ANKARA YILDIRIM BEYAZIT UNIVERSITY

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GRAPHENE REINFORCED SILVER NANOCOMPOSITE BY ELECTRODEPOSITION FOR ELECTRICAL CONTACT MATERIALS

M.Sc. Thesis by

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Lujain Alfalahi

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M.Sc. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"Graphene Reinforced Silver Nanocomposite by Electrodeposition for Electrical Contact Materials"** completed by **Lujain Al-Falahi** under the supervision of **Assist. Prof. Dr. Ramazan KARSLIOĞLU** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

Silver has been a widely used material for a large range of applications essentially in the field of electrical circuits and contactors due to excellent electrical and thermal conductivity properties.So that silver coating is one of the preferable selected coating material for the contact parts of connectors. Due to lower silver mechanical strength and weldability, and with considering to the natural operational of contacts parts, silver electrical contacts coatings have to be reinforced with second phase material that has superior mechanical and electrical properties. Graphene which is a strongest thinnest material known, has been chosen in this study as the best candidate for using as a reinforcement material for silver coatings.

In this study, pure silver coating and graphene reinforced silver matrix nanocomposite coatings were produced by using the electrodeposition technique and deposited on the cupper substrate to enhance the electrical and mechanical properties of electrical contact materials. Different current types which are, Direct current (DC), Pulse current (PC), and Pulse reverse current (PRC) and different amount of graphene addition to deposition bath was used to produce nanocomposite coatings. The effect of different current types and graphene amounts on the microstructure, crystallographic orientation, mechanical, electrical properties were investigated by Scanning electron microscope (SEM), X-ray diffraction methods, microhardness test and electrical contact test in respectively. XRD analysis showed decreasing in peak intensity and smaller grain size in coatings produced with PRC method. The nanocomposite deposition was improved electrical and mechanical properties of copper due to the unique enhanced reinforcement (GR) and superior matrix materials (silver) properties.

Keywords: Silver, Electrodeposition, Electrical contact materials, Graphene

ELEKTRIKSEL KONTAKT MALZEMELERİ İÇİN GRAFEN TAKVİYELİ GÜMÜŞ NANOKOMPOZİTLERİN ELEKTRODEPOZİSYON İLE ÜRETİMİ

ÖZ

Gümüş, elektrik ve termal iletkenlik nedeniyle elektrik devreleri ve kontaktörler alanında çok çeşitli elektrik uygulamaları için yaygın olarak kullanılan bir malzemedir.Bu yüzden gümüş kaplama, konnektörlerin temas parçaları için tercih edilen seçilmiş kaplama malzemelerinden biridir.Gümüşün daha düşük mekanik mukavemet ve kaynak imkânı sayesinde ve kontak parçalarının doğal çalışması göz önüne alındığında, gümüş elektrik kontak kaplamaları, üstün mekanik ve elektriksel özelliklere sahip olan ikinci faz malzemesiyle takviye edilmelidir.Bu çalışmada en güçlü en ince malzeme olan grafen, gümüş kaplamalar için bir takviye malzemesi olarak en iyi aday olarak seçilmiştir.

Bu çalışmada, saf gümüş kaplama ve grafen takviyeli gümüş matrisli nanokompozit kaplamalar üretmek için farklı akım türleri, doğru akım (DC), darbe akımı (PC) ve darbe ters akım (PRC) ve biriktirme banyosuna farklı grafen ilavesi kullanılmıştır. Farklı akım türlerinin ve grafen miktarlarının mikroyapı, kristalografik yönelim, mekanik ve elektriksel özellikler üzerindeki etkisi, sırasıyla Taramalı elektron mikroskobu (SEM), X-ışını kırınım yöntemleri (XRD), mikro sertlik testi ve elektriksel temas testi ile incelenmiştir. XRD analizi, PRC yöntemi ile üretilen kaplamalarda pik yoğunluğunda ve daha küçük tane boyutunda azalmayı göstermiştir. Nanokompozit birikimi, takviye malzemesi olarak grafen ve gümüşün üstün matris özelliklerine bağlı olarak bakırın elektriksel ve mekanik özelliklerini iyileştirmiştir.

Anahtar Kelimeler: Gümüş, Elektrodepozisyon, Elektriksel kontakt malzemeleri, Grafen

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NOMENCLATURE

Abbreviations

Gr	Graphene
Ag	Silver
mV	Millivolts
kV	Kilovolt
I	Current
A	Ampere
V	Volt
Cu	Copper
Ni	Nickel
Al	Aluminium
Si	Silicon
Fe	Iron
Mg	Magnesium
Ti	Titanium
Rm	Conductor resistance
Rc	Constriction resistance
Zn	Zinc
Cr	Chromium
Au	Gold
µA	Microampere
µm	Micrometre
Å	Angstrom
Al_2O_3	Aluminium oxide

cm^2	Square centimetre
Cm^3	Cubic centimetre
mΩ	Milliohm

Acronyms

DC	Direct current
PC	Pulse current
PRC	Pulse- reversed current
EDM	Electric discharge machining
CMs	Composite materials
MMC	Metal-matrix composites
CC	Carbon-carbon composite
NPs	Nanoparticles
MMNC	Metal Matrix Nanocomposites
CMNC	Ceramic Matrix Nanocomposites
PMNC	Polymer Matrix Nanocomposites
TiC	Titanium Carbide
Ag NPC	Silver Nanoparticles
CNT	Carbon Nanotubes
MA	Mechanical Alloying
PM	Powder metallurgy
PVD	Physical Vapor Deposition
CVD	Chemical Vapor Deposition
T_{ON}	Pulse current on-time
T_{OFF}	Pulse current off-time
rGO	Reduced graphene oxide

HV	Vickers Pyramid Number
PH	Power of Hydrogen
N	Newton
KW	Kilo watte
MWCNT	Multay wielding carbon Nanotubes
SEM	Scanning Electron Microscopy
EDS	Energy Dispersive Spectrometer
XRD	X-ray diffractometer
GNP_s	Graphene Nanoplates

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CHAPTER 1

INTRODUCTION

Electrical contacts are substantial components in each system in which a transfer of electricity occurs. Electrical contacts considered the most essential parts in a wide range of applications such as circuit breakers, relays and switches [1] [2]. During the life service of these parts, many functional problems occur due to the making and breaking operations. Arc erosion and welding are at the top of these problems [3]. Thus many attempts had been made by researchers to improve the performance of these parts. These improved performances require excellent physical, mechanical, and chemical properties like high electrical and thermal conductivity, high hardness, high corrosion resistance, and these parts should have good mechanical workability [2]. In contacts fields, the coating has the main role in protecting and enhancing the surface quality and improve substrate properties. The efficiency of the coating depends on the materials and the technologies that can be used.

Silver, which has the highest electrical conductivity of all metals, high resistance to oxidation, and ductility[4] is considered the best candidate used as electrical and electronic conductors whether as alloys, or composites, or plating material for the contacts part[5]. Recently, with advanced in the nanotechnology field, silver matrix nanocomposites coatings are widely used in electrical contact systems due to their excellent thermal and electrical conductivity, high wear and welding resistance. The mechanical properties of this types of coating need improvement in order to extend the contactors function life, the enhancement of nanocomposites coatings workability significantly depends on the nature and properties of the reinforcement material.

Graphene, a newly discovered material. It is one of carbon allotrope and the basic structure of all of them. Graphene is one carbon atomic layer materials, this unique structure enables graphene to own unexceptional characteristics with excellent mechanical properties. Graphene has the highest known intrinsic strength (130 GPa), and Young Modulus (1 TPa) [6] [7], also its well-known electrical and thermal properties committed new seek material for expansion advanced coating [8] [9] and

attracting vast attention in a wide range of scientific fields. Gr is a good candidate for addition to silver as the second phase for electrical contact systems.

Electrodeposition process is one of the most important coating techniques especially in electrical and electronic devices [10]. It is the process in which a thin film of material can be deposited onto a conducting substrates surface to enhancing their function and improve the properties such as increasing conductivity, hardness, corrosion resistance, wear resistance and other physical and mechanical properties[11] [12]. Electrodeposition process is an economical technology with no compelx equipment required. Through this technique, we can easily control the parameters like time, temperature, ph. of the path, coating layer thickness and surface morphology. Another advantage of this type of coating methods is a possibility to coating the compelx parts and shapes and revise the coating properties[8] [9]. Many electrodeposition methods had been introduced such as pulse current method PC, pulse reverse current method PRC in addition to the conventional direct current method DC. In PC and PRC methods more parameters controlled the electrodeposition process than the conventional DC methods[13].

Considering the electrical and mechanical problems in electrical contacts with the field of application. Development of provided contacts materials with higher mechanical efficiency while maintaining the electrical features, has been an intrinsic issue.

So that, the main aim of this study is producing a nanocomposite coating material by electrodeposition technique to improve the electrical and mechanical properties of the electrical contacts. The materials used as nanocomposite coating were silver as the matrix material and nanoscale graphene particle as a second phase addition to the coating. Nanocomposite (silver-GR) deposited on a copper substrate with different current types and different amount of graphene added to coating bath in order to determine their effect on the coating properties of the substrate. Scanning electron microscope examinations, X-ray diffraction analysis, and Raman spectroscopy were performed as characterization, hardness measurements, carried out as mechanical tests, also, the electrical contact performance for the produced coating was executed.

CHAPTER 2

LITERATURE REVIEW

2.1 Electrical Contacts Materials

An electrical contact can be described as the interaction between the current-carrying component of electrical/electronic devices that ensure the continuity of electric circuit, the current-carrying component in contact, often made of solids, are called contact members or contact parts [5].

These contact parts are usually made from metals as seen in Figure 2.1 which have high electrical conductivity, Silver, copper, gold, platinum, and palladium are in general the wide metals used for contact alloys. Graphite, molybdenum, nickel, and Tungsten are materials which are used as the structural properties of highly conductive improvement metals and some are used individually for specialized contacts and components, the best example of this croup is electric discharge machining (EDM) electrode which made of graphite with high conductivity and arc erosion resistance.

Electrical Contacts. Are electromechanical parts that are operated in any system through which an electrical current flow. Generally, in these kinds of systems, many problems occur during operation such as the arc generation which leads to increase the temperature and welding also the effect of current density on the surface of contactors and current discharge that can cause in removing some parts of contacts metal. These problems and others require special properties for the materials in this type of application. Many of these properties are determined by ingrained characteristics of the material such as high conductivity, high corrosion resistance, hardness, current load, form, and size [14].



Figure 2. 1 Electrical contacts parts [15].

As it clearly known, the most important characteristic in electrical contacts is the higher electrical conductivity which is an essential property in materials and it can be defined as the movement ability of the particles carrying current. This ability comes from free electrons move under electric field through the material. As previously, metals are the most effective conductors of electricity due to the free electrons multiplicity [16]. .Table 2.1. gives electrical conductivity and electrical resistivity of various materials

Table 2. 1 Electrical conductivity and electrical resistivity of various materials [16].

Table of Resistivity and Conductivity at 20°C		
Material	**ρ (Ω•m) at 20 °C**	**σ (S/m) at 20 °C**
	Resistivity	**Conductivity**
Silver	1.59×10^{-8}	6.30×10^{7}
Copper	1.68×10^{-8}	5.96×10^{7}
Annealed copper	1.72×10^{-8}	5.80×10^{7}
Gold	2.44×10^{-8}	4.10×10^{7}
Aluminium	2.82×10^{-8}	3.5×10^{7}
Calcium	3.36×10^{-8}	2.98×10^{7}
Tungsten	5.60×10^{-8}	1.79×10^{7}
Zinc	5.90×10^{-8}	1.69×10^{7}
Nickel	6.99×10^{-8}	1.43×10^{7}
Lithium	9.28×10^{-8}	1.08×10^{7}
Iron	1.0×10^{-7}	1.00×10^{7}
Platinum	1.06×10^{-7}	9.43×10^{6}
Tin	1.09×10^{-7}	9.17×10^{6}
Carbon steel	-1010	1.43×10^{-7}
Lead	2.2×10^{-7}	4.55×10^{6}
Titanium	4.20×10^{-7}	2.38×10^{6}
Constantan	4.9×10^{-7}	2.04×10^{6}
Stainless steel	6.9×10^{-7}	1.45×10^{6}
Mercury	9.8×10^{-7}	1.02×10^{6}
Nichrome	1.10×10^{-6}	9.09×10^{5}
GaAs	5×10^{-7} to 10×10^{-3}	5×10^{-8} to 10^{3}
Carbon (graphite)	2.5×10^{-6} to 5.0×10^{-6}	2 to 3×10^{5}
Carbon (diamond)	1×10^{12}	$\sim10^{-13}$
Germanium	4.6×10^{-1}	2.17
Seawater	2×10^{-1}	4.8
Silicon	6.40×10^{2}	1.56×10^{-3}
Deionized water	1.8×10^{5}	5.5×10^{-6}
Glass	10×10^{10} to 10×10^{14}	10^{-11} to 10^{-15}
Hard rubber	1×10^{13}	10^{-14}
Sulfur	1×10^{15}	10^{-16}
Air	1.3×10^{16} to 3.3×10^{16}	3×10^{-15} to 8×10^{-15}
Paraffin wax	1×10^{17}	10^{-18}
Teflon	10×10^{22} to 10×10^{24}	10^{-25} to 10^{-23}

Classification of electrical contacts can be carried out according to their nature, materials, design, current load, surface geometry, application, and by other procedures.

In accordance to materials, there are two categories, contact materials with high conductivity and low resistivity and contact material with low conductivity and high resistivity. For the first group, materials are subservient in electrical engineering products. These categories include metals such as (Silver, Copper , Gold , Aluminum) these material utilized as conductors in distribution and transmission of electrical energy also these kinds of materials are usually used as conductors for whole types of windings desired in apparatus and devices of electrical machines.

Second group has materials with high resistivity and low conductivity include materials like (Tungsten, Carbon, Manganic) which are very beneficial for electrical engineering products. This category are usually used in the production of the filaments for incandescent lamp, electric irons, space heaters, heating elements for electric heaters [17].

In general, the basic classification of the electrical contacts proceeds according to the applications and functionalities. They can be classified into two main groups, fixed electrical contacts and moving electrical contacts as seen in Figure 2.2.

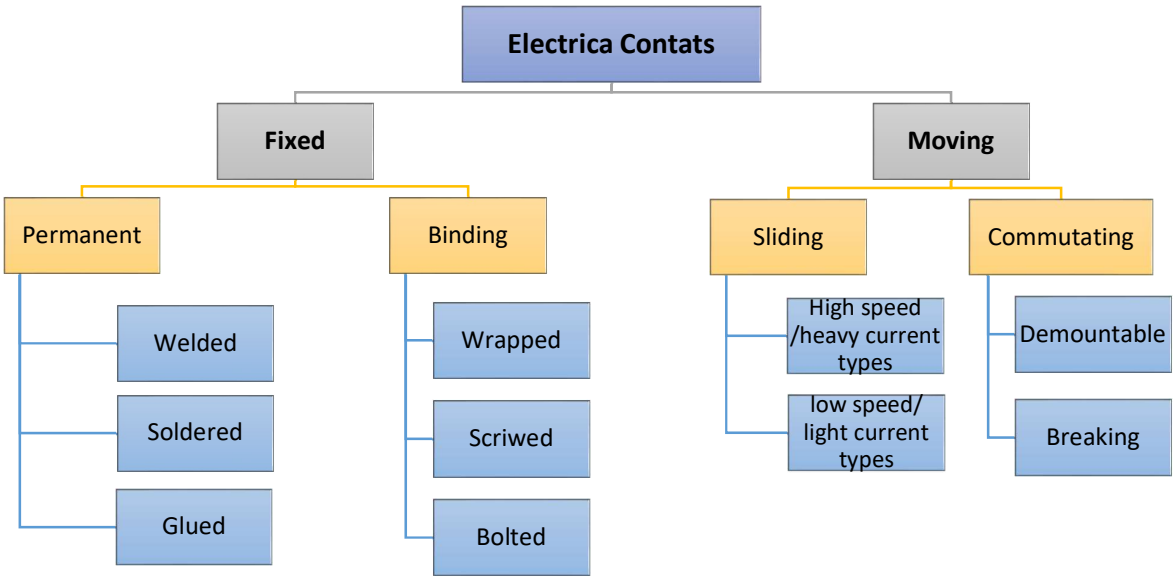


Figure 2. 2 Electrical contacts classification [5] [18].

With regard to the fixed contacts, contact members are connected statically or elastically to the steady unit of a device to provide the constant joint. Fixed contacts are divided into permanent (welded, soldered, and glued) and clamped (bolted, screwed, and wrapped). These contacts are suitable for use in all voltage and current values, for instance, large bus bars to crimped or screwed wiring connections on low voltage printed circuit boards. The working nature and implementation conditions between the two surfaces put as these contacts remain in the same position and status for a long time, and the higher contact forces, decreasing resistance. Also, increasing in temperature that generates from contact resistance under permanent load on contact materials that cause creep effect, and progressive reducing of metallic contact area due to corrosion and oxidation which progress with time as shown in Figure 2.3 and resulting in virtually disappearing of the contact points at last. so, the occurrence of sudden failure [5] [18].



Figure 2. 3 Surface of electrical contact (A) after & (B) before usage [19].

In moving contacts, there is one contact member at least is statically or elastically connected to the mobile unit of a device. Consisting of their working conditions, moving contact often has two grades: sliding contacts and commutating contacts. Sliding contacts have different types which are high speed, heavy current types such as slip rings, brushes, commutator, motors and generators, current pickup contacts in electrical transport and low speed, light current types such potentiometers [13]. The basic problems in these kinds of contacts are concerning to high sliding speed like brush/commutator and brush/slip ring in motors and generators.

During sliding the surfaces weld together, presenting high friction also generate an arc that causes arc erosion and very rough surfaces and causing high wear in the system .In order to enhance the wear resistance for this type of contacts, coating the friction surfaces of them with oxide and graphite particles could be the best choice.

Commutating contacts in an interrupted form control the electric circuit. They have two categories: Demountable (various plug connectors, circuit breakers, cable connectors) and breaking. The second one is used for a dorian closing and opening of an electrical circuit, such as in different switches, contactors, relays, and similar devices. Because of differences in breaking power, current, and voltage ranges (mV-kV) during the operation, these contacts generate arc, so that many problems can occur from arc erosion, metal transfer and welding, as shown in Figure 2.4 increase temperature across the contacts and welding can also arise due to the contact resistance in making process as shown in Figure 2.5

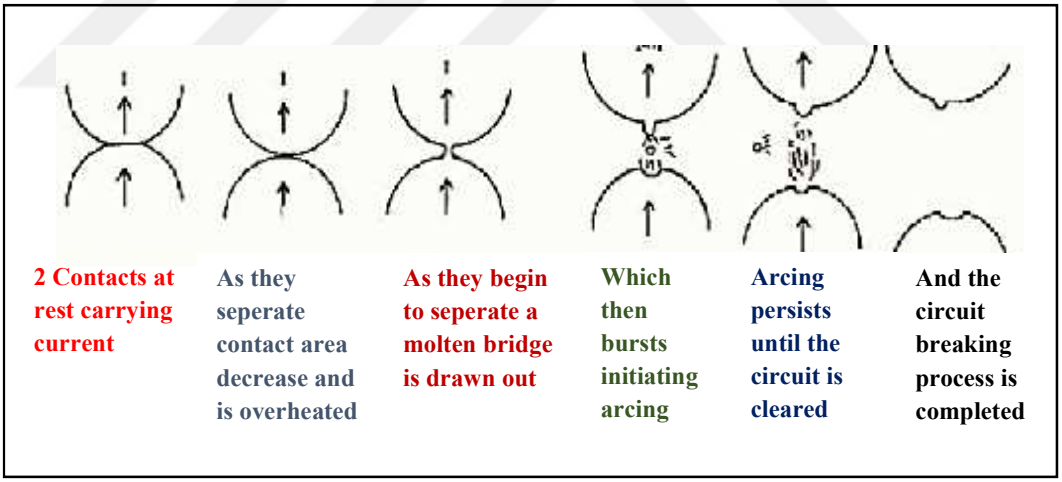


Figure 2. 4 Arc erosion and metal transfer on the breaking process [18].

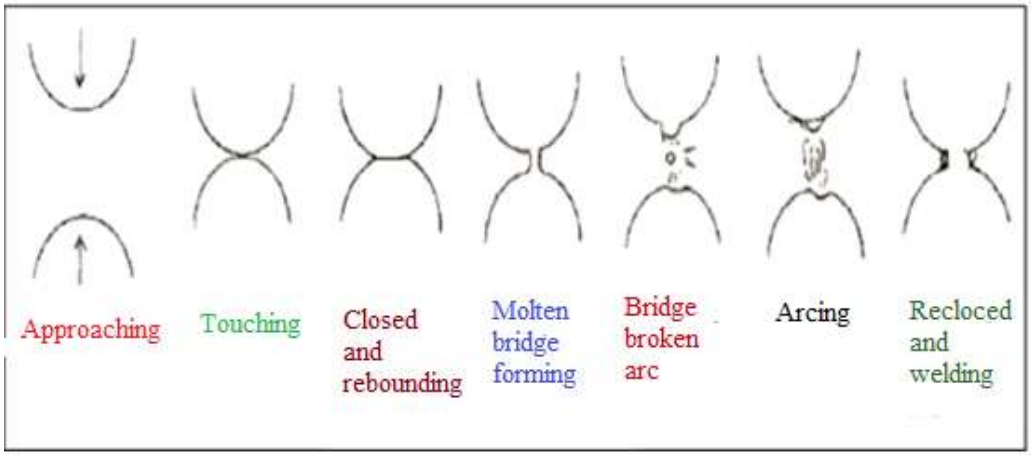


Figure 2. 5 Arc erosion and the mechanism of welding process [18].

Demountable contacts have to carry current for a long duration without disrupt contact. As same as breaking contacts, contact resistance problem occurs for these contacts. But, due to the higher contact force which is a characteristic of this contacts type, this problem is less important here. Due to the high contact resistance with using contact materials have low thermal capacity the temperature will increase. Oslo oxidation and corrosion effects make the temperature rising become excessive [5] [18].

Given all the mechanical and electrical problems that take a place with contacts above, electrical contact materials should be selected with properties that can hold out this kind of problems or improve mechanical and electrical properties of materials by coating or lubricant processes to preserve contacts functionality for a long time.

2.1.1 Composite Electrical Contact Materials

Composite materials (CMs) known as the combining of two or more materials often one of these materials have very different properties than other. The combination of materials gives the composite amended and unique properties. Within the composite, the materials do not blend or resolve into each other. It can easily tell the different materials apart as they were as an individual [20].

Composite materials are comparable to alloys but distinguished from them in the ability of using materials other than metals as a part of the combination and the unnatural forming of this combination like (reaction, phase transformation) or through natural processes such as casting for alloys [15].

Electrical contact materials seek a set of properties to satisfy the working requirements within the whole range of devices from low-current apparatuses ($I=10^{-6}$ A, $U=10^{-6}$V) to power heavy-current apparatuses (I=1000 A, U=1000 V). The procedures of wear, erosion, and friction are associated to the chemical and physical properties of materials like electric and thermal conductivity, hardness, corrosion resistance, thermal diffusion, characteristic parameters of the arc, melting temperature, heat resistance, and some other properties. Realizing an incorporation of these properties is impossible in a pure material and hard to acquire in an alloy[5]. Composites are particularly best situations that create contacts with global properties required in these types of applications.

Electrical contact CMs consist of a matrix has high conductivity, which covers a low electrical contact resistance and good heat removal from the contact area, and efficient fillers. relying on the application of an electrical contact material, an efficient filler assures, for example, low friction coefficient for sliding contacts, high mechanical and electric erosion resistance for sliding and breaking contacts, high mechanical strength, and low weldability.

