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KASTAMONU UNIVERSITY  
INSTITUTE OF SCIENCES**

**FABRICATION AND CHARACTERIZATION OF  
FUNCTIONALLY GRADED BRONZE MATRIX CERAMIC  
REINFORCED COMPOSITE MATERIALS**

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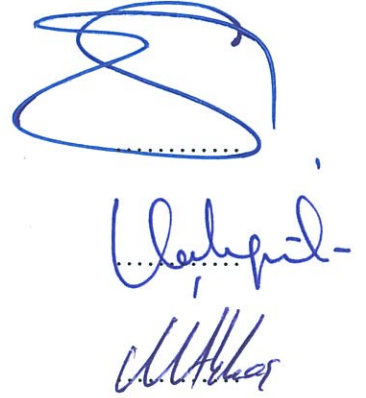
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DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING**

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## THESIS APPROVAL

The thesis study entitled "**Fabrication and Characterization of Functionally Graded Bronze Matrix Ceramic Reinforced Composite Materials**" submitted by **Aimen Mohamed ABUSHRAIDA** has been argued in front of the following examining committee members and accepted as Master's Thesis in **Department of Materials Science and Engineering, Institute of Sciences in Kastamonu University** by unanimity of votes.

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## DECLARATION

I declare and undertake that all the information in the thesis is presented within the frame of ethical behavior and academic rules and all information and statements that are not mine in this study, prepared in accordance with the thesis writing rules, have been cited fully to their sources.

Aimen Mohamed ABUSHRAIDA



## ABSTRACT

MSc. Thesis

### FABRICATION AND CHARACTERIZATION OF FUNCTIONALLY GRADED BRONZE MATRIX CERAMIC REINFORCED COMPOSITE MATERIALS

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Functionally graded materials (FGMs) have been increasingly used during the recent years for several engineering applications such as aerospace, marine, automobile, and electronic industries. In these industries, the use of many traditional metals has been replaced with new materials. If the excellent properties of functionally graded composites are taken into account, the effect of bronze matrix composites seems more significant. Functionally graded composites, which have superior properties, are produced by putting together different particles. In this case, the amount and distribution of particles are very important factors, which affect the mechanical properties of functionally graded composite materials.

For this thesis, functionally graded bronze matrix material was produced by using cold pressing method, for which, boron carbide ( $B_4C$ ), silicon carbide ( $SiC$ ), titanium carbide ( $TiC$ ), and molybdenum carbide ( $Mo_2C$ ) were used as reinforcement materials. The samples with compositions Bronze + 10%  $SiC$ , Bronze + 10%  $B_4C$ , Bronze + 10%  $Mo_2C$ , and Bronze + 10%  $TiC$  were pressed at 500MPa pressure and sintered at 750 °C for 90 minutes.

Investigations were carried out to assess the mechanical properties and microstructures of specimens. For this purpose, optical microscope, scanning electron microscope (SEM-EDS), and X-ray diffraction XRD analysis were applied for monitoring microstructures. Sample hardness testing was carried out with the help of Vickers hardness testing device at 200gram load.

Powder metallurgy method with bronze matrix ceramic reinforcement FGM composites were successfully produced. Composite layers of ceramic particles are homogeneously distributed. Little pore formation was observed. The composite layers were hard and the middle layer was ductile.

**Key Words:** Functionally graded materials, bronze, metal matrix composite, mechanical properties, microstructure.

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## INDEX OF SYMBOLS AND ABBREVIATIONS

FGM	Functionally Graded Materials
MMC	Metal Matrix Composites
SEM	Scanner Electron Microscope
XRD	X-ray diffraction
EDS	Energy-Dispersive Spectrometry
ASTM	American Society for Testing and Materials





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## 1- INTRODUCTION

In engineering applications, pure metals have very little utilization because they require materials with conflicting properties. For instance, if an application requires a hard but ductile material, no naturally occurring substance can fulfill this requirement. For solving this issue, a combination of metals or a metal-non-metal combination will be used, and that combination will be prepared in molten state. The material melting and combining is called as alloying (traditional alloying). It is prepared because its properties are different as compared to the parent metals/substances. Bronze was the first alloy prepared in the human history by combining tin and copper.

In fact, composite materials are advanced substances, which are made by combining two or more materials. Those materials have distinct chemical and physical properties in solid state. Composite materials are critical for production processes because they have excellent blends of properties, many of them behave differently as compared to their parent materials, and surprisingly, most of them are light-weight (Hon and Shiraishi, 2001).

Today's sophisticated engineering applications require more robust, lighter and cheaper materials (Tjong, 2014). Since traditional materials cannot meet the high performance demands, production of new generation materials is needed. Metal matrix composite materials (MMCs) have drawn manufacturers' attention because of their customizable combinations of features, which are needed for several engineering applications. These properties include satisfactory corrosion resistance levels, high thermal resistance, high specific stiffness, low thermal expansion coefficient, superior wear resistance, high specific strength, and good damping capacity (Alaneme and Bodunrin, 2011; Kok, 2005).

Many industries use copper and its alloys for large-scale production. These industries include machinery, automobile, and marine equipment manufacturing industries. The reason behind their use is their excellent thermal conductivity, ductility, corrosion resistance, and electric conductivity (Cui et al., 2013).

During recent years, bronze matrix composites have gained widespread importance because they are utilizable in several technological applications. Since they have high conductivity but low mechanical strength, they are taken through dispersion strengthening process, which developed new composite materials with far better properties. Particles including carbides, oxides, and borides are not soluble in the bronze matrix. Moreover, they have high thermal stability to bear high temperatures that makes them a good choice for reinforcement process. Particulate-strengthened copper matrix composites allow making desirable improvements in the mechanical properties such as high temperature tolerance, improved tensile properties, increased stiffness, and better wear resistance (Uysal, Karlioglu, Akbulut and Alp, 2012).



## **2. FUNCTIONALLY GRADED MATERIALS**

Functionally Graded Materials (FGMs) are a category of new and advanced materials, which have varying properties, which further differ along with variation in the dimensions. FGMs are different and some of them are unique because they are quite different as compared to their parent materials. FGMs are used in various applications; therefore, manufacturing some of them is costly because of the cost of parent materials, type of processes used to manufacture them and their fabrication (Mahamood, Akinlabi, Shukla and Pityana, 2012).

### **2.1. Functionally Graded Materials' Special Properties**

FGMs components have certain useful characteristic properties, which meet specific needs of some industrial processes; therefore, they effectively overcome the shortcomings of traditional composite materials. FGMs have many advantages over conventional and composite materials, which are mentioned below (Udupa, Rao and Gangadharan, 2014):

- FGMs have an interface layer, which is fully capable to attach two components made of incompatible materials; so, they substantially increase the bond strength.
- FGM coating and interface can be used to reduce the residual and thermal stresses.
- FGM coating can be used for connecting materials and eliminating the endpoint and interface stresses.
- FGM coating not only enhances the strength of the connections but it can also reduce the crack driving force.

### **2.2 Areas of Functionally Graded Material (FGM) Application**

FGMs have gained substantial significance in many human endeavors. In the sophisticated post-modern industries, FGMs are widely used. They have huge potential in several other industries and applications in the future. Many important current and future FGM applications have been mentioned in the current section. In the current era, they are used in sophisticated industries such as automobile, aerospace, biomedical,

defense, power generation, electric/electronic appliance manufacturing, marine, thermo-electronic and opto-electronic industries.

### **2.2.1 Aerospace Industry**

FGMs were initially used for making some spacecraft bodies. Their utilization has recently increased because they have been successfully tried, tested and used in the aerospace industry. A majority of aerospace structures and equipments are now manufactured using FGMs. They are a good option for manufacturing components of rocket engines, heat exchange panels, spacecraft truss structures, and equipments including cameras, reflectors, solar panels, turbine blade coatings, turbine wheels, missile tips of shuttles and missiles. FGMs offer excellent sound and thermal insulation properties; therefore, they are used in structural walls. Many important automobile parts of high-efficiency automobiles are made with the help of functionally graded materials, which are mentioned in the subsection given below.

### **2.2.2 Automobile Industry**

It is one of the industries that require variety of materials with varying properties but the utilization of FGMs is still quite limited because high cost is the only impediment that limits their use but some leading car manufacturers use them to manufacture functionally significant components of high-value automobiles. Currently, they are used to make spark plugs, engine cylinder liners of diesel engine pistons, leaf springs, drive shafts, combustion chambers, flywheels, shock absorbers, components of car bodies, racing car brakes and window panes. Moreover, they are also used for enhanced car body layers with the help of FGM particle coatings, for example, mica or dioxide.

### **2.2.3 Biomedical Equipments**

Nature has used its own FGMs to make human body. Actually, teeth and bones are functionally graded materials, which are now replaceable in case they get damaged or aged. Biocompatible engineering materials can be used to replace the natural body parts with the help of natural functionally graded materials. So far, many functionally graded materials have been successfully experimented and placed in the human bodies in the shape of implants. For bone and tooth replacements, porous gradient FGMs are generally used because their properties match the properties of natural bones. Generally, porosity gradient FGMs are used to manufacture skeletal replacement



implants because their appropriately graded porosity assists in minimizing stress shielding (Thieme et al., 2001). Some gradient porous dental implants, which are made using titanium, improve the Osseo-integration implant properties (Suk, Choi, Kim, Do Kim and Kwon, 2003). Moreover, the hydroxyapatite (HA) is almost like the bimodal human bone structure that allows growth of new tissues, and also provides a patient with the valuable mechanical properties for movement (Tampieri, Celotti, Sprio, Delcogliano and Franzese, 2001; Rodríguez-Lorenzo and Ferreira, 2004).

#### **2.2.4 Defense Production**

FGMs have remarkable penetration-resistance that limits crack propagation in a surface, which is very useful for utilization in the defense equipments. Some FGMs are utilized for manufacturing defense equipments such as armor plates, cutting plates, and bullet-proof vests/shields. They are also placed on the vehicle bodies to make them bullet-proof.

#### **2.2.5 Energy/Power Generation**

Power generation and energy conservation industries are rapidly changing industries, which are continuously in search of useful new materials. They make use of FGMs for increasing the efficiencies of their equipments. They are used to manufacture sensitive equipments such as inner nuclear reactor walls, solar panels, energy conserving thermo-electric converters, solar cells, pressure vessels/tubes, and graded electrodes to produce solid oxide fuel. Moreover, some piezo-electric FGMs are used to make ultrasonic transducers, fuel cells, thermal barrier coatings, and coatings of turbine blades.

#### **2.2.6 Electrical/Electronic Equipments**

FGMs are widely used to make electronic and electric devices. They are mainly applied to reduce the field-space and electrode field stresses (Shumiya, Kato and Okubo, 2004), manufacture semi-conductors such as diodes, sensors and insulators. These thermal-shielding elements are extensively utilized for manufacturing micro-electronic devices, and generally, they are manufactured with carbon nanotube FGMs (Kato et al., 2006).

### **2.2.7 Marine Industry**

FGMs are extensively used in marine equipments. They are used for manufacturing different components and bodies of ships and submarines. The components, which are manufactured using functionally graded materials, include diving cylinders, propeller shafts, piping systems, sonar domes, and cylindrical pressure hulls.

### **2.2.8 Opto-Electronics**

These materials are also used to manufacture different opto-electronic components and devices. This industry mainly uses optical fibers, GRINSH lasers, lenses, solar cells, high-efficiency photo detectors, tunable photo-detectors, magnetic storage devices, and semiconductors with different refractive indices.

### **2.2.9 Sports Equipments**

Some FGMs are utilized in sports equipment manufacturing specifically for manufacturing durable skis, golf clubs, and tennis rackets. They are made using selective FGMs.

