EFFECTS OF COPPER ELECTROPLATING PARAMETERS ON MICROSTRUCTURE AND MECHANICAL PROPERTIES OF Al-Cu BRAZED JOINTS

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ABSTRACT

EFFECTS OF COPPER ELECTROPLATING PARAMETERS ON MICROSTRUCTURE AND MECHANICAL PROPERTIES OF Al-Cu BRAZED JOINTS

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Almost 25, 50 and 75 microns of copper were deposited on aluminum alloys by using copper sulfate and copper pyrophosphate baths. And also, 20, 40 and 60 mA/cm^2 current density were applied during electroplating process. After electroplating process, copper deposited aluminum pieces were brazed at 570℃ for 15 minutes by using furnace brazing in the first part of study. Shear test were applied to samples and strength of the joint which was brazed with sample that had 75 microns thickness coated at 60 mA/cm^2 current density was measured higher than the others.

Electroplating parameters of the highest shear strength sample in the first part were used in the second part. 560℃, 570℃ and 580℃ were used as brazing temperature and brazing process was performed for 5 and 15 minutes. It was observed that shear strength of joint was affected from changing brazing temperature and time and the highest shear strength was measured as 3302 N. This sample was brazed at 580℃ for 15 minutes.

Keywords: Brazing, Electroplating, Copper, Aluminum, Current Density

ÖZ

BAKIR ELEKTROKAPLAMA PARAMETRELERİNİN SERT LEHİMLENMİŞ Al-Cu EKLEMLERİNİN MİKROYAPISI VE MEKANİK ÖZELLİKLERİ ÜZERİNE ETKİLERİ

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Bakır sülfat ve bakır pirofosfat solüsyonları kullanılarak alüminyum üzerine yaklaşık 25, 50 ve 75 micron kalınlığında bakır kaplanmıştır. Ayrıca elektrokaplama prosesi esnasında 20, 40 ve 60 mA/cm^2 akım yoğunluğu uygulanmıştır. Çalışmanın birinci bölümünde yüzeyine bakır kaplanmış alüminyum parçalar 570 ℃'de 15 dakika süre ile fırın içerisinde sert lehimlenmiştir. Bağlantılara çekme testi yapılmıştır ve 75 micron bakır kalınlığına ve 60mA/cm^2 akım yoğunluğuna sahip parça en yüksek mukavvemete sahip çıkmıştır.

Çalışmanın birinci bölümünde en yüksek kayma mukavemeti değerine sahip olan numunenin kaplama parametreleri ikinci bölümde de kullanılmıştır. 560℃, 570℃ and 580℃ sert lehimleme sıcaklıkları ve 5 ile 15 dakika bekleme süresi kullanılmıştır. Kayma mukavemeti değerinin sert lehimleme ve sıcaklığının değişiminden etkilendiği görülmüştür. En yüksek kayma mukavemeti 580 ℃' de 15 dakika boyunca lehimlenen numune için 3302 N olarak ölçülmüştür.

Anahtar Kelimeler: Sert lehimleme, Elektrokaplama, Bakır, Alüminyum, Akım Yoğunluğu

To my family

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CHAPTER 1

INTRODUCTION

In the last few decades, aluminum alloys have been used widely in several industries. Aluminum is a cheaper material than steel for various application areas. Aluminum has been also used in electronic applications. Its usage area is wide because of its light weight, high strength and relatively low price [2]. Also, heat sink of electronic applications has been produced from aluminum alloys. The heat sink is formed by joining aluminum parts to each other by brazing process. Many different filler metals have been tested for brazing aluminum parts. In one of these studies, Al-Si-Cu-Zn filler metal was tried to join aluminum matrix composites and the shear strength was measured as 35.6 MPa [27]. According to study of Niu et al. (2016), when parts of 6061 aluminum alloy were brazed by using Al-Si-Ge-Zn filler metal and brazing flux, a strong brazed joint was produced. In another study, the shear strength was measured as 23 MPa when 6061 graded Al parts were brazed by using Al-12Si filler metals under vacuum condition at 600 °C for 60 min. in reference to Chang et al. (2009).

1.1 Problem Statement

A strong joint can be obtained when aluminum parts are brazed using several brazing filler metals. Al-12Si alloy is generally used as brazing filler metal for aluminum brazing process. Working temperature of Al-12Si is a little bit higher than eutectic temperature of Al-Si, which is about 577℃ and it is relatively close to melting point of aluminum. Aluminum melting point is about 660℃ and melting points of aluminum alloys are lower than 660℃. Because brazing temperature of Al-12Si is very close to melting temperature of aluminum alloys, localized melting regions can be formed when some engineering aluminum alloys are brazed by using Al-12Si.

For example, the melting point of Al 6061 alloy is almost the same as liquidus temperature of Al-12Si filler metal. Because of this reason, the studying about low melting point filler metal is important for Al brazing.

1.2 Objectives

Electroplating of copper is one of the important processes to obtain a low temperature brazing filler metal. It is important that when electroplating parameters are changed, the behavior copper as a brazing filler metal will change. Surface properties of brazing filler metal can affect the properties of brazed joints. Type of electrolyte and current density can also affect the surface structure [16]. One of the purposes of this study is to obtain filler metal with different surface properties by using different electroplating parameters and to observe their effects on diffusion of brazing filler metal to interlayer of base metals. So, surface properties of electrodeposited copper must be characterized.

Brazing is another important process for this study. Except from the traditional brazing process, a different brazing technique will be performed in this study. This technique, called contact reactive brazing technique, is similar to the diffusion brazing technique. Diffusion and eutectic reaction between Al and Cu are important processes for contact reactive brazing. So, brazed joints will be characterized to observe eutectic reaction and elemental analysis will be performed to understand Cu diffusion into the aluminum parts. Since the phases at the interface of a joint influence mechanical properties of the joint, the phases formed by Al and Cu will be determined by using the binary phase diagram of Al and Cu [36].

1.3 Methods

Brazing is a joining process applied to different types of materials, usually metals. In the brazing process, the molten filler metals flow into the joint and cool to form a

strong joint. To obtain good brazement, application of the following steps is necessary [31]:

1. Preparing surface
2. Suitable clearance and fit.
3. Suitable flux
4. Proper fixtures
5. Heating the joint
6. Cleaning the joint after brazing.

Aluminum vacuum brazing reduces distortion of the part because of uniform heating and cooling as compared to localized joining process. Contact reactive brazing is a type of diffusion brazing process. The strong joint is formed by the eutectic liquid phase formed as a result of the eutectic reaction [25].

The purpose of study is obtaining strong brazing aluminum joint by using electroplated copper as brazing filler metal. So, first of all, copper electroplating mechanism should be understood and effects of electroplating parameters should be observed on the aluminum brazed joints. For this reason, depth knowledge of electrodeposition is required. The second part of the study is determining the optimum brazing parameters to obtain the strong joint so effects of brazing parameters should be known in detail. The basic principles and procedures of brazing and electroplating will be given in Chapter 2.

CHAPTER 2

LITERATURE REVIEW

2.1 Electroplating

Electroplating is a coating method which is used for depositing metal on a substrate by using electrical current in the electrolyte. Aqueous solutions such as acid, salt or base are used as electrolytes [8]. Metal which is plated is called a cathode and the metal which may be plated on the cathode is called an anode. Both anode and cathode are dipped into the electrolyte and if electric current is applied to solution, electrons flow from anode to cathode. When applying electric current, the anion starts to release electrons, which is the oxidation reaction and the cation starts to catch the electrons, which is the reduction reaction [2].

$$M(s) \rightarrow M^{Z+}(aq) + ze^{-} \text{ (oxidation reaction)}$$

$$M^{Z+}(aq) + ze^{-} \rightarrow M(s) \text{ (reduction reaction)}$$

When an external power source is applied, the potential difference forms between anode and cathode and electrodes become polarized. Metal ion concentrations are reduced on the cathode surface and a metal layer forms on the electrode surface. The thickness of plating layer depends on temperature and deposition rate of the metal ions. The plating step is controlled by current or ampere-hours [3]. The weight of deposited metal is calculated theoretically with the help of Faraday's law [13]. Also, the deposition thickness can be calculated by Faraday's Law which is shown in Eq.1. According to Faraday's law, the weight of the deposition is directly related to the amount of applied electrical charge [2].

$$W = \frac{m.I.t}{n.F}\eta \qquad \text{Equation 1}$$

Where;

W: deposited weight (g)

n: valence of metal deposited from solution (eqv/mole)

F: Faraday's constant = 96485 A.sec

m: molecular weight of deposited metal (g)

I: current (A)

t: time required to plate (sec)

η: current efficiency

$$\eta = \frac{Actual\ weigth\ of\ deposition}{Theoretical\ weigth\ of\ deposition} \qquad \text{Equation 2}$$

2.2 Copper Electroplating

Copper is the most common nonferrous material in industrial application because of good properties such as conducting of electric and heat [13]. Also, copper thin film is used as interconnection material of electronic devices because it has low electrical resistance and high electrical and thermal conductivity [15]. There are four major types of plating baths for copper electroplating. Copper cyanide and copper pyrophosphate baths are alkaline while copper sulfate and copper fluoroborate are acidic baths. Basic schematic of copper electrodeposition is shown in Figure 2.1.

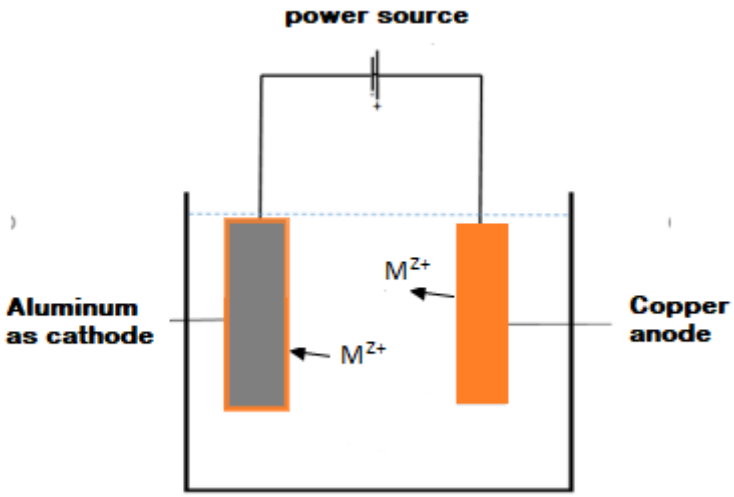


Figure 2.1 Basic schematic of copper electrodeposition

2.2.1 Alkaline Copper Plating Baths

Alkaline copper plating baths are easily controlled processes to use and produce thin deposits with uniform thickness on all surfaces. Also, they are widely used as strike baths. Because of the waste and hazard problems, non-cyanide baths are chosen instead of cyanide baths in many applications [3].

2.2.1.1 Cyanide Copper Plating Baths

Alkaline cyanide copper solutions can be used to plate a strike, which is the initial deposit, on a variety of substrates [9]. Cyanide copper baths are stable to ionic impurity contamination so they are used in many application areas depending on their concentration although they may cause health hazard and waste problems [10, 29]. Low concentration cyanide baths are generally used to deposit strike, which is a copper coating prior to plating of other metals and high concentration baths are generally used to plate thicker layer [29]. The concentration of cyanide baths specifies some parameters of electroplating process. In dilute solution, higher voltages can be necessary. Current efficiency is also affected by concentration, so it

is lower in dilute solution. Dilute cyanide and Rochelle cyanide baths are generally preferred to deposit a strike coating. However, when thicker layers are produced, high-efficiency sodium and potassium cyanide electrolytes are used. [3]. Corrosion of the anode increases with increasing concentration of free cyanide in dilute solution, but excess free cyanide lowers cathode efficiency and as a result of this, thinner deposits per unit time are obtained [1]. The dilute cyanide bath can be operated at room temperature. High efficiency sodium and potassium cyanide electrolytes are used to obtain thicker deposits [4]. Concentration and operation conditions of cyanide baths are given in Table 2.1 [1].

Table 2.1 Chemicals and operating conditions of cyanide baths

Chemicals (g/L) and operating conditions	**Strike**	**Rochelle**		**High Efficiency**	
		Low Conc.	**High Conc.**	**Sodium Cyanide**	**Potassium Cyanide**
Copper cyanide (CuCN)	22	26	60	80	80
Sodium cyanide (NaCN) or Potassium cyanide (KCN)	33	35	80	105	105
	43	-	-	-	-
Sodium carbonate (Na_2CO_3)	15	30	30	-	-
Sodium hydroxide (NaOH)	To pH	To pH	To pH	30	-
Rochelle salt	15	45	90	-	-
Potassium hydroxide (KOH)	-	-	-	-	35
Temperature (°C)	30-50	55-70	60-75	60-75	60-75
Cathode Current Density (mA/cm^2)	10-15	10-40	20-50	20-60	20-60
pH	12-12.6	12-12.6	13	>13	>13

2.2.1.2 Copper Pyrophosphate Plating Baths

Copper pyrophosphate solution requires more control and maintenance than copper cyanide bath [4]. However, when using a copper pyrophosphate bath, a better surface finish can be obtained compared to cyanide solution [29]. It has good plating rates, so it is used to obtain thick layer [3]. Its ingredients are copper pyrophosphate, potassium pyrophosphate, sodium salt, nitrate and ammonia in the solution [3]. Electrode efficiencies are almost 100% and also throwing power is well [1]. Anodes should be high purity copper [metal finish]. The anode to cathode ratio should be 2:1 [1, 10] and pH should be between 8 and 9 [4]. The solution must contain an excess amount of complexing agents because of promoting anode corrosion and increasing electrical conductivity [3]. Conductivity and corrosion are obtained by finding free or excess pyrophosphate in the bath [10]. Potassium pyrophosphate salt is generally added to the solution because it increases solubility of copper pyrophosphate in the solution [1]. Nitrate addition results in a higher maximum current density [1, 3]. Ammonia addition helps to increase the brightness of deposited metal and control the pH of solution [1, 12]. Also, it increases anode corrosion and acts as grain refiner [4]. Orthophosphate is not directly added to solution but it forms by hydrolysis of pyrophosphate. It supports anode corrosion and acts as a buffer [4]. Because of high temperature and low pH of solution (less than 7), rapid formation of orthophosphate occurs in solution [4, 10]. Low concentration of orthophosphate is not harmful. However, if orthophosphate concentration increases excessively in solution, throwing power and efficiency of solution decreases and ductility of deposits also decreases [3, 4]. Because orthophosphate cannot be removed chemically from the solution, pyrophosphate solution is discharged, diluted or rebuilt to reduce concentration [1]. Good agitation is also essential for consistent operation. Concentrations and operating conditions are shown in Table 2.2 [1].