Metal-matrix composites (MMC) are the general grade of (CMs) utilizes as electrical contact materials. Generally, in this type of composite metal or metal alloys are the matrix, intermetallic compound, oxide, carbide or nitride can be used as reinforcement materials. Most popular composite contact materials are (AgW, AgWC, CuW, AgC , AgMo, AgNi, copper graphite CuC) Figure 2.6 presents some of these materials. Silver or copper phase provides high electrical conductivity for the contact, whereas the second phase additives improve the resistance to mechanical wear, electrical erosion, and welding. Compositions can be produced by powder metallurgy processes, solid-phase sintering of blanks compacted from powders and other processes, these composites are widely used for circuit breakers and other

power switching devices, like, arcing contacts, heavy-current breaking contacts, fixed and sliding contacts.



Figure 2. 6 Composite contact materials[15].

Carbon-matrix composite is also named carbon-carbon composite (CC) or carbon - graphite composite because the most form of carbon-matrix composites use graphite or carbon fibers as reinforcement substance, which means reinforcement and matrix are carbon [15]. In general, this type of composite contact materials can be obtained by Powder metallurgy method from graphite, coal, and black. graphite or carbon contacts have been used in many applications requiring distinct properties such good conductivity, good arc, and welding resistance characteristics that graphite has. Electrical machine brushes is the most common application of this type of composite. Carbon contained in brushes provide a relatively low friction coefficient and good commutation attitude. The main characterization of these brushes is high chemical resistance, low linear thermal extension coefficient, satisfying electrical and thermal conductivities, and antifriction properties that ensure good execution of contact under normal condition.

2.1.2 Nanocomposite Electrical Contact Materials

Nanocomposites are usually known as materials consisting of two or more distinct materials with well manifest interfaces, in which one of the components at least has a

nanoscale (1 nm = 10^{-9} m) structured in one, two, or three dimensions. İn general, one material forms the matrix in which the nanoparticles of the other materials have been added as a reinforcement [21].

The nanostructured reinforcement materials which include atomic clusters, layered films, and bulk nanostructured materials with a mutual feature which is the nanoscale dimensionality (1-100) nm have an observable effect on properties of the composite, such as electrical and thermal conductivity, optical properties and mechanical properties like hardness, wear resistance, strength and stiffness. Nanoparticles (NPs) and nanocomposites acquire huge attention in scientific and engineering studies also increasing interest in these materials enables many applications in various technological area and a wide range of fields, such as engineering parts, medical devices, optics, sensors, coatings and others.[22].

Nanocomposite materials classification is the same as micro composites which are classified according to their matrix materials, into three categories. Metal Matrix Nanocomposites (MMNC), Ceramic Matrix Nanocomposites (CMNC) and Polymer Matrix Nanocomposites (PMNC). as shown in Table 2.2.

Table 2. 2 Classification of nanocomposite[22].

Class	Examples
Metal	Fe-Cr/Al2 O3 , Ni/Al2 O3 , Co/Cr, Fe/MgO, Al/CNT, Mg/CNT
Ceramic	Al2 O3 /SiO2 , SiO2 /Ni, Al2 O3 /TiO2 , Al2 O3 /SiC, Al2 O3 /CNT
Polymer	Thermoplastic/ thermoset, polymer/layered silicates, polyester/ TiO2, polymer/CNT

Electrical and mechanical properties are critical issues for the long-range properties of electrical contacts. Electrical conductivity, wear and corrosion resistance properties have great impact on the long-term functionality of electrical contacts. Because of the improved and unique properties of nanocomposite materials as compared to a classic coarse-grained system, an essential improvement in execution

of electrical contact system can be achieved by using nanocomposites as substrate conductors or thin film coating for contact parts [23].

2.2 Nanocomposite Electrical Contact Production Methods

2.2.1 Nanocomposite Coatings

Nanocomposite coatings pointing to coatings with the addition of one or more nanoscale phases in coating matrix. In last decade nanocomposite coatings have been one of the most interesting and rapidly growing areas of research, due to the massive possibilities for offering superb advantages, e.g., higher hardness, good wear resistance, energy conversion, self-lubrication, antibacterial performance, electrical conducting, etc. the forming of this type of coatings by incorporation of nanoscale phases in host matrix is the best methodology to recognize the properties of the nanoscale materials for wide range of applications and industries particularly electronic and electrical fields [24].

For electrical contact applications, utilizing of protective and wear-resistant coatings is a substantial requirement for extending the functionality of the conductors, such tendencies offered besides cost-benefit instance, many valuable functions such as wear and corrosion protection, conductive circuit elements, diffusion barriers, and others. Electrical and mechanical properties of the contacts surface layers controlled to a large extent, the quality of various electrical devices and systems. Relying on the coating material properties, contacts operating conditions, and intentional functions, the coating thickness onto the contacts surface varies from (0.1–100 μm) [5].

In usual, bulks of the electrical contact are made from a high conductivity and inexpensive metal, the conducting area between two contact members surfaces consists of small conducting areas, called a-spots. For electrical point of view, a large conducting area means better electrical characteristic, the increasing of real contact area is directly proportional to the rising of contact spots number, that known as a-spots. In generally, a-spots comprise only a portion of the real contact area or load bearing area as shown in Figure 2.7.a. This is because of the existence of insulating films, like oxides, sulphide, and latter inorganic films can present on contact surfaces. that should be ruptured so that metallic bridges qualified for conducting

current can create, and This will cause a contraction resistance, the most of the contact resistance occurs from the constriction of the current influx through a- spots see Figure 2.7.b, in addition to the film resistance which presents in conducting area in all types of electrical applications are operating in uncontrolled atmosphere, hence the contact resistance can have obtained through the following equation

$$R_c = R_s + R_{f.} \quad (2.1)$$

Where Rs represent the contraction resistance which depends on contact member resistivity where expressed as ρ1, ρ2, and a is the radius of the metal-to-metal contact area. see Figure 1.5 C. contraction resistance is given by the following equation

$$R_s = (\rho 1+\rho 2) /4 \quad (2.2)$$

Where Rf is the resistivity of the contamination film and can give through the equation

$$R_f = \sigma/\pi a\ 2 \quad (2.3)$$

where σ is the resistance per area of the contamination film.

The contact resistance is taken into consideration as one of the most significant characteristics for all electrical contacts categories and the changing occur in the real contact area and some other factors may cause a significant effect on the functionality of the device, up to malfunctions [5] [25].

Over nanocomposite coating, a favorable combination of electrical and mechanical properties for conducting members can be achieved. The nanoscale incorporation of two or more phases has some respectable tirbo-electrical properties that enable these materials to be a good candidate for contact applications. Good mechanical characteristic such as hardness, wear resistance, corrosion resistance…etc., usually are obtained from the ultra-fine reinforcement particles that embedded in a matrix phase that has some acceptable electrical properties which allow the material to deform to increase the true contact area, giving a low contact resistance, and provides low friction, (Ag-Gr) nanocomposite coatings studied here contain both of nanocrystalline and amorphous phases. and reasonably conductive crystallin silver phase perform a possible solution to increase the contact area, while graphene

particles represent mechanical stability, hardness, also provide an electrical conduction to the coating film due to its excellent electrical properties.

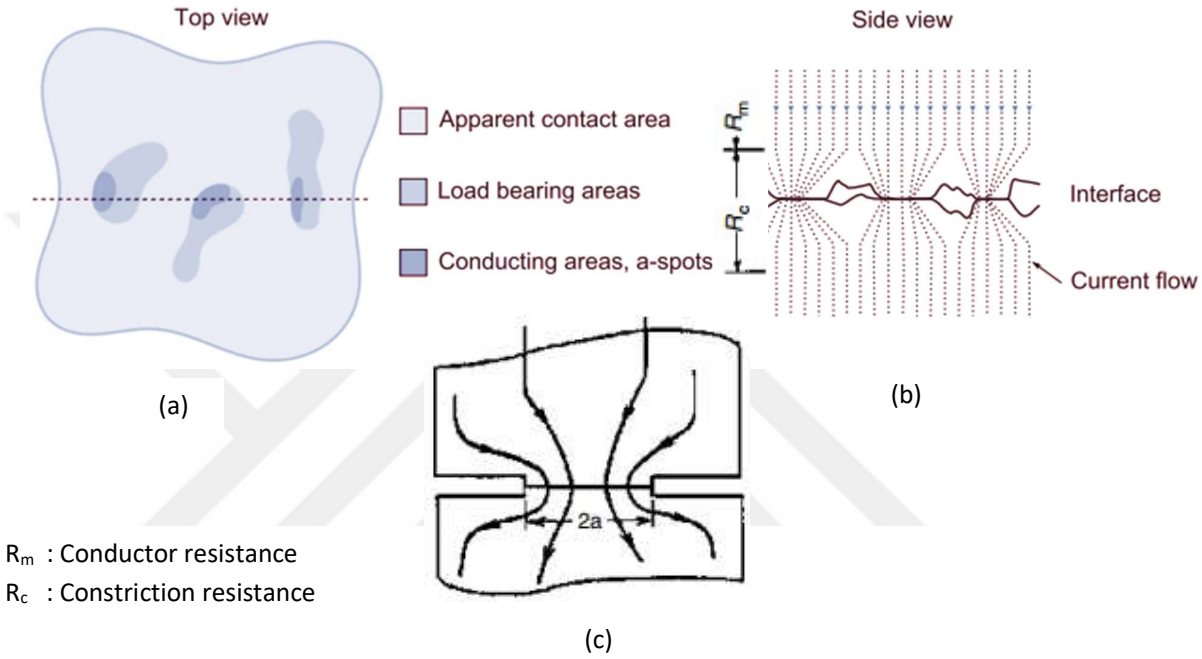


Figure 2.7 Current constraction & real contact area Graphic [26].

There are many factors which can affect the characteristics of virtually all kinds of coated electrical contacts. Among them, the imperfections of the surface (porosity), hardness (softness), adhesion to the substrate, and oxidation resistance and the corrosive environment effectiveness are the most important factors. On the other hand, and because of the environmental conditions and operating nature, the coating layer may lose adhesion and spilt up from the substrate surface, the ability to combat this tendency is critical. Thus, the prosperity of coatings in electrical applications being in the ability to reduce the adverse influence of environment, in coincidence with the substrate material, and reservation of the meant functionality of a device. Different requirements have to be considered when selecting or depositing nanocomposite coating for contacts. In general, the following common norms are used: the contact functionality, operating conditions, the contact members material (substrate), the coating and substrate materials compatibility, coating cost, and environmental integrity of coating deposition. For example, the selection of coatings for moving with low-current contacts requires a set of conditions such: coating appearance (bright or matte, cracks), co-deposition of ingredient when depositing composites, hardness property, porosity, thickness, adhesion to the substrate, resistance, corrosion, wear and electroerosion, multilayer coatings; internal stresses, and costs. The combination of all previous requirements determines the processes that used in the production of coatings for these types of contact [5].

Many techniques have been used for processing metal matrix nanocomposites the most common of them are Spray pyrolysis, Liquid metal infiltration, Vapor techniques (PVD, CVD), Rapid solidification, electrodeposition and Chemical methods, which include colloidal and sol-gel processes [15] [16].

Each one of these processes has special parameters, procedures, advantages and limitations, and diversity of systems and composites prepared by these techniques. Table 2.3 shows different types of metal matrix nanocomposite systems and their main properties.

Table 2. 3 MMNC systems [15] [16].

Matrix	Reinforcement	Properties
Ag	Au	Improvement in catalytic activity
Al	SiC	Improved hardness and elastic moduli
Cu	Al_2O_3	Improved microhardness
Cr	SiC	Improved morphology and hardness
Co	TiO_2	Improved microstructure and functional properties
Zn	MoS_2	Improved corrosion resistance
Ni	Al_2O_3	Improved Hardness of composite

2.2.2. Electrical Nanocomposite Coating Matrix Materials

Many metals had been used as matrix coating materials in electrical applications. These metals include aluminium alloys, copper, gold, titanium, nickel and nickel-cobalt alloys.

- **Copper** is widely used in electrical applications as a matrix coating materials. This is mainly due to its high electrical and thermal conductivity. On the other hand, it has poor mechanical properties. These poor characteristics of copper such as hardness and wear resistance limited its usage lifetime. Similarly, adding a proper reinforcement material can improve the mechanical and electrical properties of copper coatings. Thus, this reinforcement materials increases copper coating usage lifetime [27].
- **Nickel**, In power generation field as well as in electrical applications, nickel and its alloys are attractive coating materials. This is due to their high corrosion resistance [28], especially to alkali corrosion. This resistance can be more improved by the adding of Al_2O_3 particles reinforcement materials to the Ni-Cr alloy coatings. Also, it increases its resistance to cavitation erosion [29].

- **Gold**, another metals used as a coating material in electrical applications are gold and gold alloys [5]. Gold alloys coatings are used especially in highly miniaturized electrical contacts with relatively low contact forces such as low digital signals connectors. The use of gold coating becomes indispensable in high standard of safety components. One of the main problems of using gold in sliding contact applications is the adhesive wear. This problem can be solved by alloying gold with Ni, Co, Cu, Ag and Pd elements [30]. In general, the galvanic deposition method of gold is used in coating the electrical connectors. This method is the most cost-effective.

- **Silver**

  Silver metal is known since earlier decades. İt has been indicated that first separated silver from lead as early as 3000 BC. Silver metal can be existed in native and in ores. Or through some ores sources like copper, Lead, lead zinc, or from pure deposits [31]. Silver as a chemical element has Ag as a symbol and its atomic number is 47 located in the 11th group of the periodic table. Silver is a white lustrous, soft, ductile and malleable metal and has the highest electrical and thermal conductivity of all metals, Table 2.3 presents the basic elemental properties of silver. Also (Ag) consider as one of the noble metal because of its high corrosion and oxidation resistivity that made it ideal for industrial applications. Historically, silver has been used in jewelry and coins, nowadays, these employments have become less than half of all silver exhaustion, Silver has become an innovation material that can be found in wide applications and fields such as energy, photography, brazing and soldering, chemical production, silverware, medicine (antimicrobial property), and due to silver unparalleled thermal and electrical conductivity, it has been the metal number one in the electrical and electronics industries as shown in Figure 2.8. which indicates the percentage of silver uses in various applications.[32] [33].

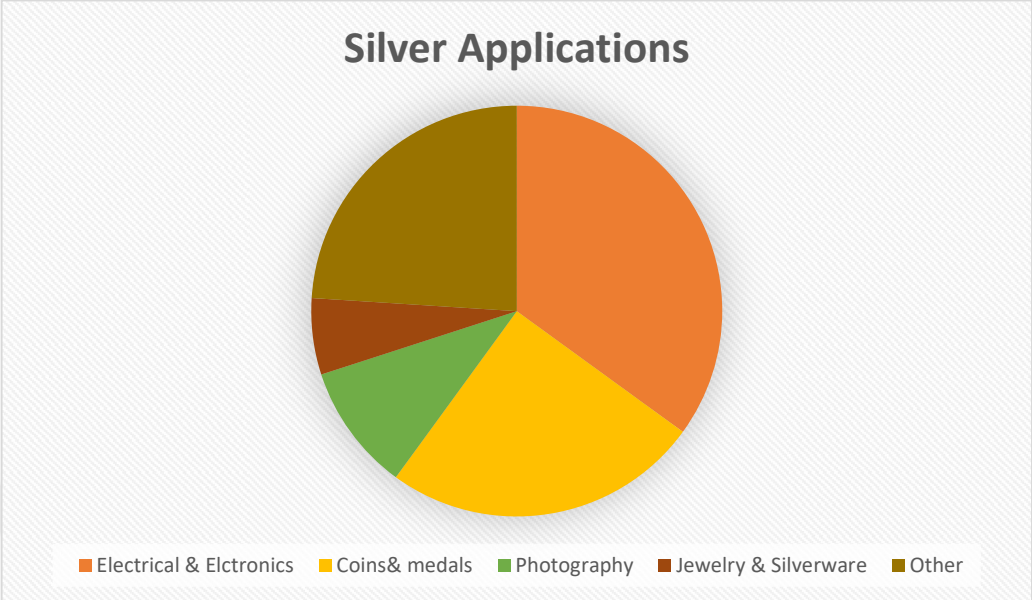


Figure 2.8 Application areas of Silver [33].

Table 2.4 Silver elemental properties [33] [34].

Atomic number	47
Atomic weight	107.868
Crystal structure	FCC
Boiling point	2428 K (2155 °C)
Density	293 K:10.5 g/cm^3
Melting point	1235.1 K (961.95 °C)
Hardness	25
Electrical conductivity	63.0 x 10^6 S m^{-1}
Thermal conductivity	429 W m^{-1} K^{-1}
Young modulus	79 Gpa
Resistivity at 20 °C (ohm m)	1.59 × 10^{-8} Ωm

As it is seen from the graph above, electrical and electronics application has the highest range of silver utilizing. Electrical contacts such as switches, relays, contactors circuit breakers, voltage regulators, arcing tips are considered as one of the most important electrical applications that applied widely in variety voltage electric devices [35]. (Ag) with its unique electrical properties is the most used metal for a significant range of breaking contacts in range (1-600 A) operating current value and more than 15 g contact force. Due to silver ductility, many designs, including solid buttons, tubular, and composite rivets fabrication can be obtained. alloying silver with other metals such as copper, palladium, cadmium, nickel, gold, or platinum generally improved its mechanical properties and increased the resistance to wear and tarnishing. the effect of these elements on different silver properties are given in Table 2.5. However, the most using of silver in electrical applications is as coating or plating material for the contact parts of connectors [10]. in usual, physical properties of the coating material determines the quality and performance of the electrical contacts. Real contact area of contact parts (a-spots) formation with large scale and high conductivity depends on some important properties like coating conductivity, surface roughness, contact force and Mechanical properties of the contact material such as hardness and Young's modulus.

Table 2. 5 Effective of different elements on silver properties [5].

Property	Additions
Arc resistance	Sb, Li, Pd, Mg, Zn, La
Abrasion resistance	Li, Ni, Cu, Pd
Lubrication	Zn, In, Sn, C
Weld resistance	Zn, In, Mn, metal oxides

Silver establishing as a coating metal is due not only to the excellent electrical conductivity but also to its unreactive surface at normal operating temperatures. Formation of oxide or sulfide layers on silver surfaces can be placed only under

specific conditions. Usually damaging effects of these layers on electrical contacts does not occur or little existed, if the contact force is high enough to break through the weakly imperfection layers .these layers can be formed because of atmosphere and decompose at a temperature around 200 °C [36].

There are several techniques used for coatings production, but the most common three processes for coating contact surfaces with silver are plating by dip immersion process, plating by swabbing process, and electroplating [5].

Silver coating produced by electroplating has a higher hardness and electrical erosion resistance than conformable bulk materials and coatings deposited by other methods. Brinell hardness of Silver through electroplating can rise up to 100, generally, higher hardness coating has higher wear resistance, and improve the coating resistance toward brittle fracture [5]. Also silver particles with nanoscale size that can be obtained through these types of techniques, recently become a better candidate as a coating for different kinds of electrical contact parts due to the characteristic of high electrical conductivity and low friction property which is considered as a critical issue for contacts applications[37].

Silver nanoparticles (Ag NPc) are usually reinforced by additional phases like ceramic, metal oxides, and carbon allotropes such as carbon nanotubes (CNT) or graphene (Gr) in order to enhance silver mechanical properties when used as a coating for many printed circuit systems.

2.2.3 Electrical nNanocomposite Coating Reinforcement Materials

Many materials with different shapes were used as reinforcing materials. These materials include carbon-nanotubes, cobalt and titanium carbide. These materials do not form a mixture with the base matrix materials neither in the solid nor in liquid states. They can add to the matrix coating in different shapes such as nanoparticles, discontinuous fibre or continuous fibre.

- **Carbon nanotubes (CNT)**

  Carbon nanotubes are widely used in many engineering fields including electrical applications. This is due to their appropriate electrical, mechanical, and physical properties. These applications include high strength and

conductive composites, energy storage devices, aerospace and automobile industries [38].

The addition of CNT as a reinforced coating material improve the wear resistance, microhardness and electrical properties of the coating. Wang et al.[39] used CNT-Sliver-graphite composite material to enhanced the sliding wear characteristics and reducing the electrical resistance of electrical contacts.

- **Metals Oxide**

  Another reinforced materials used in electrical contacts applications are the metals oxides. These reinforced materials include Al_2O_3, CdO, SnO, and ZnO. These materials flashed to materials matrix have aroused interest in electrical contacts applications. This is due to their high electrical and thermal properties and oxidization resistance.

- **Titanium Carbide (TiC)**

  Another reinforced material used in electrical contacts applications is titanium carbide. Many researches indicated that the hardness and the wear resistance of the coatings reinforced by TiC particles were improved significantly compared to the substrate whereas the coating possesses a lower friction coefficient. Also, TiC gives good mechanical stability and it has a good electrical conductivity [40]. In addition, The TiC particle showed good wettability and compatibility with many matrix materials and alloys.

- **Graphene (Gr)**

  Graphene is the first two-dimensional crystal material that was discovered at the beginning of the 21st century [41]. It consists of a single layer of carbon atoms packed tightly in a hexagonal honeycomb lattice [42], and the last form of carbon allotropes in sp^2-bonded atoms plane structure as shown in figure (1.8) [43]. It is stronger than diamonds and has a superior connection to electricity and heat than any other conductive material.

Graphene was theoretically studied in the 1940s, where scientists thought it was impossible to have a two-dimensional material, so they did not try to isolate graphene.

In 2004, two scientists of Russian origin working at the University of Manchester in Britain, Andrei Jim and Kostansen Novosilov, succeeded in producing, isolating, identifying and characterizing graphene atoms, and discovered its physical properties using a normal adhesive tape. After a series of experiments, the two scientists extracted a one-atom layer of graphene. And won the Nobel Prize in Physics in 2010 for their pioneering work in the field of two-dimensional atoms crystals.

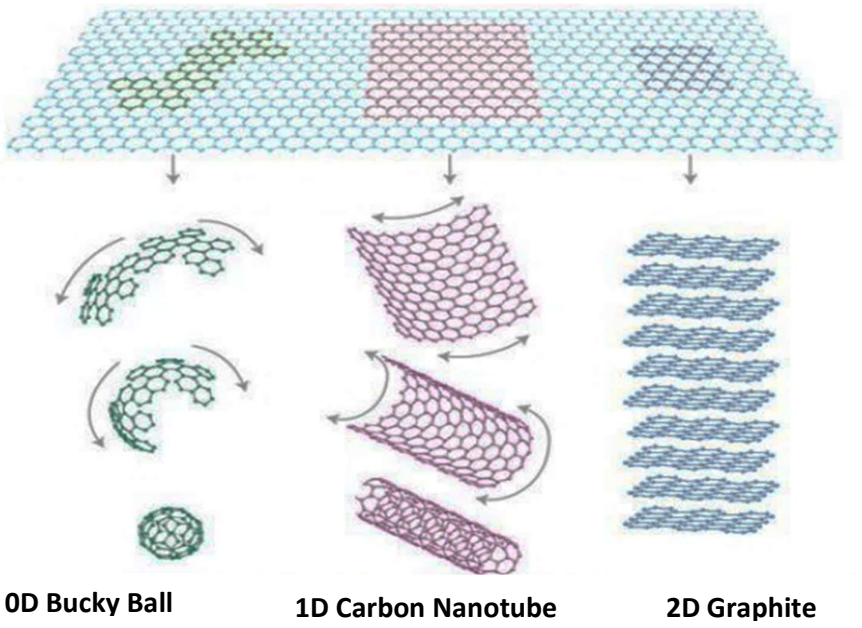


Figure 2. 9 Graphene plane structure [43].