### **2.2.10 Others**

Utilization of FGMs is widespread. They are used to make cutting tools, tools requiring high thermal strength, dies, fire-fighting equipments, fire-proof doors, stainless steel razor blades, helmets and spectacle frames (Miyamoto, Kaysser, Rabin, Kawasaki and Ford, 2013). They are also used to manufacture pressure vessels, MRI scanner cryogenic tubes, laptop bodies, fuel tanks, x-ray tables and musical instruments. They are used on a large scale in Japanese products, which is comprehensively mentioned by Miyamoto (Miyamoto, 1996). In future, the FGM application is likely to increase, and it will substantially increase in case their production costs are decreased.

### 3. PRODUCTION METHODS OF FUNCTIONALLY GRADED MATERIALS

#### 3.1. Filtration/Slip Casting

When a porous structure is dipped into a sequence of slurries, which have different characteristics, the liquid enters the pores with the help of capillary forces. These forces leave the layers on the surface with a stepped gradient (Moore, 1993). These principles also apply in case of sequential slip casting. Filtration and slip casting have a potential for large-scale production in case a few layers fulfill the application needs (Kieback, Neubrand and Riedel, 2003).

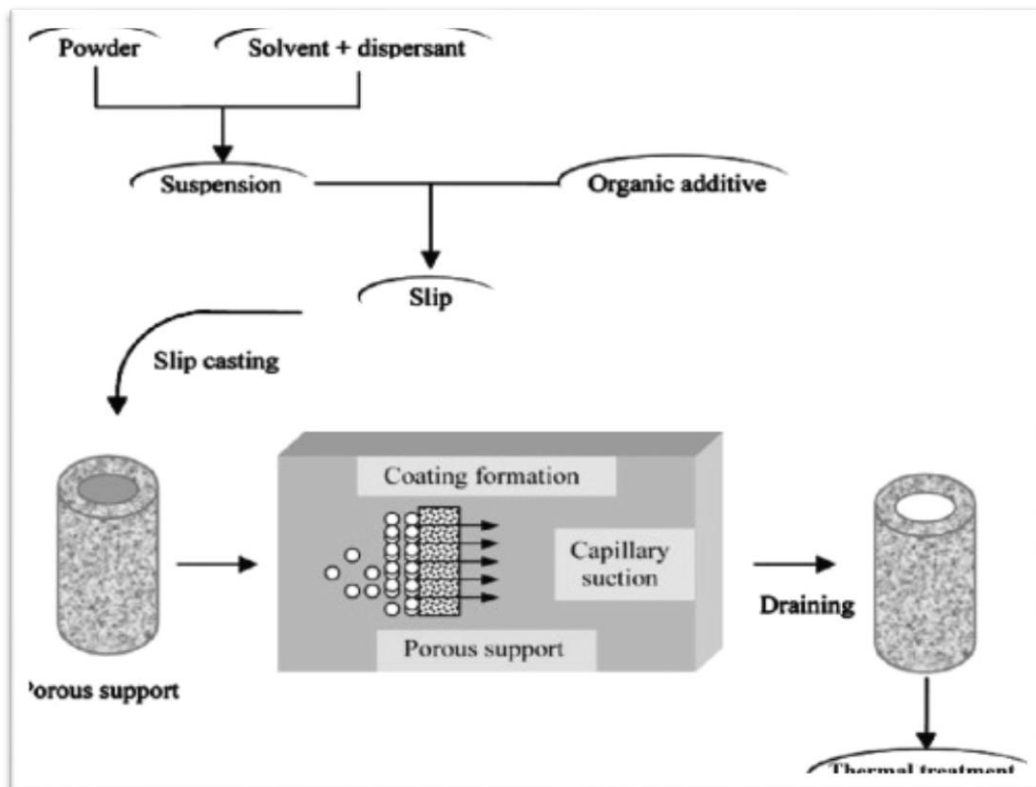


Figure 3.1. Filtration/Slip Casting process

#### 3.2. Liquid Metal Infiltration Method

Infiltration suits those FGMs, which have varying melting points. For this process, a semi-processed form is first developed that has appropriate porosity gradient. It is later infiltrated with the melted material of the component, which has lower melting point. The semi-developed form only has open pores, and it should not dissolve in the melt. The mentioned infiltration procedure suits ceramic, metal and glass FGMs but

generally, metals and ceramics are not wet (at wetting angle  $\theta > 90^\circ$ ), and the pre-developed forms/pre-forms aren't spontaneously infiltrated. For infiltrating large pores, pressure is applied during the infiltrating process (Kieback, Neubrand and Riedel, 2003).

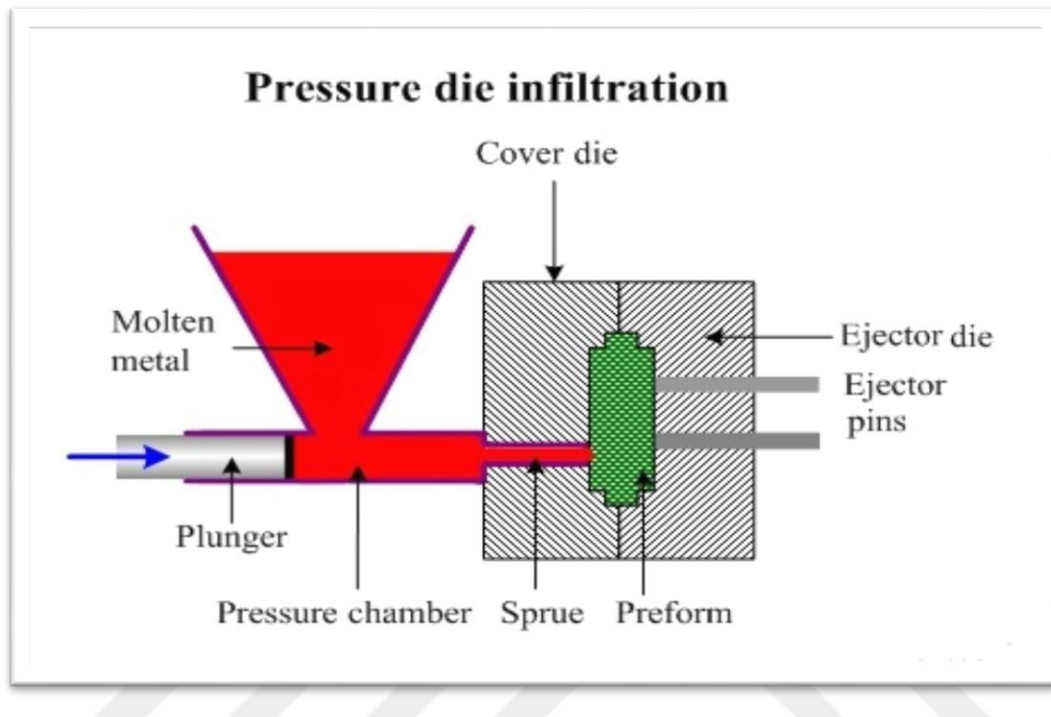


Figure 3.2. Pressure die infiltration process

### 3.3. Centrifugal Casting Method

The gravitational force and its impacts are used in this process for producing FGMs by spinning the mold. This process is applied for manufacturing cylindrical components. In this process, molten metal is released in a rotating mold. The molten metal solidifies during the rotation of the mold. Centrifugal casting has some advantages such as low porosity, high mechanical properties and uniform microstructure. The compositional gradient has been mainly obtained through the centrifugal force difference that is generated by the density differences between the solid particles and molten metal (Gupta and Talha, 2015; Watanabe, Yamanaka and Fukui, 1998; Watanabe, 2000).

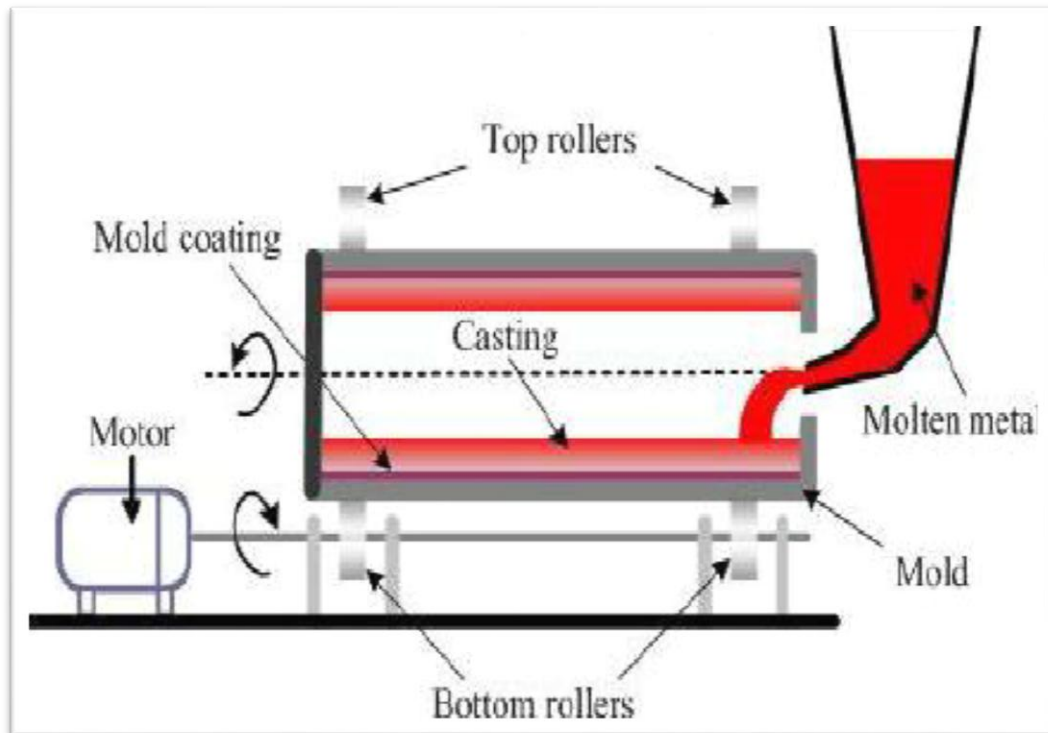


Figure 3.3. Centrifugal casting process

### 3.4. Ribbon Casting Method

The ribbon/tape casting method is implemented when the slurry mixture is spread on a moving belt, which passes under the blade edge on the moving belt. This shapes the slurry to make it acquire uniform thickness. For preparing the slurry mixture, the powder mixture is mixed in an organic solvent. Appropriate binders and plasticizers are applied. Then, the slurry is shaped to make it film-thick that finally acquires the tape shape. In this case, the size may be variable, which may be several meters maximum or at least a few millimeters thick. The thickness is set with the help of a casting blade (Gasik, 1998). Then, the solvent is dried, which releases a green residue. Stepped FGM gradients are manufactured through stacking the tapes, which have different compositions. When the tape stack is produced, it is sintered at a high temperature (50°-200°C) and 3-30MPa pressure. At high temperature and pressure, the stacked graded part is sintered that helps removing the organic binder. It is useful for increasing the components' density. A major benefit of this process is producing high-resolution FGMs; however, this process leads to limited component strength but that depends on

sintering pressure and temperature (Rhee, 2007; Chumanov, Anikeev and Chumanov, 2015).