Table 2.2 Chemicals and operating conditions of copper pyrophosphate baths

Chemicals and conditions	Strike	General
Copper Pyrophosphate Trihydrate ($Cu_2P_2O_7.3H_2O$) (g/L)	25-30	52-84
Potassium Pyrophosphate ($K_4P_2O_7$) (g/L)	112-205	235-405
Potassium Nitrate (KNO_3) (g/L)	1.5-3	3-12
Ammonium Hydroxide Solution (mL/L)	0.5-1	3.75-11
Temperature	22-30	43-60
Current density	10-30	10-70
pH	8.0-8.5	8.0-8.7
Anode to cathode ratio	2:1	2:1

2.2.2 Acidic Copper Plating Baths

Copper electrodeposition from acidic baths is widely used for electroforming, electroplating and electro refining because it has low-cost chemicals and it is simple and easily controllable process [4]. There are two types of acidic baths; copper sulfate and copper fluoroborate baths. Deposition of copper from acidic solution requires less voltage than that from alkaline solution because solution has high conductivity and polarizations of anode, and cathode are small [4].

2.2.2.1 Copper Sulfate Bath

The chemical composition of copper sulfate bath is simple. The primary ingredients of the copper sulfate electrolyte are copper sulfate pentahydrate and sulfuric acid [1]. Copper sulfate bath is highly conductive and can be operated at room temperature

[10]. Metal ions are furnished with copper sulfate. Copper sulfate concentration is not critical. Sulfuric acid concentration is more critical than copper sulfate because changes in its concentration affect concentration of copper sulfate in solution, conductivity of solution and anode and cathode polarization [3]. When sulfuric acid concentration increases, the solubility of copper sulfate decreases. Also, it prevents precipitation of salts and improves throwing power [10]. High sulfuric acid concentration increases the anode dissolution [1]. Chloride can be added to the solution to reduce anode polarization [4]. The chloride ion influences the surface appearance, structure, micro hardness and crystallographic orientation of the deposits [4]. The efficiency of anode and cathode are close to 100%. Concentrations and operating conditions are shown in Table 2.3 [1].

Table 2.3 Concentrations and operating conditions of copper sulfate baths

Ingredients or conditions	**Range**
Copper Sulfate ($Cu_2SO_4.5H_2O$) (g/L)	200-240
Sulfuric Acid (H_2SO_4) (g/L)	45-75
Temperature, ℃	20-50
Agitation	300 rpm, mechanical stirring
Current Density, mA/cm^2	20-100

2.2.2.2 Copper Fluoborate Bath

Copper fluoborate is more soluble than copper sulfate so there are more metal ions in the fluoborate solution than in the copper sulfate solution. [4]. Primary constituents of the copper fluoborate bath are copper fluoborate and fluoboric acid [1]. They produce high speed plating and dense deposits so they can be used in thick

deposition process [3]. Concentration and operating conditions are shown in Table 2.4 [1].

Table 2.4 Concentrations and operating conditions of copper fluoborate baths

Ingredients or conditions	**Low Copper**	**High Copper**
Copper fluoborate, (g/L)	225	450
Fluoboric acid	To pH	40
Temperature, ℃	20-70	2070
pH	0.8-1.7	<0.6
Current Density, mA/cm^2	70-130	120-350

2.3 Brazing

Many products are formed by several components. They are assembled with different joining methods. Adhesives, fasteners and welding are generally used for joining and brazing is one of the joining methods in the manufacturing industries [24]. Brazing and soldering can be classified under welding. [9]. Brazing is defined by the American Welding Society (AWS) as a process which produces coalescence of materials by heating them to a suitable temperature and by using a filler metal having liquidus temperature above 450℃ and below the solidus temperature of the base materials. Brazing filler material is placed between surfaces of the joints and it spreads to faying surface by capillary attraction. Brazing and soldering is similar joining processes, but brazing is performed above 450℃ and soldering is used below it. Brazing is a completely different process from welding because joint is welded by different way [12]. The base metal doesn't melt in the brazing process. Only filler metal melts but during welding process both filler and base metals melt and fuses. The brazing temperature is always lower than the melting temperature of the base metals in the brazing [12]. The joint forms with metallurgical bond between brazing

filler metal and surfaces of the base metal. A schematic of welded and brazed joints are shown Figure 2.2.

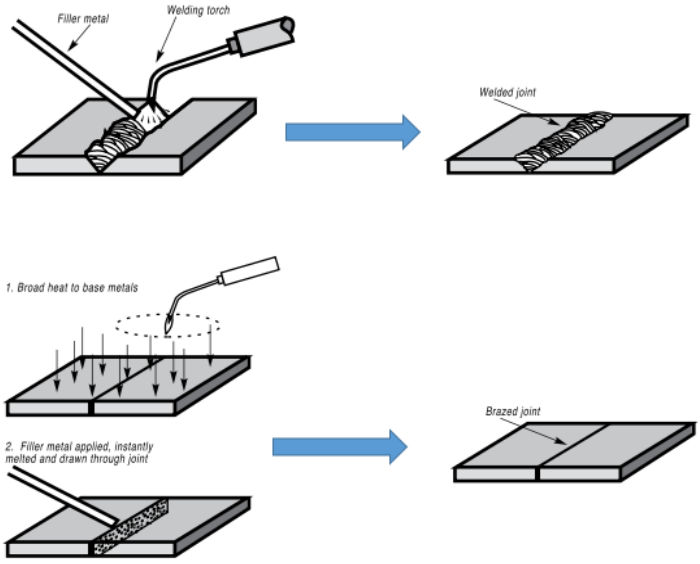


Figure 2.2 Welded and brazed joints [12]

Clearance is the most important design criteria for obtaining good brazement joint. The clearance means the distance between the joint's faying surfaces. As shown in Figure 2.3, for the molten filler metal to be evenly distributed between the base metals' surfaces, capillary action is necessary [12].

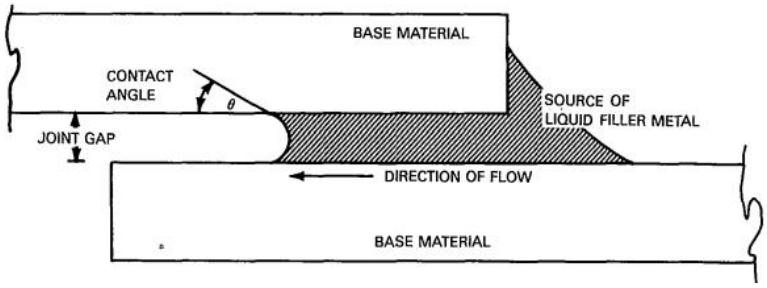


Figure 2.3 Schematic representation of a braze joint [9]

It is simple to maintain the clearance between assemblies with similar material members. However, the clearance is the critical parameter for designing with dissimilar material members and it must be calculated by using the brazing

temperature [5]. Also, if different materials are to be brazed, thermal expansion coefficient is an important parameter to be determined the joint clearance [11]. In brazing different parent materials, the clearance may increase or decrease depending on the thermal expansion coefficients and their positions. Therefore, the clearance at the room temperature is adjusted to reach the clearance at the brazing temperature when brazing dissimilar materials [5]. Figure 2.4 shows the relationship between thermal expansion coefficient and clearance. Mechanical properties of the brazed joints are impacted by the joint clearance [9]. The smallest acceptable clearance is better for resulting in the strongest joint because when the clearance is small, the filler metal easily distributes throughout the joint area with capillarity and voids, or shrinkage cavities do not form much when the filler metal solidifies [9].

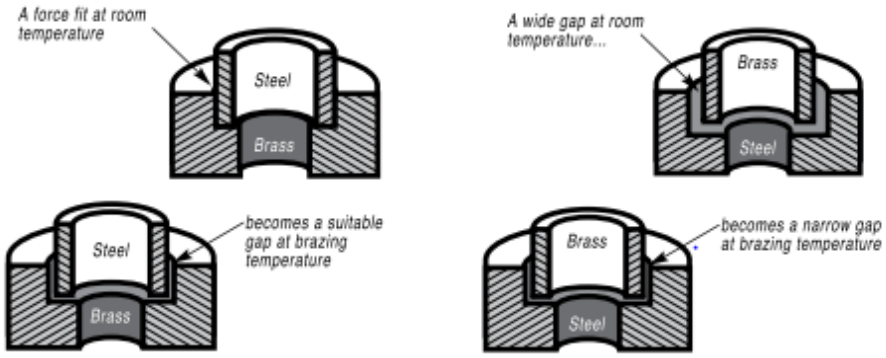


Figure 2.4 Brazing process of dissimilar materials with different thermal expansion coefficients and joint gaps

The surface finish of the parent materials is important for flows of filler metal because brazing is often a capillary process and micro scratches on the surface provide a pathway to enhance the flow of the filler metal [11]. The filler metal is preplaced at the joint in furnace brazing whereas the brazing filler metal is fed from one side of the joint in manually brazed joints [9]. Types of preplaced filler metals are generally wire, foil, powder or shim. If brazing filler metal is preplaced in the

joint, the filler metal flows between the parent materials without any capillary action so capillary action is not an important factor for preplaced filler metal [9].

Selecting a suitable brazing temperature is another important factor to obtain good brazement. Brazing filler metal flows and spreads in a joint after it is completely molten [5]. When it is heated to its solidus temperature, it begins to melt and if the temperature is increased, more of the alloy becomes molten. And then, when the temperature reaches to the liquidus of filler metal, it becomes 100% liquid [11]. For this reason, the liquidus temperature may be considered the lowest temperature required for brazing [5]. During heating to brazing temperature, temperature differential becomes between external and internal sections of the joint. The temperature of the internal section may be lower than external section when the joint is rapidly heated. To minimize the temperature differential and uniformly heat the joint, slower heating methods such as furnace may be used, heat may be concentrated according to mass of assembly and the location of heat may be conducted to brazed area [5].

Brazing filler metal (BFM) is a metal to be added when making braze [5]. BFM is a metal or alloy and it has liquidus temperatures above 450°C (840°F) but below the solidus temperatures of the parent metals [5, 9]. Brazing filler metals should have some basic characteristics [12]. First, they should have the ability of wetting of surfaces of parent materials. Also, they should have suitable melting point and fluidity to permit its spread by capillary attraction. They should form joints providing suitable physical and mechanical properties for the intended service application after the brazing process. And finally, they should provide or avoid interaction between base metal and filler metal depending on requirements [5]. There are literally hundreds of different compositions of brazing filler metals [9]. AWS lists them in eight categories. Also, brazing filler metals have several forms which are rod, ribbon, powder, wire [9]. Filler metal may be preplaced on the joint before starting to heat cycle of brazing or may be fed to a face after heating starts. Furnace brazing and high production brazing operations require preplaced filler metal [5]. Many different shapes and forms of filler metals can be produced for specific applications by using

preforms [9]. There are several advantages of preforms filler metals. Preforms filler metals are suitable for automation and they help minimizing and optimizing the production costs [12] because amount of filler metal can be controlled more precisely and excess filler metal consumption can be decreased [9]. Brazing filler metal can also be applied at least to one of the surfaces of parent materials by using thin film coating technique such as vacuum deposition, electroplating etc. [33].

Another important factor to good brazement is surface preparation of the joint. Cleaning of all surfaces of the joint is necessary to obtain successful and repeatable brazement [9]. When surfaces are clean, capillary action can work properly [12]. If there are contaminants which are oil, grease, dirt, rust and oxides on one or both surfaces, they may form a barrier that prevents the uniform flow and bonding between parent metals and filler metals. For this reason, voids forms in the joint and non-uniform brazed joints are obtained and mechanical properties of the brazed joints are reduced [9, 12, 5]. There are two common cleaning techniques: chemical and mechanical. Chemical methods as alkaline cleaning, solvent cleaning and acid pickling are more widely used than mechanical methods to clean the parent metals [9].

2.3.1 Brazing Techniques

There are four commonly used brazing process types. These are torch brazing, furnace brazing, induction brazing and dip brazing.

2.3.1.1 Torch Brazing

Torch brazing is a simple and widely used process because it requires low initial investment for equipment. A fuel gas flame is used in the torch brazing process to provide the heat needed to melt and flow the filler metal [5]. It is performed without a protective atmosphere. Except from the joining of pure copper base metal with phosphorus-bearing filler metal, flux is required with torch brazing process [9]. Post-

braze cleaning must be applied to the brazement joint to remove flux residue and heat scale after torch brazing [5].

2.3.1.2 Induction Brazing

Induction brazing process includes selective heating of the components at the joint area to the brazing temperature by using the resistance to the flow of electricity induced by coils [9, 19]. Heat is applied to only joint region and is not applied to base materials. For this reason, metallurgical changes of joining components are minimized and minimal or no distortion are observed at the parts. The brazing filler metal can be preplaced [9]. However, this technique is not suitable for complex shapes. It is not difficult than other brazing methods but it requires special knowledge [5].

2.3.1.3 Dip Brazing

There are two types of baths in the dip brazing. One is molten salt bath and the other is chemical flux bath. The assembly is dipped or immersed into a heated molten metal or flux bath of molten salt during dip brazing technique. In both dip brazing methods, the temperature of molten bath is lower than the solidus temperature of the parent metal and higher than the liquidus temperature of the brazing filler metal [5]. Dip brazing in molten metal bath has limited brazing applications because of high application temperature. However, dip brazing in molten salt bath is widely used to braze to aluminum, copper alloys and ferrous parts [5]. In the chemical flux bath, flux is used rather than molten metal. In both processes, after the parts are joined and held together, they are immersed in the bath. And then, when the parts reach a temperature of the bath, the molten metal flows into the joint [9].

2.3.1.4 Furnace Brazing

Furnace brazing is a commonly used brazing technique because of its comparatively low cost of equipment and the adaptability of furnace. It is a repeatable process for mass production of quality parts. Furnace brazing provides a protective atmosphere and the ability to control and record every stage of the brazing cycles with computerized instrumentation [5]. Many brazing assemblies do not require a special fixture. Only the weights of the parts are enough to hold them together [9]. The precleaning is important the same as other brazing processes. Special chemical and mechanical cleaning methods can be used to clean the surfaces of parent materials from oil, grease, oxides or other foreign substances that can contaminate the braze joint [5]. Joint design is also critical because no observation can be made during furnace brazing [9]. Brazing filler metal is preplaced into the joint and then the assembly is inserted into the furnace. The furnace is heated to a temperature above the liquidus of the filler metal and below the solidus temperature of the parent metals under suitable atmospheric conditions. The heating cycle should be designed to melt and solidify the filler metal to join the parts with minimum distortions, and the shape of assembly should remain the same at the end of the brazing process [9]. Pure, dry inert gases can be used to obtain suitable atmospheric properties, but vacuum is an economical method for this purpose. Brazing filler metals with high vapour pressures are not suitable for furnace brazing because their volatilizations reduce the service life of the furnace [5]. Because of this reason, brazing filler alloys which contain elements such as cadmium, zinc or lead cannot be used in the furnace brazing [11].