Graphene Characterized as less thickness and more flexible with high stiffens (modulus ~1 TPa) and strongest (strength ~100 GPa) materials. which is superior to copper in its ability to supply electricity and heat exceeds the ability of other materials, so that it is considered as a perfect choice in the field of solar cells and the liquid crystal industry [6].

Despite the flexibility, graphene has a hardness 300 times more than steel, and these require hardness that carries the equivalent weight of an elephant to the head of a needle to break ,also It has a unique electronic properties with high electron motility reach to (250000 cm^2/Vs) at room temperature which higher than silicon as much as 30 times that allows electrons pass through it with very little resistance, and few percent temperature increasing, besides it is a good conductor of heat and all

exceptional properties that make it suitable to use in different fields and applications such as, electronics, sensors, energy storage devices, electrodes, fuel cells and nanocomposites [44] .

Recently, in composites technology, graphene has been considered as a best promising nano-filler used to improve composites quality due to its unique electrical and mechanical properties. Different materials include metals, such as (Al, Cu, Mg, Ag) [45], polymers (PANI, PPS, PVA, PS, PET, etc.) [46], and ceramic-like (Si3N4, Al2O3, zirconia) [47] have been reinforced by GR successfully.

In electrical engineering and electronics fields, graphene and graphene thin films had been established in various kinds of applications as it refers to above, in the last few years, graphene and because of its high conductivity , low contact resistance ,and low resistivity which is about of only $1.0x\ 10^{-8}\Omega.m$ for single layer [41], besides super thermal (high thermal resistivity and low thermal expansion coefficient) and mechanical properties, has been investigated in the systems of new electrical contact materials.

Graphene becomes an excellent candidate material used for producing such attractive types of coatings can offer highly desired requirements like low-friction, long-lasting, and high conductivity for electrical contacts functionality.

Graphene was able not only to restrain wear and friction but also it has potential to repress the surface oxidation due to its impermeability to gas molecules which can play a role in protecting contacts surface against corrosion during the operation to maintain a successful performance for long times.[48] [49].

2.3 Nano Composite Coating Fabrication Methods

Coating surfaces with nanocomposite materials are one of the most important issues in order to enhance and modify the surface of a material by improving mechanical, chemical, electrochemical, electrical, and tribological properties of materials so that improving the performance of the materials for various application purposes.

Nanocomposite coating is consisting of two or more phases which are immiscible, this coating must contain the nanometer scale in at least one dimension even in its

base component which called matrix or in its second phase which dispersed in the matrix and known as fillers.

Nanocomposite coating has several classifications, one of them deals with the type of matrix materials, which could be an organic matrix like polymer, or inorganic matrix like metal and metals alloys, For the last type of nanocomposite coating could be prepared by various techniques such as:

2.3.1 Chemical Vapour Deposition Method (CVD)

CVD is one of the oldest and widely used methods for the fabricating of metal matrix composite coatings, in this process volatile molecular in the vapour phase is transported to a heated substrate where a chemical reaction occurs forming a solid film which is deposited onto substrate surface [50]. CVD technique is a suitable for coating the complex shapes and parts due to its non-line-of-sight nature, also it can be used for production variety types of solid films (metallic, ceramic compound, semiconducting films) and these coatings can include elements, metals and alloys, oxides, carbides, borides, and nitrides, and the thickness of the coatings which is deposited by this process ranges from sub-micrometer to several millimeters[50] [51]. Propagated CVD process diagram can show in Figure 2.9.

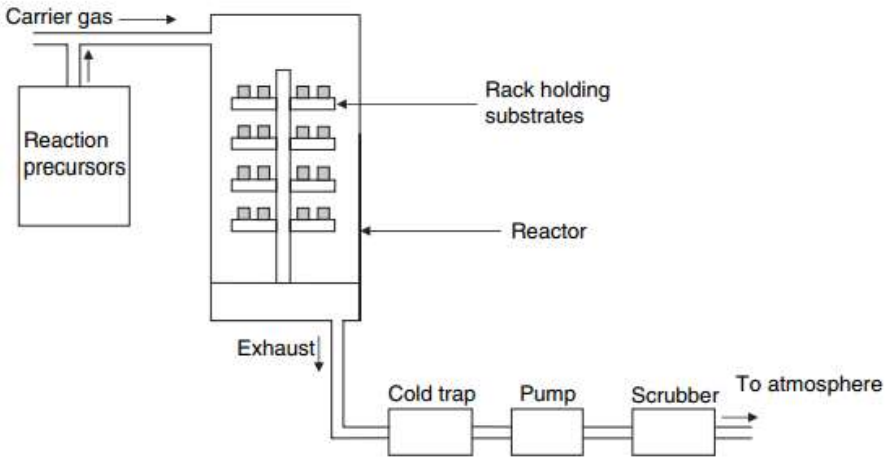


Figure 2. 10 CVD process diagram [51].

2.3.2. Physical Vapour Deposition Method (PVD)

In this technique, a physical process such as sputtering, or evaporation, used to create coating vapour flux from a solid target in vacuum conditions and condensed it as a film on the substrate surface as it demonstrated in Figure 2.11. This method used in general for producing nanocomposite coating containing inorganic matrix and inorganic fillers.[52] with a range that can vary from angstroms to millimetres in thickness. generally, properties such as hardness, wear resistance, oxidation resistance, and multilayer composite coatings could be improved by using PVD coatings. Thus, this technique is useful in a wide range of applications such as automotive, medical/surgical cutting tools, and aerospace. PVD has an excellent coating adhesion and easy regulation of microstructure by selecting the coating parameters. But coating the geometrically complex parts by this process is kind of difficult [51].

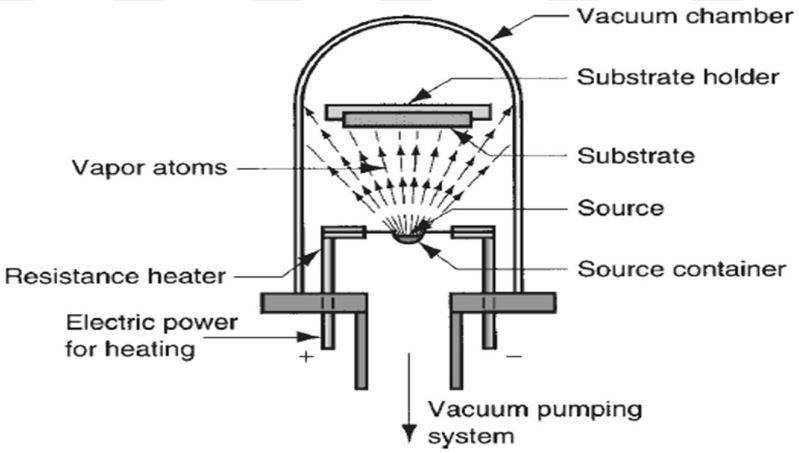


Figure 2. 11 PVD process Schematic diagram [51].

2.3.3 Thermal Spray Coatings

It is a technique which is often used for producing hard nanocomposite coatings with a matrix of metal or alloy on the selected surface. This process involves the projection of heated or melted material (liquid or partly liquid particles) that mixed in a gassy medium with high velocity onto a substrate surface. Upon impacting the

surface of substrate, molten particles compact and transmit the heat to the cold surface and solidify fastly and formed the coating layer. Wires, rod, and powders can be used as feedstock materials in this method as shown in Figure 2.12. Abundant processing paths can be used relying on materials properties and satisfied performances of the coating. These processes include plasma spraying, detonation flame spraying, high-velocity oxy-fuel (HVOF) spraying, and flame spraying. Different materials and components like metals, ceramics, and polymers coated by this technique in ranges of 50-300 μm deposit coating thickness. Line-of-sight nature of this deposition technique considered as the main disadvantage inheres [50] [51].

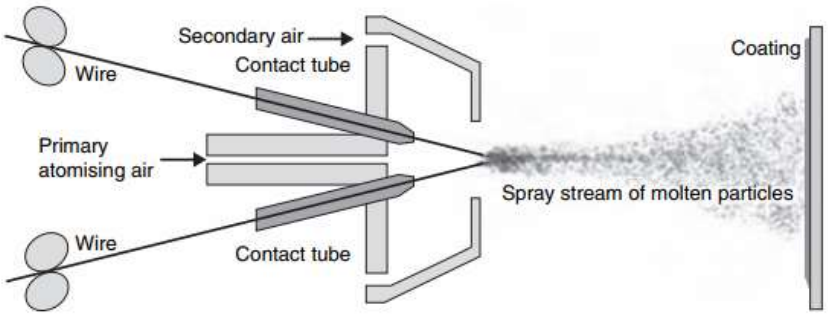


Figure 2. 12 Sketch of thermal spraying method [51].

2.3.4 Cold Spray Method

Cold spray technique differs from traditional thermal spray processes (gas-flame, plasma, and detonation spraying) in coating fabrication temperatures. In this process, solid powders usually below (50 μm) deposited on the surface of the substrate without melting. Powder particles are fed to the high-velocity gas stream (300-1200 m/s) obtained by compressed gas as shown in Figure 2.13 [53], using this process avoids some of materials deterioration phenomena like oxidation, decomposition, as well as phase transition during the process and that is due to the lower temperature required. Metallic matrix coating like Cu, Co, Al, and alloys could be obtained through this process which has low porosity ≤ 1% and strong adhesion (>70 MPa),

and high strength (≥ 280 Mpa). Processes such as mechanical alloying (MA) could be used in order to fabricate the metallic powders that used in this method [54].

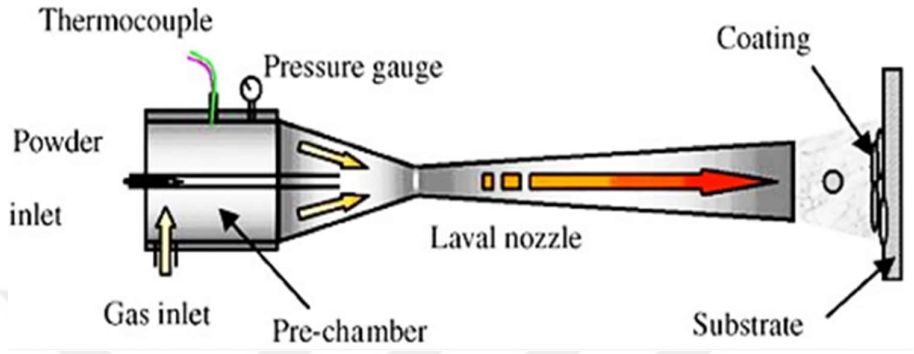


Figure 2. 13 Schematic diagram of the cold spray process [53].

2.3.5 Powder Metallurgy (PM)

Powder metallurgy is the process in which metal or ceramic powders are mixing to form finished or semi-finished components. This process in general consists of four main steps as shown in Figure 2.14 that include: powder manufacture, powder mixing, compacting, and sintering [55]. Usually, ball milling of the metal powder is required in this method for preparing metal matrix nanocomposite in order to get more homogeneity in particle size after that compressing the powder using a hydraulic press, then sintering of the compact is establishing in controlled atmosphere furnace so that to achieve favourable density and strength. occasionally, in order to remove leftover porosities secondary processes such as rolling, extrusion or stamping are required in order to eliminate the residual porosities from the product. Powder metallurgy has a wide range of applications as follows:

- Automotive applications
- Refractory carbides
- Refractory metals

There are some factors that can influence on the characteristics of (PM) processed (MMC) such as:

- the reinforcements type

- Phase and microstructure that could be affected by the parameters and heat treatment of process.
- The bonding between matrix and reinforcements [56].

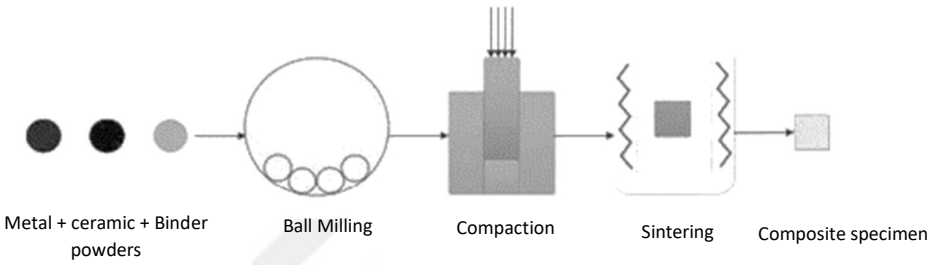


Figure 2. 14 Schematic diagram of Powder Metallurgy Process [55].

2.3.6 Electroplating Processes

2.3.6.1 Electroless method

The first description of electroless deposition for metals was as early as 1844 [51], but the first reported for this process was for nickel and cobalt coating in 1946 [50] . Electroless plating is a chemical reduction process that depends on a catalytic reduction of metal cation in a chemical reducing medium. then deposition of metal occurs subsequently with no need to an external electrical source[57], which is the main diverse than electrodeposition process that requires an electrical energy to reduce metals ions as shown in Figure 2.15. Variety metals such as copper, gold, palladium, platinum, silver and alloys embrace one or more of these metals have been successfully plated via this process. Generally, electroless deposition depends on some important characteristics includes path composition, operating conditions, pretreatment of the substrate surface, and electrolyte age (electrolyte lifetime can be less than 5 or 6 metal turnover before replaced). The electroless coating has good wear resistance, corrosion resistance, hardness, electrical resistivity,and less porosity with uniform deposition layer even for complex shapes and geometrical parts. that makes this method so attractive for a wide range of applications such as automotive, aerospace, biomedical and electronics industries [50].

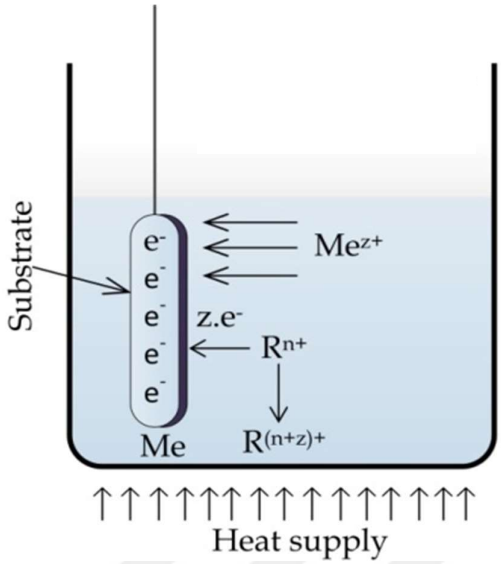


Figure 2. 15 Schematic diagram of electroless plating process [57].

2.3.6.2 Electrodeposition method

Electrodeposition is an important technology in the electronic industry field. This economical technology is used to enhance the characteristics of metal surfaces by the production of dense metallic nano-crystals coatings [58]. This technology is also used in many other industries including home appliances, jewellery, automotive, aircraft and aerospace engineering. A magnetron sputtering targets of well-defined shapes can be fabricated using electrodeposition technology. The main advantages of this technique are increasing the desired mechanical and electrical properties of metals and eliminating waste by deposition precisely where needed. Sputtering targets of Ag, Cr, Au, Fe, Ni, Co and alloys have been prepared by electrodeposition.

Many methods were used to perform metallic coatings. These methods are direct current (DC), pulse current (PC) and pulse- reversed current (PRC). For many decades the DC electrodeposition method was widely used for fabrication of metal matrix coatings. Recently, the PC and PRC electrodeposition methods have received more attention. This is due to the improved corrosion and mechanical properties of coatings obtained by using these methods. Many researchers observed that by using the PC and PRC methods a significant improvement in hardness and wear resistance were obtained compared to DC electrodeposited coatings [59].

In the DC electrodeposition method, only one parameter affects the electrodeposition process, which is the current density as shown in the Figure 2.16.

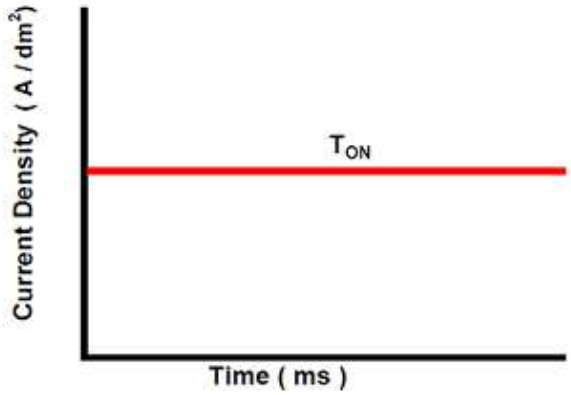


Figure 2. 16 Typical Direct Current DC waveform.

In PC and PRC electrodeposition methods many parameters are influencing the techniques which make the techniques much more flexibility. These parameters include the peak current density, pulse current on-time (T_{ON}), and pulse current off-time (T_{OFF}). This resulting in a unique combination of composition and microstructure in deposited coatings, which can be obtained by varying these parameters. Also, a series of pulses of equal amplitude, duration, and polarity separated by zero current can be obtained in PC method by alternating the electrodeposition current between two different values [60]. A typical pulse current and pulse reverse current waveforms are shown in the Figure 2.17. In this figure, the current is alternated between a peak positive current value applied for T_{ON} time and zero applied for T_{OFF} in the PC technique and between a peak positive and peak negative current values applied for T_{ON} and zero current value applied for T_{OFF} in the PRC technique.

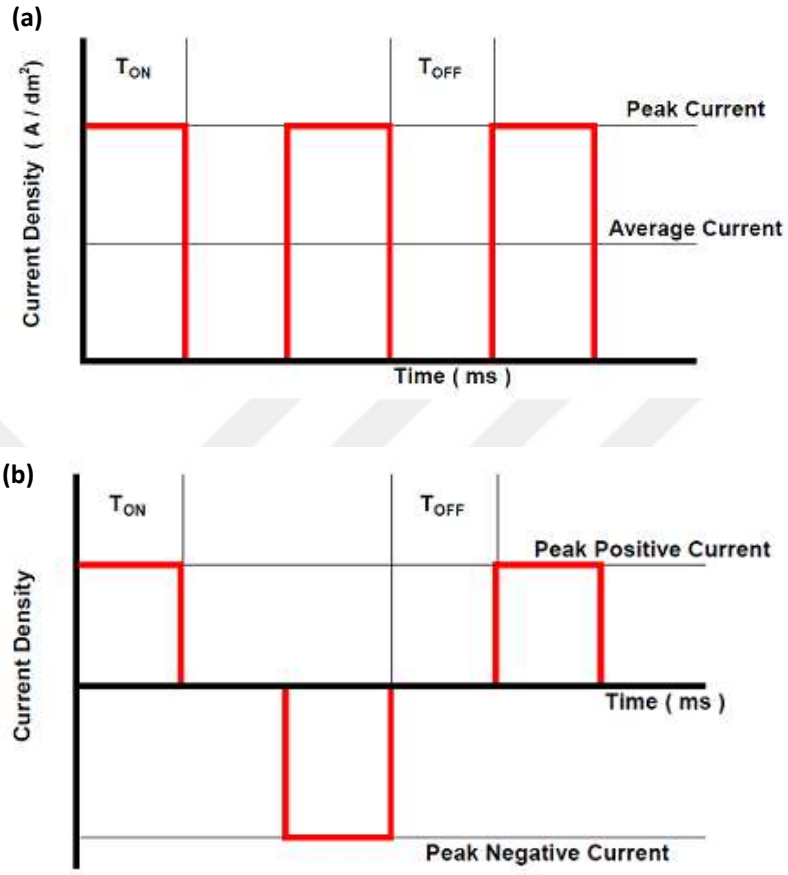


Figure 2. 17 Typical (a) Pulse Current PC and (b) Pulse Reverse Current PRC waveforms.

The main advantages of PC and PRC techniques are [60] [13]:

1. Replenishing metal ions in the diffusion layer only during off time increases significantly the limiting current density.
2. The process limitations are reduced due to the flexibility in pulse parameters.
3. Improves adhesion of deposit, creates a uniform thickness.
4. Fine-grained deposit with lower porosity and reduced stress.
5. An improvement in physical and mechanical properties can be obtained using a higher rate of deposition.

The main disadvantages of PC and PRC methods are the pulse generators are more expensive compared to DC unit. In addition, in order to obtain better results, this technique needs proper planning with a series of procedures.

2.3.6.3 Principles of Electrodepositing

Electrodeposition is the process of coating a thin layer of coating metal on the surface of different conducting materials by electrochemical reduction of coating metal ions from a solution containing ionic species (electrolyte) [61]. A typical set up for small-scale electrodeposition is shown in the Figure 2.18.

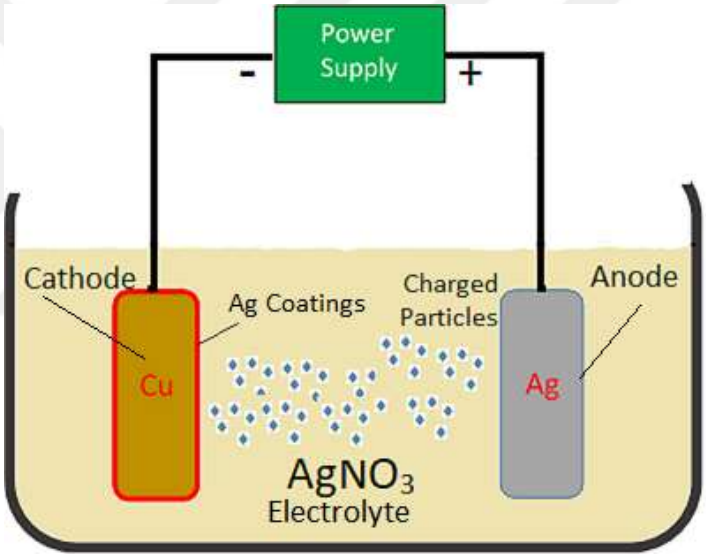


Figure 2. 18 Schematic representation of Ag electrodeposition cell.

2.3.6.4 Faraday's Laws of Electrolysis

From his experiments, Faraday deduced two fundamental laws, which govern the phenomenon of electrolysis. These are:

(i) First Law. The mass of ions liberated at an electrode is directly proportional to the quantity of electricity i.e. charge which passes through the electrolyte.

(ii) Second Law. The masses of ions of different substances liberated by the same quantity of electricity are proportional to their chemical equivalent weights.

In another word, the mass of a substance liberated from an electrolyte in a given time is proportional to the quantity of electricity passing through the electrolyte. The Faraday law that governs the electrodeposition process is given by the equation in 2.4:

$$m = \frac{Q\ A}{n\ F} \tag{2.4}$$

Where:

'm' is the mass of the deposited metal (in grams)

'A' is the metal atomic weight.

'F' is the Faraday constant (F = 96485 $C.mol^{-1}$).

'n' is the valence electron of metal.

'Q' is the net charge passes through the system, and equal to current multiplied by time (Q = I t).

This equation can be expressed as:

$$m = Z\ Q \tag{2.5}$$

Where Z is a constant called electro-chemical equivalent.

If i = 1 ampere and t = one second then, m = Z which gives the definition of Z which can be expressed as the amount of the substance by weight liberated in unit time by the unit current.

Electrodeposition can occur from a simple solution. The electrolyte may be any soluble compounds or salt containing the metal in the form of anion or complex. In order to facilitate the current flow between the electrodes, some additives such as inorganic acid or alkali may be added to the plating bath. These ions increase the electrical conductivity of the solution. This also can decreases the voltage applied. Also, these additives can be used as PH regulator.

