peaks detected except for Cu and Ag in both sonicated samples. This means no alloying occurred in the collision area of the copper substrate when the silver particles hit the surface. Ag peaks in both samples sonicated at 25 °C and 50 °C match the one in untreated pure Ag graph, indicating a similar surface area of Ag, while the Cu peaks of sonicated samples do not exactly fit those in the related pure copper curve. The higher Cu peaks in the two sonicated sample curves compared to the one for untreated copper, indicate that the copper surface area has been increased; this is especially obvious in the backwards scan of the sample sonicated at 50 °C that the current density in the area of Cu has enhanced confirming the development of the surface area of copper. This can be attributed to the copper surface porosity enhancement due to displacement reaction occurrence during the treatment, and/or erosion damages.
4.5.2 Corrosion studies

The corrosion behaviour of two samples; untreated copper and copper sonicated at 50 °C for 30 min in 5 mM AgNO$_3$ was investigated. The potentiodynamic scan was carried out in 0.1 M Na$_2$SO$_4$ and 0.01 M NaHSO$_4$ buffer solution. The potential was controlled versus MSE reference electrode with a scan rate of 3 mV/s.

![Potentiodynamic Scan](image)

Figure 45 Potentiodynamic curves of untreated copper and copper sonicated at 50 °C for 30 min in 5 mM AgNO$_3$. The tests were carried out in deaerated 0.1 M Na$_2$SO$_4$ and 0.01 M NaHSO$_4$ solution with a scan rate of 3 mV/s.

Figure 45 the corrosion current density for two untreated copper and copper sonicated in 5 mM AgNO$_3$ are approximately measured at 0.4 µA/cm$^2$ and 3 µA/cm$^2$, respectively. Therefore the current density has increased by a factor of 7.5. By increasing the corrosion current density we can conclude that the corrosion rate has increased as well. With zero copper in the solution, copper will start to dissolve at low potential with hydrogen evolution as cathodic reaction (at a very low rate). Therefore, physical conditions of the surface of copper substrate which was negatively affected by the treatment and also the porous nature of the silver coating layer can cause the copper sonicated sample to show higher corrosion rate. There is another possibility for
this corrosion rate increase; it could be the galvanic effect of deposited silver, although some residual dissolved oxygen, despite the deaeration, may be required to show such an effect.

4.5.3 The effect of sonication on limiting current density for oxygen reduction

Several investigations have been pursued on the effect of sonication on mass transport, and they are all in agreement that ultrasound will increase the mass transfer rate to a surface, thus increasing the limiting current density of the cathodic reaction [56, 57, 58, 71]. In the current work, the limiting current density was measured by performing potentiodynamic scans on copper substrate using a mercury sulfate reference electrode (MSE). The cathodic polarization curve was plotted by measuring the oxygen reduction of the sample in the 0.1 M Na₂SO₄ and 0.1 M NaHSO₄ buffer solution, open to air, applying different reaction conditions; untreated sample, sample sonicated at 25 °C and sample-probe distance of 1 cm, sample sonicated at 50 °C, sample-probe distance of 1 cm and sample sonicated at 25 °C and sample-probe distance of 0.5 cm.

![Potentiodynamic Scan](image)

**Figure 46** Potentiodynamic curves of copper with and without the effect of sonication with a probe-distance of 1 cm at room temperature. The tests were carried out in 0.1 M Na₂SO₄ and 0.1 M NaHSO₄ solution in equilibrium with air with a scan rate of 3 mV/s.
Figure 46 shows the oxygen reduction reaction of the untreated sample and sonicated sample 1 cm away from the sonicator tip at 50 °C. As it is obviously seen in the graph, under the effect of sonication, mass transfer will be increased significantly. As a consequence of that increase, the limiting current density increases by an approximate factor of 35 ($i_L = 2.5 \times 10^{-3} \text{ A/cm}^2$). The usual equation for measuring limiting current density, $i_l$, is shown below:

$$i_l = \frac{D_z n F C_B}{\delta}$$

In the above equation, $i_L$ stands for limiting current density, $n$ is the number of transferred electrons, $F$ is the Faraday constant (96500 coulombs per mole), $D_z$ is the diffusion coefficient of oxygen, $C_B$ is the concentration of oxygen and $\delta$ refers to the thickness of diffusion layer formed on the surface of the substrate.

Using a typical value for $D$ (1 $\times$ $10^{-5}$ cm$^2$/s), and $C_B$ (8 ppm or 0.25 mM, 2.5 $\times$ $10^{-7}$ mol/cm$^3$), we obtain $\delta = 0.14$ mm for the blue curve in the figure, and $\delta = 0.004$ mm (4 microns) for the red curve.