2.3.2 Aluminum Brazing

Aluminum is one of the versatile, economical, and attractive metallic materials for a broad range of engineering applications [31]. Aluminum alloys are extensively used in automobiles, ships, structural and electrical applications and military fields because of their excellent properties of high strength and stiffness, light weight,

corrosion resistance, good thermal and electrical conductivity, low price and other advantages [10, 29, 30]. There are several mechanical or metallurgical joining techniques. Melting temperature of Aluminum is 660 °C. Brazing requires less heating than welding so brazing is generally used for heat treatable aluminum alloys such as ASTM 6xxx. [22]. Binary Aluminum-Silicon filler metals that have solidus temperatures above 590 °C (1090 °F) (see Figure 2.5) are commercially used for aluminum alloys [9]. The filler metal may be wire, shim, paste or it may be coated on one or both surfaces of parts. Aluminum brazing temperature is between 555°C and 645 °C (1030 and 1195 °F) [9]. Aluminum can be brazed by several brazing techniques such as torch, furnace, dip or others. Precleaning is an important step before Al brazing because all aluminum alloys have naturally oxide films on their surfaces [34]. Chemical cleaning is required for heat-treatable aluminum alloys to remove thicker oxide films from surface [5]. There are two general methods, named caustic acid cleaner and acid cleaner, for chemical cleaning [5].

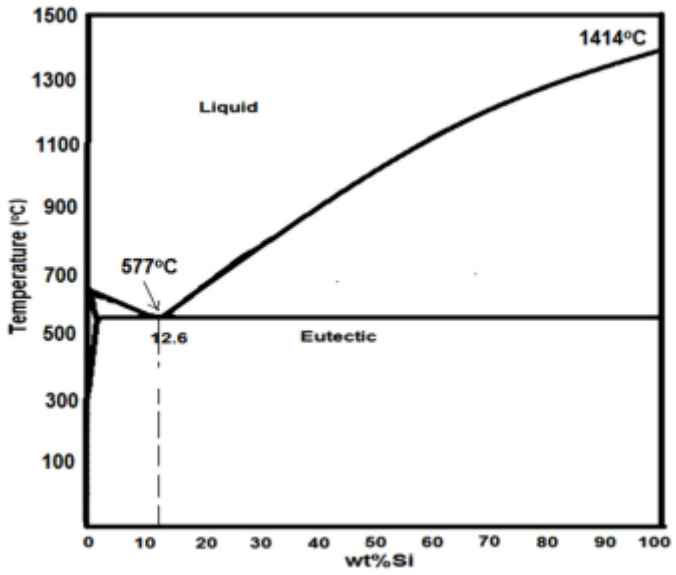


Figure 2.5 Phase diagram of Al-Si [31]

A sound joint can be obtained by using Al-12Si brazing filler metal to braze Aluminum parts. As it can be seen in Figure 2.5 the eutectic point of Al-12Si brazing filler metal is about 577°C and it is relatively close to melting point of aluminum.

For this reason, localized melting regions may be observed in some engineering aluminum alloys after brazing [19]. For instance, melting point of Al 6061 alloy is almost the same as liquidus temperature of Al-12Si filler metal so it can be difficultly joined. Because of this reason, the development of low melting point filler metal is important for brazing of aluminum alloy [22]. Diffusion brazing may be one of the development techniques of low melting point filler metal. It can also be called as eutectic brazing [22] or contact reactive brazing [25].

2.3.3 Contact Reactive Brazing

Contact reactive brazing is a diffusion brazing process. The joint is brazed by using the eutectic reaction [25]. Low melting liquid phase is produced between parent materials [35]. When the brazing temperature reaches the eutectic temperature, the eutectic liquid is formed between the substrate and reactive material. And then, the eutectic liquid wets the surface and spreads on the surface of the substrate to form joints [3, 18]. Contact reactive brazing is important because it is a low temperature joining technique. After contact brazing, it is observed that there is almost no deformation on base materials and few defects on the brazing joint [15]. Flux is not required for contact reactive brazing [18]. Copper, zinc, silver or gold can be used as reactive material with aluminum substrate. Eutectic points of binary Al-Si, Al-Ag, Al-Cu, Al-Au, Al-Zn and Al-Sn are shown in Table 2.5 [22].

Table 2.5 Eutectic temperatures of binary aluminum systems

Materials	**Eutectic Temperature (℃)**
Aluminum-Silicon	577
Aluminum-Silver	554
Aluminum-Copper	548
Aluminum-Gold	527
Aluminum-Zinc	382
Aluminum-Tin	242

Especially, joining aluminum to copper is difficult because of their different melting points and the occurrence of the brittle intermetallic compounds at the interface. Different joining methods such as friction welding, diffusion bonding and ultrasonic welding have been reported to join aluminum to copper. However, these methods require high pressure, and the base metal surface must be treated specially. Therefore, these methods are limited in mass production in industries. Contact reactive brazing can be applied in assemblies of Al alloys and materials with high melting temperature such as copper [9]. Aluminum-copper phase diagram is shown Figure 2.6. Although copper has a melting point of 1080°C, to braze aluminum and copper, heating above 548°C, which is the eutectic point may be sufficient [22]. Cu atoms diffuse in Al during brazing process and when the temperature reaches to eutectic point and composition of Cu and Al reach to 33 and 67% by weight at the interface, eutectic reaction occurs and eutectic liquid forms. And then, it wets the surface and spreads into the joint [10]. Pressure may be required for contact reactive brazing [5].

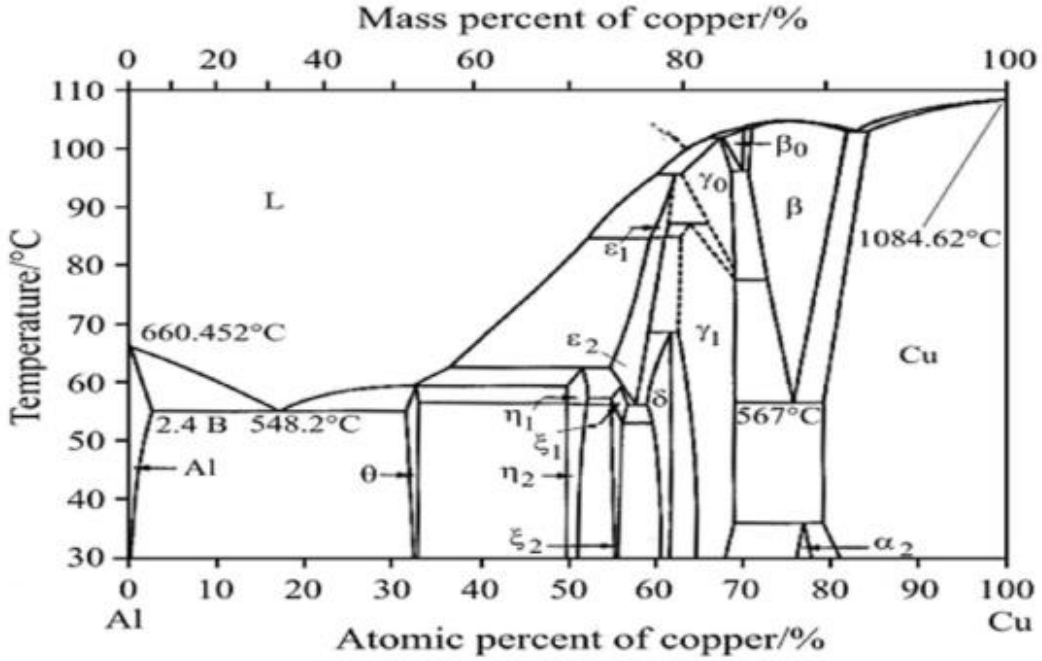


Figure 2.6 Phase Diagram of Al-Cu [36]

CHAPTER 3

OPTIMIZATION OF ELECTROPLATING PARAMETER

This thesis study involved two experimental parts. Firstly, copper was deposited on Al using different electroplating parameters. Copper plated Al pieces were brazed with another Al piece applying the same heat cycle. And then, shear test was applied to joints and optimum electroplating parameters for strong brazed joint were determined. Secondly, Al pieces were coated with copper by using optimum elecroplating parameters and optimum brazing parameters for strong joint were obtained.

3.1 Experimental Procedure

In the first step of thesis study, 18 different aluminum samples were plated with copper by using different electroplating parameters. Two types of solutions, three different thicknesses and current densities were used for electroplating. And then, they were brazed by following the same brazing profile and were tested by using tensile test machine to measure their shear strength. The electroplating parameters of the sample that yielded the highest strength were determined as optimum electroplating parameters and electroplating process was performed according to the optimum conditions in the second step of thesis study.

3.1.1 Copper Electroplating on Aluminum

Rectangular 6063 graded Al alloy pieces were used as cathode in electroplating part of the experiments. 3.6 cm^2 area of Al was plated with copper. Oxide free copper anode was placed 5 cm away from the cathode surface.

Copper sulfate solution and copper pyrophosphate solution were prepared for electroplating. Before copper was deposited on surfaces of Al pieces, according to ASTM B253-11, alkaline and acidic cleaning procedures were applied. Deionized water was used in each rinsing step to avoid any interaction that may change bath performance. Precleaning steps of copper electroplating were given as follows;

1. Measuring weight of the Al piece
2. Cleaning the surfaces of Al piece with hot and soapy water.
3. Rinsing in water.
4. Caustic dipping in alkaline solution of NaOH (0.5 M) for 30 s to 1 min.
5. Acid cleaning in solution of H_2SO_4 (25%) for 1 min to 2 min.
6. Rinsing in water.
7. Acid cleaning in solution of HNO_3 (50%) for 30s to 1 min.
8. Rinsing in water.

After precleaning step was applied successfully to Al piece, electrodeposition process was started immediately to protect the homogenous surface activity. Also, copper anode was dipped to 0.5 M sodium hydroxide solution for 1 min and then dipped into 50% nitric acid solution for 30 sec to clean the surface and to remove oxides from the surface.

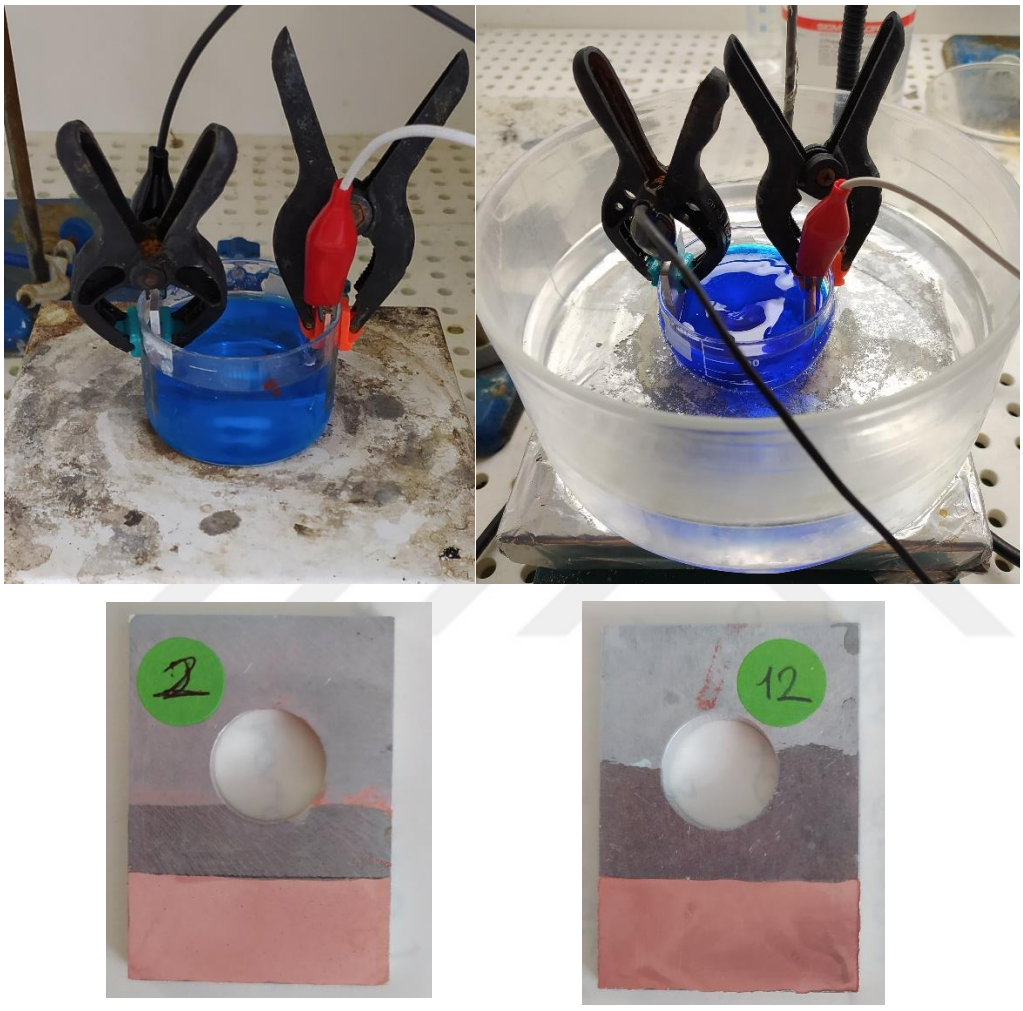
As shown in Table 3.1, three different current density and thicknesses were chosen for each solution. 25, 50 and 75 microns copper were plated on Al pieces by applying 20, 40 and 60 mA/cm^2 current density.