In order to obtain a fine-grained deposit with a smooth appearance, many conditions have to be provided. Many factors affect the electrodeposition process of metals. These factors are:

- Current density: The electrodeposition process depends upon the rate at which crystals grow and the rate at which fresh nuclei are formed. At low current densities, the deposit will be coarse and crystalline in nature. The quality of deposit becomes more uniform and fine-grained on account of the greater rate of formation of nuclei at higher values of current density. PRC Method eliminates thickness build up at high current density areas during current reversal and improves step coverage without pores reaching down to the substrate [60].

- Electrolyte concentration: The electrolytic Concentration is more or less complementary to the first factor. This is because a higher current density can be achieved by increasing the concentration of the electrolyte. In PRC method, the electrochemical polarization of cathode increases when applying the reverse current. At this point, the current transition occurred opposite to the current direction, which decreases the nucleation energy and increases the rate of nucleation. therefore, we can obtain a more smooth surface and compact coatings structure [62].

- Temperature: The temperature of the electrolyte has two contradictory effects. First, the diffusion increases at a comparatively high temperature and even at relatively high current density, smooth deposits may be produced. Second, the rate of crystal growth increases the possibility of coarse deposits. At moderate temperatures, the deposits are good.

- Addition agents: To improve the quality of the deposits, some agents may add to the electrolyte. These agents may be a colloidal matter or an organic compound such as gelatin, agar, glue, gums, rubber, alkaloids, sugar etc. The addition agents are supposed to be absorbed by crystal nuclei and prevent their growth into large crystals. Otherwise, the metal deposits in the form of large crystals and the surface become rough. In order to obtain a completely homogenous bath in terms of acidity, buffer agents can be also added into the bath. Some of the additives can reduce the electrode surface energy so they can inhibit the attachment of hydrogen bubbles to surface. These bubbles lead to undesirable pitting that is macroscopic

point defects. PC method reduces the additive requirement by 50–60% whereas PRC enhances the bath stability and efficiency with negligible additive consumption [60].

- Nature of electrolyte**:** The formation of a smooth deposit largely depends upon the nature of electrolyte used.

  - Nature of the metal on which the deposit is to be made

    It is believed that the operation of crystals is in continuation of these in the base metal. Thus, the nature of the metal on which deposit is to be made influences the growth of crystals.
  - Throwing power of the electrolyte

    For a cathode having an irregular shape, the throwing power of an electrolyte may be regarded as the quality that produces a uniform deposit on irregular surfaces. For these types of surfaces, the conductance of the electrolyte is not the same for all parts of the cathode because of the distance between the cathode and anode not equal for the cathode parts. In an electrolyte of low conductance, the current will concentrate on the parts of the cathode, which are nearer the anode resulting in poor throwing power. This problem can be solved by using a good conductance electrolyte, which increases the throwing power. Also by keeping a good distance between the cathode and the anode, this led to improving the throwing power thereby providing more or less the same conductance for all parts of the cathode. Presence of colloidal matter improves the throwing power but increase of temperature may produce the opposite effect.

2.4 Review of Related Works

Silver composites and silver composite and nanocomposite coatings have been attracting much attention in the electrical and microelectronics field due to higher conductivity characteristic. One of the methodologies used to improve the metal mechanical and electrical characteristics is using the nanocomposite coatings. This is a significant topic in the material science field. In this chapter a quick review of experiments and research conducted in the field of producing nanocomposite coating and successfully deposition of silver and greaphene through electrodeposition method, also a quick review of some researchs deals with the investigated of DC, PC, PRC deposition current types and their effects on improved coatings properties. Besides, survey of some studies spotted the light on the development of electrical contact component by graphene implementation.

Karslioglu et al. [63] investigated the effect of different deposition current types which are direct current (DC), pulse current (PC), and pulse reverse current (PRC) on the surface microstructure, crystallographic structure, microhardness, and wear behaviours of Ni-Co alloys and Ni-Co/MWCNT composite coatings. When compared according to the three current types, they indicated that hardness values for both of alloys, and composites were the lowest in DC deposition current, and increased with PC, and PRC respectively. This increasing in microhardness attributed to the changing in the crystallographic grain growth, and results showed that the smaller grain size achieved with PRC method (see Figure 2.19). They also reported, that the co- depositions of MWCNT in electrodeposited layer increases with PC, and PRC respectively. The increasing of MWCNT promoted the changing of particles morphologh from polyhedral structure to spherical and somehow porosity structure (see Figure 2.20). They also mentioned that coating thickness layer was the thinner in Ni-Co/MWCNT coating which produced by PRC method. They attributed this result to the fact that the (PRC) method increases and promotes the MWCNT co-deposition. Higher amounts of MWCNT acts as physical parier that inhibits grain growth.

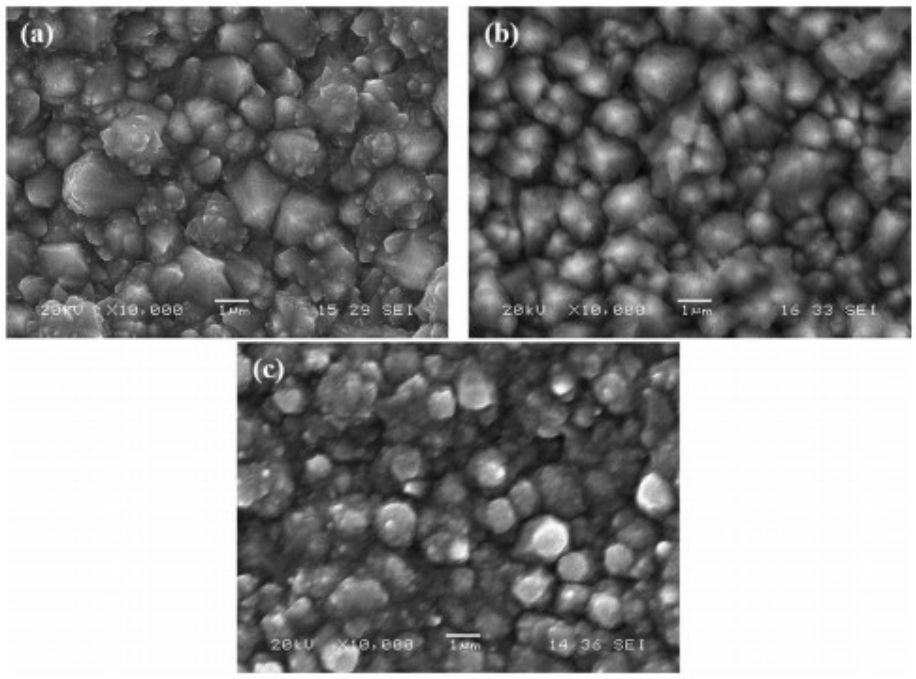


Figure 2. 19 Ni–Co alloy coatings at 50ºC for 30 min at 5 A/dm2 current density; a) DC, b) PC and c) PRC methods [57].

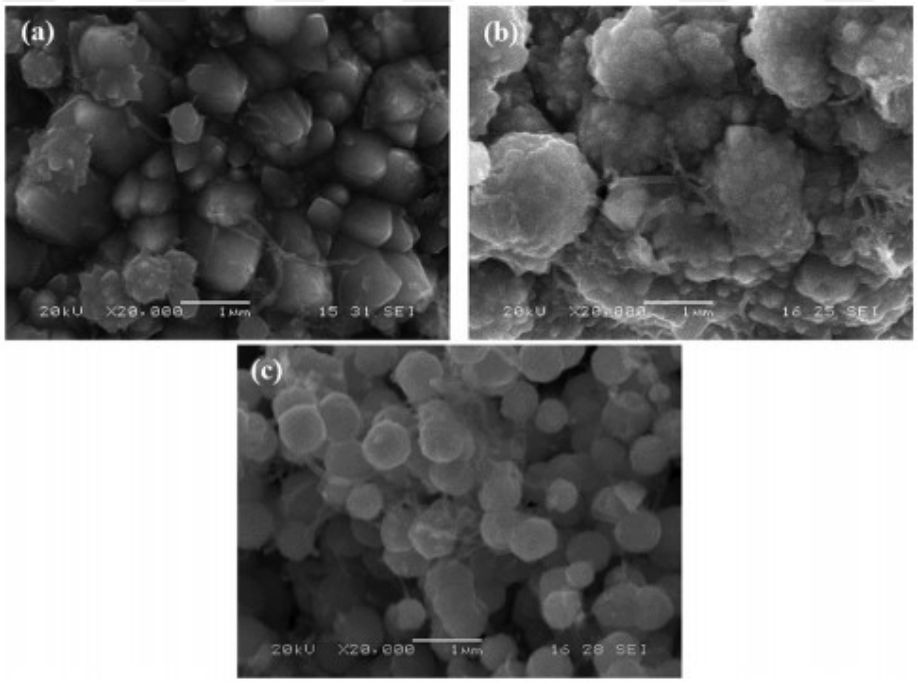
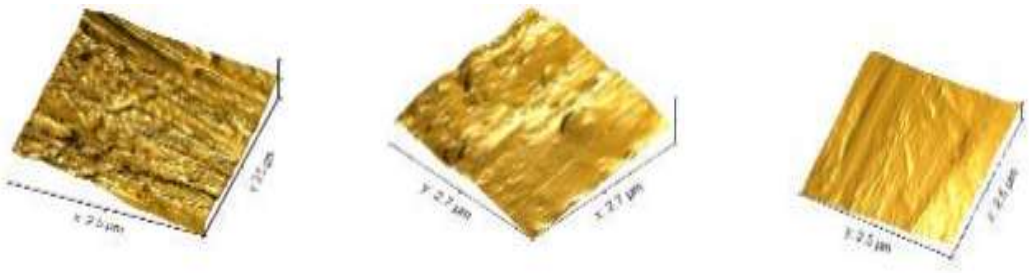


Figure 2. 20 Ni–Co/MWCNT nanocomposite coatings at 50 ◦C for 30 min at 5A/dm2 current density; (a) DC, (b) PC and (c) PRC methods [57].

C. Shanthi et al. [64] made a comparative investigation for DC and PC platings of Ag on Ag alloy with the studying the effects of the peak current density on the current efficiency and the thickness of deposition process, they mentioned that a thinner thickness layer of deposit obtained with the applying of pulse current .The interruptions of current during PC did not allowed thicker growing films. Otherwise an equilibrium concentration for the metal ions during PC occurred, so by increasing current density when considering PC is necessary in order to recover the OFF time where is no deposition places. For this study it has been clarified that Ag plating by applying pulse current has a uniform with lower thickness layer, less porosity and smaller grains compared to the case of DC plating.

V.Vaghela et al. [65]investing in the influences of pulse electrodeposition method on the surface morphology to pure Ag deposited on Al alloy from cyanide path. They studied the impact of variables parameters of the pulse like (duty cycle, peak current density and the frequency of pulse) on the hardness, grain size, anti-tarnishing , porosity, thickness and brightness of the surface deposition. By increases the duty cycle of the pulse , the thickness of deposited Ag electrons and hardness increasing with the increasing the frequency , higher frequencies that mean (shorter pulses) caused an enhancement of the nucleation rate that led to decreases the deposits grain size and building up surface with these fine-grained so less porosity and higher hardness.



(a) (b) (c)

Figure 2. 21 Morphology analysis of Ag deposition a)with DC,b) with PC, and c) with PRC[59].

The investigation of surface morphology in respected to various current methods were evaluated in this study by SEM & AFM. Three morphologies analysis by AFM

presented in Figure 2.21 showed that the deposit prepared by DC current exhibit higher surface roughness with 900 nm compared with the roughness of surface obtained by PC and PRC that had 200nm and 10nm in respectively, likewise, a significant decreasing in the average of particle size was obtained in the deposits obtained by PC , PRC , arrange of (200 -500 nm) for PC and (30-40nm) for PRC which were much smaller than of (1300-2500nm) obtained by DC. They reported that so good quality of deposits with a finer grain size, less porosity and uniform plating can be obtained with lower pulsed duty cycle and used alternative to deposition method type like PC, PRC methods.

L. Stappers et al. [66] co-deposited carbon black nanoparticles with silver from a hydantoin containing the electrolyte. To keep particles suspended during electrodeposition, they used an ultrasonic agitation. They indicated that high amounts of relatively uniformly distributed carbon nanoparticles in the coatings were successfully obtained. In order to study the coating behaviour for electrical connector applications, the contact resistance of the coatings was measured during reciprocating fretting. Their results indicated that the wear rate and the electrical properties drastically change. The wear rate is lowered by a factor 14 and the contact resistance during fretting is below 1 mΩ without spikes.

M. Uysal et al. [67] examined the effect of graphene addition on the structure and tribological behaviours of electroless Ag, and Ag-WC nanocomposite coatings. They found that the addition of even small quantities of Gr can significantly improve the anti-wear and anti-friction properties of Ag matrix Nanocomposites. They indicated that graphene co-deposition in the deposition coating not only enhanced the resistance of wear but also offers a topical protective layer which effect in reducing the friction on the surface of contacts. The introduction of WC and Gr in the Ag-WC-Gr nanocomposite coatings resulted in a decrease in Ag matrix grain size which confirmed by XRD data analyses besides, a makeable changing in the nucleation and growth mechanisms of silver matrix. The incorporation of hard WC in the coating effected in increasing the hardness of the deposition coating while the introduction of nanosheet graphene resulted in decreasing the hardness value concurrently with an increase in surface roughness and porosity. They attributed this result to the

deposition of Gr sheets, in the end wise geometry of Ag coating due to the changing and shifting in the nucleation and growth mechanism of Ag. Although, the addition of Gr caused high wear resistance and decreased the friction coefficient of nanocomposite coating due to surface lubrication characteristic of Gr. It has been concluded in this study that controlling the decoration of Ag on the Gr sheets in a form of multilayer nanocomposite coatings can constribte in produce an efficient type of micro and nano contact materials. Also they reported that WC / Gr nanocomposites considered an excellent candidate for MEMS devices contact materials.

Pengpeng Wang et al. [45] fabricated an enhanced silver-graphene properties of composite materials. An improved mechanical tensile strength, hardness and ductility properties composite product was obtained. The hardness of the silver-graphene composite produced was much higher than most carbon-reinforced silver contact materials. Also, their electrical endurance test showed that the silver- reinforced graphene Ag-rGO composites have excellent electrical properties. Their results showed that the contact resistance of Ag-rGO is as low as ~ 0.0012 mΩ, which is much lower than that of pure silver (0.0035 mΩ). They concluded that the interaction of rGO and Ag nanoparticle is a critical factor that determines the final performance of the resultant product and influenced the dispersion of rGO in the Ag matrix.

Song Wang et al. [68] investigated the microstructure, electrical conductivity and the arc erosion behaviour of silver-graphene Nanoplates electrical contact materials prepared by powder metallurgy process with different (GNP_s) content (0.5,1.0,1.5,2.0) wt. %. The influence of graphene amounts on the surface morphology of the composites was clarified and presented in Figure 2.22 they observed that by addition lower amounts of (GNPs) (0.5, 1.0, 1.5 wt.%), (dark area) to the silver matrix (grey areas) the Ag- GNPs showed fewer agglomeration contents compared with Ag-GNPs contact materials prepared with 2.0% GNPs additions.

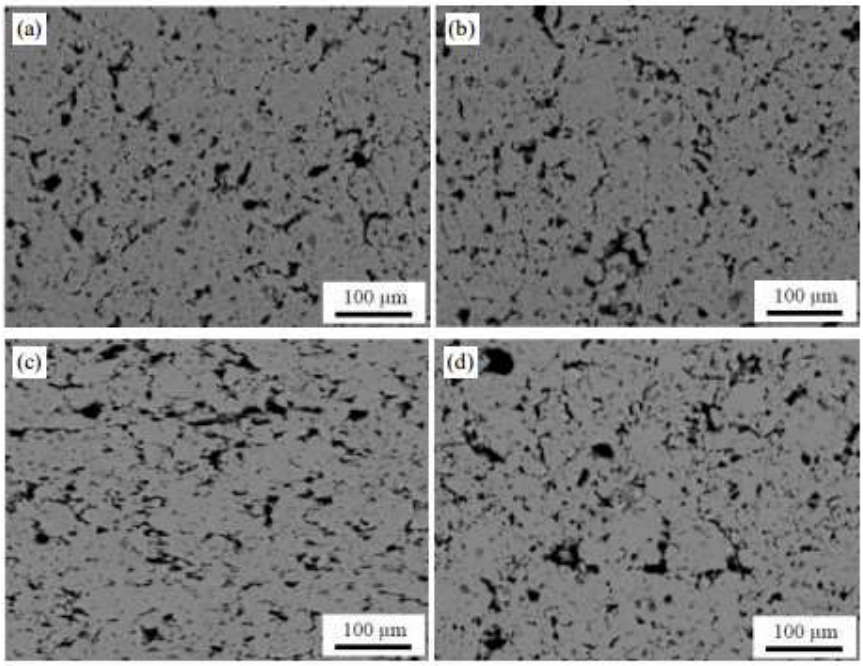


Figure 2. 22 SEM images of Ag-GNPs materials: (a)0.5% GNPs, (b)1.0% GNPs, (c)1.5% GNPs and (d)2.0% GNPs.

Higher agglomeration with higher GNP_s contact caused decreases the electrical conductivity of Ag-GNPs prepared with 2.0 wt.% graphene contacts. They indicated that the agglomeration ration regions caused high porosity and a lot off particles boundaries concurrent with high CNPs contact caused electrons dissipation so conductivity decrease. Further more they examined the arc erosion behaviour of Ag-GNPs electrical contact materials with different GNPs contact. Figure 2.23 showed the surface morphology of Ag-GNP_s composite contacts after 30000 operation cycles under DC 25/15A the Arc erosion contact showed paste- like erosion morphology with big and deep pits. Arc erosion of Ag-1.5 wt. % GNP_s surface exhibited very shallower erosion pits with the relatively flat surface. While Ag more uneven surface with more rough erosion pits obtained with the increasing of GNP_s contacts in Ag-GNP_s electrical contact materials.

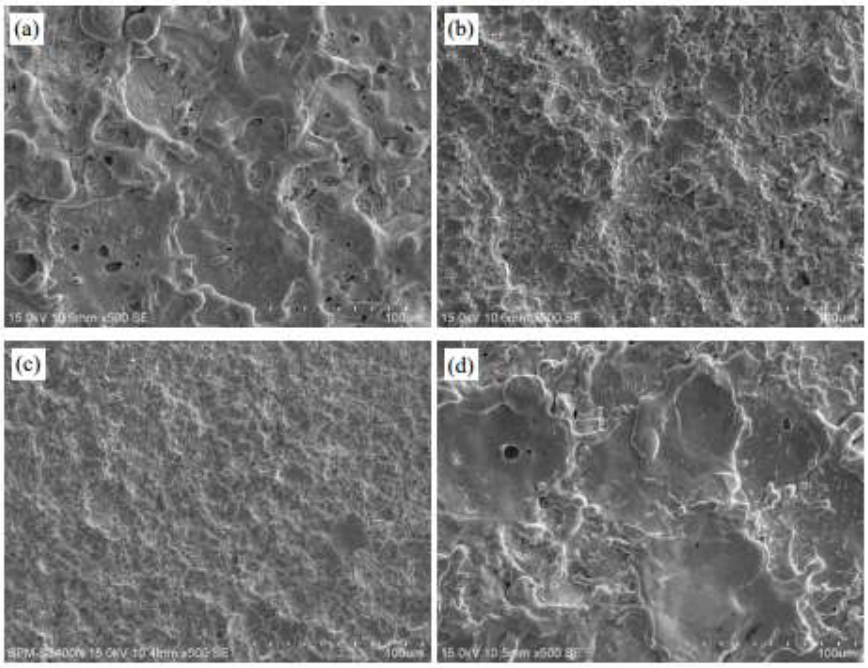


Figure 2. 23 Surface SEM of Ag-GNPs materials: (a)0.5%GNPs, (b)1.0%GNPs, (c)1.5%GNPs and (d)2.0%GNPs.

The Potential for graphene to be used as a lubricant for sliding electrical contacts had been evaluated by Diana Berman et al. [48] They investigated the effect of graphene on friction and wear behaviour of sliding Gold/Titanium Nitride substrates. The demonstration was conducted both in the humid and dry environment. They measure the coefficient of friction along with the contact resistance for revealing its potential to maintain high electrical conductivity of the macroscale contacts and also for indicating any modification of graphene layers at the sliding interface as shown in the Figure 2.24.

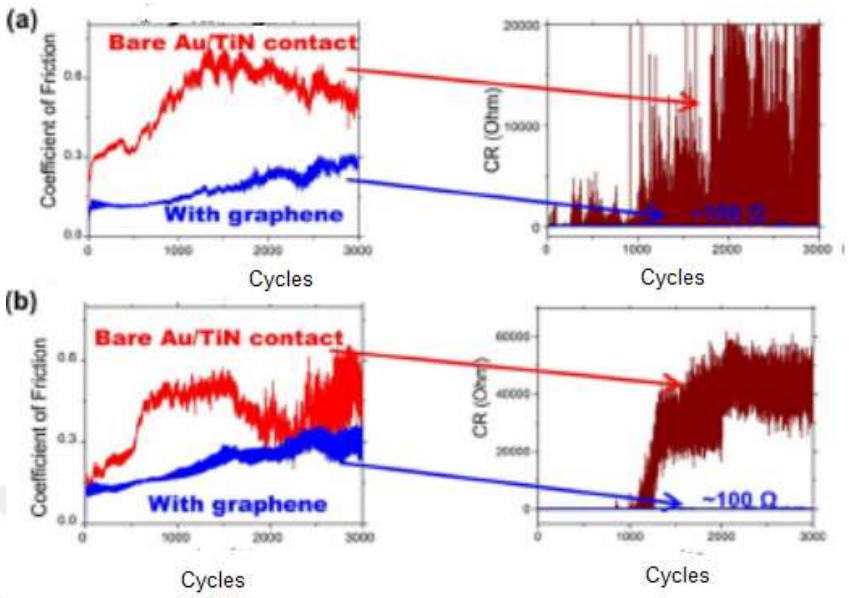


Figure 2. 24 Coefficient of Friction with the corresponding Contact Resistance evolution for bare gold/titanium nitride contact and with graphene both in a) dry nitrogen. b) Humid air [42].

From This figure, we can see that the graphene not only suppresses the friction and wear but also maintains low contact resistance of the sliding interfaces.

CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1 Introduction

Present chapter discusses the particular experimental procedures, the materials used and the equipment accessed to verify the performance of the coatings developed through experimentation. All the experimental procedures and processing were carried out at Ankara Yıldırım Beyazıt University laboratories, for characterization purpose the equipment that located in these laboratories in addition to one examination executed at the laboratories of Fatih Sultan Mehmet University are mentioned below with their particular utilization within the investigation also their specifications and details obviously. The materials and chemicals components needed for the fabrication of the composite coatings and electrolyte baths for deposition study also were provided during this chapter.

3.2 Experimental Procedures

The experimental processes were started with optimizing procedures according to the literature studies. Electrolytic baths have been used for electrodeposition processes with a temperature that usually kept in the range of (50-60)˚C. The average of current was selected as 10 mA (5A/dm^2) for all current types, and PH of the bath was adjusted to 10-12. BARAKUDA electroplating device has been utilized not only as a power source, but also as a currents supplier through providing different current types such direct current (DC), pulse current (PC), and pulse-reverse current (PRC) that had been applied within deposition processes. The average of current density with 10 mA was applied for the three deposition current methods, by applying 10 mA in DC, and 20 mA for the T_{ON} and 0 mA for the T_{OFF} in PC method according to the equation 3.1, and 40, 0, -10 mA for T_{ON}, $T_{OFF,}$ and anodic(reverse)T_{ON} in respectively for PRC method which represented in equation 3.2 ,where is the on-time and off-time and reverse on- time of applied current were 10 ms ,keeping the duty cycle of current for all current types 50% in accordance to Equation 3.3 .

$$I_A = I_{Ton} + I_{Toff} / 2 \quad (3.1)$$

$$I_A = I_{Ton} + I_{Toff} + I_{Ton(reveres)} / 3 \quad (3.2)$$

$$\text{duty cycle} = \frac{T_{ON}}{T_{ON} + T_{OFF}} \quad (3.3)$$

Where is I_A is the average current, I_{Ton} is the current density in cathodic (forward) time, I_{Toff} is the current density in the OFF time which equal zero, and $I_{Ton(reveres)}$ is the current density in e anodic (reverse) time, 2 and 3 are the number of current durations in PC, PRC respectively.T_{ON} is the ON time and T_{OFF} is the OFF time in pulse cycle. Average current was selected 10mA (5 A/dm^2) for all current type.