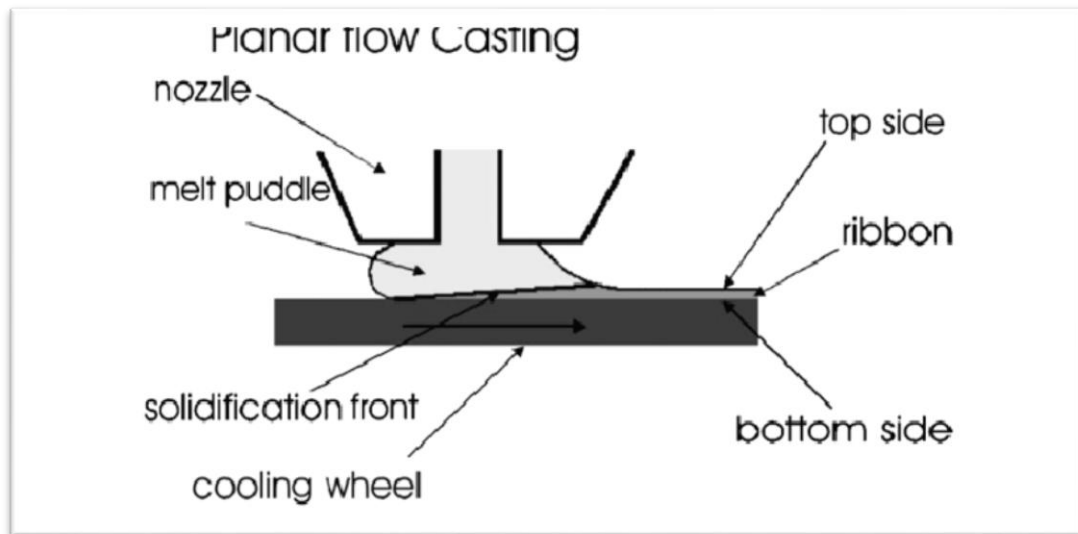


Figure 3.4. Ribbon casting process

### 3.5. Coating Methods

Sulzer-Metco recently developed PS-PVD (plasma spray–physical vapor deposition) method, which is in fact a hybrid deposition process. This process is a combination of PVD process, and economical and conventional low-pressure plasma-spraying (LPPS) methods that evaporate the coatings. The LPPS method is used in the pressure range 50-200mbar, which allows deposition of very thick and very thin coatings (at least 1mm thick) (Udupa et al., 2014). When the operating pressure is reduced, the plasma flame ranges between 50 and 500mm, which assures homogenous and uniform coating. For stable PS-PVD procedure, the operating pressure should be between 0.5 and 2mbar with more than 2m plasma flame length. In this case, the flame diameter ranges from 200 to 400mm. Obviously, the pressure requirement for PS-PVD procedure is more than the PVD process. A high plasma stream velocity (more than 2000m/s) along with high plasma stream temperature easily vaporizes the feedstock, which consequently allows coating deposition in other places besides the inner places (Udupa et al., 2014).

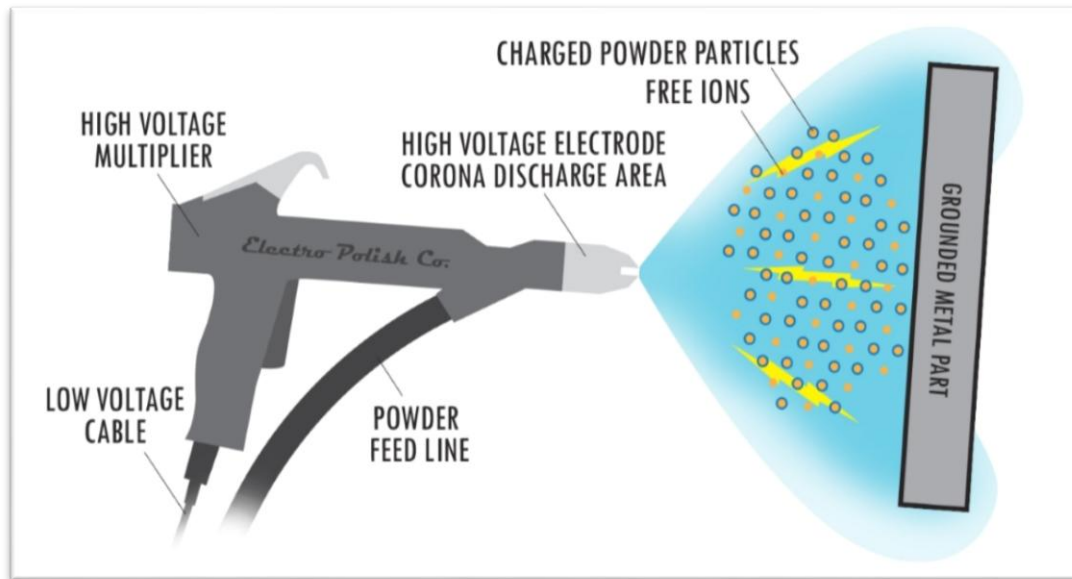


Figure 3.5. Coating process

### 3.6. Powder Metallurgy Method

Powder metallurgy is applied when there is a need for blending or molding. In this method, fine powdered materials are first blended and then they are pressed until they acquire the needed shape. Later, the mixture is heated to join the surfaces. This method is also used in places, which involve tiny components and there is a need for high precision. A small amount of material waste and unusual mixtures can be used for manufacturing parts for the automotive industry, home appliances and recreation equipments (to name a few). When the metallic powders are produced and classified, the classical PM process sequence is followed in three main stages: (1) mixing powders, (2) compression and (3) sintering. Some optional and final secondary operations are also conducted.

#### 3.6.1. Powder Production

Powder production method determines other properties such as amount, size, purity, shape, and production cost of powder. The advantage of powder production is to predict the shape and size of the powder grains. Almost any material can be converted into powdered form but the production method selected for making powder depends on the cost, reactions, and characteristics. Mechanical methods, electrolytic production,

chemical production, atomization techniques, and vaporization methods are among those methods, which are used for powder production.

#### **3.6.1.1. *Production with Mechanical Methods***

Both mechanical methods and other production methods are mainly based on creating new surface areas when the energy is applied. Mechanical production methods have four basic forms. Impact is separation of the desired materials into small pieces at a high speed with the help of hammer or other heavy tools. Abrasive milling is a process, in which, abrasive balls (these balls vary according to the properties of the material) are placed in a drum and the raw material is separated into small pieces by frictional force of the balls. The process is generally used to make powder of brittle materials. It is unsuitable for ductile materials because they deform instead of converting into powder. It is a production method, which is performed with basic machining processes such as cutting (machining), turning, and grinding. Irregularly shaped large pieces are produced by implementing these processes. Although it is suitable for small-scale powder production, it is not the first choice for powder production because it is inefficient and slow. Powders like silver, which is used as amalgam filler in the dental filling, is produced by this method. All the materials, which are exposed to compressive force, show tendency to transform into powder when they come to the breaking point. Based on this property, desired materials are transformed into powder by compression force. One of the most commonly used methods is mechanical alloying process. In order to obtain a finer and more homogeneous microstructure, it is assured that solid powders are periodically welded and then they are ground to make powder.

#### **3.6.1.2. *Atomization Techniques***

In this technique, the desired material is passed in the liquid form. This process is carried out by degrading the molten liquid into droplets. The droplets are frozen, which help obtaining particles. The most commonly used ones are gas atomization and liquid atomization. Gas atomization is done by breaking down liquid metal droplets with the help of air, nitrogen, argon or helium. Pure powders can be obtained through gas atomization, which completely takes place in the inert gas environment. The obtained particle shape is generally spherical. Liquid and water atomization is a method of breaking up molten liquid droplets by using oil and water. Cleaning is required when the process is over because the obtained material might react with water.



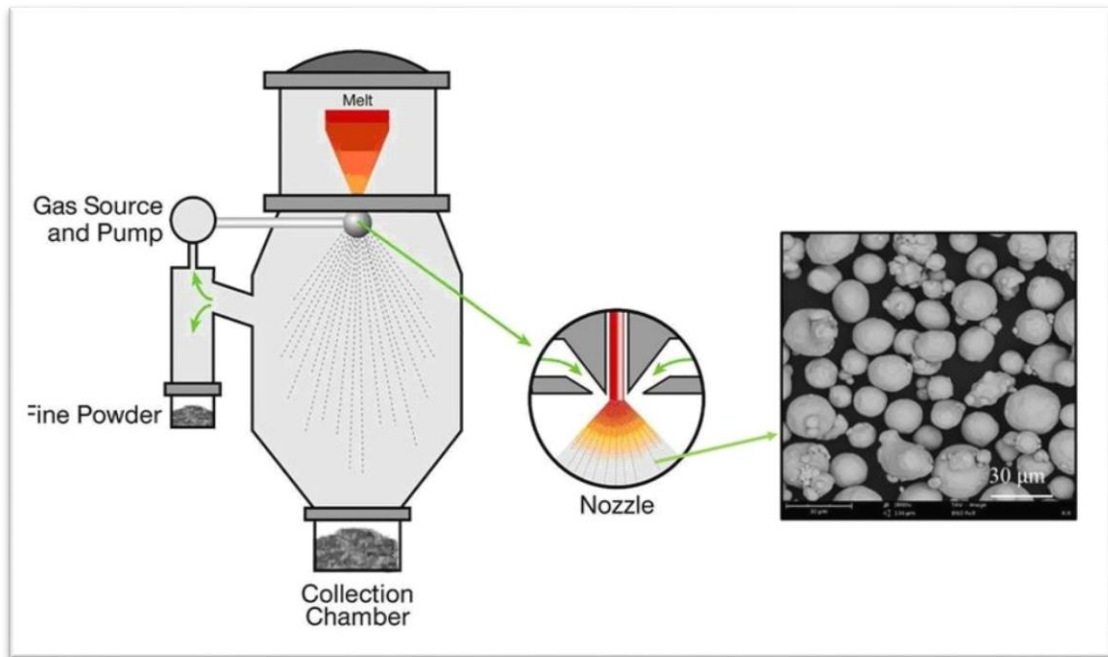


Figure 3.6. Gas atomization technique

### 3.6.2. Powder Mixing and Blending

Mixing: When a chemical compound powder is mixed in different sizes, the mixing process combines different material powders, these processes produce unique composites, which can be either wet or dry. In order to obtain the desired characteristics in the finished products, a great majority of the powders are mixed with other powders, binders and lubricants. During sintering, sufficient diffusion must be assured to create uniform chemistry and structure.



Figure 3.7. Powder mixing and blending machine

### **3.6.3. Compression**

The mixed powders are pressed into molds under high pressure for molding them in the desired shapes. A workpiece is called "green compact" or just "green" when it undergoes compression process. It means that the workpiece is "not yet completely processed." Most of the compressions are made with mechanical, hydraulic and pneumatic pressing equipments, and rigid tools. Powders do not flow like liquid, they are pressed until their particles become homogenous and counter force is generated; this counter force is formed by the combination of friction between the particles, the mold surface, and the lower punch resistance.

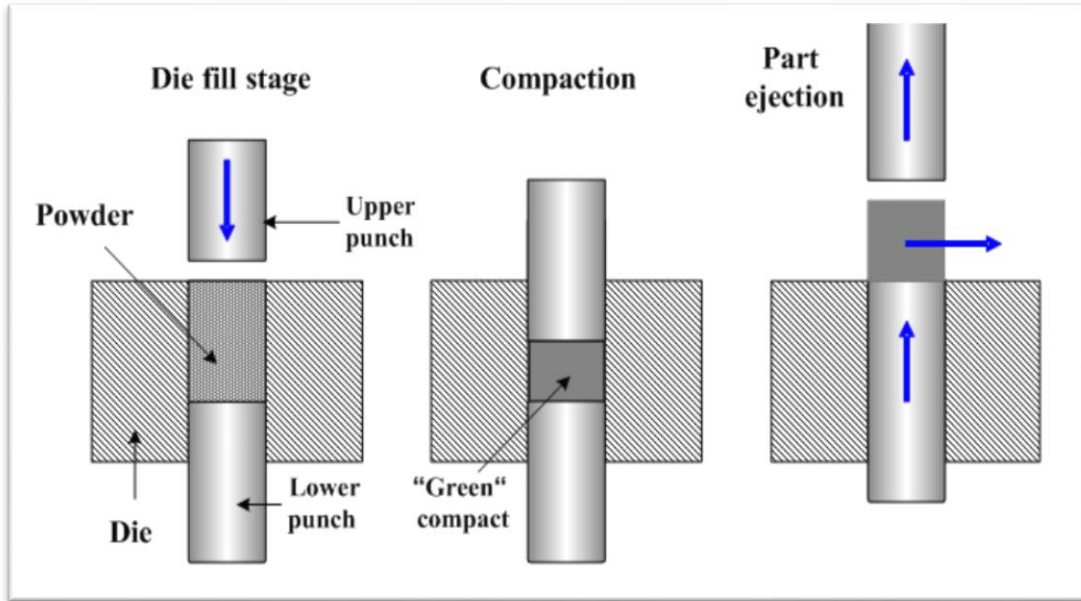


Figure 3.8. Compression process

### 3.6.4. Sintering

Sintering is one of the most important processes in powder metallurgy. Bonding during sintering involves significant events such as polymer burning, dimensional change, and coarsening of the microstructure. Solid state diffusion and bonding occur at high temperatures. The cooling process reduces the temperature of the products in temperature-controlled atmosphere. This process is carried out in oxygen-free conditions.