This decrease of diffusion layer thickness and increase of limiting current density can be attributed to the effect of agitation induced by microstreaming and turbulent flow made by ultrasound. In another words, an increase of limiting current density could be credited to the oxygen reduction increasing due to solution agitation made by ultrasound and possibly a small contribution to the reduction of OH\(^{\cdot}\) (hydroxyl) and H$_2$O$_2$ molecules.

For further development of this method, it is useful to express the mass transfer enhancement in terms of a mass transfer coefficient for oxygen (which will be the same as for any other species, such as silver ions, with a small adjustment for their slightly different $D$ values). The mass transfer coefficient is defined, using flux rather than current density, as

$$j_{Lim} = K_m \cdot C_B$$
Data will be required for D values at different temperatures. Interesting variations of $K_m$ with the other sonication parameters can be expected.

4.5.3.1 The effect of temperature

Besides the impact of ultrasound agitation which decreases the thickness of the diffusion layer, by increasing the temperature to 50 °C the diffusivity of the reacting species, $D_z$, will be increased. As a result, based on the equation for $i_L$, the limiting current density will increase. As seen in

Figure 47, the limiting current density of the sample sonicated in 0.1 M Na$_2$SO$_4$ and 0.1 M NaHSO$_4$ at 50 °C is $3.2 \times 10^{-3}$ mA/cm$^2$, which is increased by a factor of 45 and 1.5 compared with the untreated sample and sample sonicated at room temperature, respectively.

![Potentiodynamic Scan](image)

Figure 47 Potentiodynamic curves of untreated copper, a copper sonicated with a probe-distance of 1 cm at room temperature and a copper sonicated with a probe-distance of 1 cm at 50 °C. The tests were carried out in 0.1 M Na$_2$SO$_4$ and 0.1 M NaHSO$_4$ buffer solution in equilibrium with air with a scan rate of 3 mV/s.
However, temperature has an inverse influence on the solubility of oxygen in water. At 50 °C, the solubility of oxygen in water is approximately 5.5 ppm. Then, the concentration of oxygen, \( C_{O_2} \), will be 0.17 mM or \( 1.7 \times 10^{-7} \) mol/cm\(^3\).

![Graph showing solubility of oxygen in water with respect to water temperature.](image)

**Figure 48** The solubility of oxygen in water in equilibrium with air with respect to water temperature.

The increase in limiting current density under sonication, between 25 °C and 50 °C, is about a factor of 1.5, which could be rationalized by correcting for the different D and C values at 50 °C; any remaining discrepancy between the two datasets would be due to changes in the sonication process itself with temperature.

### 4.5.3.2 The effect of sample-probe distance

By decreasing the sample-probe distance to 0.5 cm, the agitation induced by ultrasound increased, but the limiting current density compared with the one with distance of 1 cm seemed to remain unchanged. However the limiting current density in this case, compared with the untreated one, has been also enhanced by a factor of 35 (Figure 49).
Figure 49 Potentiodynamic curves of untreated copper, a copper sonicated with a probe-distance of 1 cm at room temperature and a copper sonicated with a probe-distance of 0.5 cm at room temperature. The tests were carried out in 0.1 M $\text{Na}_2\text{SO}_4$ and 0.1 M $\text{NaHSO}_4$ buffer solution in equilibrium with air with a scan rate of 3 mV/s.
5 Summary, Conclusions and Future Work

5.1 Summary and conclusion

A surface modification method was developed to deposit silver particles on the surface of copper by means of simultaneous effect of displacement reaction and ultrasonic irradiation. The physical and electrochemical analysis proved the deposited materials as silver. A continuous porous uniform layer of silver with a thickness of 2µm was deposited on the surface of copper under the optimal reaction conditions of 5 mM concentration of AgNO₃, reaction temperature of 50 °C and sonication time of 30 min.

The electrochemical studies on the surface of silver coated copper revealed that there was no chemical connection built-up in the area of collision of silver particles to the surface of copper. The proposed mechanism for this silver deposition is that the sonochemically produced silver particles and also the silver particles synthesized by displacement reaction are thrown to the surface of copper by microjets, strong adhesion of particles to the surface will be achieved upon the collision. The high temperature and speed of thrown silver particles to the surface of copper are believed to be the reason for the silver coating.