Coatings were achieved in a glass beaker of 100 ml capacity with (ISOTEX) speed controlled magnetic stirrer positioned in a fume hood. As an anode material, a high purity silver plate with 5 g. in weight and dimensions of 1 cm in width, and 2 cm length. As cathodic material, two kinds of copper substrates were used, first one was high purity copper rod cut to cylinder pieces with the dimensions of 8 mm in diameter, and 3 mm as thickness, which used for coatings characterization purposes, second one was electrical contact pairs (buttons) with the same surface area of copper cylinder pieces for both of upper and lower buttons, were obtained from commercial electrical contractor (Himel HDC6-9) that used for electrical and erosion behavior analyses after removing the available coating layers by manual grinder machine and coated with the prepared coatings . Coating baths contained silver nitrate ($AgNO_3$), potassium cyanide (KCN), and distilled water. For composite coatings, graphene with (3 nm x 1,5 μm) dimensions that was purchased from Nomography company has been used. In order to prevent agglomeration of the graphene and getting well homogeneity in the bath an ultrasonic mixer was used.

In this study, the effects of the different deposition current types and graphene additions to the silver coating were investigated on microstructure, phases, hardness, electrical contact performance, and erosion properties. The experimental procedure flow chart that followed during this investigation was given in Figure 3.1.

3.2.1 Substrate Preparation

In this study, two different copper substrates were selected as a cathode for the deposition of silver and silver-graphene composite coatings. First substrates type was hot rolled copper rod and cut by BUEHLER Iso Met Low Speed Saw apparatus into cylindric pieces with averagely 8 mm in diameter, and 3 mm in thickness. Metallographic preparation for these samples by belt grinder was obtained by different grade size 400, 800, and 1000 mesh SiC emery paper. Later the substrates were cleaned with distilled water and rinsed with acetone. Copper wire was soldered to the un grinded side of these samples in order to dip them in the electrolyte path and to supply current by attaching this wire to the power source as shown in Figure 3.2.

The other substrates type were electrical contact pairs (buttons) of HDC60911M AC contactor had been taken out after dismantled the contractors as illustrated in Figure 3.3. Basic coating of these buttons has been removed by manual grinder machine in order to coat these parts with the investigated coatings. After grinding, cleaning samples with acetone and distilled water was established.

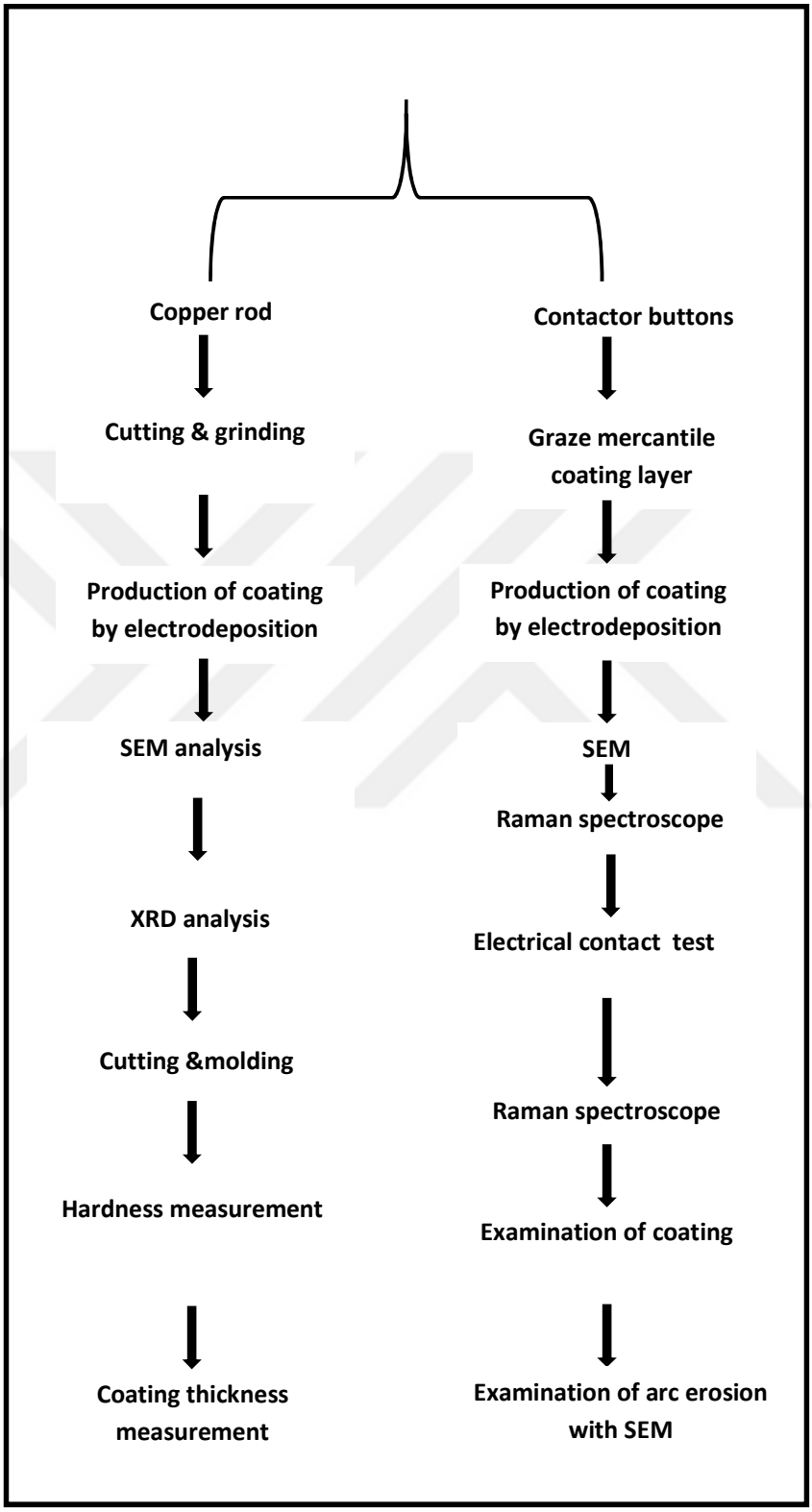


Figure 3. 1 Experimental procedures chart.

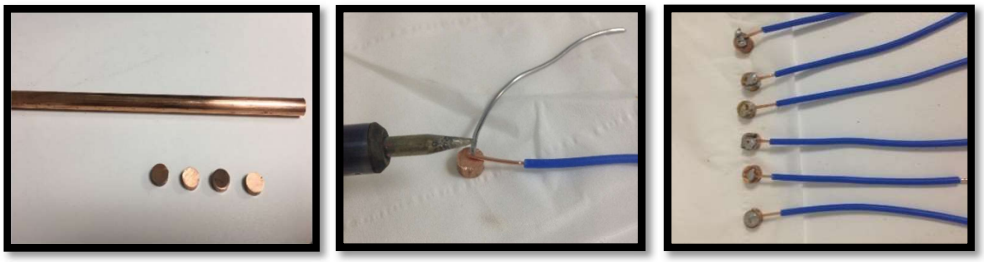


Figure 3. 2 Copper rod samples.



Figure 3. 3 Electrical contact samples.

3.2.2 Coating Baths Composition

Two types of electrolyte baths of silver deposition which are pure silver coating bath and Silver-Graphene nanocomposites coating bath were prepared. Both baths carried out in a 100 ml glass beaker. Pure silver coating bath consists of silver nitrite ($AgNO_3$), Potassium cyanide (KCN), and distilled water. The second bath contained the same chemical components with the addition of different amounts of graphene reinforcement material. Both baths were stirred for 10 minutes with a magnetic stirrer. For silver graphene nanocomposite coating bath, the ultrasonic stirrer was used for 30 minutes in order to prevent graphene agglomeration and homogeneously dispersion during a deposition in the silver matrix. All coating systems were adjusted in 55±5 ºC average temperature and placed in the fume hood position. All the depositions developed by electrodeposition was controlled by using three different current types which are Direct current (DC), pulse current (PC), pulse-reverse current (PRC). After electrodeposition of 120 min, the coatings were washed with distilled water. All used chemical components and experimental procedures parameters are indicated in table 3.1.

3.3 Electrodeposition Processes Ag and Ag-Graphene Nanocomposite Coating

Parallel silver plate and copper buttons electrode configuration and surfactant silver nitrite baths for the deposition of Ag and Ag-Gr nanocomposite (where the addition graphene Nano-sized particles deposited in the silver matrix) were used. Silver deposition electrolyte bath and according to the literature researches commonly consist of silver nitrite ($AgNO_3$) and potassium cyanide (KCN), which adopted in this study. ($AgNO_3$) used as silver source and (KCN) used as an inducer for higher solution conductivity, higher solubility, higher limiting current densities, and also its ability in increasing the polarizations of anode and cathode, which improves power passing in electrolyte [69]. pH value of the electrolyte was 12 and it should have maintained over 10.5 due to the probability of complex deformation of silver ions below this range which decreased the rate of plating. A magnetic stirrer with a heat probe was used for stirring of the bath during deposition for homogeneously

dispersed particles in the solution also keeping constant temperature at 55±5˚C that required during entire depositions, for graphene electrolytic baths ultrasonic homogenizer stirrer was used for 30 minutes before deposition processes in order to prevent the sedimentation and agglomeration of Gr nanoparticles in the electrolyte solution and homogeneously dispersed during a deposition in the silver matrix. All the depositions had been produced by DC, PC, and PRC deposition current types, and the effects of these current methods on mechanical and electrical properties of the coatings had been observed and characterized. Coating baths parameters are given in table 3.2.

Table 3. 1 Coating Systems Parameters.

Coating baths parameters	**Pure silver coatings**	**Silver - Graphene nanocomposite coatings**
AgNO3 (silver source)	10 g/L	10 g/L
KCN	10 g/L	10 g/L
Graphene (reinforcement material)	—	0.5g/L ,1 g/L , 2g/L , 4g/L
Current density	5A/dm^2	5A/dm^2
Current type	DC,PC,PRC	DC,PC,PRC
PH	12	12
Temperature	55^0 C	55^0 C
Ultrasonic stirring	–	magnetic stirring: 45 minutes before coating progress
Magnetic stirring	150 rpm	150 rpm
Cathode	Copper	Copper
Anode	Silver	Silver

Table 3. 2 Test Current Parameters of all Specimen.

Specimen No:	Current type ($I_{average}$=5A/dm^2)	Graphene	$AgNO_3$/ KCN(g/l)	T_{on} / T_{off} / - T_{on} (ms)
1.	DC	_	10/10	∞/0/0
2.	PC	_	10/10	10/10/0
3.	PRC	_	10/10	10/10/10
4.	DC	0.5 g/l	10/10	∞/0/0
5.	PC	0.5 g/l	10/10	10/10/0
6.	PRC	0.5 g/l	10/10	10/10/10
7.	DC	1 g/l	10/10	∞/0/0
8.	DC	2 g/l	10/10	∞/0/0
9.	DC	4 g/l	10/10	∞/0/0

3.4 Characterization Methods

3.4.1 Scanning Electron Microscopy Analysis (SEM)

The microstructure images analysis of the coatings was scanned using HITACHI Tabletop Microscope model (TM4000Plus) as shown in Figure 3.4. The results obtained from the characterization process were studied and analyzed. This device was also used to study the changes of the grain structure under different conditions.

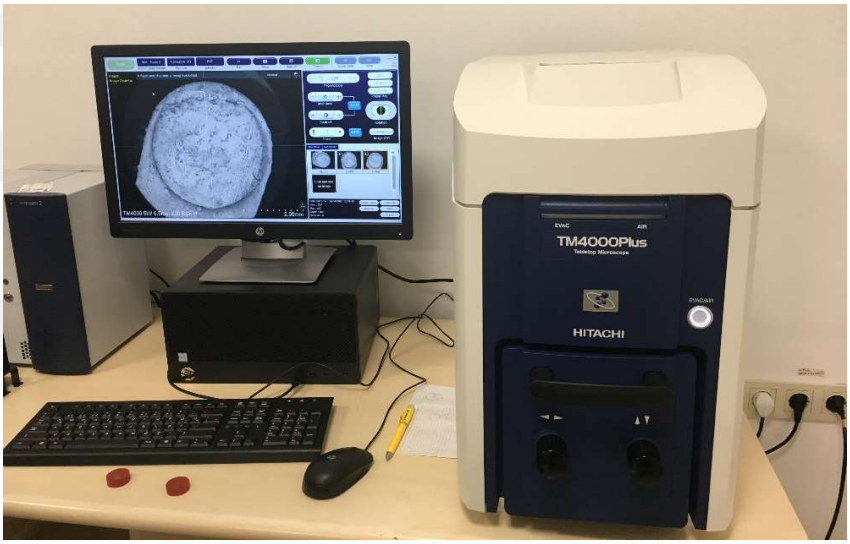


Figure 3. 4 HITACHI Tabletop Microscope (TM-4000 plus).

3.4.2 X-Ray Diffraction Analysis

In this work, XRD analysis had been used to characterize the structure and the crystalline phases in the produced coatings and to determine the size of the crystallite. The equipment used in this research is (Rigaku Miniflex 600) X-ray diffract-meter as shown in Figure 3.5.

This XRD equipment uses a Cu-Kα radiation value of wavelength 1.54059 and operates at 40 kV. A scan rate of 2°/min between 35° to 85° 2θ angles was performed. A Halder-Wagner method was used to calculate the crystallites size.



Figure 3. 5 X-Ray Diffraction analysis device.

3.4.3 Raman Spectroscopy

Raman spectroscopy is a useful non-destructive tool used to distinguish ordered and disordered carbon structures either graphene, graphite or Nano-tube carbon exist in the composite coating. Each of these forms has a characteristics peak measured in Angstrom, known as Raman shift. These peaks indicate the type of the structure exists in the coating. Raman spectroscopy performed by Jasco NRS 4500 with applied scattering spectra 532 nm wavelength laser light source, and a low excitation power of 5 mA had been used in this study for characterization the presence of graphene. The graphene has a peak located at ~1365 cm^{-1}.

3.4.4 Micro-Hardness Measurements

The micro-hardness of the produced composite coatings was examined using a Vickers hardness test. A SHIMADZU HMV-G Vickers micro-hardness tester equipment, shown in Figure 3.6, was used for this purpose. The measurements were performed on coatings cross section that was prepared by metallographic procedure and conducted using a load of 5 N with holding time of 10 seconds. The procedure was accomplished by obtaining the average hardness value of testing each specimen for six times at least. The device was also used to measure the thickness of the coating layers.



Figure 3. 6 A SHIMADZU HMV-G Vickers micro-hardness tester.

3.4.5 Coating Thickness Measurements

A SHIMADZU HMV-G Vickers micro-hardness tester equipment was used to measure the coating thicknesses. Thickness measurements were obtained from the coatings cross sections after cutting the coated substrates with Low Speed Saw apparatus mounted the samples with Bakelite by hot mounting machine. Then grinding operation for the samples was applied by using SiC emery papers with 600, 800, 1000 and 1200 grinding size. After that, polishing surfaces by using 3 μm diamond suspension on the MD Mol, and cloth thus reach the mirror-like surfaces finish. Then, the average of five measurements from the different area was calculated with computer software.

3.4.6 Electrical Contact Test

Electrical performance was carried out with Handmade electrical contact test device that had been established in Yıldırım Beyazıt University laboratory for examining the electrical contact performance of all prepared coatings. Figure 3.4 shows the device structural set up, and Figure 3.5 schematically shows electrical contact test setup. Contact tests were carried out at a constant load of 4 kW with a current of ~18 A /DC, and voltage of 220 V. Each contact coated pairs were tested for 10000

operation cycles. Operating frequency with 2 seconds for both Ton and Toff was selected. Electrical contact test was applied for analyzing arc erosion, melting and break-down of the coated contactors. The surface morphologies of all contacts after the test is completed were characterized by (Hitachi TM-400). scanning electron microscope.

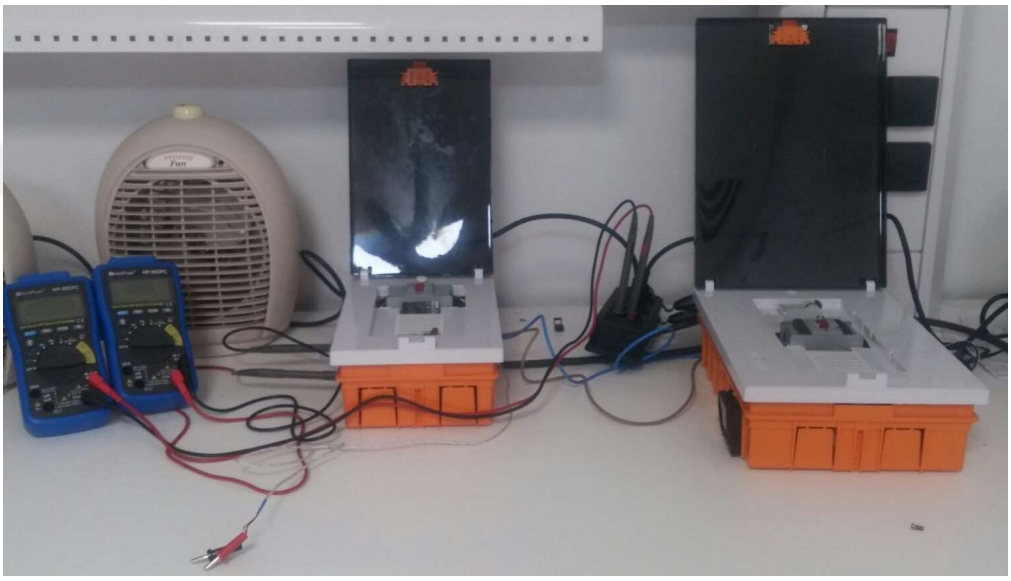


Figure 3. 7 Electrical contact test devise.

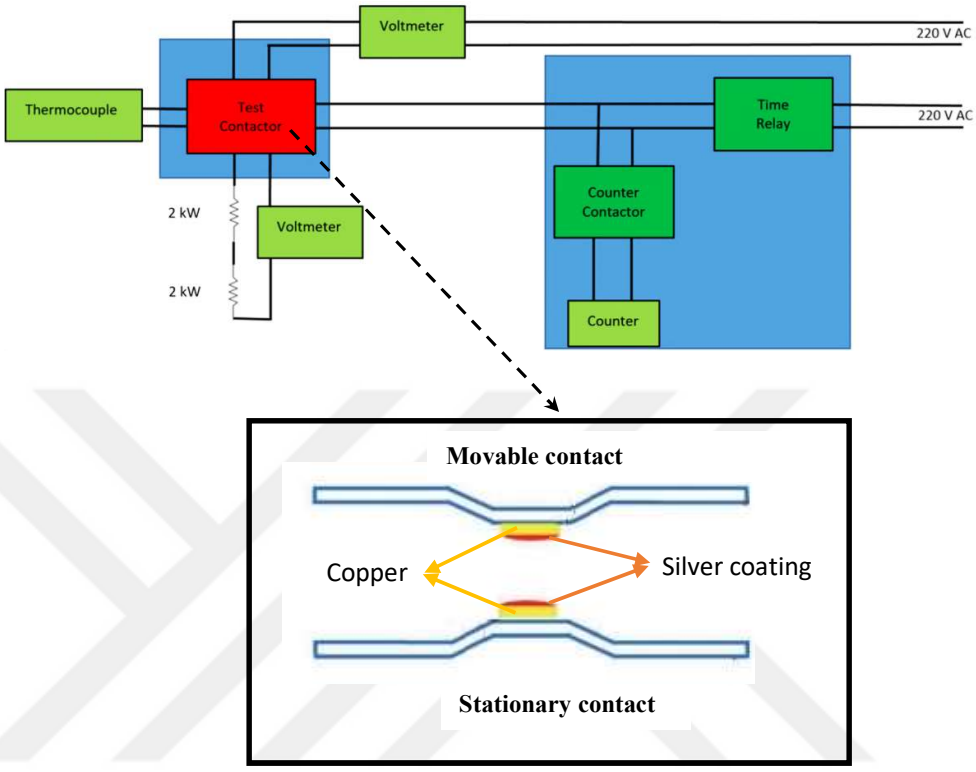


Figure 3. 8 Schematic diagram of Electrical contact test.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Structural Analysis

4.1.1 Microstructural Analysis

Electrical contact parts are commonly coated with silver, that used for electroplating as it is a good conductor of electricity. It is often plated onto electrical contacts for use in the electrical and electronics industry [70]. According to some literature studies achieved for silver plating for this purpose, several types of coating baths have been used and optimum bath composition that providing required electrical and mechanical properties for this study was adopted [71] [72] [21]. The influences of different current types and different amount of graphene reinforcement additives to coating bath on the structural and mechanical and electrical behaviour were examined. For this purpose high purity copper substrate was chosen as a cathode material and high purity silver used as an anode. During the deposition, temperature for coating bath kept constant at around 55˚C when the avarege of current density with $5A/dm^2$ was used [73]. Cyanide solutions the most common used for silver electroplating [72] due to offering proportional deposition quality with low cost. So that, with accordance with the above evaluation, the bath composition consisted of $AgNO_3$, KCN and pure water has decided for this study.

Typical surface morphologies of DC, PC, and PRC electrodeposition of pure silver (Ag) and silver -graphene nanocomposite (Ag-Gr) coatings were observed under a scanning electron microscope (SEM) and the images are given in Figure 4.1. From these images, it can be clearly observed that the morphologies of these coatings changed with the changing in current types during the deposition. The surface of pure Ag coating deposited with DC current method has relatively bigger grain size and showed irregular polyhedron crystal with less compacted structure compared to the same coatings produced using PC and PRC techniques that exhibited better

uniformity and finer grain structure. Highly instant of current density throughout PC and PRC deposition seems to increase the nucleation of the grains on the surface [64] performing in finer grain structure in the Ag coating. In case of PC deposition , the interruption of current allow equilibrium concentration of metal ions deposition, besides, higher peak pulse current is necessary in order to deposit a given amount of metal in a set of time , in order to compensate for OFF time . A consequence of using higher current density in the case of pulsing is that higher deposition over potentials result, which promotes nucleation process and increased the amount of deposition resulting in uniformity and finer grained deposition. Ag PRC deposited showed smaller grain size with more homogenous and compacted structure compared to DC, and PC deposits. In PRC process the forward pulses T_{on} restrict mass transfer operation and dominate the grain size; while reverse pulse T_{on} helps to remove entrapped hydrogen and minimizes the random morphology during each pulse hence finer grained with more compacted surface can be obtained.

Similar results were obtained by C. Shanthi et al. [64] through investigated the influence of DC and PC current deposition of Ag on the surface morphology of Ag alloys, they concluded that the deposition by using PC method result in finer grain size and less porosity structure compared to DC method at the same current density.