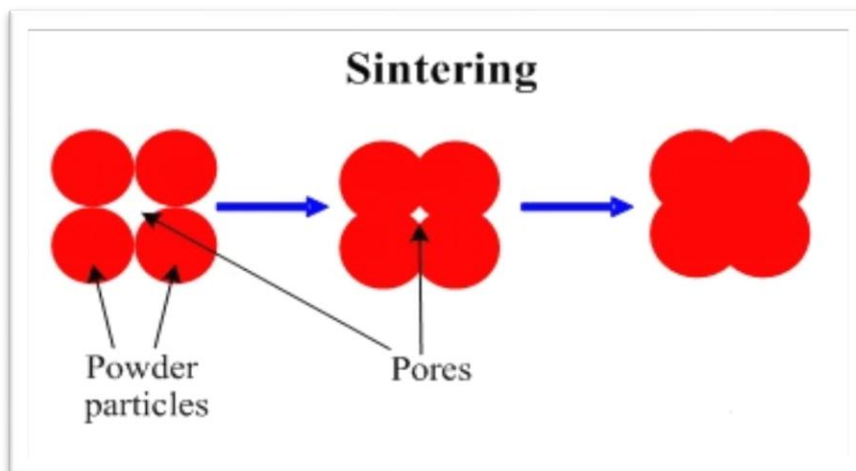


Figure 3.9. Sintering process

#### **4. BRONZE ALLOYS**

Bronze is one of the very useful alloys. It is a combination of copper, 12% tin and some other metals including zinc, nickel, manganese or aluminum. In some cases, metalloids or non-metals including silicon, phosphorous or arsenic are also added because they help increasing hardness of the alloy, which becomes substantially harder than the pure copper. Moreover, it has useful characteristics including ductility, stiffness, and machinability.

Archeological researches show that bronze has been the hardest alloy, which was commonly used in a historical era termed as the Bronze Age. Bronze Age was witnessed in Western Eurasia and India in 3000BC. It was popular in China in 2000 BC (Thorp, 2006). Iron Age replaced the Bronze Age that began in 1300 BC, and the widespread use of Iron was witnessed in Eurasia in 500 BC despite the fact that bronze remained popular during the Iron Age.

Since many historical pieces had been made with the help of different bronzes and brasses (combinations of copper and zinc), the scholarly descriptions of older remains and modern museums call them "copper alloys".

##### **Physical properties of bronze include:**

- Bronze has copper color.
- It is odorless.
- It conducts electricity and heat very well
- It is tougher than iron/copper
- It has low friction.
- The melting point of Bronze ranges between 950C and 1050C
- It is solid at room temperature.
- Relative density of Bronze is 8.8g/cc
- It does not dissolve in water
- It is ductile.

##### **Chemical properties of Bronze include:**

- Bronze oxidizes in the air that deposits a thin copper oxide layer on its surface.
- It reacts with several pollutants and their sulfur compounds.
- It reacts with strong acids to produce hydrogen.
- At room temperature, it is normally stable.
- Bronze resists seawater corrosion.

## **Applications of Bronze alloys**

It is a necessary alloy for making medals, musical instruments and sculptures. It is helpful to make bearings and bushes of many machines because of its low metal friction. Bronze is widely used for several marine equipments and bodies because it offers excellent corrosion resistance against the sea water.

Bronze is used to make bells but for making bells, 23% tin is added to form the alloy.

Almost all the professional cymbals (brass plates for drummers) are manufactured using bronze that provides both appropriate sound as well as durability.

Coin-making industry uses bronze because almost all the “copper” coins are in fact made of bronze. For making coins, 1% zinc and 4% tin are added.

In addition to coins, bronze has been used for manufacturing medals and prize shields for centuries. Now, bronze medals are given to honor third position holders in different competitions.

## 5. REINFORCEMENTS FOR COMPOSITE MATERIALS

Composite materials undergo reinforcement stage to gain more strength than they have in the matrix form. It provides following characteristics:

- Less density
- Good chemical and mechanical compatibility
- Good thermal stability
- High Young's modulus
- High tensile strength and compression
- Good processability
- Cost effectiveness

Normally, inorganic non-metals (ceramics and carbon fibers) have acceptable combinations of the mentioned properties but aligned fibers acquire the most effective reinforcement; so, they are very popular because they are needed for manufacturing high-performance equipments. Moreover, development of the textile technology can result in providing the needed properties and fabrication ease. A majority of fiber reinforcements consist of tough/brittle carbon or ceramics including graphite, glass fiber, silicon carbide fiber, boron fiber, aramid fiber, alumina fiber, and high-density polyethylene fiber (Chawla, 2012). In this project, we used the following reinforcements:

### 5.1. Silicon Carbide (SiC)

It is a ceramic that is so hard that it is the hardest substance after diamond, boron carbide and cubic boron nitride. Obviously, it is chemically inert and wear resistant, which makes it a reliable ceramic and abrasive for challenging operating situations.

SiC is generally produced when petroleum, coke, quartz or silica are combined in an electric resistance furnace. The mixture chemically reacts within the temperature range 1700-2500°C, which forms  $\alpha$ -SiC. The reaction is given below:



Table 5.1. General characteristics of Silicon Carbide (SiC)

Properties			
Chemical formula	Csi	Compression strength(MPa)	3900
Molecular weight	40.11	Crystal structure	FCC
Color	Black,Green	Melting Point (°C)	2730
Density (g/cm <sup>3</sup> )	3.21	Thermal conductivity (W/m K)	120
Hardness (GPa)	29	Specific heat (J/kg K)	750
Young's modulus (GPa)	410	Lattice parameters (nm)	a <sup>0</sup> =0.189, c <sup>0</sup> =0.308
Poisson's ratio	0.14	Unit cell volume (10 <sup>-22</sup> cm <sup>3</sup> )	1.259

For long time, silicon carbide has been a popular material in the power electronics because it has impressive electrical and physical properties that enable it to endure very high temperatures and voltages. The applications, which made use of SiC, include ball valve components, turbine parts, seals, vanes, bearings, kilns, wear plates, heat exchangers, and semi-conductor wafer-processing equipments.

## 5.2. Boron Carbide (B<sub>4</sub>C)

As mentioned earlier, B<sub>4</sub>C, is the third toughest substances after diamond and boron nitride. Another useful property is that it directly synthesizes from carbon and boron elements with the help of metallothermic procedure. Moreover, another popular procedure called as carbothermic reduction makes use of inexpensive chemicals such as boron anhydride (B<sub>2</sub>O<sub>3</sub>) or boric acid (H<sub>3</sub>BO<sub>3</sub>). Using this procedure, boron carbide is produced using carbon reduction.



Boron carbide provides excellent hardness (2900-3100kg/mm<sup>2</sup>) to things it is used to make. Besides that, it has excellent electrical, thermal and mechanical properties. Moreover, it has low cost and density (2.51g/cm<sup>3</sup>), and substantial inertness that makes

it suitable for micro-electronics, spacecrafts, military equipments, medical equipments and nuclear devices (Ryan et al., 2002). Table 5.2 shows general characteristics of B<sub>4</sub>C.

Table 5.2. *General characteristics of Boron Carbide (B<sub>4</sub>C) (Pierson, 1996)*

Properties			
Composition	(B <sub>11</sub> C)CBN	Compression strength(MPa)	2750
Molecular weight	55.26	Crystal structure	Rhombohedral
Color	Black	Melting Point (°C)	2450
Density(g/cm <sup>3</sup> )	2.52	Thermal expansion(1/°C)	5x10 <sup>-6</sup>
Hardness(GPa)	27.4-34.3	Electrical conductivity(Ω <sup>-1</sup> m <sup>-1</sup> )	140
Young's modulus(GPa)	290-450	Lattice parameters(nm)	a <sup>0</sup> =0.55991, c <sup>0</sup> =1.20740
Slip modulus(GPa)	165-200	Unit cell volume(nm <sup>3</sup> )	3.27809
Bulk modulus(GPa)	190-250	Space group	R3m
Poisson's ratio	0.18		

### 5.3. Molybdenum Carbide (Mo<sub>2</sub>C)

Molybdenum carbide is an excellent transition metal carbide that has useful chemical and physical properties including hardness, high melting point, oxidation, corrosion resistance, electrical conductivity and high abrasion resistance (Chen et al., 2011); therefore,, it is considered as significant for heterogeneous catalysis. Table 5.3 shows general characteristics of molybdenum carbide.

Table 5.3. *General characteristics of molybdenum carbide (Mo<sub>2</sub>C)*

Properties			
Compound Formula	Mo <sub>2</sub> C	Compression strength(MPa)	901
Molecular weight	203.91	Crystal structure	BCC
Color	Gray	Melting Point (°C)	2690
Density (g/cm <sup>3</sup> )	9.18	Young's modulus (GPa)	227-553
Vickers Microhardness	1950		

Molybdenum carbide (Mo<sub>2</sub>C) is an affordable and cheap material, which is basically used for hydrocarbon reformation since its electronic structure is just like noble metals (Dantas, Lopes-Moriyama and Souza, 2018). During the recent years, Mo<sub>2</sub>C was successfully tried and used during the active phase both as powder for producing



electrodes to detect several substances, and for high-performance power storage devices.

#### 5.4. Titanium Carbide (TiC)

TiC acts in the homogeneous phase in the limit  $0.47 < x < 1$ , and it has structure of table salt (NaCl). Since it has a reasonable chemical inertness, high melting point, hardness, and good electrical conductivity, TiC is widely used in large number of applications in different industries. They are mainly used for cutting tools, and also as wear-resistant materials, and anodes (lithium-ion batteries) (Gou, Zhang and Chou, 2017). Table 5.4 shows general characteristics of TiC.

Table 5.4: *General characteristics of Titanium carbide (TiC).*

Properties			
Density (g/cm <sup>3</sup> )	4.93	Enthalpy (kJ/g )	2.8
Molecular weight	59.89	Poisson's ratio	0.19
Color	Black	Melting Point (°C)	3065
Crystal structure	FCC	Thermal expansion (ppm/°C)	7.9
Hardness (GPa)	30	Electrical resistivity (μΩ.cm)	105
Young's modulus (GPa)	460	Lattice parameters (nm)	a <sup>0</sup> =0.430-0.433
Space group	Fm3m	Specific heat (J/g .K)	0.56

## 6. LITERATURE REVIEW

Mahamood et al. (2012) in their study, FGMs are advanced materials, which have different properties based on their composition. FGM properties vary according to the constituent materials, so, they are used in several applications, which raise the fabrication and material processing costs. If these processes are improved, their cost will decrease, which will promote their overall utilization. The fabrication processes, application areas, and excerpts of some recently conducted researches have been discussed. There is a need to increase research efforts to develop a more convenient, feasible and economically viable FGM fabrication method, also termed as SFF method. Developing the SFF procedure is needed, and further research in this area will reduce the cost of FGM manufacturing and increase their productivity (Mahamood, Akinlabi, Shukla and Pityana, 2012).