Under the effect of sonication, the oxygen reduction limiting current density was increased by up to 45 times due to increase of solution agitation and turbulent flow made by ultrasound, therefore, the limiting current density was increased. However, the corrosion resistance of the sample sonicated in silver nitrate solution appeared to be decreased. This increase of corrosion rate is attributed to the surface area of the copper substrate which was negatively affected by the treatment and also the porous nature of the silver coating layer. It is hypothetically possible that the porosity nature of silver coated layer caused the creation of a galvanic couple of silver and copper in which the corrosion rate of copper was increased by the galvanic effect of deposited silver.

As far as we are aware, this is the first time that silver is deposited on the surface of copper by aid of high intensity ultrasound. In the earlier attempts, silver was ultrasonically deposited on the surface of soft materials such as polymers and glass. The achievement of electrochemical
monitoring with and without sonication suggests ways forward to optimize such a process with the aid of electrochemistry. Promising results were also obtained on the synthesis of copper hydride by sonication of Cu$_2$SO$_4$ solution.

5.2 Future Work

The suggestions for future will be to:

- Find a way to measure corrosion rate under sonication, despite the electrochemical noise (linear polarization?).

- Find ways to separate the contributions of displacement and particle collision to the growth of the silver layer.

- Improve the apparatus so that the environment can be changed dynamically, and/or samples can be inserted or removed without changing the environment. For example, it is essential in future work to be able to pump already deaerated solution into the cell.

- Perform more detailed microscopic analysis to address the issue of possible surface alloying; select the most promising systems for such studies.

- Vary the substrate and depositing metal, respecting the limitations of which metal ions can be reduced to the metallic state by sonication. Initial work with molybdate, not included here, showed that it could be reduced to Mo (V) but not to metal.

- Generally, exploit electrochemical measurements and control to probe the mechanism of sonication.

- Development of preliminary results (shown in Appendix E) on sonication of nanoscale electrodeposited metal layers on metal substrates, looking for alloying or other interesting effects.
References


[34] J. Hihn, F. Touyeras, and M. Doche, “Sonoelectrodeposition : The Use of Ultrasound in Metallic Coating Deposition.”


Appendices

Appendix A. Sonochemical reduction of different metal salts

Different metal salts including lab-made copper(I) and copper(II) oxide (Cu$_2$O, CuO), cupric nitrate (Cu(NO$_3$)$_2$), nickel sulfate (NiSO$_4$), copper(I), copper(II) chloride (CuCl, CuCl$_2$) and sodium molybdate have been irradiated by high intensity ultrasound to see if any nanoparticles will be produced. Irradiation of none of the above listed metal salts led to reduction of related metal nanoparticles.

Appendix B. Calculation of the potential of the silver wire reference electrode

The potential of reference electrode (Ag wire) was calculated for the given reaction conditions using Nernst equation for different values of the concentration of AgNO$_3$ and the reaction temperature.

For the half reaction of $aA + ne \rightarrow bB$ the Nernst equation will be:

$$E_{cell} = E^0 - \frac{2.303RT}{nF} \log \frac{[B]^b}{[A]^a}$$

Therefore, Nernst equation for the following reaction Ag$^+$ + e $\rightarrow$ Ag will be,

$$E_{cell} = E^0 - \frac{2.303RT}{nF} \log \frac{[Ag]}{[Ag^+]}$$

And [Ag] = 1 then,

$$E_{cell} = E^0 + \frac{2.303RT}{nF} \log [Ag^+]$$

E= electrode potential

$E^0$= standard electrode potential of Ag$^+$/Ag which is 0.80 V
R= gas constant = 8.3 J/Kmol

T= temperature (Kelvin)

N= number of electrons

F= Faraday constant= 96500 C mol$^{-1}$

\([\text{Ag}^+/\text{Ag}]\)= concentration of silver ions

For \([\text{Ag}^+] = 5 \text{ mM at } 50 \degree \text{C}]: \ E_{\text{cell}} = 0.8 + \frac{2.303 \times 8.3 \times 323}{1 \times 96500} \log [5 \times 10^{-3}] = 0.65 \, \text{V}

For \([\text{Ag}^+] = 20 \text{ mM at } 50 \degree \text{C}]: \ E_{\text{cell}} = 0.8 + \frac{2.303 \times 8.3 \times 323}{1 \times 96500} \log [20 \times 10^{-3}] = 0.69 \, \text{V}

Appendix C. Sonication of a copper slug in 20 mM AgNO$_3$ for 60 min at 40 \degree \text{C}

Some supplementary experiments were done on the effect of temperature on the surface coating homogeneity of the copper sonicated in 20 mM AgNO$_3$.