As well as, the trend is similar to the results mentioned by Vaishali et al. [65] after studying the improvement of surface morphology of Al alloys deposited with pure Ag by pulsed electrodeposition. They found that deposited obtained by PRC has the lower holes and the grain size was reduced to 40nm which is smaller than 1.5μ in case of DC. Also, the surface roughness was minimized from 900nm in DC method to 200nm with PC, till 10nm with PRC current type.

For (Ag-Gr), nanocomposite coatings, SEM images showing an obvious effect of (Gr) content on the coating morphology, a significant increasing of graphene content which indicated through EDS analysis (Figure 4.4) was obtained by PC and PRC methods. Also the reinforcement content (Gr) is less in the coatings deposited through DC method because of co-deposition is lower in the DC deposited coating when comparing with PC and PRC deposited composites. The periodically current

alternation (from positive to zero values in PC, and positive to negative values in PRC) caused in discharging the electric double layer that formed around the cathode, and allowing better passage of ions adsorbed on the surface, that way better permeation of nanoparticles towards cathode occurred. These adsorbed ions onto nanoparticles surface thereafter get reduced at the cathode giving rise to entrapment (graphene reinforcement) of the nanoparticles in the growing coating.

The incorporation of Gr caused by modulating the surface to spherical crystals which exhibited a relatively rough surface compared with unreinforced coating surface. This change in surface morphology can be related to the changing of several crystallite planes for the Gr reinforced nanocomposites. Since Gr co-deposition as illustrated from the surface morphology of coating is lower in the DC composites deposition, the Ag crystals are still in the polyhedrons morphology but smaller than pure Ag coatings.

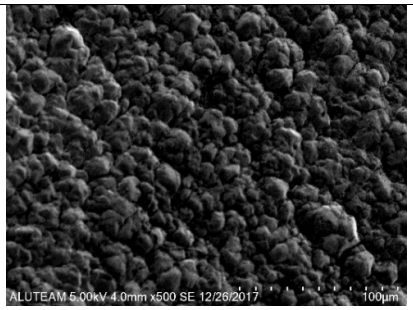
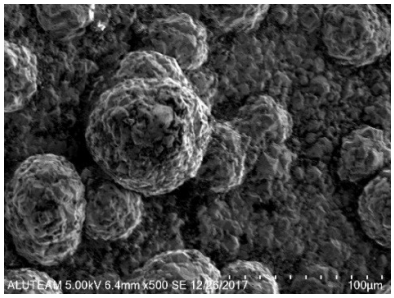
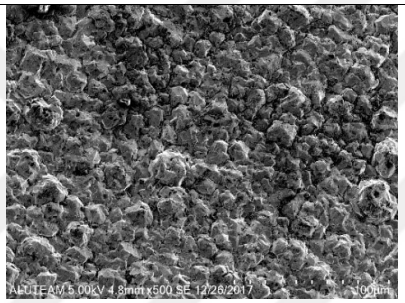
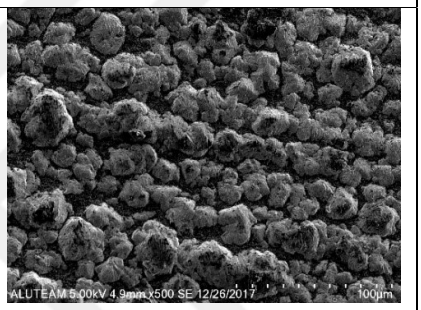
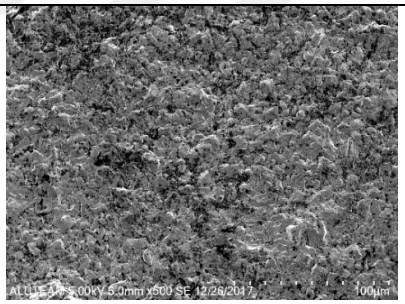
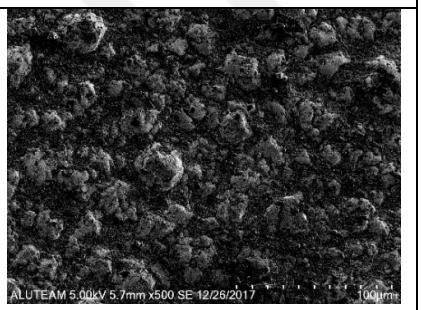
Current type	Ag	Ag/Gr
DC		
PC		
PRC		

Figure 4. 1 Surface morphology of pure Ag and Ag-Graphene coatings deposited by DC, PC, and PRC current methods.

The surface morphologies of the Ag-Gr nanocomposite coatings, deposited with varying amounts of Gr nanoparticles in the electrolytic bath (1, 2, and 4 g/L), are presented in Figure 4.2. All these coatings are deposited using DC current type. The images clearly indicate that; when the quantity of Gr nanoparticles in composite increases the surface of the coatings turn into a surface with coarser grainy features. As it is clear the Ag-Gr coating, deposited with 1g/L Gr, the deposited surface was piled with spherical cluster morphology. By increasing Gr content in electrolyte up to 2 gm/L, Ag-Gr coating showed a spherical surface arranged with a large number of grains has nearly equally sized with spherical-shape. This changing in morphology in accordance with some studies[63] can be associated with the adding of nano-sized reinforcement material. The incorporation of Gr nanoparticles caused in decreasing the grain size by acting as physical barriers inhibit the grain growth of Ag matrix, this decreasing in Ag crystallite size can transform the particles from polyhedral into spherical structure. also the hardness value of coating has increased. As well as, the concentration of Gr continues to increase a changing with crystallographic morphology from spherical crystal to polyhedral crystal occurred which caused by decreasing of hardness value. With increasing Gr reinforcement in the coatings up to 4g/L the composite change significantly with high roughness with a considerable amount of porosity in the deposited composite structures, which is an indication of partial permeability of Graphene for ions to deposit on substrate. Also it can be found some endwise sheets penetrated into the coated layer on the surface of the composite. These endwise dispersions are signs of homogeneous dispersion of Graphene sheets in the silver matrix . As shown in Figure 4.2.C. the Ag/Graphene composite coatings, the layers of the Graphene sheets dispersed between the silver depositions resulted in decreasing the grain size of the silver matrix structure as it have been clarifed in XRD analysis (Figure 4.9).

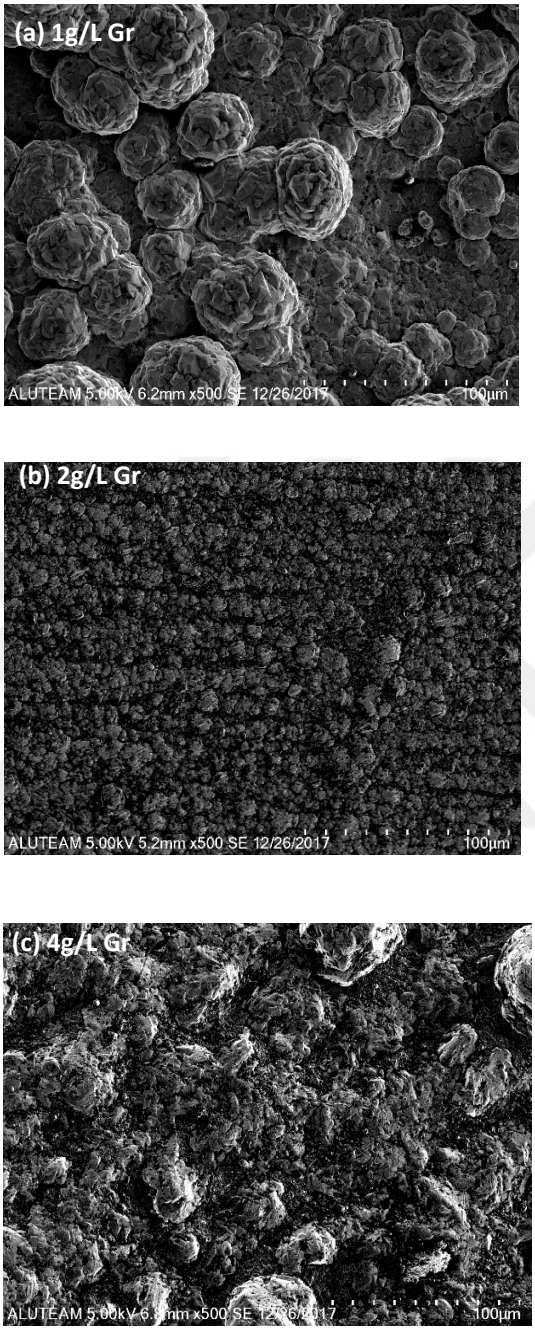


Figure 4. 2 Surface morphology of Ag-Gr coatings deposited with different amount of graphene produced by DC current method.

4.1.2 Energy Dispersive Spectrometer (EDS) Analysis

The elements and their ratios in the pure coating and nanocomposite coatings were determined by Energy Dispersive Spectrometer. This technique has been used in some studies [67]. EDS Map Sum Spectrum of Ag-Gr composite coating contains 1g/L Gr and produced by DC is shown in Figure 4.3

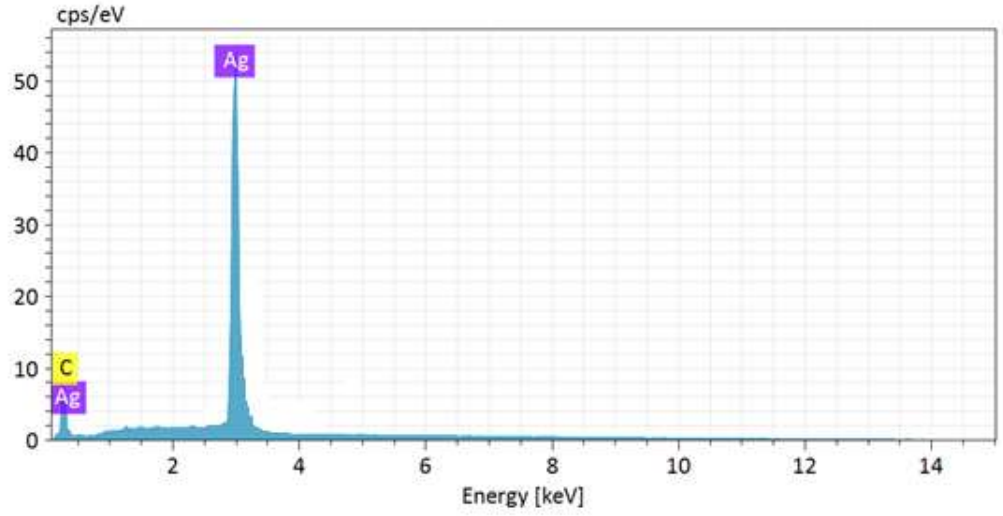


Figure 4. 3 EDS Map Sum spectrum of Ag-Gr coating with 1g/L Gr addition produced by DC.

Energy dispersive spectra graphs of Ag-Gr nanocomposite coatings that confirmed the variation of graphene in the deposition as a function of DC, PC, and PRC coating methods was shown in figure 4.4.The figure clearly indicated that the presence of Gr effected by the three current types. Gr ratio is the highest in coating produced by PRC deposited type and smallest in coating produced via DC deposited method. The disparity of graphene ratio in accordance to deposition current methods can be explained as follows: in case of PRC deposition the alternation of pulses during deposition allowed higher incorporation and loosely adsorbed of graphene into Ag matrix, while in DC case the continuous current application result rapid deposition at the nucleation site forming Gr cluster in the matrix. This affected the mechanical properties of the nanocomposite and the highest hardness was obtained in the PRC deposition coating. EDS results of Ag-Gr nanocomposite coatings clarify the ratio of Gr as a function of different amount of this component into the coating bath

produced by DC type are graphically shown in figure 4.5. Graphene ratio is the highest in the addition amount of 4 g/ L. And smallest in the amount of 0.5 g/L produced via DC too. This illustrates that the wt.% of graphene in the deposited coatings (obtained using similar electrodeposition conditions) increased significantly with increasing graphene content in the electrodeposition bath. The increasing of graphene amount in coating structure caused by decreasing both of hardness and thickness layer of the coating produced coatings.

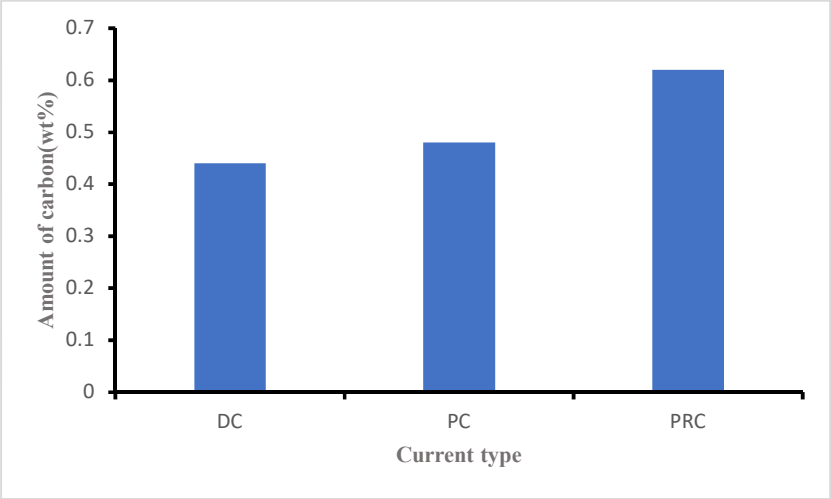


Figure 4. 4 Weight percentage of carbon in Ag-Gr coatings produced by DC, PC, and PRC deposition methods.

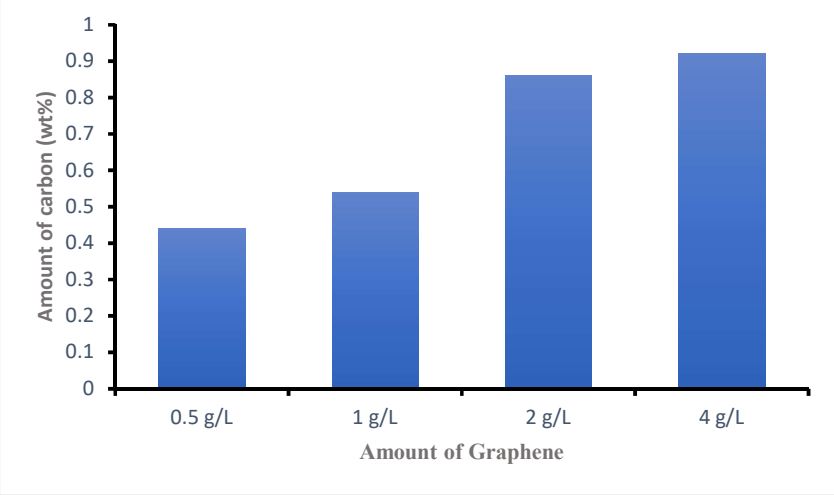


Figure 4. 5 Weight percentage of carbon in Ag-Gr coatings produced with different graphene amounts.

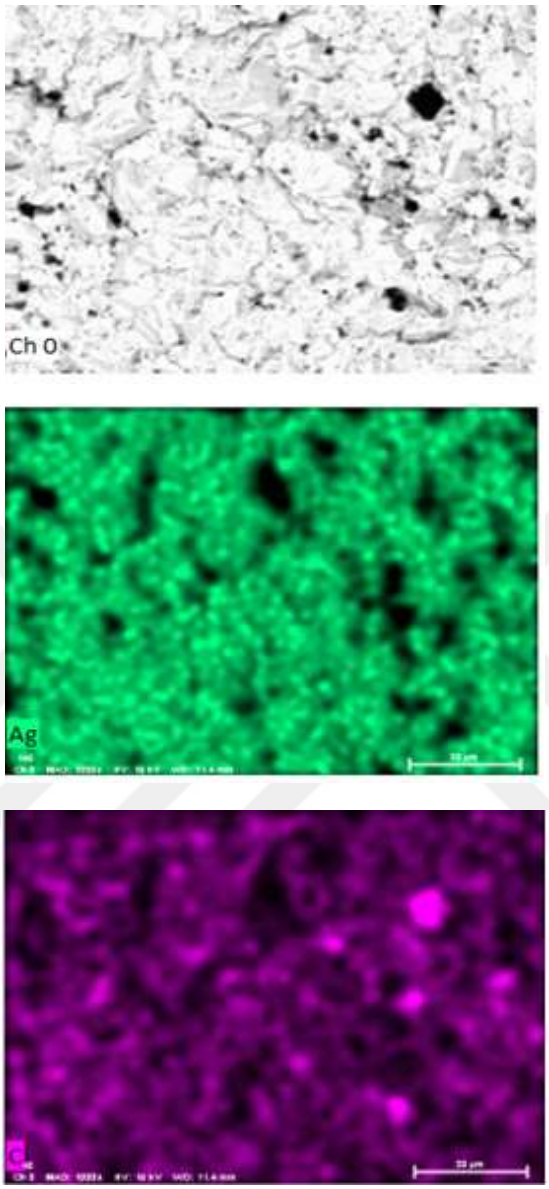


Figure 4. 6 EDS dot map analysis of Ag /Graphene coatings produced by PC deposition method.

EDS map results of Ag-Gr coating prepared with 0.5g/L Gr amount and PC method are shown in Figure 4.6. It can be seen that the elements are homogeneously distributed in deposits. Whereas the carbon in the deposits refers to the graphene.

4.1.3 X-Ray Diffraction Analysis

Crystallographic structure of pure Ag and Ag-Gr coatings prepared in this study were examined by using XRD analysis. The wavelength of X-ray beam was selected as 1.54059 Å. JPDScard number used in the analysis was 04-0783 [74]. XRD patterns of pure silver coatings, deposited with DC, PC , and PRC electrodeposition current types are shown in Fig 4.7.a. It can be clearly observed that there are four main peaks at 2θ = 37.87˚ and 2θ = 44.05˚, 2θ = 77.16˚ , 2θ = 81.29˚ for Ag coating produced via DC method and four peaks at 2θ =38.14˚ , 2θ = 44.31˚ , 2θ = 77.45˚ , and 2θ = 81.59˚ for Ag coating produced via PC and the peaks at 2θ =38.25˚ , 2θ =44.42˚ ,2θ = 77.49˚, and 2θ = 81.64˚ for Ag coating produced via PRC method . All the indicating peaks for the three current types were corresponding to (111), and (200), (311) and (222) crystallographic planes, respectively. The (220) reflecting peak has not changed or affected with the changing in deposition type. For all these coatings the intensity of (111) peaks is the highest elucidated preferred orientation of (111) plane parallel to the Ag coating surface. Also, it can be observed increasing in the intensity of (200) peak and decreasing in the intensity of (311) peak with no observable changing for (220) nor (222) peaks When Ag deposited type changed from DC to PC, and PRC. The highest and sharpest (111) peak was obtained in DC deposition type and decreased in PC and PRC type. This decreasing for PC and PRC deposition indicates for more random crystallographic texture in the coatings and refining in grain size [75].

The crystallite sizes of the pure Ag electrodeposited coatings were measured from the width of the (111) peak detected in the X-ray diffractograms by using the Halder-Wagner method. According to results gained from this method, the crystallite size of Ag decrease with the changing in current type in the pure Ag coatings. Grain sizes of the coatings produced with DC, PC, and PRC were 30.7, 21.8, and 11.72 nm., respectively. The highest grain size of pure Ag coatings was achieved with DC current deposition. While the finest grain size was for the Ag coating prepared with PRC current deposition.

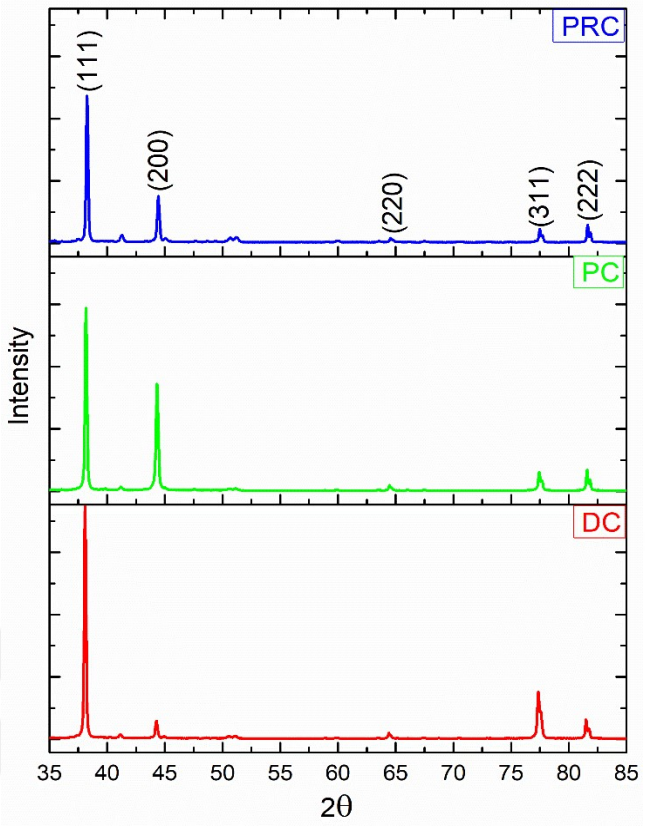


Figure 4. 7 XRD patterns of the pure Ag coatings deposited by DC, PC, PRC methods

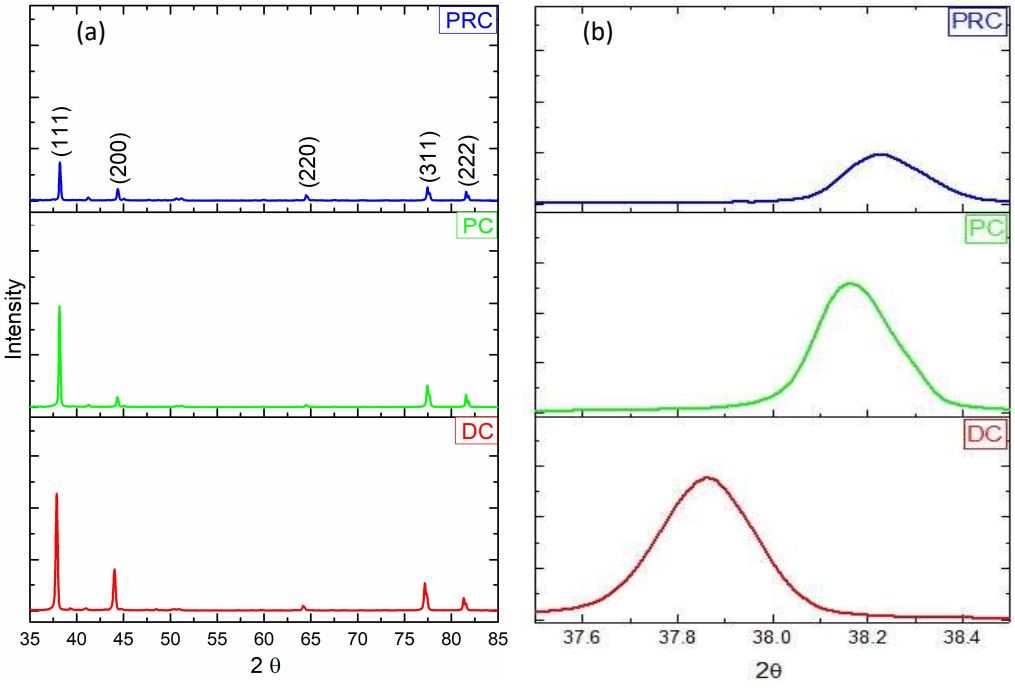


Figure 4. 8 (a) XRD patterns of the Ag-Gr coatings deposited by DC, PC, PRC methods, and (b) detailed (111) diffraction of Ag-Gr coatings.