Table 3.1 Copper electroplating parameters

Sample	Electroplating Baths	Current Density (mA/cm^2)	Theoretical Thickness (μm)
1	Copper Sulfate	20	25
2	Copper Sulfate	40	25
3	Copper Sulfate	60	25
4	Copper Sulfate	20	50
5	Copper Sulfate	40	50
6	Copper Sulfate	60	50
7	Copper Sulfate	20	75
8	Copper Sulfate	40	75
9	Copper Sulfate	60	75
10	Copper Pyrophosphate	20	25
11	Copper Pyrophosphate	40	25
12	Copper Pyrophosphate	60	25
13	Copper Pyrophosphate	20	50
14	Copper Pyrophosphate	40	50
15	Copper Pyrophosphate	60	50
16	Copper Pyrophosphate	20	75
17	Copper Pyrophosphate	40	75
18	Copper Pyrophosphate	60	75

Also, two different electroplating baths were used for copper depositions as can be seen from Figure 3.1. Electrodeposition from copper sulfate baths was performed at room temperature and electrodeposition from copper pyrophosphate baths was performed at 50 ℃.

Concentrations of baths and their operating conditions are given Table 3.2 and Table 3.3. Pictures showing eelectrodeposition from copper sulfate baths and copper pyrophosphate baths together with electroplated Al samples are shown in Figure 3.1.



(a) (b)

Figure 3.1 Electrodeposition from (a) Copper Sulfate Baths (b) Copper Pyrophosphate Baths

Table 3.2 Concentrations and operating conditions of copper sulfate bath

Ingredients or conditions	**Range**
Copper Sulfate ($Cu_2SO_4.5H_2O$) (g/L)	219
Sulfuric Acid (H_2SO_4) (g/L)	60
Temperature, °C	25
Agitation	300 rpm, mechanical stirring
Current Density, mA/cm^2	20, 40, 60

To plate copper from pyrophosphate bath, 2 microns of strike was applied on Al surface by using copper pyrophosphate strike solution. Bath concentrations and operation conditions of pyrophosphate strike and general plating solutions are given in the Table 3.3. Concentrations and operating conditions of these baths were determined according to thesis study of Burcu Hamat [29].

Table 3.3 Concentrations and operating conditions of copper pyrophosphate strike and general plating baths

Concentrations and operating conditions of Copper Pyrophosphate Strike		**Concentrations and operating conditions of General Copper Pyrophosphate**	
Copper Pyrophosphate Trihydrate ($Cu_2P_2O_7.3H_2O$) (g/L)	27.5	Copper Pyrophosphate Trihydrate ($Cu_2P_2O_7.3H_2O$) (g/L)	68
Potassium Pyrophosphate ($K_4P_2O_7$) (g/L)	135.8	Potassium Pyrophosphate ($K_4P_2O_7$) (g/L)	275
Potassium Nitrate (KNO_3) (g/L)	2.25	Potassium Nitrate (KNO_3) (g/L)	4.5
Ammonium Hydroxide Solution (mL/L)	0.75	Ammonium Hydroxide Solution (mL/L)	7.375
Temperature, ℃	25	Temperature, ℃	50
Current density (mA/cm^2)	11	Current density (mA/cm^2)	20, 40, 60
Mechanical Stirring	300rpm	Mechanical Stirring	300rpm

Before and after electrodeposition process, weigth of Al pieces were measured and current efficiency was calculated. After calculating the current efficiency, plating time of each sample was calculated by using Faraday's Law, current density and thickness of coating.

3.1.2 Aluminum Brazing

In this step of experiments, uncoated Al pieces were joined to Al pieces which were coated with Cu by using brazing process. Before brazing process, precleaning was applied to both Al pieces because capillary action works properly only when the surfaces of the metals are clean. If there are contaminates such as oil, grease, rust on the surface, they will form a barrier between the base metal surfaces and the filler materials. Steps of precleaning are given below:

1. Caustic dipping in alkaline solution of NaOH (0.5 M) for 30 s to 1 min.
2. Rinsing in deionized water.
3. Acid cleaning in solution of HNO_3 (50%) for 30s to 1 min.
4. Rinsing in deonized water.

Heavy surface contaminants were removed with caustic etching and oxide films were removed from the surfaces of base metals with acid etching.

After precleaning steps, it should not be waited to braze the parts. Lap joint was chosen as joint type as shown Figure 3.2. Furnace brazing was used under vacuum condition and some pressure was applied on joint during brazing process. Heating cycle of brazing is given in Figure 3.3.

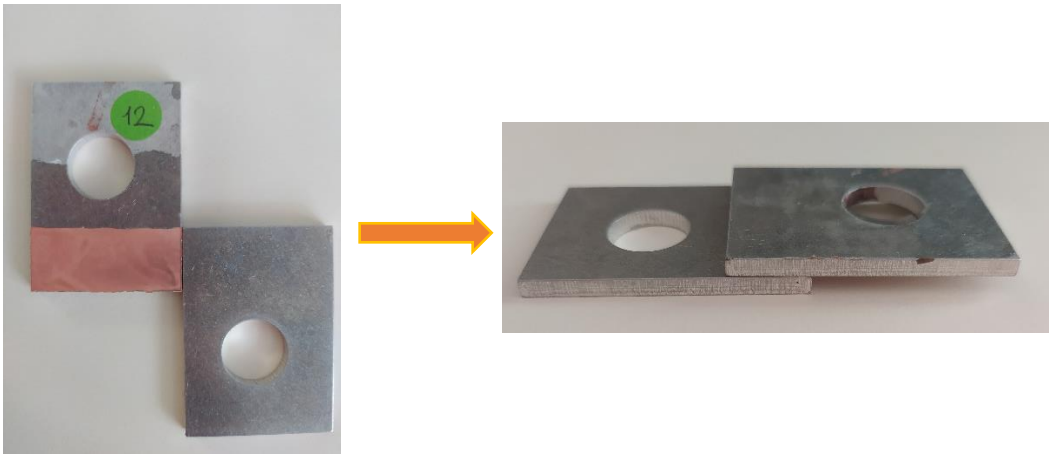


Figure 3.2 Aluminum pieces subjected to brazing and a typical lap joint formed after brazing

First of all, joint was heated to 200 ℃ and waited for 15 min to remove contaminants in the furnace and then it was heated again to 520℃. It was waited for 30 min at 520 ℃ for the joint to be properly heated. Until this step, heating rate was 5℃/min. Afterwards, joint was heated at 2℃/min to 570℃,which is almost 20℃ above the eutectic temperature, and waited for 15 min at this temperature. Finally, joint was cooled down in the furnace.

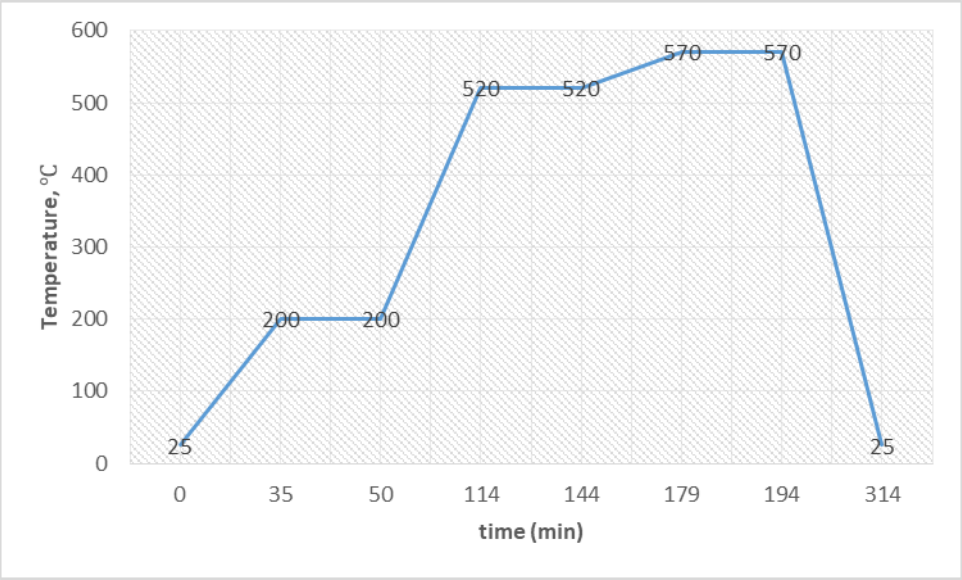


Figure 3.3 Heating cycle during brazing of aluminum parts

After aluminum pieces were brazed successfully, shear tests were done by using tensile testing machine to all joints which was brazed by using heating cycle given in Figure 3.3. The results of shear tests were compared and optimum current density, electroplating solution and thickness were obtained. SEM images, which were taken by the Central Laboratory at Middle East Technical University, and optical microscope images and their results were given in the next chapter.

3.2 Results and Discussion

Copper deposition process was applied to 18 specimens and their weigths were measured before and after the process. Theoretical weight was calculated by using density of copper, deposition area and theoretical thickness of deposits according to Eq.3. The current efficiency, η, was calculated by using experimental and theoretical weights of coatings by using Eq.2. Current efficiencies of processes were calculated almost 100% as shown in Table 3.4.

Table 3.4 Current efficiency results of electroplating solutions

#	Baths	Theoretical Thickness (µm)	Weigth (t_0)	Weigth (t_1)	Weigth Th.	η (%)
1	Copper Sulfate	25	9.12	9.20	9.20	100
2	Copper Sulfate	25	9.12	9.19	9.20	100
3	Copper Sulfate	25	9.14	9.20	9.22	100
4	Copper Sulfate	50	9.12	9.28	9.28	100
5	Copper Sulfate	50	9.10	9.26	9.26	100
6	Copper Sulfate	50	9.14	9.28	9.30	100
7	Copper Sulfate	75	9.13	9.37	9.37	100
8	Copper Sulfate	75	9.14	9.37	9.38	100
9	Copper Sulfate	75	9.15	9.39	9.39	100
10	Copper Pyrophosphate	25	9.15	9.23	9.23	100
11	Copper Pyrophosphate	25	9.11	9.19	9.19	100
12	Copper Pyrophosphate	25	9.11	9.18	9.19	100
13	Copper Pyrophosphate	50	9.11	9.27	9.27	100
14	Copper Pyrophosphate	50	9.14	9.30	9.30	100
15	Copper Pyrophosphate	50	9.07	9.22	9.23	100
16	Copper Pyrophosphate	75	9.09	9.33	9.33	100
17	Copper Pyrophosphate	75	9.12	9.36	9.36	100
18	Copper Pyrophosphate	75	9.14	9.37	9.38	100

$$Weight_{theoretical} = \rho_{Cu} \times thickness \times area$$ Equation 3

3.2.1 Copper Sulfate Solution

Shear tests were applied to joints of aluminum and copper coated aluminum pieces, which were brazed by using brazing cycle in Figure 3.3. ASTM D1000 standard was used to determine test conditions, because the brazed joints are similar to adhesive joints. Shear test results of samples produced by copper sulfate solution are shown in the Table 3.5.

Table 3.5 Shear Test Results of samples produced by copper sulfate solution

#	Electroplating Baths	Current Density (mA/cm^2)	Theoretical Thickness (µm)	Shear Strength (MPa)
1	Copper Sulfate	20	25	0.44
2	Copper Sulfate	40	25	0.63
3	Copper Sulfate	60	25	1.01
4	Copper Sulfate	20	50	1.30
5	Copper Sulfate	40	50	1.60
6	Copper Sulfate	60	50	1.90
7	Copper Sulfate	20	75	2.29
8	Copper Sulfate	40	75	2.74
9	Copper Sulfate	60	75	3.12

According to shear test results, given in Figure 3.4 and 3.5, shear strength increased when current density of electroplating process increased. There could be several reasons for this result. If current density was changed, surface morphology of plated Cu also changes because adsorbed hydrogen content in the deposit increases with increasing current density. The increase in hydrogen content of deposit influences the structure of deposited metal.

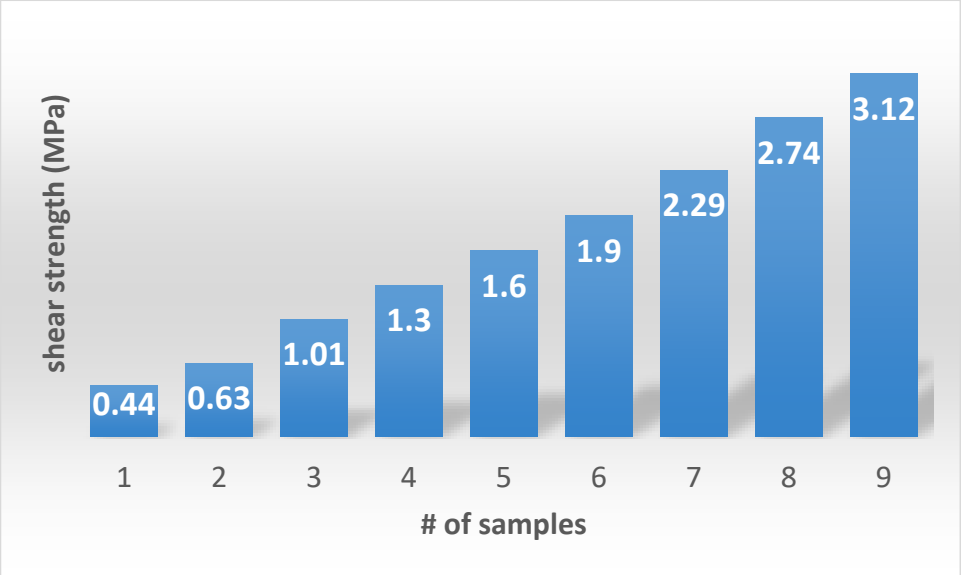


Figure 3.4 Force at break versus # of sample for copper sulfate solution

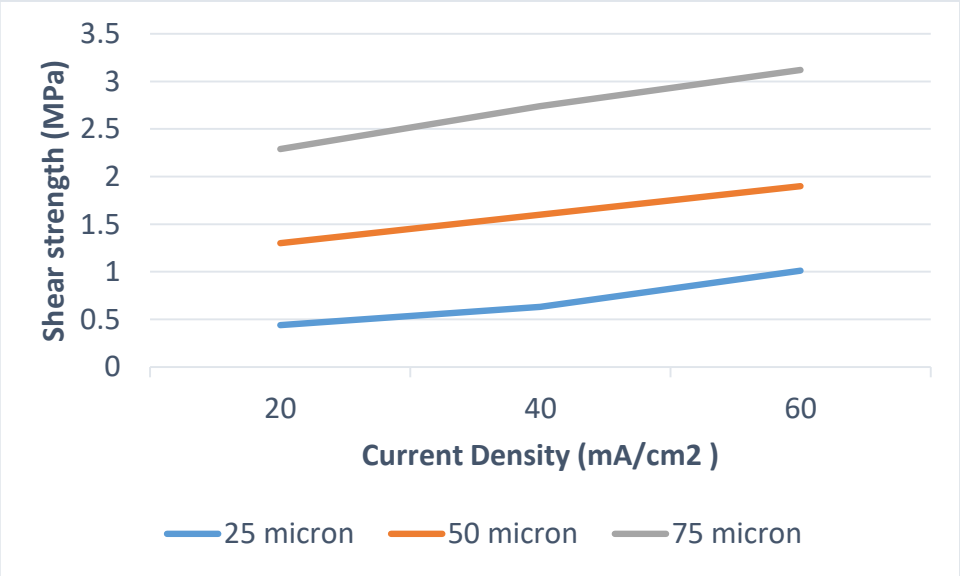


Figure 3.5 Shear strength versus current density for copper sulfate solution

Furthermore, shear strength of joints increased with the thickness of electroplated copper as can be seen in Figure 3.5. The reason for this result may be explained with reference to joint strength vs joint clearance chart [28] given in Figure 3.6. The strength of joint increases when the joint thickness or gap increases until a certain thickness. And then after the critical thickness, it starts to decrease. When thickness of electroplated copper increases, interaction layer between filler metal and substrate increases and the brazing seam thickness also increases. As shown in Figure 3.7, when brazing filler metals diffuse more in the substrate, the brazing seam behaves the same as substrate materials and shear strength of joint is close to shear strength of substrate and when shear force is applied to joint, the joint breaks from the substrate. However, when thickness of brazing seam increases too much, brazing seam also increases and when shear force is applied to joint, the joint breaks from the brazing seam because the brazing seam does not behave the same as substrate material.