Toudehdehghan et al. (2017) pointed out that, Material engineering is an important corner stone of several engineering applications. Continuous exploration and experiments resulted in conversion of many basic materials into many inorganic as well as organic compounds, which finally resulted in the FGM development. FGMs are cutting edge substances, which offer specific material properties. In addition to reviewing FGM applications, also mathematical idealization of the FGMs has been discussed. FGMs are heterogeneous, and their mechanical properties smoothly change their spatial coordinates. For correctly analyzing FGMs, their complicated heterogeneous microstructures and homogenization schemes should be simplified. Through this process, some closed-form solutions of basic solid mechanical problems can be found. Consequently, FGMs are unique because of their individual material structures; therefore, there are limitless possibilities of their use in the futuristic engineering applications (Toudehdehghan, Lim, Foo, Ma'arof and Mathews, 2017).

Sharma et al. (2001) noted that, The metal matrix composites (MMCs) have interesting tribological properties because they are needed for many applications including cylinder liners, bearing sleeves, aircraft brakes, and pistons. The SiC particles and unreinforced particles (reinforced phosphor-bronze alloy) have been studied in terms of applied loads and sliding speed when there is no lubrication. The SiC content within composites varied 1-5% (in steps of 2% by weight). For analyzing their wear rate, a

pin-on-disc wear testing machine was used, for which, the counter face was used in the form of EN24 steel disc. 20-160N loads were applied in 20N steps at 1.25, 1.56 and 1.87m/s speeds. Results of the experiment show that wear rate increased both in case of matrix alloy and composites when the load and the sliding speed were increased but the composites wore out quicker than the alloys. When the critical load was applied, mild wear transformed into severe wear in case of composites and the unreinforced alloy. It is important to mention that the transition loads for the unreinforced alloy were substantially lower than the loads for composites; therefore, transitional loads increased when the SiC particles' weight percentage was increased but they decreased when the sliding speed was increased (Sharma, Satish, Girish and Somashekar, 2001).

Ali et al. (2016) mention, Bronze-40%w composites are successfully prepared by compacted mixture of powders. The green compacts of bronze (40wt %) were sintered for 60 to 120mins at 750, 850, and 950°C. Scanning Electron Microscopy (SEM) technique was used for testing microstructures of the raw powders and composites. The results revealed that the densities increased when compaction load, sintering time and temperature were increased. The average of Vickers hardness for composites 60wt% bronze (40wt %) was 91.5. Tin electroplating improves corrosion resistance of the bronze by electroplating with tin-based electrolyte with suitable current (0.01A) for 4 hours. In this way, coating layers of 45-60µm were obtained. Corrosion rate measurements were done for different samples under different conditions (non-coating, coating and scratched coating). The corrosion current of the scratched coating sample was found more than the unscratched samples because of cathodic protection of the exposed area of the composite substrate. Consequently, the corrosion rate of scratched coating sample was more than the unscratched sample (Ali, Suppiah and Muayaduldeen, 2016).

Bannan et al. (2003) in their study, Investigation was carried out to understand the composites such as aluminum bronze (AB2) and titanium carbide (TiC) reinforced copper, and their in-situ fabrication, which takes place when aluminum composites undergo carbo-thermal reduction of titanium in an induction furnace. For this purpose, inert atmosphere was assured, and carbon monoxide was obtained as a byproduct when the reaction took place between graphite lid, induction field, and graphite crucible. The particles of titanium carbide (order 1-3µm) were processed in aluminum bronze at almost 1250°C. On the other hand particles of order 1-6µm were produced in copper at

around 1330°C. Dispersion concentrations (20% and 6.5%) of titanium carbide were found for copper and aluminum-bronze. Moreover, the evidence was found, which proved that iron can be utilized as a dispersion medium in case of particles of titanium carbide in the aluminum-bronze alloy (Bannan, Temple and Jones, 2003).

İpek et al. (2017) pointed out that, Boron carbide (B<sub>4</sub>C) reinforced copper-based metal matrix composites (MMCs) were manufactured using powder metallurgy method and tribological behavior of compacted composites were investigated. B<sub>4</sub>C reinforcement was selected at different ratio from 2%wt to 10%wt. Powders was compacted under 735±1MPa pressure in a die using the cold pressing method. Sintering of the samples was performed for two different sintering durations: 1 hour and 3 hours in Ar gas atmosphere at 900°C. Computerized pin-on-disc setup was used to conduct tribological tests in dry sliding condition. Tribological tests durations were from 1 to 5 hours. Wearing surfaces were investigated with the help of a Scanning Electron Microscope (SEM), which helped understanding wear mechanisms. In addition, porosity and tribological behavior of the manufactured samples were explored. It was found that the porosity of the samples increased when the B<sub>4</sub>C content increased. Moreover, wear resistance increased with increasing reinforcement content. Wear loss was decreased with increasing sintering time. Hardness of the composites were increased with increasing sintering time (İpek, Cuvalci and Celebi, 2017).

Xie et al. (2017) noted that, Powder metallurgy was used to prepare bronze/ceramic composite with mass ratio of bronze bond: mCu: mSn =85:15 and ceramic bond: 3:1. The sintering temperature influences the structure of ceramic/bronze composite bond; so, the mechanical properties were analyzed with the help of electro-mechanical universal testing machine. Moreover, scanning electron microscope (SEM), Rockwell hardness tester, and X-ray diffraction were used, and the findings show that the rise in the sintering temperature increases the blending strength, density, and impact strength for both ceramic and bronze composite bonds. They first increase with increasing temperature but later reduce when the temperature is increased further. At 620°C sintering temperature, the ceramic/bronze composites' mechanical properties are at peak with bending strength 170MPa, density 5.43g/cm<sup>3</sup>, impact strength 9.76kJ/m<sup>2</sup>, and 126HRB hardness. The increasing temperature of Cu and Sn alloy caused bronze and ceramic to interact with each other. At 620°C sintering temperature, copper and tin

are  $\alpha+\delta$  eutectoid, and the ceramic and metal bonded well that improved the ceramic/bronze composite bond properties (Xie, Hou, Li, Huang and Ding, 2017).

Naebe and Shirvanimoghaddam (2016) mention that, FGMs are increasingly becoming the much needed modern materials because of their broad range of applications in several critical industries. A majority of the researches on FGMs have been conducted on ceramics or metal-based materials; therefore, the available knowledge on applications and properties of polymer FGMs is limited. Availability of many processing methods and wider applications may be the reasons, because of which, very few researchers focused on them. Gradient microstructures, which exist in nano-reinforced polymer composites, have great potential in terms of futuristic engineering applications. Fabrication of biopolymer FGMs uses advanced techniques including use of nano substances (e.g. graphene, carbon nanotube (CNT) and boron nitride (BN)) and near-field electro-spinning, which can ultimately lead towards multi-functional material development. Those materials need improved physical, mechanical, and chemical performance, after which, they will be usable in bio-applications. Other than well-established methods for FGM fabrication, several less utilized methods are available, which may be used to develop next generation gradient structures in the future. High temperature microwave sintering assures valuable energy and time saving, and hopefully, it will be useful to develop new FGMs in the future, which will have more density and better thermal stress distribution. Microwave sintering is an efficient and effective method for metals, ceramics, and polymers. Along with advancement in the additive manufacturing processes, several significant opportunities exist to develop new and multifunctional gradient compositions for FGM applications. High control and accuracy of this technique makes it possible to grade compositions with complex geometries. These compositions are applicable in several applications including biocompatible prosthesis applications (Naebe and Shirvanimoghaddam, 2016).

Sobczak and Drenchev (2013) said in their study, The properties and graded structures of composites diverted the experts' attention towards material science and technologies because they had interesting and useful characteristics. So far, many production methods have been introduced to synthesize graded metal matrix composites. These production methods fall into the following two categories. In the first category, the arrangement of a few parts of the final product are arranged in a graded structure, which is later infiltrated through melting or sintered for obtaining composites with the required

properties and the graded structure; however, graded structure can also be obtained from the composite melt solidification, which happens in the methods of the second category. In this category, it is essential to apply external forces, which can be any of the following forces: centrifugal force, gravity, electromagnetic waves, magnetic force, or a combination of forces. Another adaptable and versatile process is plasma spraying, which helps obtaining the graded structure through thermal processes, and it mechanically and chemically resists the graded coatings on the surface. FGM development needs specific skill set and knowledge of physics, chemistry, and multiple engineering sciences because sometimes, application of FGMs is the only available option to meet the requirements of postmodern industries (Sobczak and Drenchev, 2013).

Radhika et al. (2018) pointed out that, One of the major objectives of the current project is fabricating Cu-10Sn/SiC composite ( $\text{\O}_{\text{out}}100 \times \text{\O}_{\text{in}}70 \times 100$  mm) and functionally graded unreinforced copper alloy (Cu-10Sn) applying horizontal centrifugal casting process. The tribological and mechanical properties of the obtained structure have been investigated. Also, the hardness and microstructure of the obtained structure along the radial direction of the castings have been analyzed and conducted the tensile tests at both the outer and the inner zones. The composite microstructure was evaluated, which showed that across the radial direction, the reinforcement particles created a gradient structure while in the inner periphery, highest reinforcement concentration was discovered. In this case, maximum hardness was found on the surface, which was 205HV. The results of the tensile test show that the inner zone of the composite had high tensile strength (248MPa). It was more than the unreinforced alloy and the outer zone. Since the mechanical properties of the inner periphery were better, we conducted dry sliding wear experiments to analyze the composite's inner area with the help of pin-on-disc tribometer. In this case, some parameters were: Sliding distance 500-1500m, load 10-30N, and sliding velocity 1-3m/s. These values were analyzed with the help of Taguchi L27 orthogonal array. Also, the effect of these parameters has been analyzed on the wear rate through variance analysis and signal-to-noise ratio. The analyses showed that load created the greatest impact (54%) on the wear rate while sliding distance was next to it with 18.2% impact, and the sliding velocity had 3.7% impact. The composite wear rate substantially increased when the load and the sliding distance

were increased; however, it decreased along with increase in the sliding velocity (Radhika, Thirumalini and Shivashankar, 2018).



## 7. EXPERIMENTAL STUDIES

### 7.1. Raw Materials and Production of Composites

In the present study, matrix powders were chosen. They included bronze powder (85% Cu and 15% Sn, -325 mesh particle size, 99.9% purity), SiC reinforcement powder (400 mesh particle size,  $\geq 97.5\%$  purity), TiC (-325 mesh particle size, 98% purity), Mo<sub>2</sub>C (-325 mesh particle size, 99.5% purity), and B<sub>4</sub>C (-325 mesh particle size, 98% purity).

Sample preparation was carried out through several stages, which can be summarized in the following steps:

Firstly, we calculated the volume of each layer of the sample (V).

$$V = \pi r^2 h$$

Where: r: radius of the sample.

h: thickness of the layer.

$$V = 3.14 \times (0.65)^2 \times 0.2$$

$$V = 0.265 \text{ cm}^3$$

Then we used the density to calculate the mass needed for each layer.

$$\text{Mass (m)} = \text{Volume (v)} \times \text{Density } (\rho)$$

$$m_{(100\% \text{ CuSn})} = V \times \rho_{(\text{CuSn})}$$

$$m_{(100\% \text{ CuSn})} = 0.265 \times 8.69$$

$$m_{(100\% \text{ CuSn})} = 2.30 \text{ gr} \quad \text{It is the net mass of the middle layer for all the samples, and for all the layers}$$

Table 7.1: Powder weights of samples

layers	Sample 1 (B <sub>4</sub> C content) weight (gr)	Sample 2 (Mo <sub>2</sub> C content) weight (gr)	Sample 3 (TiC content) weight (gr)	Sample 4 (SiC content) weight (gr)
1 <sup>st</sup> layer	2.2035	2.1575	2.3125	2.1395
2 <sup>nd</sup> layer	2.30	2.30	2.30	2.30
3 <sup>rd</sup> layer	2.2035	2.1575	2.3125	2.1395



After the calculation, powders should be weighted accurately using a sensitive balance (Photo 7.1)



Photo 7.1. Sensitive balance (4-digit)

- 1- Mixing: For the mixing process, the powders were subjected to mixing for 45 minute at the speed of 20rpm. 10 mixing balls were used for this process, and each one of them had 10mm diameter. The ball milling machine that has been used is shown in the Photo 7.2



Photo 7.2. Mixing machine

- 2- Pressing: In the pressing process, the powder is placed in a cylindrical mold with 13mm diameter (photo 7.3). The reinforcement powder was added to the powder matrix, after which, the composite was pressed at 500 MPa to produce a 6mm thick cylindrical sample with 13mm diameter (with three 2mm layers), as shown in Figure 7.1.