The x-ray diffraction (XRD) patterns for (Ag-Gr) nanocomposite coatings prepared with the addition of 0.5 gm/L Gr to electrolyte path and deposited by DC, PC, and PRC current types are presented in Fig.4.8. a XRD patterns show five typical peaks corresponding to (111), (200), (220), (311), and (222) crystallographic planes of silver. Note that there are no peaks referring to the Graphene content since the amount of dispersed Gr is so low in deposited coatings. Although there aren't any corresponded peaks of Gr; but the influence of reinforcement Gr can clearly be observed by means of obvious decreasing in intensities of (111), and (200) peaks as well as, marked decrease in intensity for (311), and (222) reflection peaks in compared with unreinforced Ag coatings. Preferable XRD peaks of Ag-Gr nanocomposites associated with Gr dispersing which has a profound influence on the preferred orientation of Ag matrix by acting as a physical barrier and inhibit grain growth. The decreasing in intensity of (111) peak of Ag-Gr coatings for PC and PRC deposition indicating more random crystallographic texture in the coatings and refined grain size compared with the peak intensity of DC method. Also, higher embedding of graphene in the Ag matrix resulted by PRC provides new nucleation place. Thus, the peaks intensity of XRD decrease. The results obtained from EDS analysis providing the presence of graphene, Also Raman spectroscopy analysis Figure 4.19 was performed in this study in order to prove these consequences.

The stress origination in Ag lattices due to the dispersion of graphene in silver matrix deposited with DC, PC, PRC current types were determined by the shifting and broadening in the (111) plane that obtained by X-ray diffraction are shown in Figure.4.8. b. It is reported that the formation of fine grain and a high density of defects caused by a large strain in the particles and nanograins deposited as thin films [76]. As Ag deposited with the introduction of Gr, peak broadening of the Ag (111), provided a clear evidence of the build-up of microstrains in Ag lattices. Dispersing Gr into the silver matrix, significant reduction in grain size as (11.42, 10.39, 8.77) nm for DC,PC, and PRC respectively, and increase in lattice strain were observed and this may be attributed to a severe lattice distortion and grain size refinement while the shifting of the peak indicates to the macro stresses occurred in the lattice.

The patterns of XRD for Ag-Gr nanocomposite coating prepared with the addition of three different amount of graphene content which were 1g/L, 2g/L, and 4g/L produced by DC current type are shown in figure 4.9.a. Five diffraction peaks were indicated at (111), (200), (220), (311), and (222) crystallographic planes for all Ag-Gr coatings layers. As in the case of previous Ag-Gr coatings produced with different current deposition types, there is no peak assigned to graphene reinforcement additive. For these Ag-Gr nanocomposite coatings, the highest peak intensity was detected (111) plane. When the amount of graphene was increased from 1 g/L to 4 g/L, it was observed a significant decrease in the peak intensity of (111) plane which is the dominant growth direction. The smallest and lowest peak intensity was conducted with the addition of 4 g/L Gr. In accordance to the EDS results given before for Ag-Gr coatings, the addition of 4 g/L of Gr resulted in increasing its ratio also, its distribution in a silver matrix. So, EDS and XRD results verify each other.

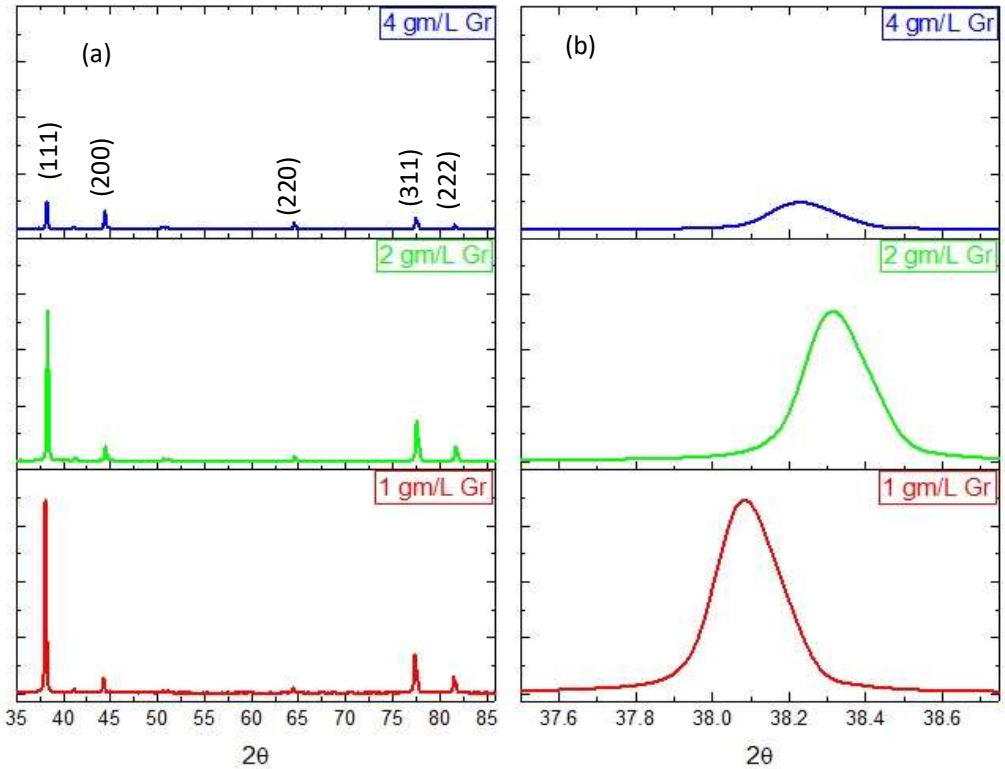


Figure 4. 9 (a) XRD patterns of the Ag-Gr coatings deposited with different graphene amounts deposited by DC method, (b) detailed analysis of (111) diffraction of Ag-Gr coatings deposited at different amount of Gr.

The crystallite sizes of the Ag-Gr deposited coatings were measured from the width of Ag (111) peak reflected in the X-ray diffractograms by Holder-Wanger method. The results were demonstrated that the crystallite size of silver decreases with the increasing of graphene additive from 1 g/L to 4gm/L in electrolyte path. Grain sizes of the nanocompositecte coating produced with the addition of 1, 2, and 4 g/L Gr were 11.2, 10.3, and 8.12 nm., respectively. The smallest grain size of Ag-Gr coatings was achieved with the addition of 4g/L graphene.

Detailed analysis of XRD patterns of the Ag-Gr coatings deposited with adding a different amount of graphene is presented in figure 4.9.b. In the coatings prepared at 1, 2, 4 g/L Gr additive, the value of (2θ) angle shifted from 38.1 to 38.3, 38.255, the detailed examination of the graph, proves that more addition of graphene decreases the peak intensities and caused in distortion during coating and shifted the peaks to the right.

4.2 Hardness of The Coatings

Vickers microhardness method was used to measure the hardness values of the all co deposited layers in this study. The hardness values of pure Ag and Ag-Gr coatings produced by using DC, RC and PRC current types that performed from the cross sections of the coatings are shown in Figure 4.10.

The figure illustrates that the microhardness of the Gr reinforced Ag matrix nanocomposites is higher than the unreinforced Ag coatings for the three methods of coatings. A maximum Vickers Hardness value of approximately 100 HV was obtained using Ag-Gr nanocomposite by using PRC current type. These results agree with many studies, which reported an increase in the hardness was obtained by the addition of fine grains as second phase to composites. This is due to the increase of the nucleation rate and the reduction of grain size. This difference in microhardness between Ag and Ag/Gr is clearer in DC and PC methods whereas the microhardness of pure Ag using PRC method is obviously higher than Ag coatings obtained by using the DC and PC methods. It can be concluded that the co-deposition of Gr improved the microhardness of nanocomposite layers and these results express the effect of deposition method on the microhardness of coatings.

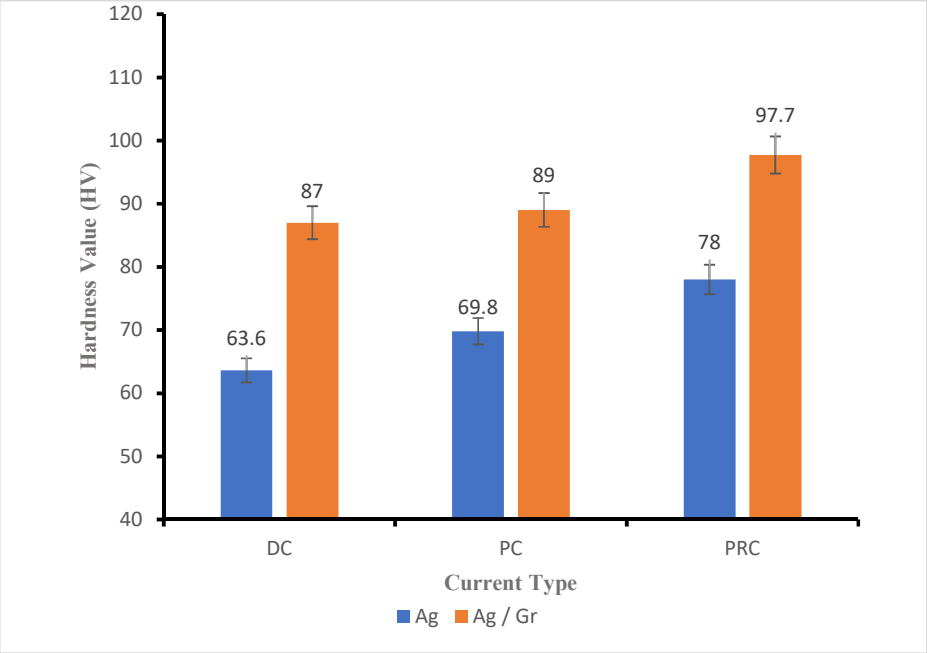


Figure 4. 10 Hardness variation of Ag and Ag-Gr nanocomposite coatings with respect to DC, PC, and PRC current types.

The improvement in the hardness of Ag depositions with PC and PRC methods are due to the change of crystallographic grain growth orientation and finer crystallite size as confirmed in SEM and XRD results. Also, by using the PRC method, the reinforcement content is increased resulting in a higher hardness of the deposition coatings than the DC and PC methods[63]. Borkar and Harimakar [77] reported a similar effect of current type on different metal depositions. This result was verified by EDS and XRD results.

Hardness values of Ag coatings reinforced with different Gr amounts deposited with the DC method are presented in figure 4.11. It is clearly illustrated that the increasing of graphene contents in produced coatings effected on the hardness of coatings thin films. Higher hardness value was obtained with addition 2g/L of graphene to the deposition bath. This rising in hardness of nanocomposite coatings depended not only on size and distribution of the reinforcement particles but also on the volume content of these particles in metal matrix [78]. When Gr amount in the electrolyte up to 4g/L, the hardness of nanocomposite remarkably decreased to (53HV) limit, this

result attributed to the agglomeration of high Gr content in electrolyte that yildes besides surface roughness, porous depositions of Ag coating layers. This changing of the surface morphologies led to a remarkable decrease in the hardness as mentioned in SEM results.

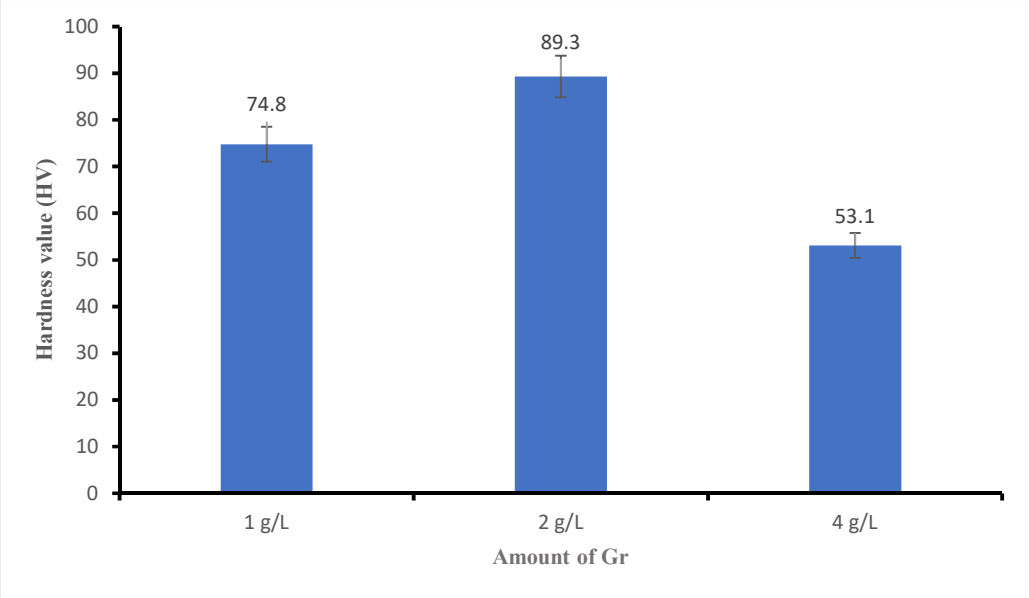


Figure 4. 11 Hardness variation of Ag-Gr nanocomposite coatings with respect to different amounts of graphene.

4.3. Deposition Rate of Coatings

Deposition ratio of all produced coatings had been calculated from divided the thickness of the deposited films which obtained from the coatings cross sections by SHIMADZU HMV-G Vickers micro-hardness tester equipment, by deposition time. The variation of deposition ratio of pure Ag and Ag-Gr nanocomposite coatings depositions as a function of current type was presented in Figure 4.12.

Interestingly, by the using of similar electrodeposition conditions, deposition ratios of all unreinforced Ag are significantly higher than Ag-Gr nanocomposites deposition ratios, it seems that the reinforcement of the Gr in the Ag matrix prohibit the normal growth of the crystal and hence less coating thickness in given electrodeposition time. Also, it can be observed that the dispositioning ratio of Ag-Gr nanocomposite coatings was decreased with DC, PC and PRC respectively, the

thickness layers of these coatings were (73.9, 66.3, 56.5) µm with DC, PC and PRC respectively, disposition ratio of pure Ag coatings was approximately having the same deposition rate and thickness (74.4, 73.2, 76.8) µm for the DC, PC and PRC methods in respectively, that can be related to the approximately controlling of the average current density in Ag deposition. This figure is clearly indicating that Ag-Gr achieved with PRC deposition type has the lowest deposition ratio. This is because of the fact that in PRC deposition method the current provides the embedding more amount of the second phase into Ag matrix. High incorporation of graphene in the Ag matrix acts as a physical barrier to grain growth and slow down the deposition rate [77].

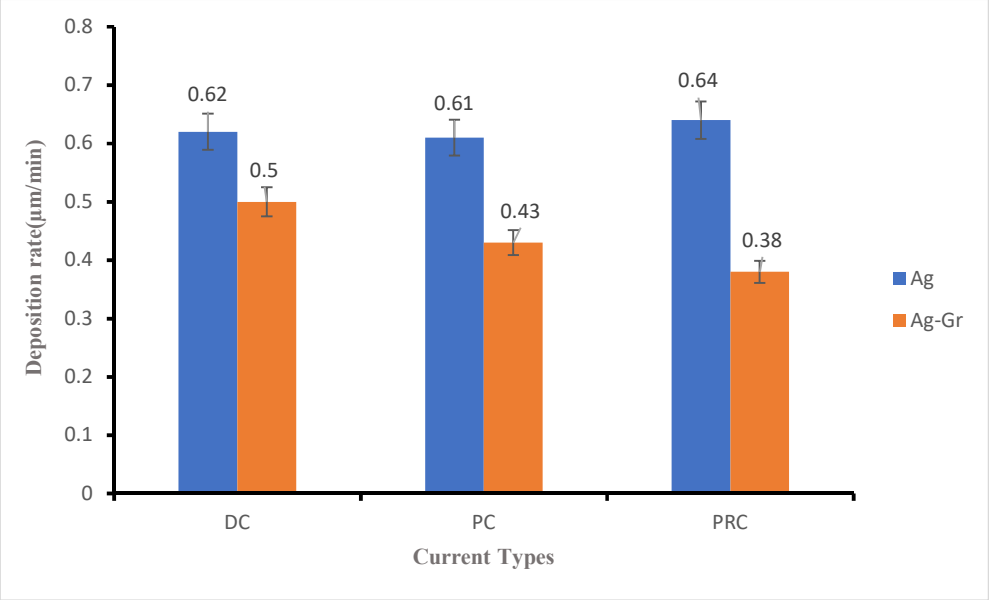


Figure 4. 12 Deposition ratio of Ag and Ag-Gr nanocomposite with respect to current types.

Similar commentary can be adopted for elucidation the decreasing of deposition rate by increasing of graphene amounts in composite coatings as showed in figure 4.13. From this figure, it can be seen that the deposition ratio increased with the increasing of Gr concentration up to 2 g/l. But by adding 4gm/Gr the dispositioning ratio was decreased, this decreasing occurred as a result of higher agglomeration of Gr particles due to higher ionic strength of the electrolyte bath

with more concentration of Gr. This agglomeration arrested the grain growth of Ag matrix during deposition, then subsequently restricts the dislocation motion during coating deformation resulting in slowing down growth rate. As well as the thickness layer measurements were (48.3µm,73µm, 44.8 µm) for the Ag-Gr coatings with (1, 2, 4 g/L) of graphene in respectively.

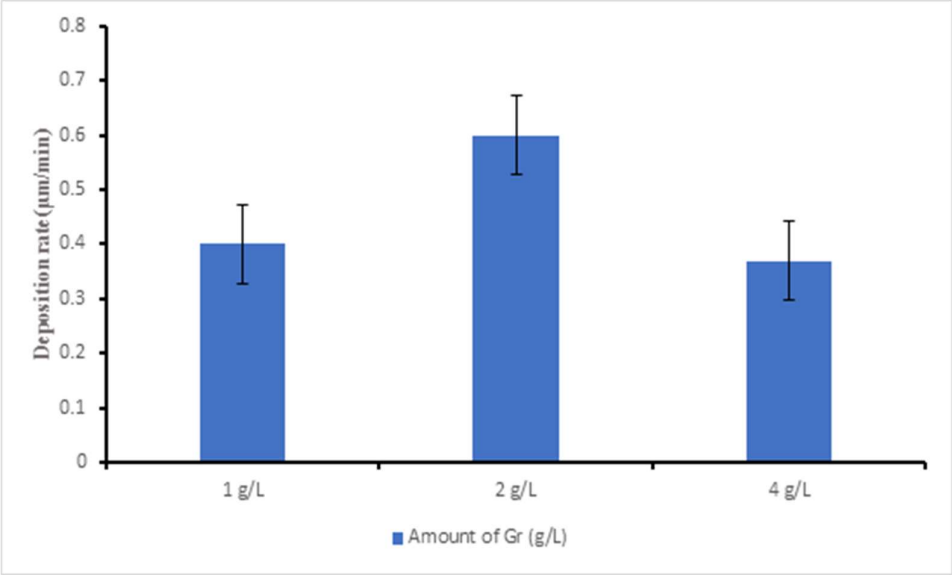


Figure 4. 13 Deposition ratio of Ag-Gr nanocomposite with respect to different graphene amounts.

4.4 Electrical Contact Performance Test

The electrical performance as a function of temperature for all coated contacts samples had been measured by handmade electrical contact test device. Tests were established at a constant load of 4 kW, 220 AC voltage, and double capacity of commercial contactor (Himel HDC6-9) allowable load (~18 Ampere), for 10 000 operation cycles. Contactor buttons coated with pure Ag and Ag-Gr coatings showed disparate ranges of temperature as a function of resistivity. The temperature of contacts that coated by pure Ag coatings using DC, PC, and PRC deposition methods were given in the Figure 4.14. It can be clearly observed that the contact temperature of Ag coatings increased gradually by increases operation cycles. Which is so familiar in most contacts systems due to the formation of oxide films caused by arc

process [18] between contacts pairs during operation, leading to high resistance. Contact temperature in Ag coating deposited with PRC method has the highest value of temperature comparing with the temperature of DC and PC coated layers, this is due to the finer grain sized structure obtained through PRC deposition. A decrease of Ag crystalline size formed a nanosized polycrystal surrounded in a network of grain boundaries acts as defects that block the carrier movement [79] result in increasing of the temperature. Similar results about the influences of grain size on the electrical resistivity of the materials have been obtained in similar studies [80] [30] [81]. This increasing of the temperature in PRC coated contact caused an escalating resistance rise resulting in ruin the contact after 8000 operating cycle, whereas the lower temperature (mean less resistivity) achieved by DC coating type.

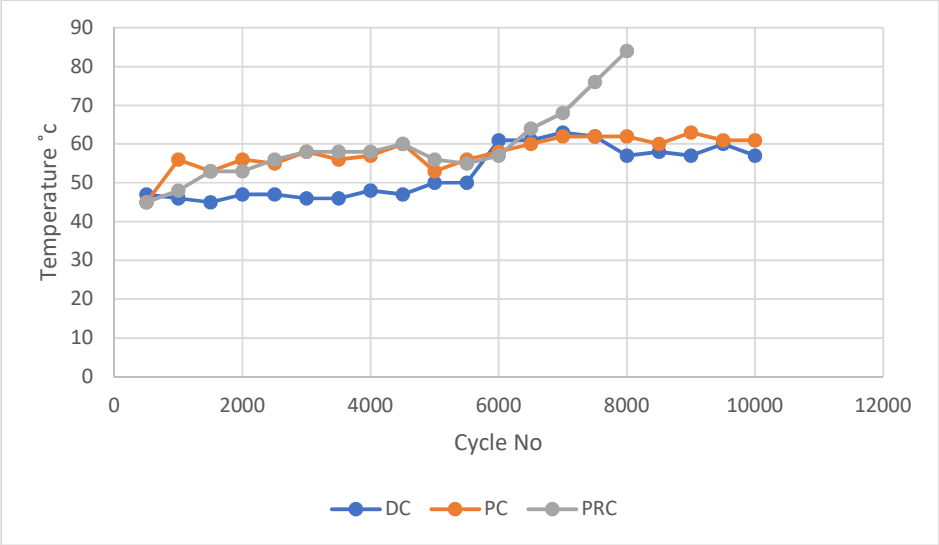


Figure 4. 14 Electrical performance measurements of pure Ag coatings produced with DC, PC, and PRC methods.

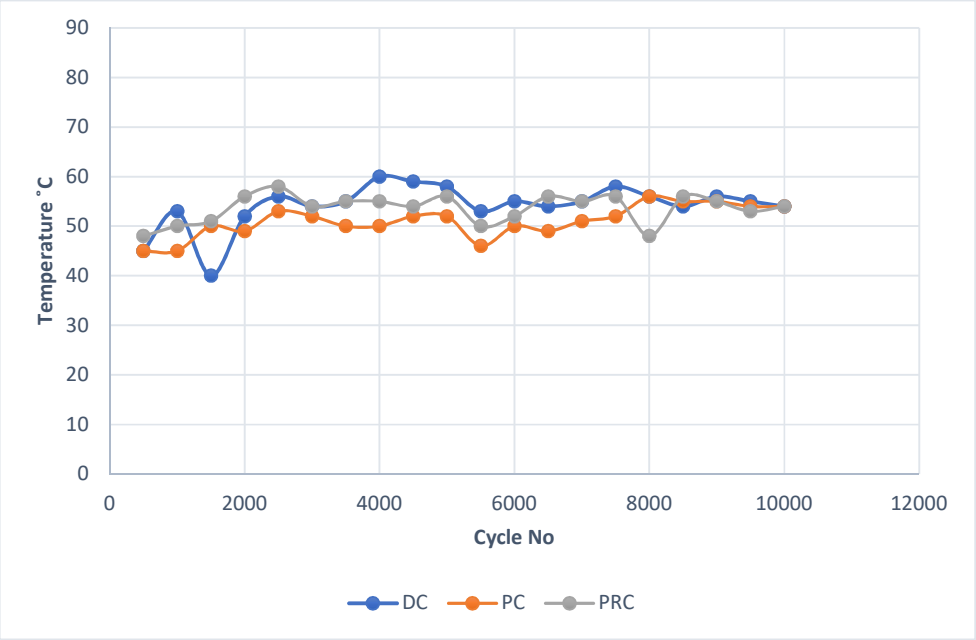


Figure 4. 15 Electrical performance measurements of Ag-Gr nanocomposite coatings produced with DC, PC, and PRC methods.