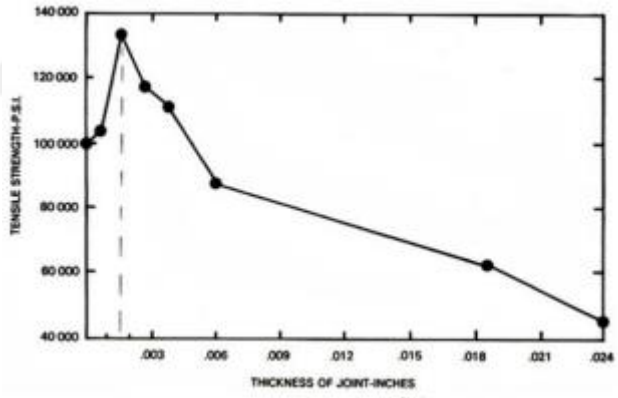
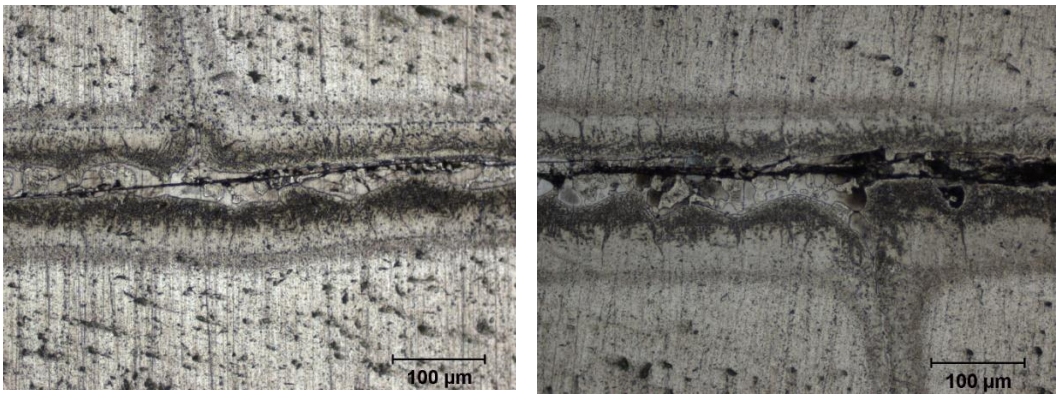


Figure 3.6 The joint strength vs joint clearance chart

To understand the effect of thickness on the brazing seam, optical microscope analysis was performed to samples number 6 and number 9 and their results are shown in Figure 3.7. It is obvious that the brazing seam thickness increases when the thickness of Cu coating was increased.



(a) (b)

Figure 3.7 Optical microscope images of samples number 6 and 9 (a) 50 microns Cu layer (b) 75 microns Cu layer

EDS line scanning analysis perpendicular to joint was performed on sample number 9 to examine Cu and Al compositions of the joint (see Figure 3.8). As can be seen from the figure, intensity of Cu atoms increased and intensity of Al atoms decreased as the brazing seam is approached.

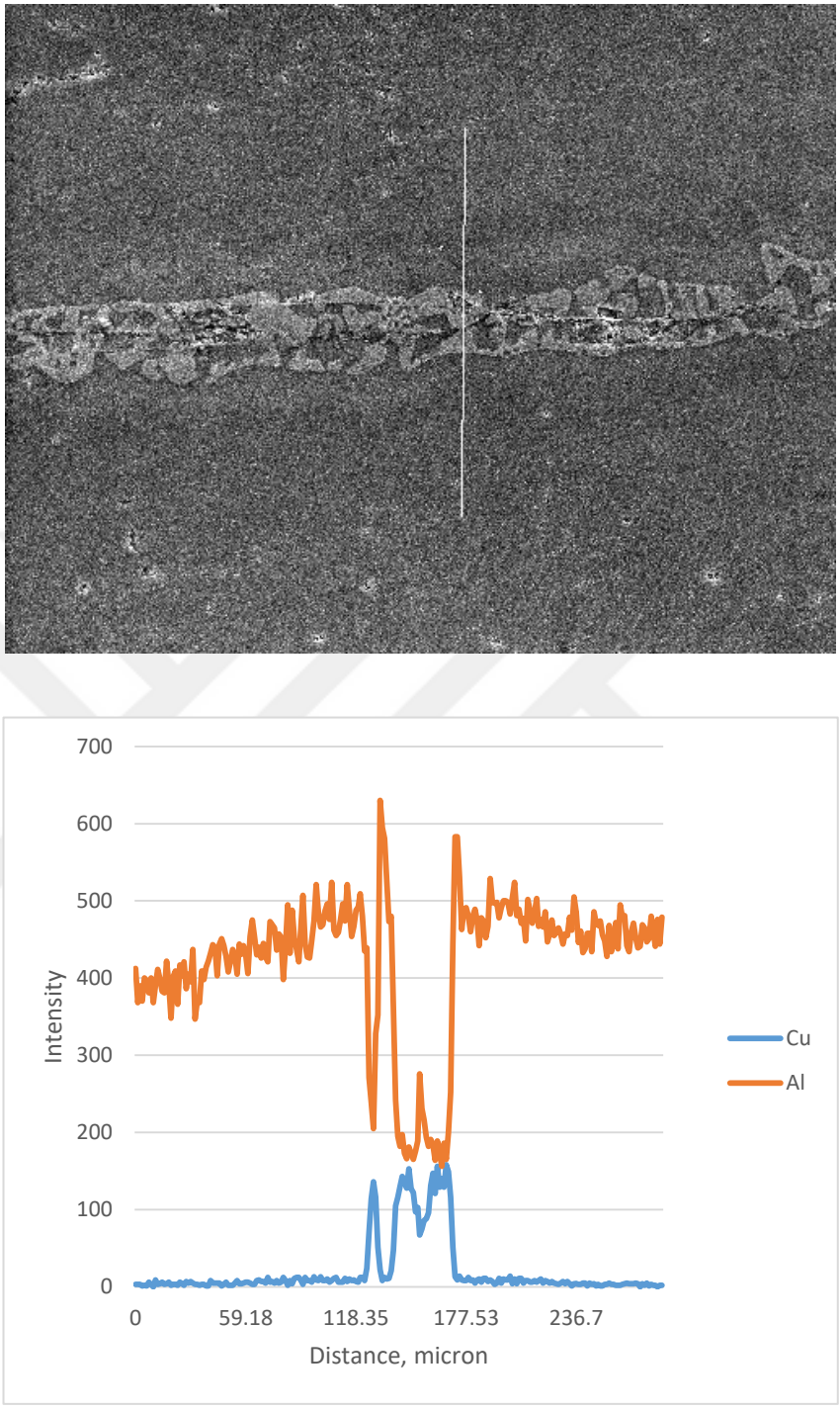


Figure 3.8 EDS line scanning analysis of sample number 9

SEM images of brazing seams of samples number 6 and 9 were also taken and shown in Figure 3.9. Effects of thickness of brazing filler metals on the brazing seam can also be seen in this figure.

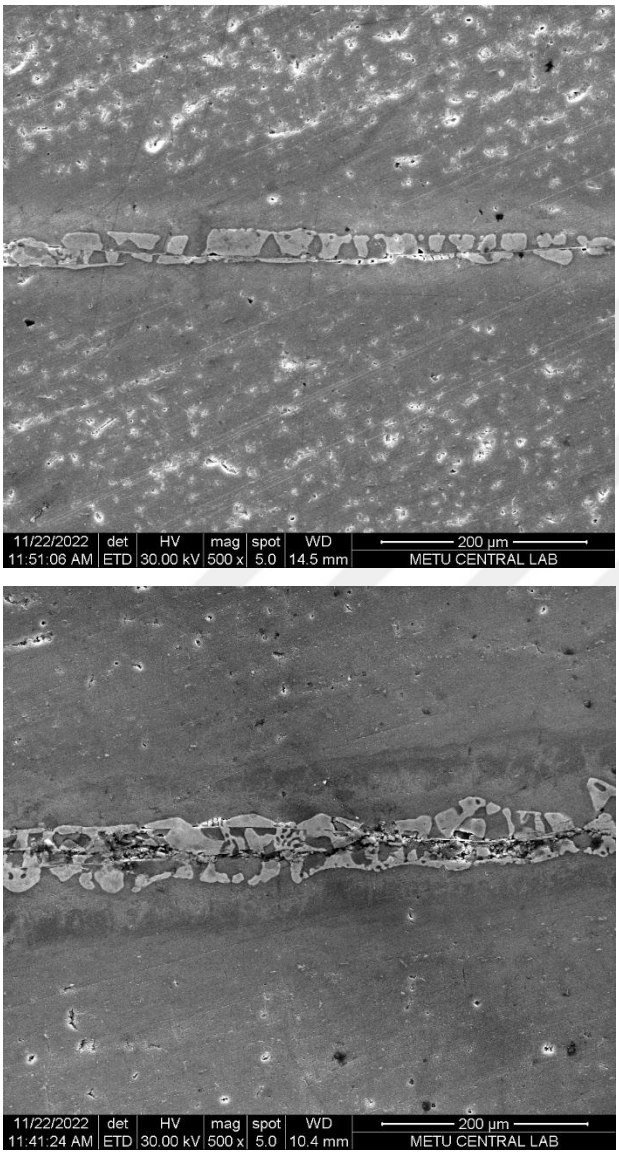


Figure 3.9 SEM images of samples number 6 and 9 (a) 50 micron (b) 75 micron

The shear strengths of joints were not measured as high as it was expected. When interlayer between Al pieces was investigated, it can be seen that base metals were joined from only localized regions (see Figure 3.10). The fracture surfaces of some

of shear tested samples shown in Figure 3.11 also reveal this feature. There can be several reasons of this. Aluminum has natural oxide on its surface so precleaning steps and accuracy of vacuum are important parameters to obtain sound braze joint. In this study, vacuum of the furnace may not be efficient so oxide may have formed on surfaces of substrates and prevented the diffusion of Cu into Al interlayer. When SEM images were analysed in detail, it was seen that there were lots of cracks or voids in the interlayers between substrates and preventing metal to metal contact due to presence of oxides on the interlayer.

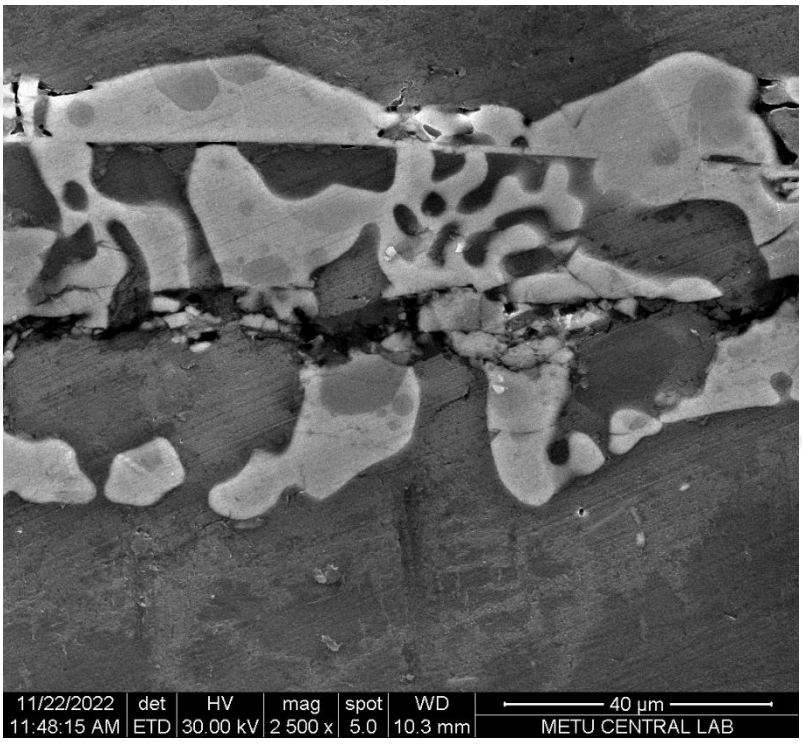
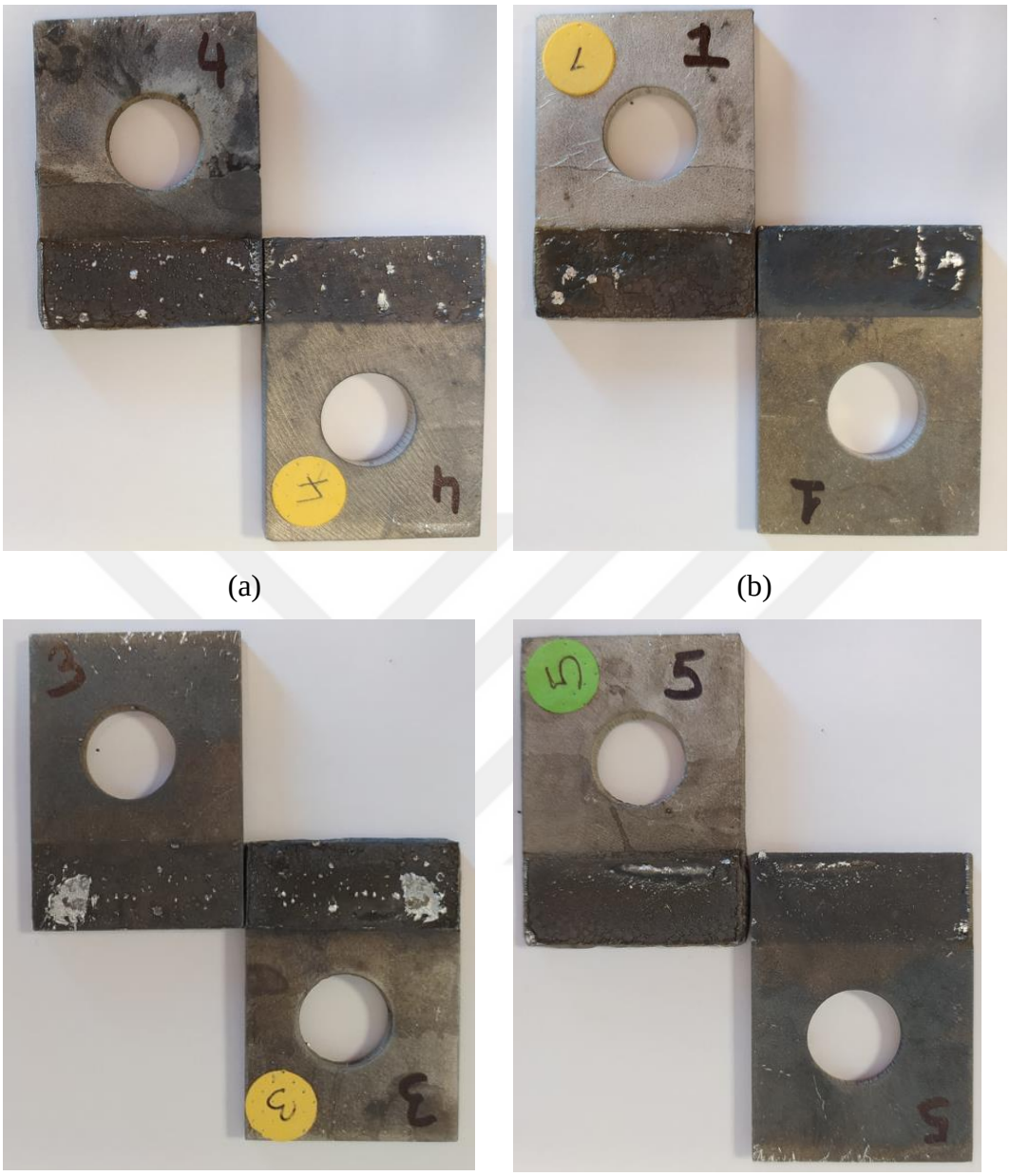