Figure 50 shows the ESEM images of the copper sonicated in 20 mM AgNO$_3$ for 60 min at the temperature of 40 \degree \text{C}. The resulting silver coating developed at 40 \degree \text{C} was almost the same as the one formed at room temperature.
Figure 50: The effect of temperature; ESEM images of the surface of copper sample sonicated in 20 mM AgNO$_3$ for 60 min at 40 °C.

Appendix D. OCP measurements

In order to monitor the OCP during the displacement reaction and also during the sonication, the OCP measurement as a function of time was carried out on the surface of copper substrates in different reaction conditions. In all these experiments, potential was measured against an Ag wire as a reference electrode with a surface area of 50 mm$^2$.

- The effect of concentration on open circuit potential change of copper surface under the effect of sonication at 50 °C
Figure 51 shows the effect of concentration on the surface potential of copper placed 1 cm away from the sonicator tip in 5 and 20 mM AgNO₃ aqueous solutions at reaction temperature of 50 °C.

Figure 51 OCP variations monitored with respect to time as a function of salt concentration in the solution under argon purging, heating period and ultrasound irradiation. Irradiation was done at 70% efficiency with a sample-probe distance of 1 cm at 50 °C.

For the sample sonicated in 20 mM AgNO₃, the OCP begins shifting towards more positive values about 200 s after the sample is placed in silver nitrate solution due to progressive nucleation of silver on the surface of copper by means of displacement reaction. As can be realized from Figure 51, for the lower silver concentration, this increase in potential does not occur until the temperature is increased, which can be expected from the lower corrosion rate and silver deposition rate at this concentration. Under sonication, the behaviour is not easy to interpret, but we observe a sharp decrease in potential for the higher concentration (indicating removal of silver from the surface), followed by a gradual rise due to new silver being deposited.
(possibly), whereas for the lower concentration the effect of sonication on the potential is less. More work is required on the meaning of such data.

- The effect of concentration on open circuit potential change of copper surface under silent conditions without the effect of sonication at 50°C

Under silent conditions, the OCP of copper sample in the solution with 20 mM AgNO₃ is more positive than the one in 5 mM AgNO₃ solution (Figure 52). This is credited to the silver dendrite formation rate increasing by increasing the ion concentration of the solution in which the displacement reaction occurs.

![Figure 52](image)

Figure 52 The OCP monitoring curves of samples in 5 and 20 mM AgNO₃ aqueous solutions at 50 °C with and without the effect of sonication.

Although the OCP is noisy under sonication, in future work, it may be possible to measure the corrosion rate under sonication by linear polarization resistance, which will help to test various theories as to what is occurring.
Appendix E. The effect of sonication after Ni electrodeposition

To investigate the effect of sonication on electrodeposition layer, a copper slug was Ni electroplated in Watts solution applying 10mA current for 120 s to get a nickel nano layer, probably discontinuous, on the surface of copper. Then, the Ni electroplated copper was sonicated in water and ethanol solution for 60 min at 50 °C with a sample-probe distance of 1 cm. Figure 53 (a) shows the potentiodynamic curves for two untreated copper and Ni plated copper samples and Figure 53 (b) shows the potentiodynamic curves for three samples; untreated copper, Ni plated copper and sonicated Ni plated copper. The tests were carried out in 0.1 M Na$_2$SO$_4$ and 0.01 M NaHSO$_4$ solution. The potential was measured against MSE reference electrode.
Figure 53  a) Potentiodynamic curves of untreated copper and Ni plated copper and b) Potentiodynamic curves of untreated copper, Ni plated copper and sonicated Ni plated copper. The tests were carried out in deaerated 0.1 M Na$_2$SO$_4$ and 0.01 M NaHSO$_4$ solution with a scan rate of 1 mV/s.

These experiments showed no conclusive evidence for alloying or other interesting effects, but this is an area for further development.

The images below show the electrochemical impedance spectroscopy (EIS) results of three copper samples; untreated copper, Ni plated copper and sonicated Ni plated copper. The tests were carried out in 0.1 M Na$_2$SO$_4$ and 0.01 M NaHSO$_4$ open to air solution with an initial frequency of 100000 Hz and a final frequency of 0.05 Hz.
Figure 54 EIS results of three copper samples; a) untreated copper, b) sonicated Ni plated copper and c) Ni plated copper. The tests were carried out in 0.1 M Na₂SO₄ and 0.01 M NaHSO₄ solution with an initial frequency of 100000 Hz and a final frequency of 0.05 Hz.