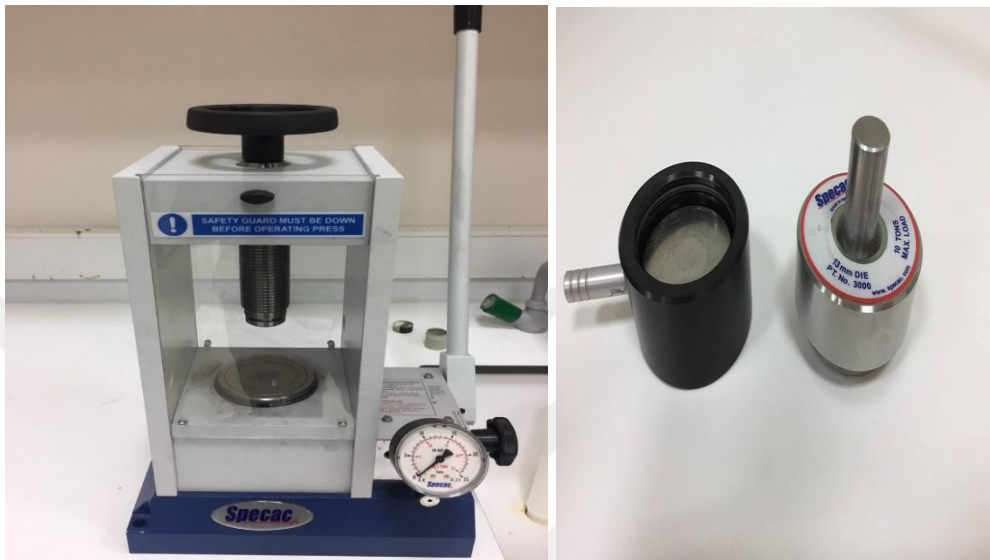


Photo 7.3. Pressing machine and the mold

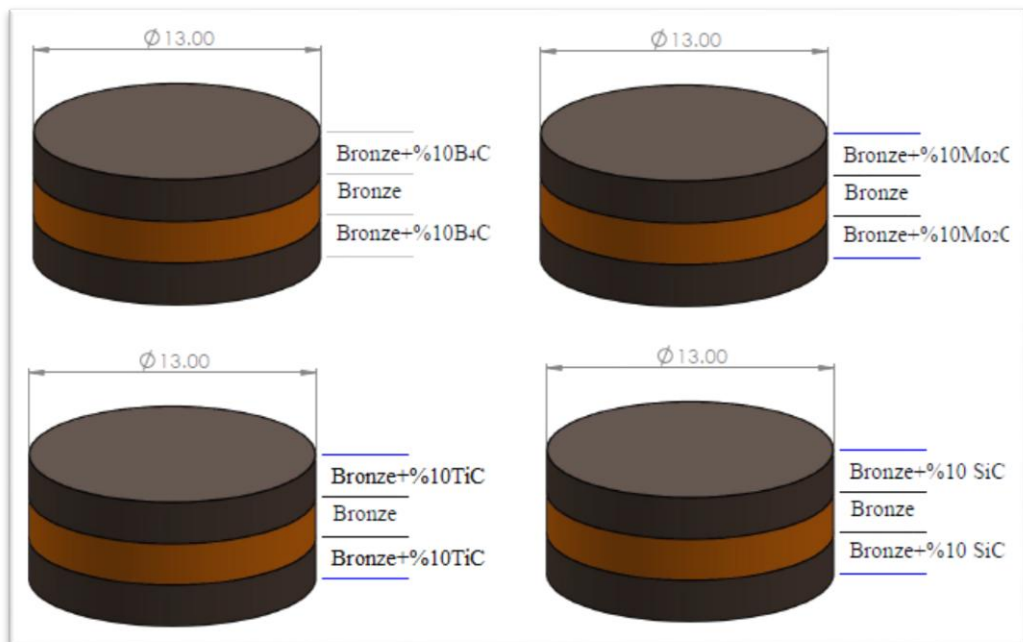
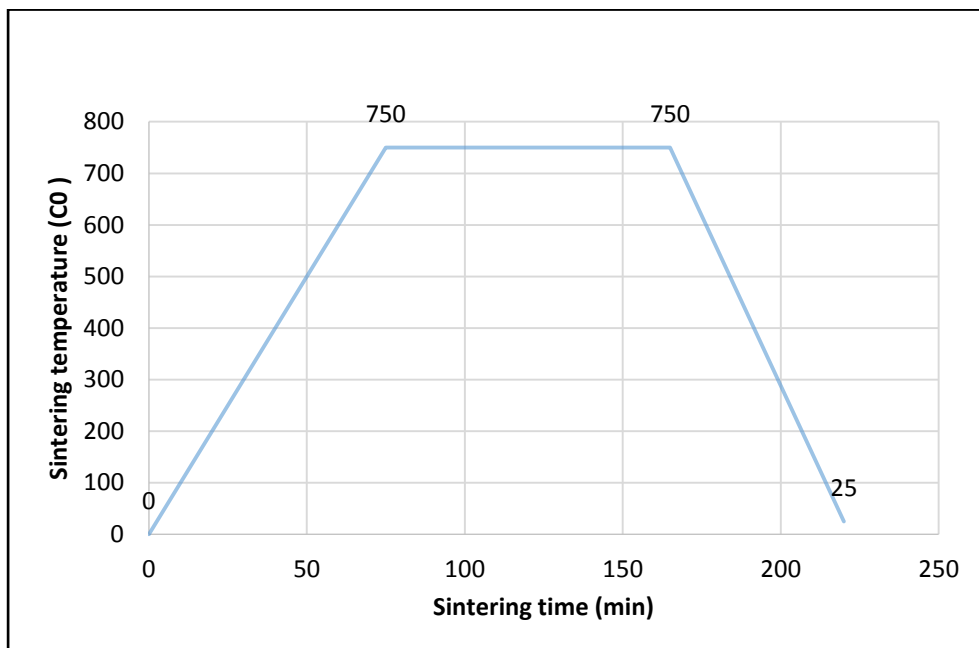


Figure 7.1. The samples shape and dimensions

- 3- Sintering: The samples were sintered in a tube furnace under protective argon gas atmosphere. The sintering temperature was 750°C and duration was 90min with heating and cooling rate 10°C/min as shown in the Chart 7.1. The photo given below shows the furnace that we used during the sintering process.



Photo 7.4. Tube furnace



Graph 7.1. Heating and cooling rate

## 7.2. Applied Tests

- Hardness Test
- Metallographic studies
- Microstructure examinations (Optical microscope, SEM-EDS and XRD)

### 7.2.1. Hardness Test

For determining the hardness level of the produced samples, we used Vickers hardness testing device at 200 gr load (Photo 7.6). For accurate determination of hardness, hardness values were measured from the upper, middle, and lower layers of the samples; so, three hardness values were taken from each sample.

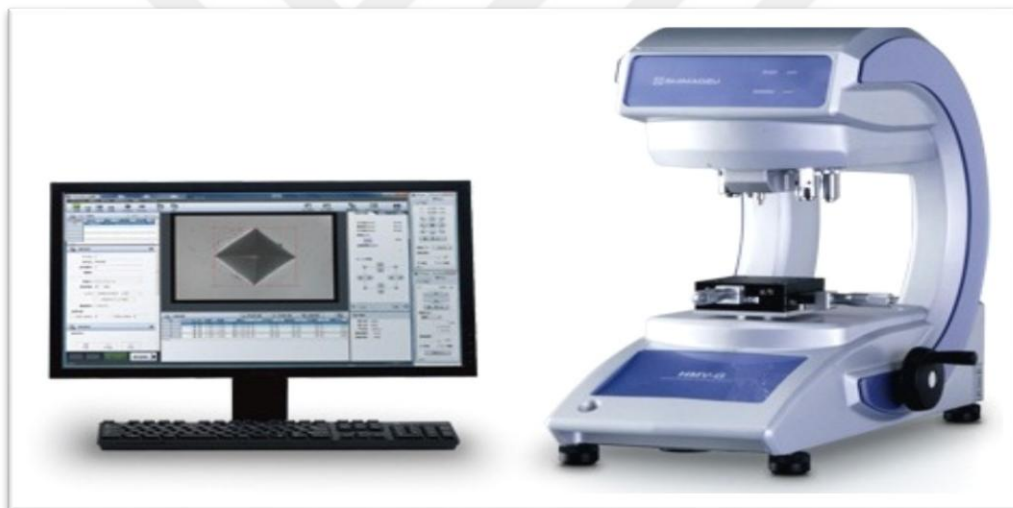


Photo 7.5. Vickers hardness testing device

### 7.2.2. Metallographic Studies

For metallographic examinations, the obtained metallography samples were cleaned on 60-1200 mesh papers. Then, the surfaces of the sockets were polished with the help of diamond spray. For microstructure investigations, the samples should be etched for 20 seconds in 5 grams  $\text{FeCl}_3$  + 50ml  $\text{HCl}$  + 100 ml  $\text{H}_2\text{O}$  solution. Energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM), and X-ray diffraction

(XRD) were used to study and understand the phase structures. Photo 7.6. Shows the grinding and polishing machine used in the faculty laboratory.



Photo 7.6. Grinding and polishing machine

### **7.2.3. Microstructure Examinations (Optical microscope, SEM-EDS and XRD)**

For optical examinations, Olympus GX41 inverted metal microscope and Stream image analysis system were used. Scanning electron microscope FEI QUANTA 250 FEG was utilized to analyze the samples' fracture surfaces. Besides SEM, EDS analysis was conducted to analyze the sample microstructural chemical composition. Moreover, X-ray procedure was accomplished to find out about the phase formation in the microstructure. For this purpose, Bruker D8 advanced device was used. Photo 7.7 shows the devices used in the microstructure imaging and phase analysis.