Figure 3.10 Voids and cracks in the brazing seam



(a) (b)

(c) (d)

Figure 3.11 Fracture surface of samples (a) 50 microns at 20 mA/cm^2 (b) 25microns at 20 mA/cm^2 (c) 25 microns at 60 mA/cm^2 (d) 50 microns at 40mA/cm^2

Among the samples produced by using copper sulfate bath, the highest shear force was obtained from sample number 9. It was brazed by using 75 microns copper coated at 60 mA/cm^2 current density. Fracture surface of sample 9 is given in Figure

3.12. As can be seen from the fracture surface, almost all joining area was brazed and filler metal spreaded to interlayer.



Figure 3.12 Fracture surface of sample #9

3.2.2 Copper Pyrophosphate Solution

Shear tests were performed to brazed samples produced by using copper pyrophosphate solution similar to those given for samples produced by using copper sulfate solution. Shear test results are shown in Table 3.6, Figure 3.13 and Figure 3.14.

Table 3.6 Shear test results of samples produced by copper pyrophosphate solution

#	**Electroplating Baths**	**Current Density (mA/cm^2)**	**Theoretical Thickness (µm)**	**Shear strength (MPa)**
10	Copper Pyrophosphate	20	25	1053
11	Copper Pyrophosphate	40	25	1082
12	Copper Pyrophosphate	60	25	982
13	Copper Pyrophosphate	20	50	1198
14	Copper Pyrophosphate	40	50	987
15	Copper Pyrophosphate	60	50	992
16	Copper Pyrophosphate	20	75	1188
17	Copper Pyrophosphate	40	75	1467
18	Copper Pyrophosphate	60	75	1590

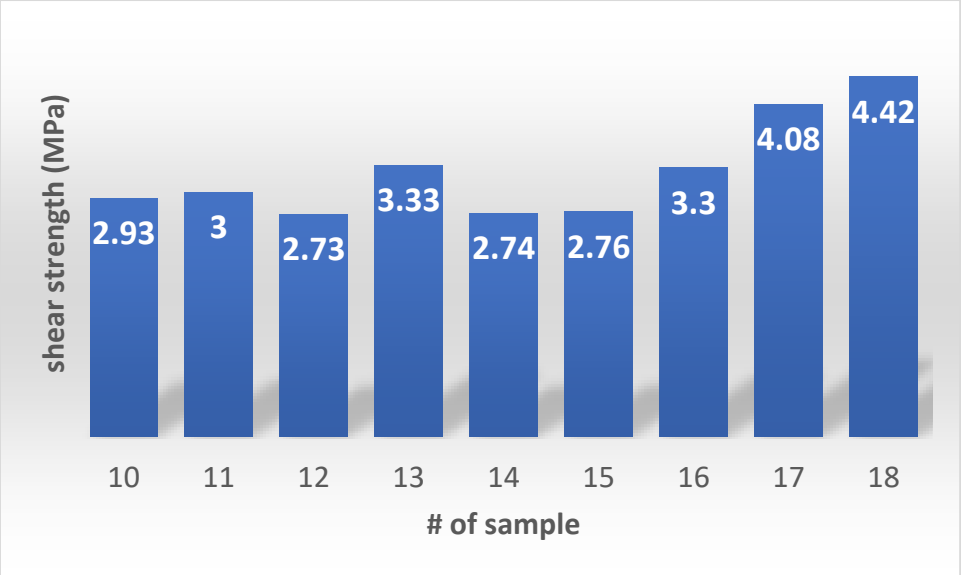


Figure 3.13 Shear strength versus # of sample for copper pyrophosphate solution

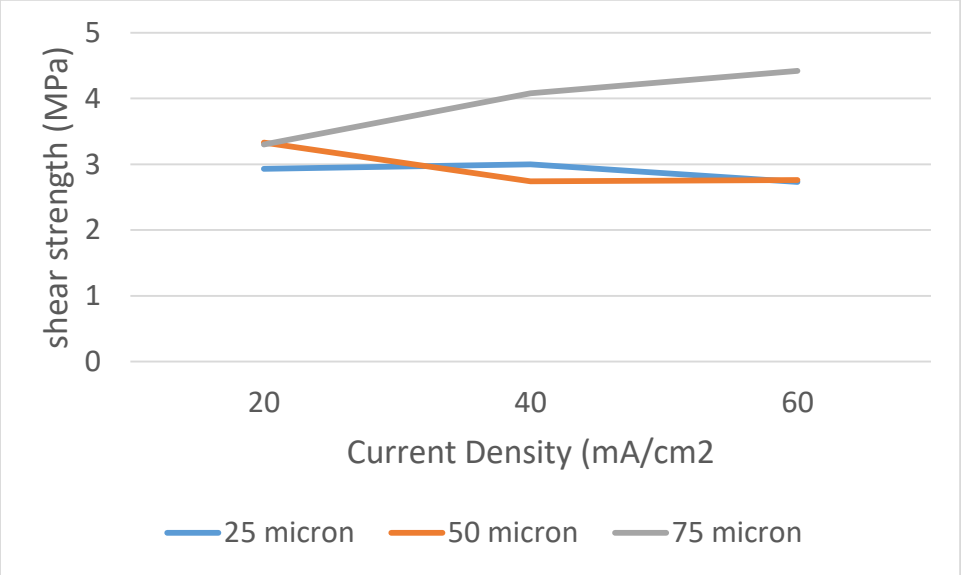
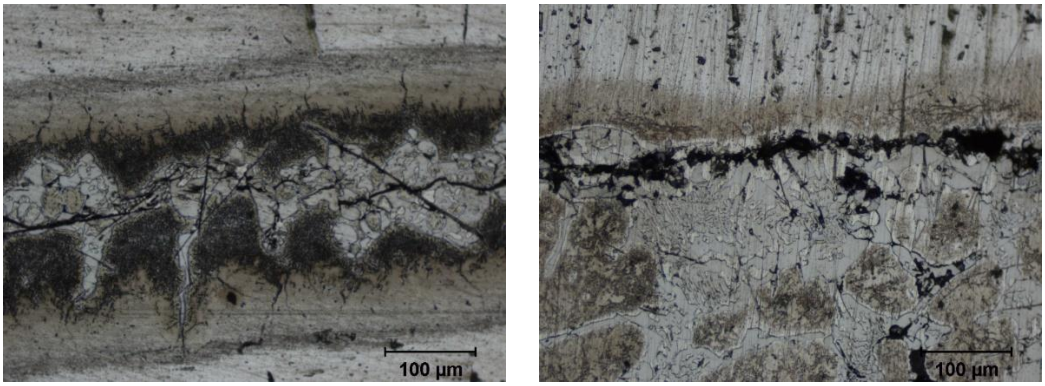


Figure 3.14 Shear strength versus current density for copper pyrophosphate solution

Similar to coatings from copper sulfate, when thickness of copper coatings increased, shear strength of samples also increased. As can be seen from Figure 3.15 and Figure 3.15, brazing seam of copper deposits having 50 μm thickness contained predominantly alpha phase. When thickness of deposited copper increased to 75 μm, a centreline eutectic and intermetallic phases formed across the joint. Until critical

thickness, intermetallic helped to increase strength but they decreased shear strength after critical thickness because of their brittle properties.



(a) (b)

Figure 3.15 Optical microscope images of sample number 15 and 18 (a) 50 micron Cu layer (b) 75 micron Cu layer

When SEM and optical microscope images given in figures 3.15, 3.16 and 3.17 were analysed, there were lots of cracks or voids again because of the same reason as sulfate solution.

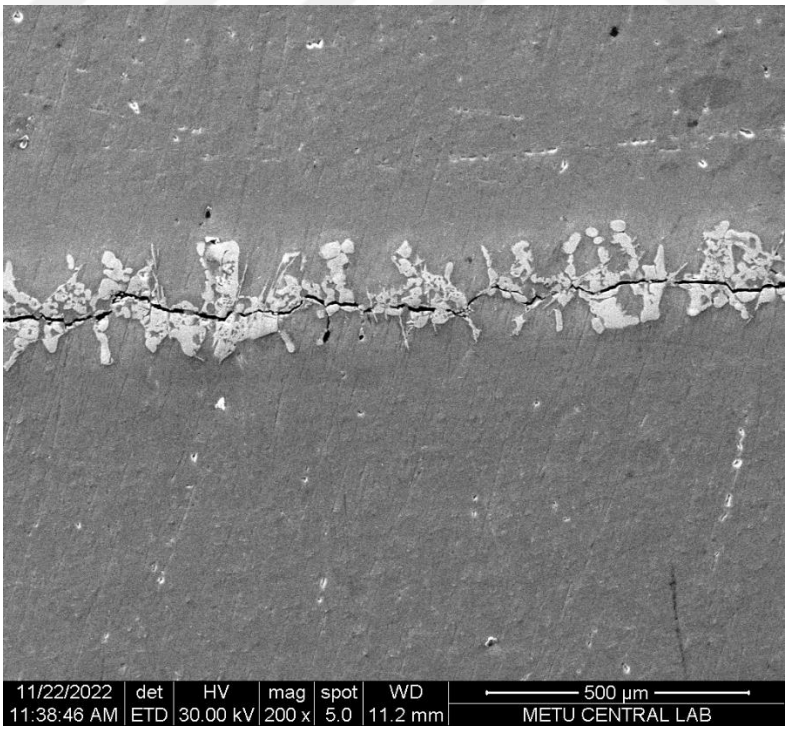


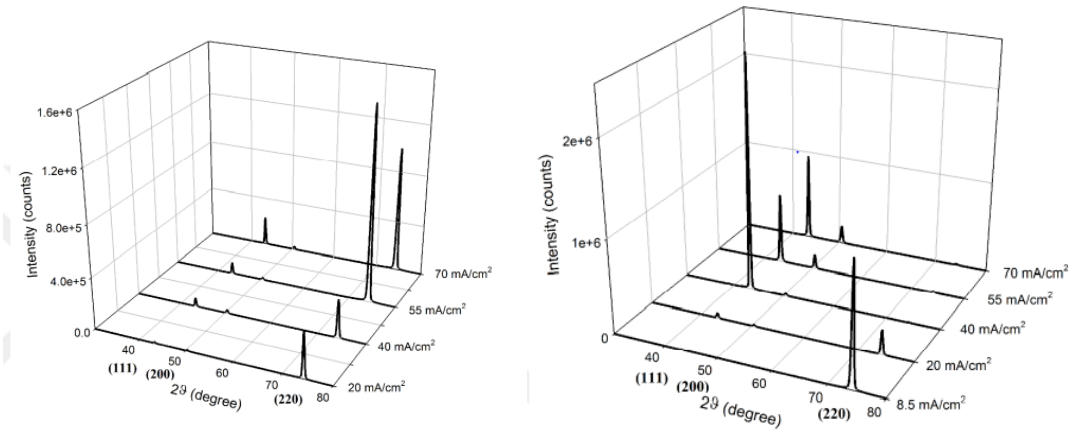
Figure 3.16 SEM image of sample number 17