Figure 4.15 presents the electrical contact temperature of Ag-Gr nanocomposite coatings prepared with DC, PC, and PRC current methods as a function of contact behavior. By observing Figure 4.15. it can be seen that the average temperature of Ag-Gr nanocomposite contacts is slightly less than the average temperature of the pure Ag coatings. The preferable incorporation of graphene proving an increase in coating heat dissipation properties due to the ability of Gr to carry the thermal load that formed in contacting area in Ag matrix through PC and PRC deposition types results in less and more constant temperature level than DC deposition composite coating. Higher temperature observed in Ag-Gr nanocomposite produced via DC current type, due to the irregular distribution of graphene with DC method that leads to increasing coating thickness layer which is directly proportional with the increase of the resistance of the nanocomposite thin film [41].

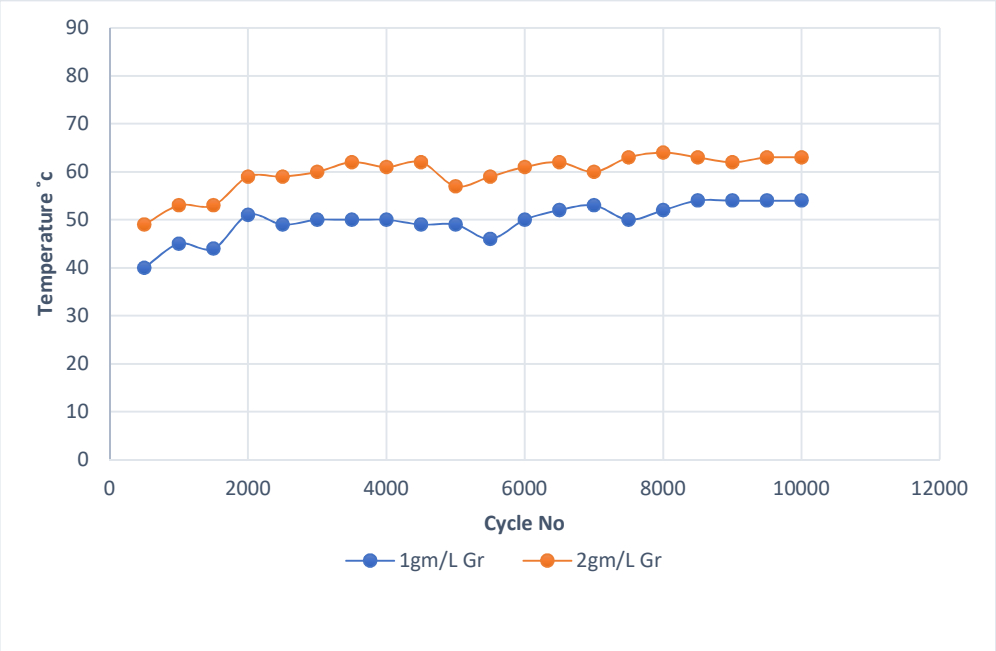


Figure 4. 16 Electrical performance measurements of Ag-Gr nanocomposite coatings produced with 1g/L, and 2g/L graphene additions.

Figure 4.16. illustrates the influence of 1g/L, and 2g/L graphene additions to Ag-Gr deposition coatings prepared by DC current type on the temperature of coated contacts. From Figure.4. 16. It can be seen that both coatings temperature slightly increase with the increase of the operation cycles. The temperature of Ag-Gr coating deposited with the addition of 2g/L Gr is higher than the temperature of the coating prepared with 1g/L Gr addition. This rising in temperature can associate to fine-grained structure formed by more concentration of Gr nanoscale, which means more grain boundaries that act as defects impede the movement of electrons caused in increasing the resistivity. As a result of this increasing the temperature rising. Whereas the highest value of hardness was obtained with the addition of 2g/L of Gr, same result was obtained by WANG Juan et al. [39], they mentioned that the increasing of graphite content in CNTs-Ag-G electrical contact materials leads to an increase in contact resistance to a specific level then still constant with the increasing of graphite amount in the composite, while the hardness of composite improved with the addition of CNTs. Also, Fehim F. et al. [82] reported that the increasing of W content in Ag–W composite contact materials prepared by powder metallurgy

process, shows increasing in electrical resistivity due to higher dispersion of W in Ag matrix that caused in decreasing the weight fraction of Ag which enables good conductivity, while the composite hardness was increased with more hard W contents.

4.5 Effect of Contact Test on Morphology

The effect of contact test on the morphology of the contacts that coated with Ag and Ag-Gr coatings by DC, PC, and PRC current types and conducted with handmade electrical contact test equipment were analyzed by SEM. The contacts pairs were placed in up and down into contact unit of the testing device, these pairs used as the stationary contact and movable contact, during operation in respectively. When electrical contact tests performed the upper part moved downward till contacted the down part, and then returned upward in current-carrying time of 2 seconds for both of T_{on} and T_{off} durations. The tests were performed at 220 AC voltage, and commercial contactor load capacity (~18 Ampere), with a constant load of 4 kW. The characterization of arc erosion morphology for stationary and movable contacts after 10 000 operations under the above parameters are represented in figure 4.17.

SEM morphology of electrical performance characteristics for movable and stationary contact that coated by DC, PC, and PRC pure Ag deposition types after 10 000 operations clearly indicate that the changing in current methods has a significant effect on the arc morphology of the contact surface. It can be observed that the surface morphology for both of movable and stationary pairs of contacts after arc erosion are almost similar.

Arc erosion morphology for coating prepared by PRC method has higher erosion pits and clear melting deformation on the contact surface than DC, and PC coating contacts. The higher arc erosion actions that caused in melting and evaporation of silver in conducting area for PRC coating contact surface associated to the higher contact resistance of PRC coating that comes from finer Ag grain sized obtained by this type of deposition. This increase in contact resistance rises contact surface temperature that caused in melting the contacts surfaces when they began to break, forming a molten metal bridge between cathode and anode, that leads to an arc generation and erosion.

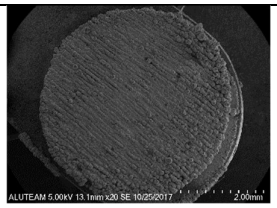
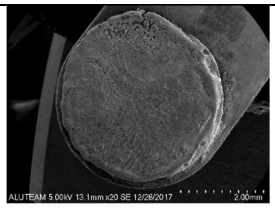
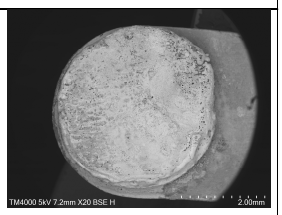
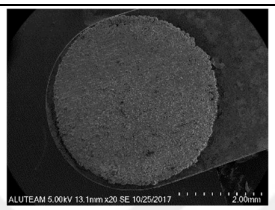
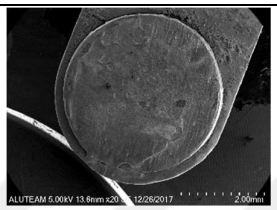
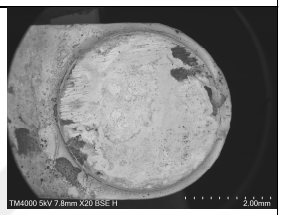
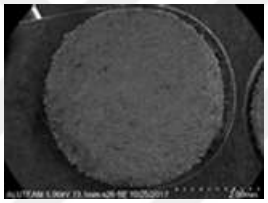
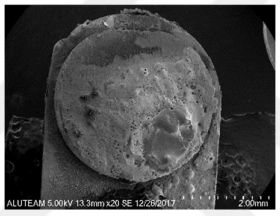
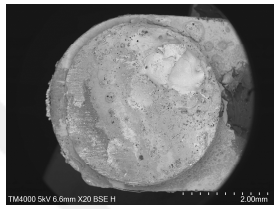
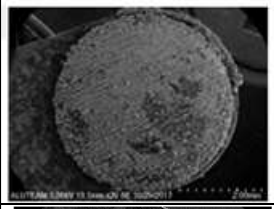
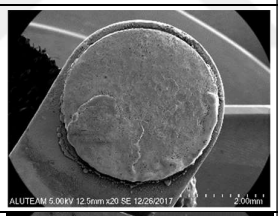
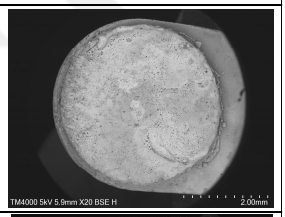
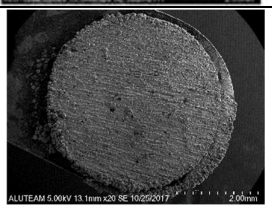
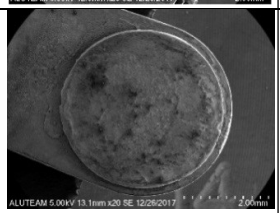
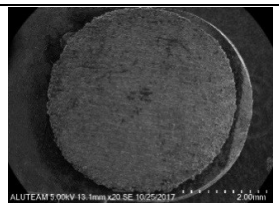
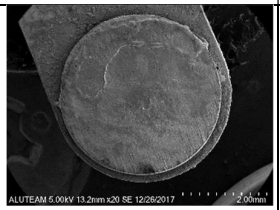
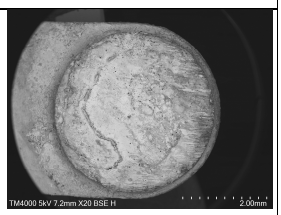
Current type	Deposited	After10 000 cycle (up)	After10 000 cycle (down)
DC Ag			
PC Ag			
PRC Ag			
DC (Ag/Gr)			
PC (Ag/Gr)			
PRC (Ag/Gr)			

Figure 4. 17 Effect of current type on pure Ag and Ag-Gr electrical contact performance.

Arc erosion morphology of Ag-Gr electrical contact parts coated via DC, PC, and PRC under the same previous operation conditions, showed a preferable erosion resistance than unreinforced Ag coatings, as seen in Figure.4.17. The disparity of arc erosion behaviours between unreinforced Ag and Ag-Gr coatings surfaces under the same operating conditions is attributed to the addition of the second phase graphene as a reinforcement material to Ag matrix, the number of phases and additive (besides some more factors) considered as substantial factors affecting contacts erosion [83]. The surface of Ag- Gr contact coatings produced via PRC current type after 10 000 arcing operations shows decreasing in erosion pits with more even surface morphology compared with DC and PC coatings surfaces after the same operations cycles. Likewise, PC arcing morphology is more uniform than that of DC method. The improver erosion behaviour of PC, PRC contact coatings associated to the decreasing of contact resistance of the coated contacts thus, diminished the arc erosion as mentioned before the explanation of this results can be associated to better and uniform distribution of graphene nanoscales through the Ag matrix with PC and PRC current types. Furthermore, uniformly distribution of finer Gr grain size in the Ag-Gr composite decreases the spacing between approach erosion areas which prevent the concentration of the arc in a fixed site. Subsequently, arc will appear in other sites, and due to the magnetic field of convergent tiny arcs, they will repulse each other and spread rapidly, the arc acts as a quick motion, caused in a shallowing and uniform distribution of erosion pits. Also, it has been reported in some previous studies [68], that the good incorporation of Gr nanoscales in Ag matrix can weaken the splatter erosion of Ag molten pool that enhances arc erosion resistance and preventing the weight loss.

The influences of increasing graphene contents in Ag-Gr nanocomposite coating produced by using DC deposition current method on the arc erosion behaviour of coated contacts have been examined. Arcing morphology of Ag-Gr coatings of electrical contacts prepared with the addition of 1g/L, 2g/L graphene to the silver matrix, and operated under the same operating conditions and cycle numbers are presented in figure 4.19. It can be observed that there is clearly inhomogeneous deformation with some clear erosion pits on the surface of Ag-Gr coatings, which was associated with the arc erosion concentration which occurred during operations.

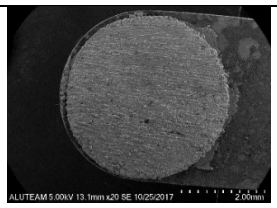
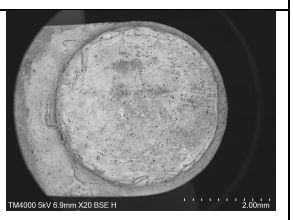
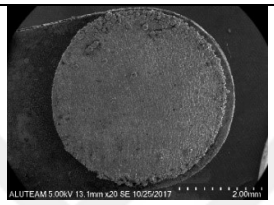
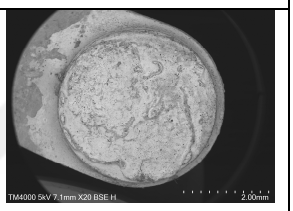
Current type (composition)	Deposited	After10 000 cycle (up)	After10 000 cycle (down)
DC Ag + 1.0 gr Gr			
DC Ag + 2.0 gr Gr			

Figure 4. 18 Effect of graphene amounts on Ag-Gr electrical contact performance.

The structure of erosion looks a paste-like morphology. This figuration of erosion pattern can be attributed to the non-wetting between Ag matrix and Gr, that caused in the splashing and solidification of silver liquid during arc erosion. However, higher graphene amounts ineffectively restrained the splash and the solidification of the molten silver. Ag-Gr coating with 1g/L Gr addition shows very shallower erosion pits with a relatively flat surface. While, with the increase of graphene amount 2g/L in the Ag-Gr coating, the surface becomes uneven, with more rough erosion pits. The increasing of the contact due to the arc energy action, caused by silver melting, while the graphene which has a higher melting point are still in the solid state. The melting of silver formed a silver liquid pool containing graphene. Due to the buoyancy actions, Gr with a density of (2.2g/cm^3) which is less than that of silver (10.5g/cm^3), will move from down to up and floats in the molten pool. Gr at most, will distribute over silver coat when the melted silver rapidly cools. Resulted in, mainly Gr distribution on the surface of the molten pool. The increasing of Gr amount in the coating composition, caused in easier gathering and agglomeration of Gr particles, that resulted in reducing the electrical contact performances.

4.6 Raman Spectroscopy Analysis

Raman spectroscopy analysis was performed in order to determine the presence of graphene Since there was no reflection referring to this component in Ag-Gr nanocomposite coatings when examined with XRD analysis. Also, to determine the effect of electrical contact test on the subsistence and deformation of Gr after the test. So that Raman spectrum had been obtained from the surfaces of deposited Ag-Gr and Ag-Gr arc erosion tested contact sample, both of them were deposited with PC type. Raman spectrum of these two surfaces are shown in Figure 4.19 It is clearly observed that there are two main peaks corresponded 1362.4 cm^{-1} and 1584.4 cm^{-1} bands, these peaks correspond to the D band sp^3 and the G band of sp^2 carbon atoms respectively [79]. Mechanical, electrical and optical properties of atoms are strongly depend on sp^2 and sp^3 content [80] [81]. the ratios of sp^3/ sp^2 were calculated with Spectra manager software (Jasco NRS-4500 computer software) and Curve Fitting module according to Gaussian method. After applying 10.000 electrical contact cycle the ratio of I_D/I_G decreased from 2.77 to1.75, in sum I_D/I_G ratio 36.8 % decreased. Which means that the graphene structure turned to the more graphitic structure. The changing in the structure is attributed to the increase of temperature which occurs at the acuity contacts during electrical contact test. The elevation in temperature generates from arc between the contact surfaces at T_{on} and T_{off} moment. It has been reported in some literature that graphitization and decreasing in I_D/I_G ratio caused by high temperature [39] [82].

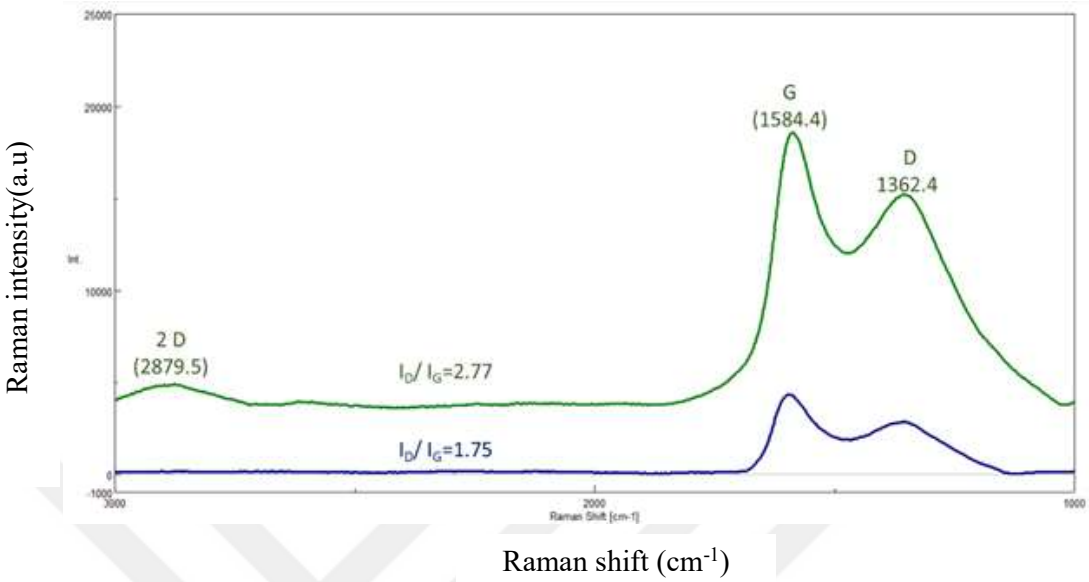


Figure 4. 19 Raman spectra of Ag-Gr nanocomposite coating before and after 10000 cycle of electrical contact test.

CHAPTER 5

CONCLUSIONS AND FUTURE WORK

5.1 Conclusion

In this study, pure silver and graphene –reinforced silver matrix nanocomposite was deposited by means of electrodeposition process on high purity copper substrates with two categories. The first category was cylindrical specimens of high purity copper rod used for characterizing the microstructural and mechanical properties of coatings.

The second copper category was electrical contact buttons used to investigate the electrical contact performance and arc erosion behaviour of the coatings after contact test. The Electrodepositing of pure Ag and Ag-Gr nanocomposite coatings were produced by applying three different current types which are DC, PC, and PRC and different amounts of graphene addition into the coating bath. The influence of these parameters on the coatings characterization and performance were investigated and the results were summarized as follows:

- Microstructure analysis for pure Ag, and Ag-Gr Nanocomposite coatings which produced by PC, PRC deposition types exhibited a homogenous crystallographic morphology with finer grain sized for pure Ag coatings, and high amount of Gr co-deposited reinforcement in the Ag-Gr coatings. Compared with DC deposition. While the microstructure of Ag-Gr coatings deposited with different Gr amounts exhibited rough surface with non-homogeneous structure by increasing Gr content. Ag-Gr coating produced with adding 4g/L Gr has maximum surface roughness due to the agglomeration of more Gr during deposition.
- EDS analysis determines the value of components ration (in this analysis C element indicates the presences of Gr) EDS analysis result for Ag-Gr nanocomposite coatings denoted that the amount of graphene in the prepared coating was frequently influenced by current type. Graphene ratio was the highest in the coating produced by PRC and decreases with PC and DC, respectively.

EDS analysis of Ag-Gr produced with different graphene amounts showed that the higher ratio of graphene obtained with the addition of 4g/L to the coating path.

- Crystallographic texture for the pure Ag and Ag-Gr coatings produce with (DC, PC, PRC) current types exhibited dominant growth in (111) plane. The highest and sharpest peak observed in DC deposition type. Peak intensity, as well as the grains size, decreased with PC and PRC respectively. All Ag-Gr coatings produced with different graphene amounts exhibited preferential growth in (111) plane. Smallest peak intensity observed was for Ag-Gr coating prepared with the addition of 4g/L Gr. The increases of graphene amounts did not change the growth direction but decrease the peak intensity because of refinement grain size.
- The hardness of pure Ag and Ag-Gr nanocomposite coatings were significantly affected by current types. Highest value of hardness was obtained for Ag-Gr coatings prepared with PRC method while the lower hardness values were obtained for those coatings produced by DC method. The hardness value of Ag-Gr nanocomposite coatings prepared with the different Gr amounts exhibited higher hardness value with the addition of 2g/L Gr, by increases Gr amount till 4g/L hardness value decreased due to some porosity occurred as result of the higher amount of Gr nanosheet penetrated in Ag matrix.
- The deposition rate of pure Ag coating wasn't much influenced with the changing of (DC, PC, and PRC) deposition types as much as Ag-Gr coatings. Ag-Gr produced with PRC method exhibited lower coating deposition ratio and less coating thickness. Furthermore, deposition rate of Ag-Gr coatings decreased with the increasing of graphene amount in produced coatings, the lower deposition ratio and lower coating thickness obtained with the 4g/L Gr addition to the coating bath.
- The electrical performance of pure Ag coating was influenced by deposition current types. Ag coating produced by PRC method exhibited higher temperature. The contact temperature of Ag-Gr nanocomposite coatings produced with different current types and different amount of Gr were considerably affected by both of deposition types and graphene amounts. Ag-Gr coating produced by DC exhibited higher temperature in compared with Ag-Gr coating prepared by PC, and PRC deposition methods. As well Ag-Gr coating prepared with the addition

of 2g/L Gr exhibited higher temperature value than the coating produced with 1g/L Gr. According to the electrical contact arc erosion behaviour of pure Ag, coating was considerably affected with current types. Arc erosion morphology of Ag coating produced by PRC exhibited higher number of erosion pits with heavy deformation on the contact surface according to the electrical contact test result. Arc erosion behaviour of Ag-Gr nanocomposite coatings produced with different current types showed that Ag-Gr coating produced by PRC method has fewer erosion pits and more even contact surface. According to the electrical contact test result. Arc erosion morphology of Ag-Gr coatings produced with different Gr amount, erosion morphology of Ag-Gr coating prepared with 2g/L Gr exhibiter uneven surface with high deformation areas. Anti-erosion resistance of Ag-Gr coatings was better than unreinforced Ag coatings

- In this study, uncoated contact pairs had been tested by the electrical contact test device, and burned after 700 operating cycle, while the coated contacts continued operating until 10 000 cycles with no burning or breakdown, with a likely continuity of action over this limit.
- Raman spectroscopy analysis clarified the presence of graphene in Ag-Gr Nanocomposite coatings in corresponding to the D band sp^3 and the G band sp^2 Carbon atom. Furthermore, it is revealed the changing of C atoms after the electrical contacts from the graphene structure to the graphite structure.

5.2 Future work

- For Ag-Gr nanocomposite coatings corrosion resistance can be measured.
- For all prepared coatings, electrical conductivity measurement can be examined.
- For all prepared coatings, surface roughness must be measured.
- For all Ag-Gr coatings, Transmission electron microscope (TEM) analysis must be applied for confirming the feasibility of Ag-Gr composite electrodeposition.

- The effect of varying plus parameters (duty cycle, current density and frequency) on the structure growth of pure Ag, and Ag-Gr coatings can be examined.
- To analyzing more information with clearer detailed arc erosion morphologies 3D optical profiler analysis should be achieved.

- To investigate the efficient electrical performance of all coatings, operating cycles of coated contact test should be continuing to work unto break down.

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TOPICS OF INTEREST

- Electrodeposition
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