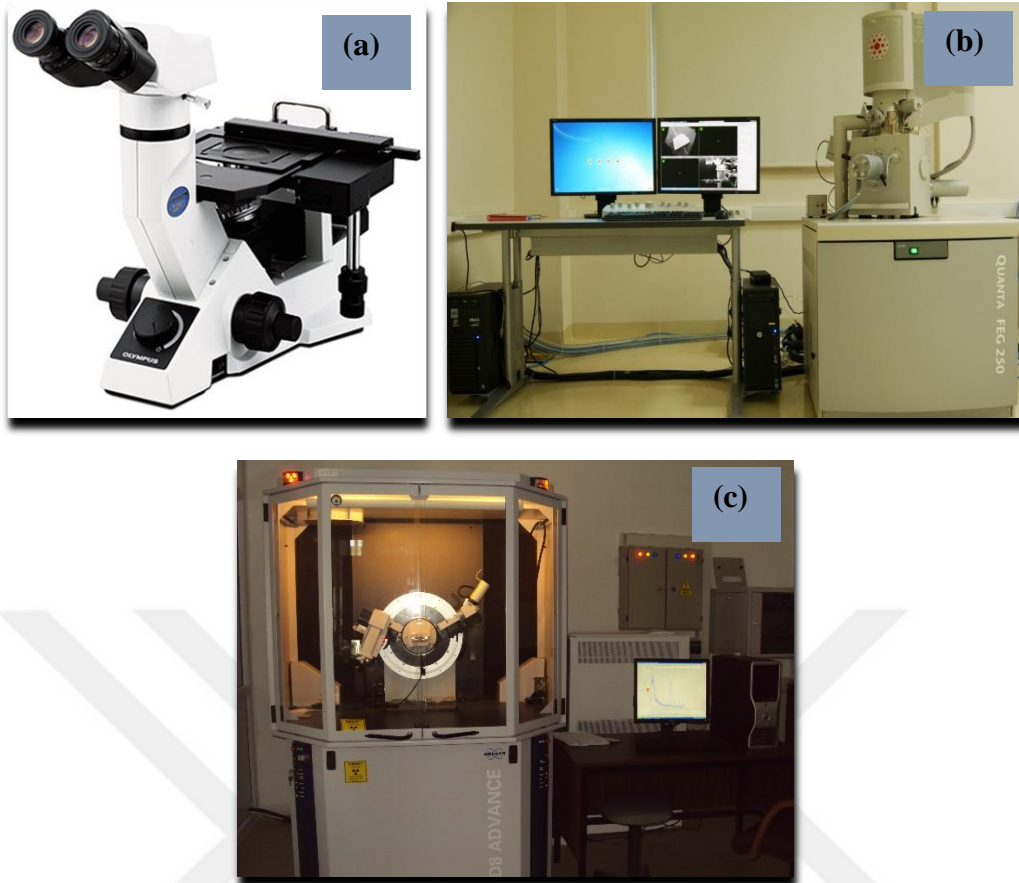


Photo 7.7. The devices used for imaging and phase analysis detection: (a) Optical microscope, (b) SEM and (c) XRD



## 8. RESULTS AND DISCUSSION

### 8.1. Microstructure Results

Photo 8.1 shows SEM images of powders used in the production of functionally graded bronze matrix ceramic reinforced composite materials. Bronze powders have a spherical and rounded morphology with different sizes. Boron Carbide and Silicon carbide powders have a sharp angular morphology, molybdenum carbide and titanium carbide powders have an aggregated morphology.

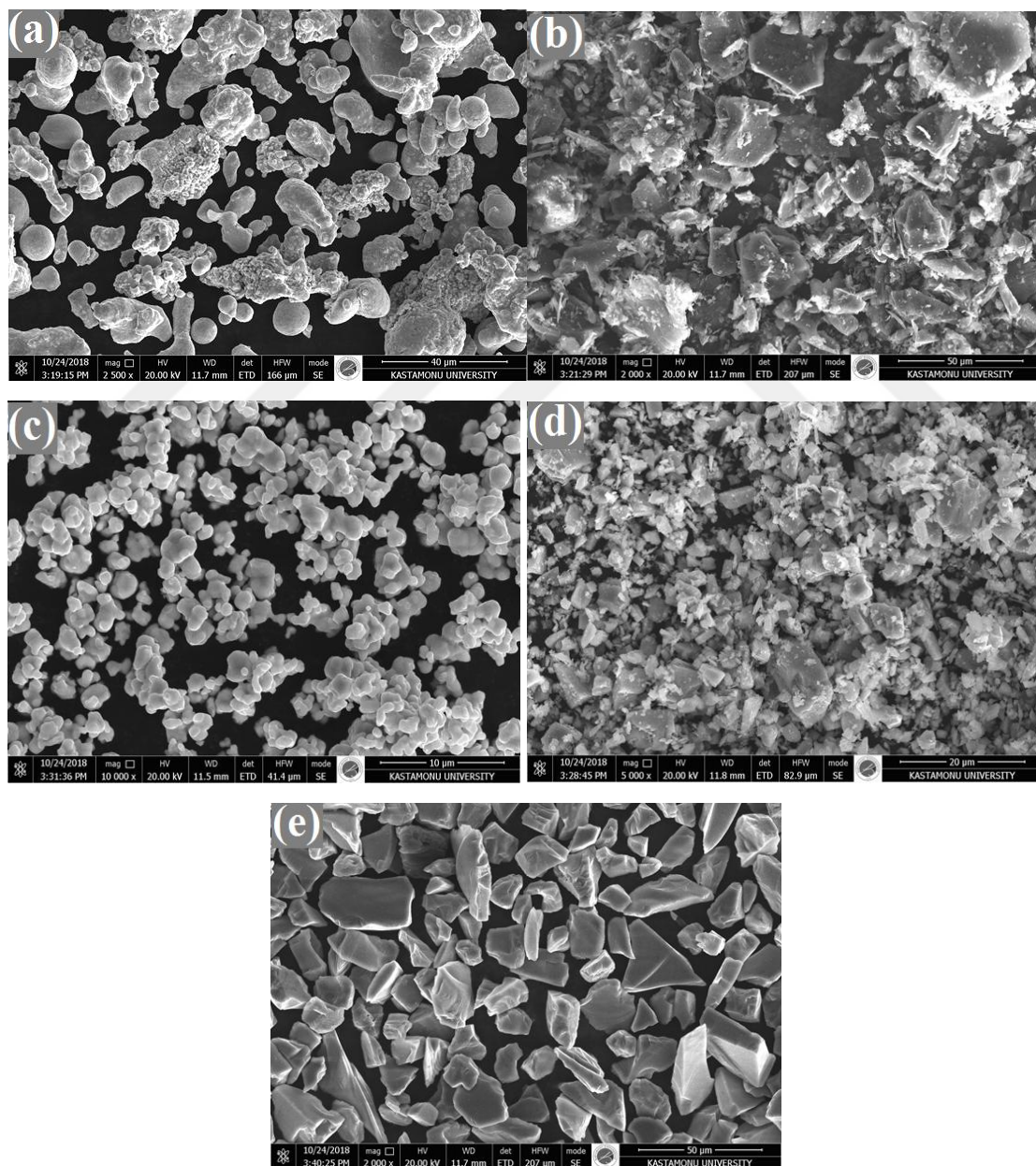


Photo 8.1. SEM images of powders:(a) CuSn, (b) B<sub>4</sub>C, (c) Mo<sub>2</sub>C, (d) TiC, and (e) SiC

Photo 8.2, Photo 8.3, Photo 8.4 and Photo 8.5 shows SEM images of boron carbide, molybdenum carbide, titanium carbide and silicon carbide reinforcement bronze matrix functionally graded composite with different magnifications. It's obvious from the ESM images that the reinforcement ceramic particles are homogeneously distributed and Microstructures were generally similar in all composites. A uniform dispersion of ceramic reinforcement powders in the bronze matrix offers improvement in density and the mechanical properties of resultant composites.

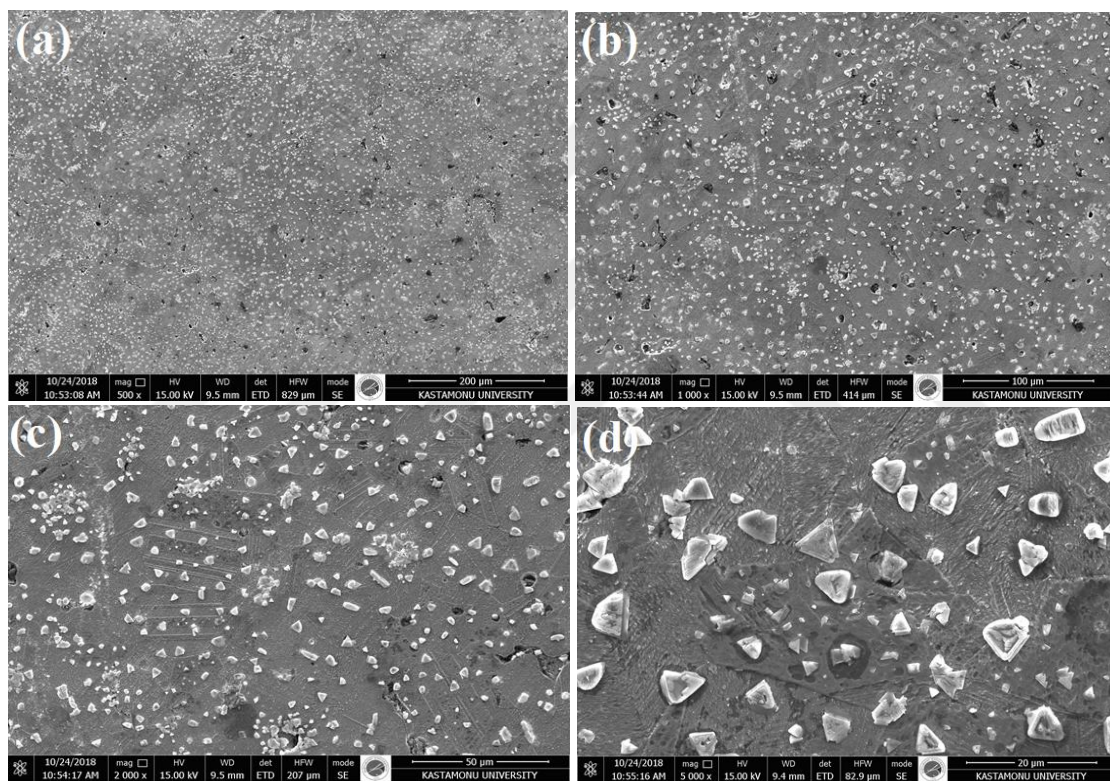


Photo 8.2. SEM images of  $B_4C$  reinforcement bronze matrix FGM: (a) 500X, (b) 1000X, (c) 2000X, and (D) 5000X



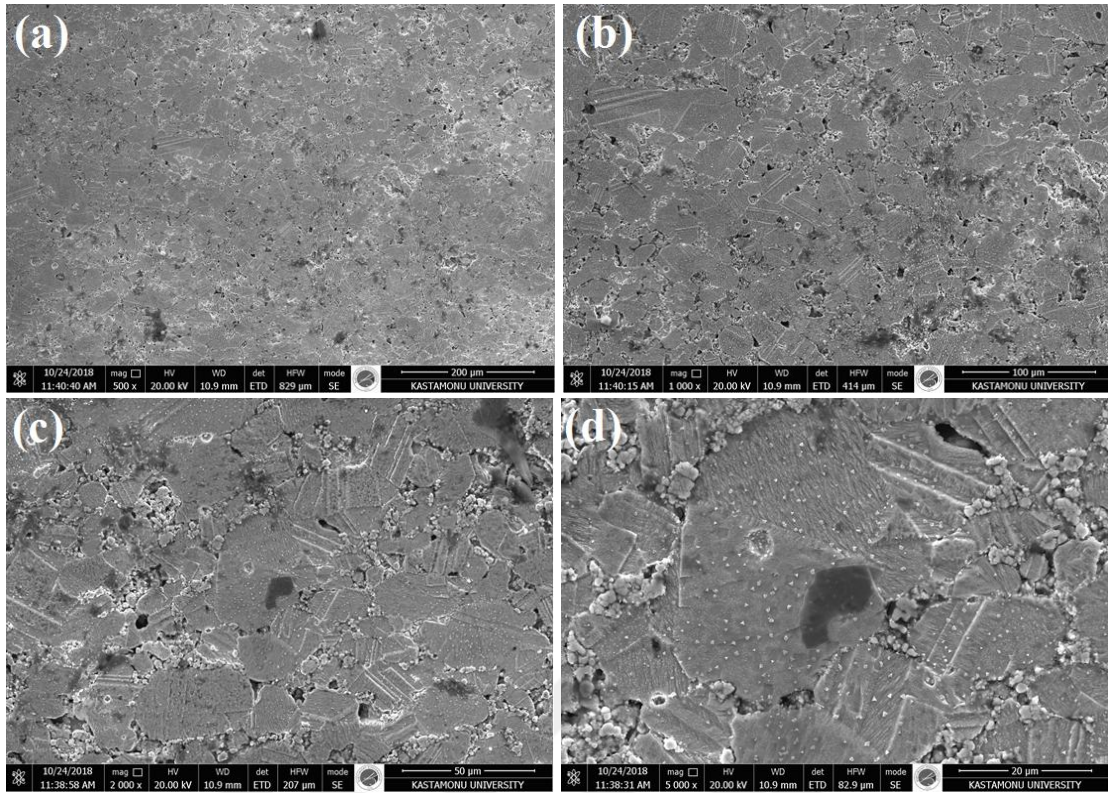


Photo 8.3. SEM images of Mo<sub>2</sub>C reinforcement bronze matrix FGM: (a) 500X, (b) 1000X, (c) 2000X, and (D) 5000X