Figure 3.17 Optical microscope image of sample number 18

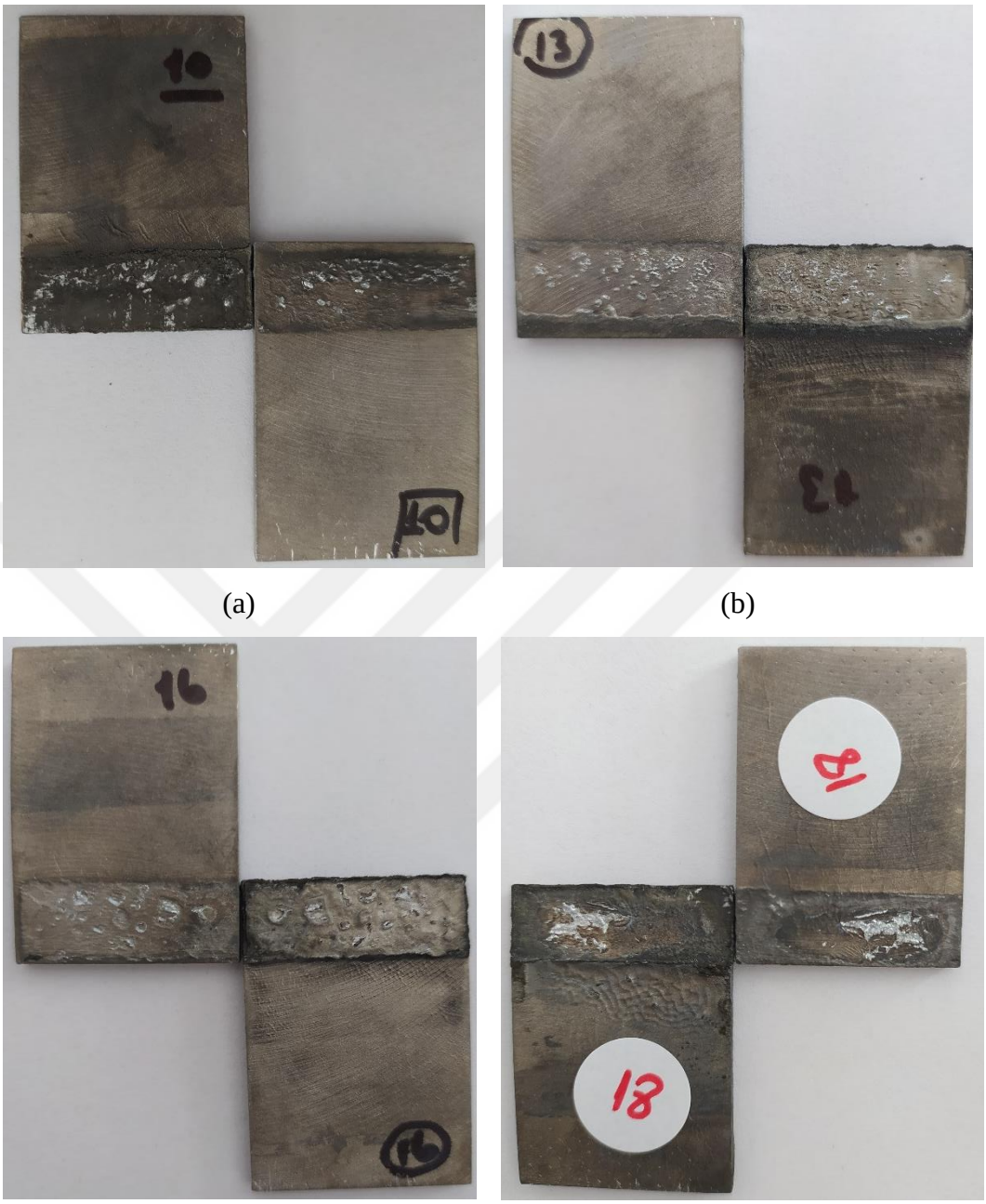
However, strengths of samples produced by using copper pyrophosphate solution were higher than strengths of samples produced by using copper sulfate solution.

The reason for obtaining higher strengths from samples produced by using copper pyrophosphate solution can be explained by using XRD pattern of copper deposited from copper sulfate and copper pyrophosphate as given in Figure 3.18. Copper has face centered cubic structure so its growth direction was expected to be (111) plane. However, deposition from copper sulfate solution favoured (220) plane. The growth and deposition from copper pyrophosphate solution favoured (111) and (220) planes when current density increases. The extra surface energy occurred when growth direction was different from (111) so the change in current density affected the brazing joint property. There were more interaction regions on joints produce by using samples coated by copper pyrophosphate than joints copper sulfate solutions. The fracture surfaces of shear tested samples are shown in Figure 3.19.



(a) (b)

Figure 3.18 XRD patterns of copper deposited from (a) copper sulfate (b) copper pyrophosphate [16]



(a) (b)

(c) (d)

Figure 3.19 Fracture surfaces of samples produced by using copper pyrophosphate solution (a) 25microns/20mA/cm^2 (b) 50microns/20mA/cm^2 (c) 75microns/20mA/cm^2 (d) 75 microns/60mA/cm^2

CHAPTER 4

OPTIMIZATION OF BRAZING PARAMETERS

4.1 Experimental procedure

According to the shear test results of the first part of this study, sample number 18 had the highest shear strength. So, electroplating parameters of sample number 18 were used to deposit copper on aluminum samples in the second part. Electroplating parameters are given in Table 4.1. Surface preparation steps were the same as the first part, and they were applied to samples before electroplating and brazing processes. In total 6 samples were prepared and they were brazed according to brazing parameters shown in Table 4.2.

Table 4.1 Optimum electroplating parameters

Optimum Electroplating Parameters	
Solution type	Copper Pyrophosphate
Current density	60mA/cm^2
Thickness	75μm

Table 4.2 Brazing parameters of samples

# of sample	Brazing Temperature (°C)	Brazing Time (min.)
19	560	15
20	570	15
21	580	15
22	560	5
23	570	5
24	580	5

The brazing cycle in this part was changed to complete the process in a shorter period. The change was adopted after the realization that brazing cycle was too long for present sample dimensions according to literature [25] and results of the first part. So, the brazing cycle given Figure 4.1 was used in this part. After brazing, shear test was applied to all brazed samples.

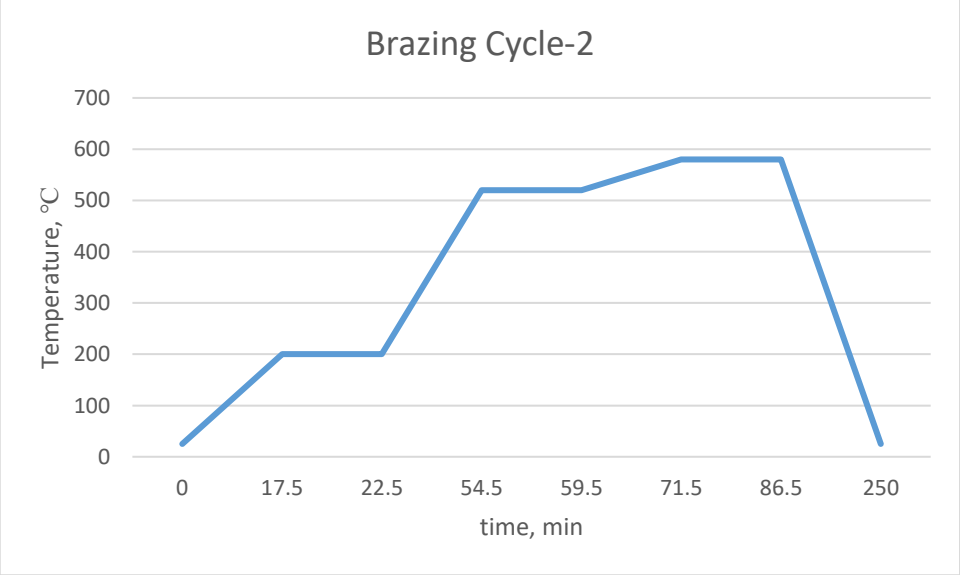


Figure 4.1 Brazing cycle used in this part of study

4.2 Results and Discussion

Shear test results of samples prepared in the second part are listed in Table 4.3.

Table 4.3 Shear test results of samples prepared in the second part of study

# of sample	Brazing Temperature (°C)	Brazing Time (min.)	Force at break (N)
19	560	15	0
20	570	15	1812
21	580	15	3302
22	560	5	0
23	570	5	0
24	580	5	627

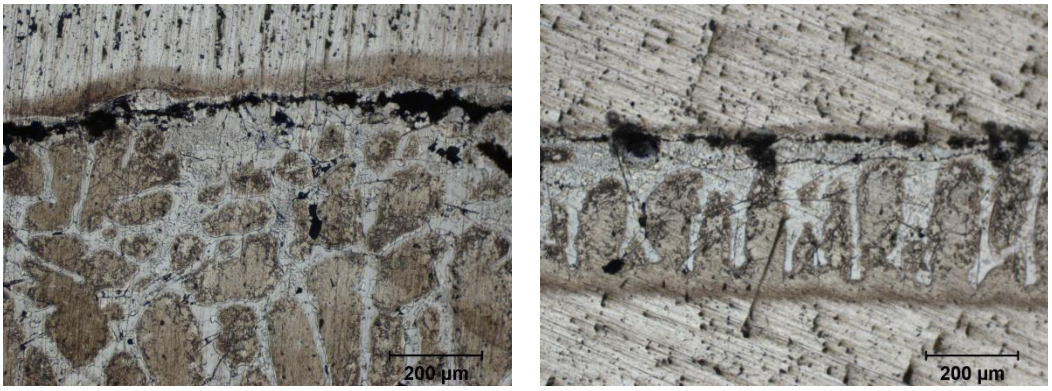
Sample number 19 was found as two parts and unbrazed when they were taken out of the furnace. This means that 560 °C was not sufficient as brazing temperature of aluminum and copper because diffusion of Cu in Al was slow at low brazing temperature. When diffusion of Cu was not sufficient, thin Cu layer reacts with aluminum to form the liquid phase and almost no interaction had occurred at low temperature in this study. The coated and uncoated parts of sample number 19 together with the fracture surfaces of samples 20 and 21 are shown in the Figure 4.2.



(a) (b) (c)

Figure 4.2 Shear tested samples (a) brazed at 560℃/15min (b) brazed at 570℃/15min (c) brazed at 580℃/15min

The comparison of shear test results of samples number 18 and 20, indicates that brazing cycle of this part seems more accurate than that of the first part. Although they were subjected to the same procedure during copper coating, shear test result of sample number 20 was higher than sample number 18. When they were analysed with optical microscope, images of Figure 4.3 were obtained. According to optical microscope results, copper diffused away from interlayer between Al and Cu in sample number 18. However, it was shown that more copper was remained in the brazing interlayer of sample number 20.



(a) (b)

Figure 4.3 Optical microscope images of sample number 18 (a) and sample number 20 (b)

Sample number 21 was brazed at 580°C and the best shear test result was obtained in this study. Microstructure of sample number 21 was analysed by using optical and scanning electron microscope (SEM) and they are shown in **Hata! Başvuru kaynağı bulunamadı.** and Figure 4.5 respectively. When images that were obtained from optical microscope were investigated, contrary to images of other samples, it could be seen that there were regions where the joining line was not visible and the diffusion region was spread equally on both sides.

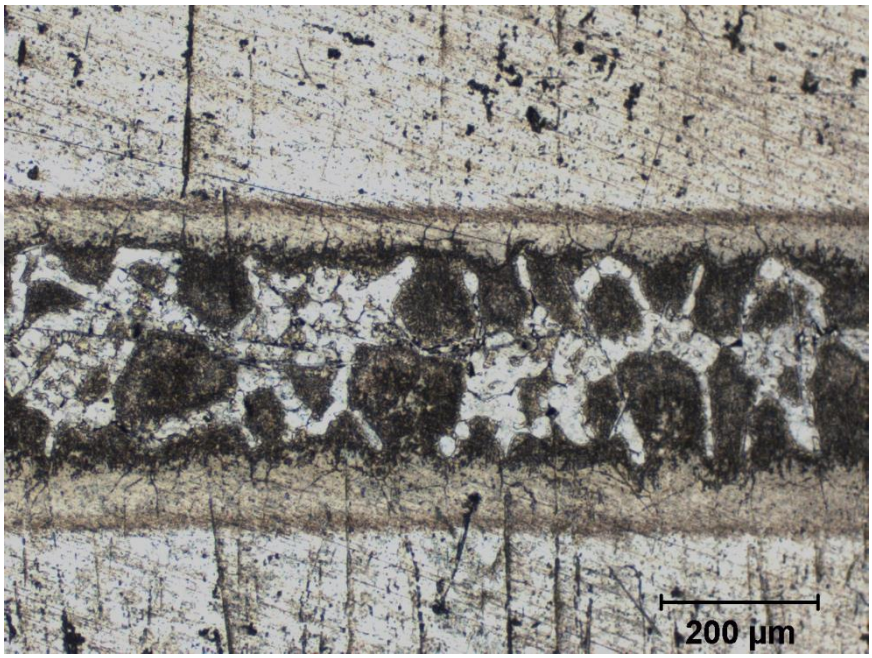


Figure 4.4 Optical microscope image of sample number 21

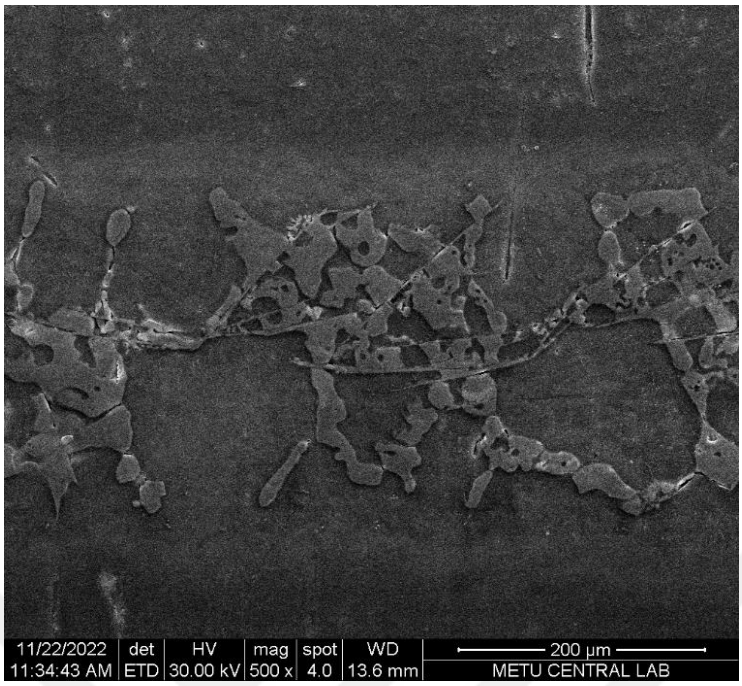


Figure 4.5 SEM image of sample number 21

Moreover, copper diffused to both sides of the joining line and eutectic phase occurred on both sides. Because brazing temperature was increased, Cu atoms in the liquid phase diffused into the substrate and more and more eutectic liquid phase formed in the brazing seam. When brazing temperature was increased, the interaction layer also increased. In order to observe the diffusion of Cu atoms at 580℃, EDS line scanning analysis was performed perpendicular to the brazing interlayer. As it can be seen in Figure 4.6, intensity of Cu atoms increased while intensity of Al atoms decreased as the brazing seam is approached.

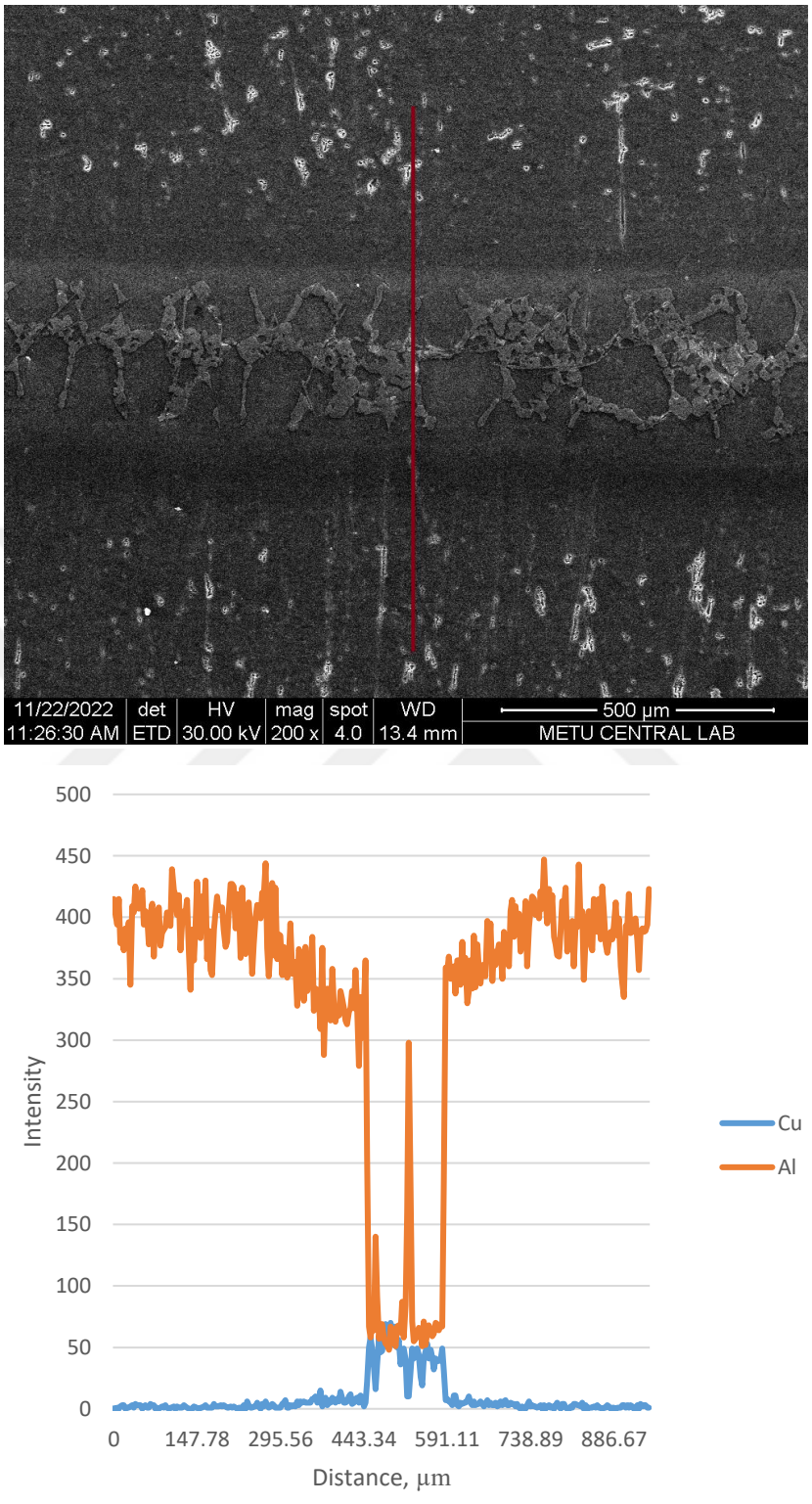


Figure 4.6 EDS line scanning analysis of sample number 21

In addition, EDS analysis was performed at positions; A, B and C as shown in Figure 4.7, to determine chemical compositions and phases in the brazing seam. The results are given in Table 4.4. Region A contains only Al. Region B contains both Al and Cu and the ratio of their atomic percentages is about 2:1 so region B may contain Al_2Cu phase. Presence of small amount of Cu together with large percentage of Al in region C may indicate the presence of α-Al phase. This means that the brazing seam was formed by the eutectic phase of Al-Cu according to phase diagram of Al-Cu [36].

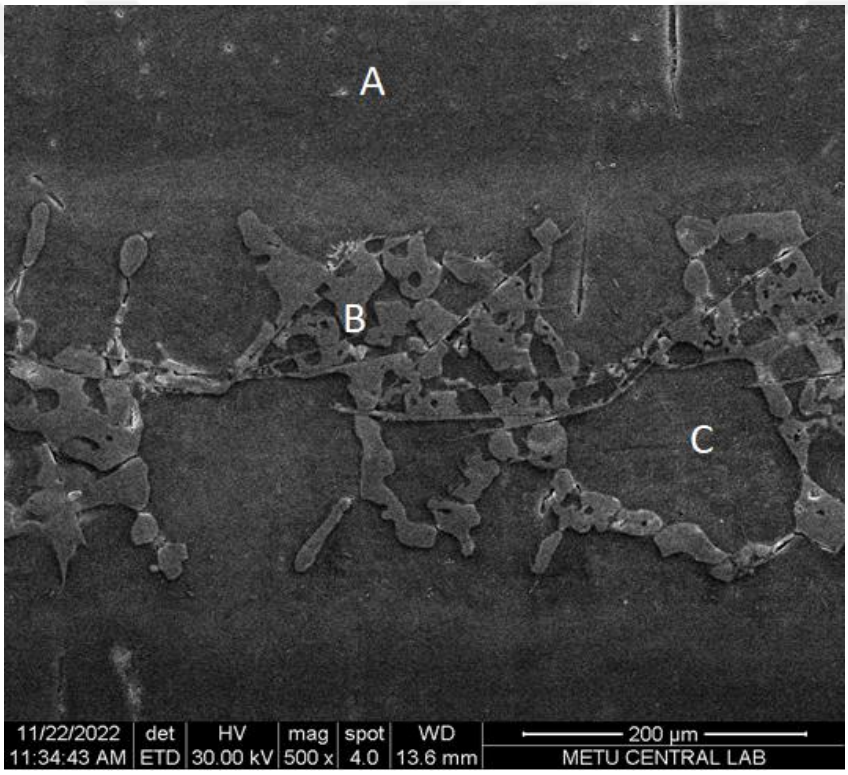


Figure 4.7 EDS analysis of A, B and C regions of brazing seam of sample 21

Table 4.4 EDS results of A, B and C regions of brazing seam of sample 21

Regions	Element	wt%	at%
Region A	Al	100	100
Region B	Al	60.75	78.47
	Cu	39.25	21.53
Region C	Al	95.68	98.12
	Cu	4.32	1.88

Another brazing parameter was brazing time. Samples number 22, 23 and 24 were brazed by using 5 minutes dwell time. Samples number 22 and 23 were not brazed and found as two separate parts when they were taken from the furnace after the brazing process. This means that 5 minutes dwell time was not enough for brazing process at 560℃ and 570℃. The coated and uncoated parts of samples number 22 and 23 together with the fracture surface of sample 24 are shown in Figure 4.8.



(a) (b) (c)

Figure 4.8 Shear tested samples (a) brazed at 560℃/ 5min (b) brazed at 570℃/ 5min (c) brazed at 580℃/ 5min

Only sample number 24 could be brazed by using 5 minutes dwell time at 580℃. However, its shear strength was measured much lower than the others. Optical microscope images of sample number 24 were taken to examine the brazing seam.

As can be seen from Figure 4.9, there are many dendritic structures in the brazing seam. Because substrate material of this study was 6063 grade Al, dendritic structure may be explained with reference to Al-Si phase. Therefore, there was not enough time for diffusion; dendritic α-Al phase may have formed in the brazing seam.

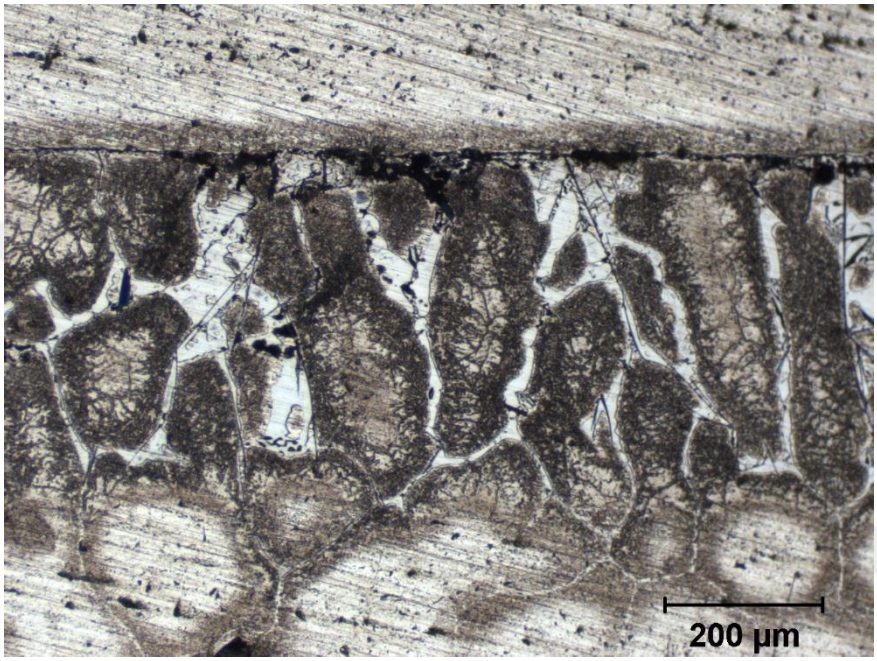
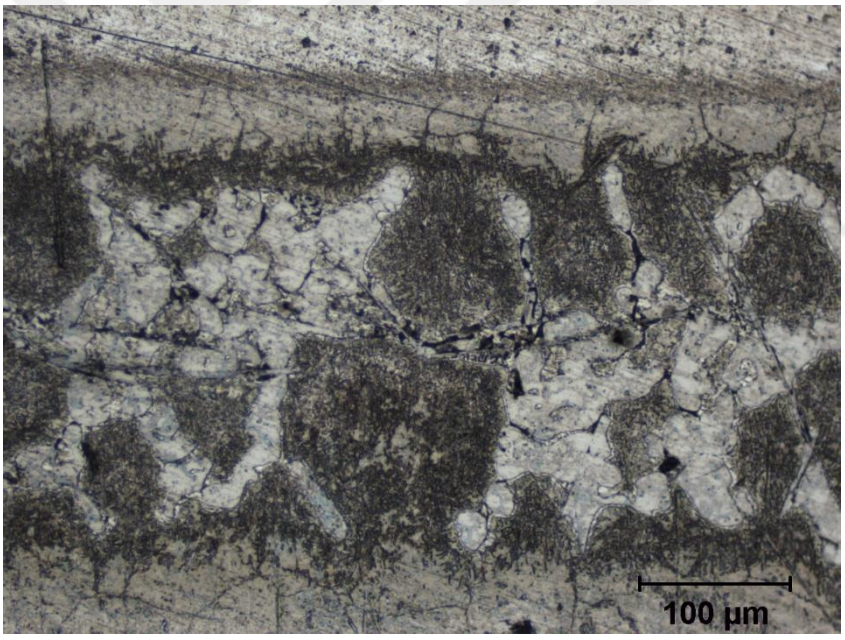


Figure 4.9 Optical microscope image of sample number 24

In addition, when brazing seams of sample number 21 and sample number 24 are compared, it is obviously seen that thickness of interfacial reaction layer decreased with increasing dwell time (see Figure 4.10). When brazing time was increased, Cu atoms in the liquid phase diffuse into the solid base metal because of the concentration of Cu. It was higher in the liquid phase than in the solid base metal. So, the width of the liquid Al–Cu phase narrowed and the Al_2Cu phase became denser. Strength of joint increased when brazing time was increased because of second phase particle effects of intermetallic.



(a)



(b)

Figure 4.10 Optical microscope images of (a) sample number 24 (b) sample number 21

A 75 μm copper foil was also used as brazing filler metal and aluminum pieces were brazed by using it at 580 ℃ for 15 and 45 minutes. However, any joining was not obtained as seen in Figure 4.11.



Figure 4.11 Two pieces of Al received after the brazing test performed by using copper foil as brazing filler metal

According to the results of the thesis study, it was obviously seen that interfacial problems between base metal and filler metal could be solved by using electroplating process to place brazing filler metal between base metals. Also, because of regional joining, brazed area which was shown in Figure 4.12 was measured as 1.16 cm^2 by using an image program and actual strength of joint was calculated as 28.5 MPa. The maximum shear strength of brazed joint by using Cu foil is almost 23 MPa in the literature [25]. The maximum shear strength calculated from the 1.16 cm^2 fractured surface of brazed joint by using coated Cu layer in this study is higher than the maximum shear strength of brazed joint by using Cu foil. The defect free joint interlayer can be obtained by using coated Cu layer and shear strength of brazed joint can be improved because of this reason.



Figure 4.12 Brazed region of sample number 21

CHAPTER 5

CONCLUSIONS

Electroplating of Cu and Al brazing parameters were studied in this thesis. It was obtained that electroplating parameters such as thickness, current density and solution types were found to affect brazed joint properties because they change surface properties of brazing filler metal.

After finding the optimum electroplating parameters which can be used in this study, brazing parameters were changed and their effects were observed on the brazing seam. It was seen that temperature, thickness and time were important brazing parameters because they affected the mechanical properties of joints. When brazing temperature was increased, shear strength of joints also increased because of accelerating diffusion of Cu atoms from the liquid phase to solid substrate. And when brazing time was increased, diffusion of Cu atoms into solid phase also increased. Because of this, denser Al_2Cu phase occurred.

No brazing was obtained by using copper foil as brazing filler metal at 580°C for 15 minutes. This means that interfacial effects decreased when electroplated copper was used as brazing filler metal.

To obtain strong Al brazing by using electroplated Cu as filler metal, 75 microns of Cu should be plated on Al by using 60 mA/cm^2 current density and copper pyrophosphate solution. And then, brazing process should be performed at 580°C for 15 minutes brazing time. It is obviously seen that when these parameters are applied, the joint which has 28.5 MPa shear strength can be obtained.

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