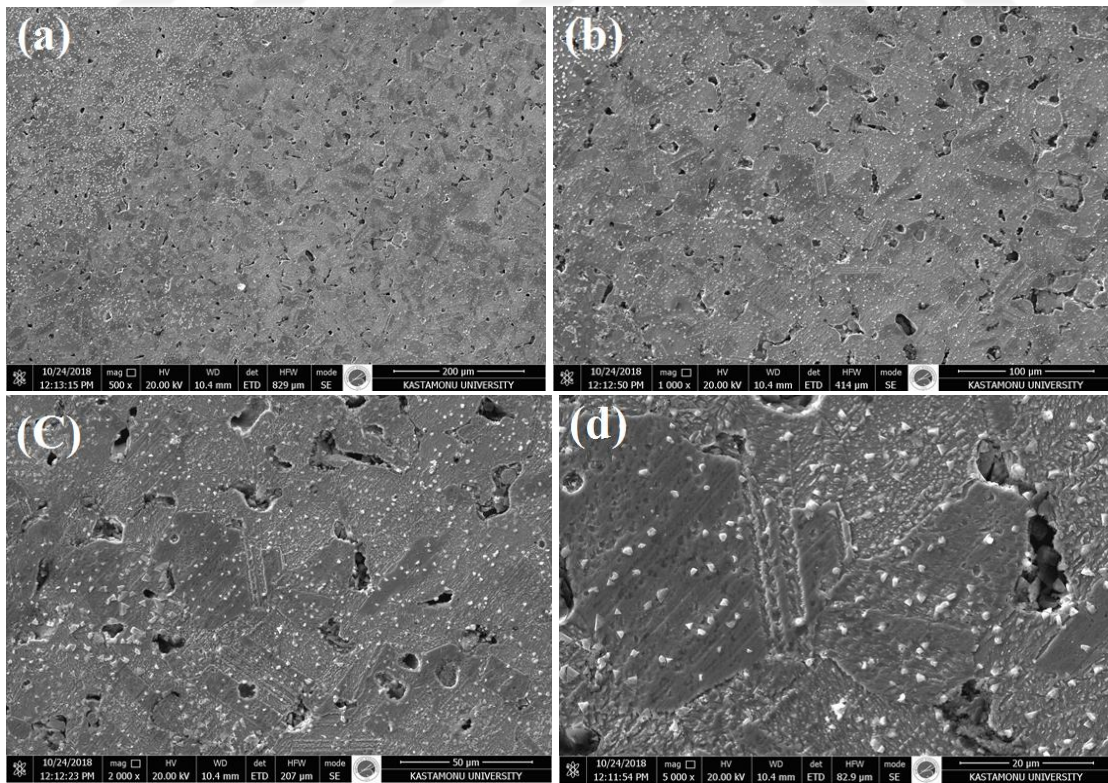


Photo 8.4. SEM images of TiC reinforcement bronze matrix FGM: (a) 500X, (b) 1000X, (c) 2000X, and (D) 5000X



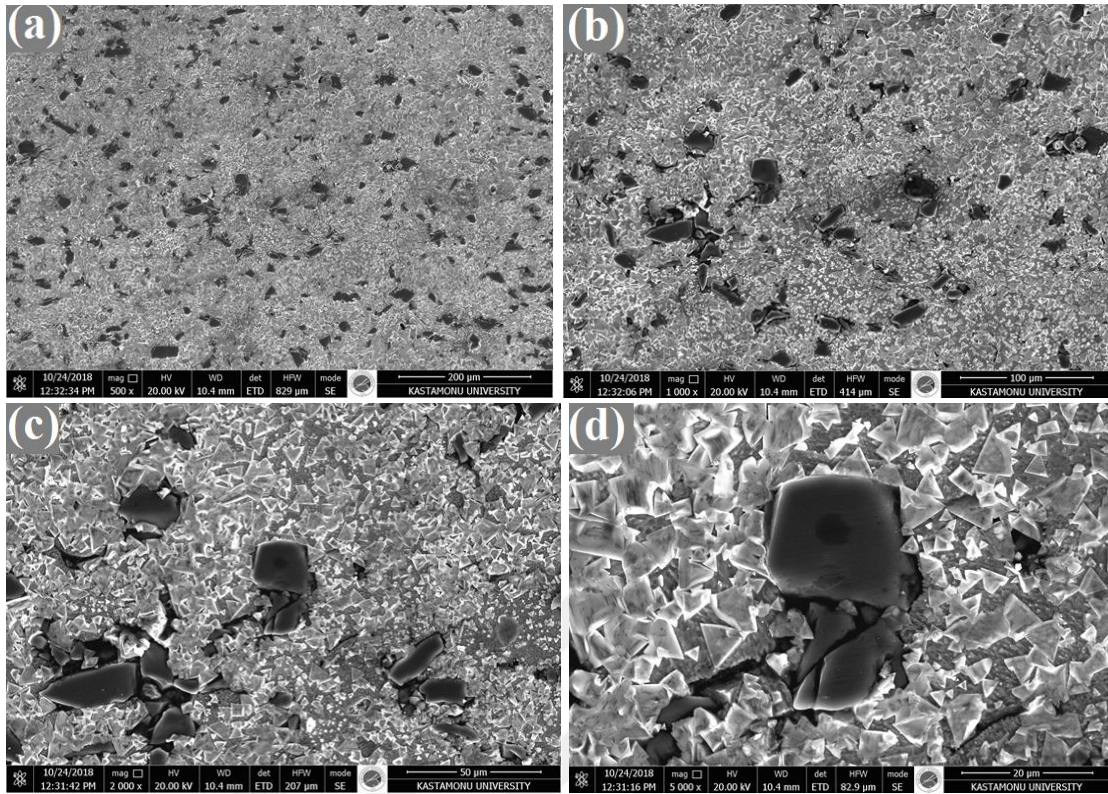


Photo 8.5. SEM images of SiC reinforcement bronze matrix FGM: (a) 500X, (b) 1000X, (c) 2000X, and (D) 5000X

Optical microscope images of FGM materials produced by powder metallurgy method are shown in Photo 8.6, Photo 8.7, Photo 8.8 and Photo 8.9. Photo 8.6 shows boron carbide reinforced, Photo 8.7 shows molybdenum carbide reinforced, Photo 8.8 shows titanium carbide reinforced, and Photo 8.9 shows silicon carbide reinforced FGMs. In these photographs, triple (composite-middle-composite) layers and enlarged photographs of these regions as well as interface parts are seen in detail. The composite layers and the middle part are clearly distinguished.

The  $B_4C$ ,  $Mo_2C$ ,  $TiC$  and  $SiC$  grains were distributed in a similar manner and relatively homogeneously in the bronze matrix. These ceramic particles are located in the parts where the bronze grains meet. There was no breakage and crack formation at the interface surface. Pore formation is observed in the FGMs.

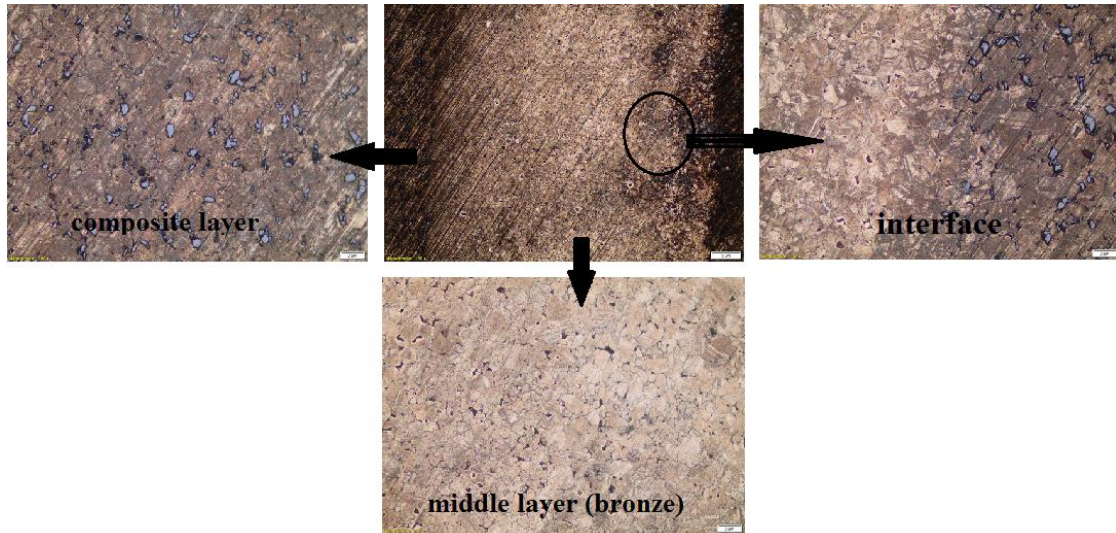


Photo 8.6. Optical microscope images of  $B_4C$  reinforced bronze matrix FGM composite

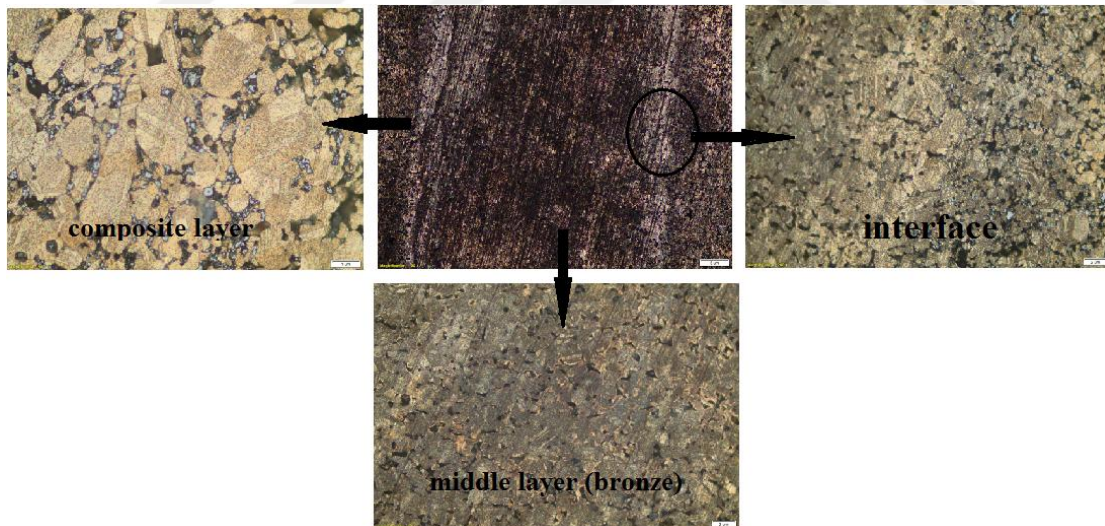


Photo 8.7. Optical microscope images of  $Mo_2C$  reinforced bronze matrix FGM composite



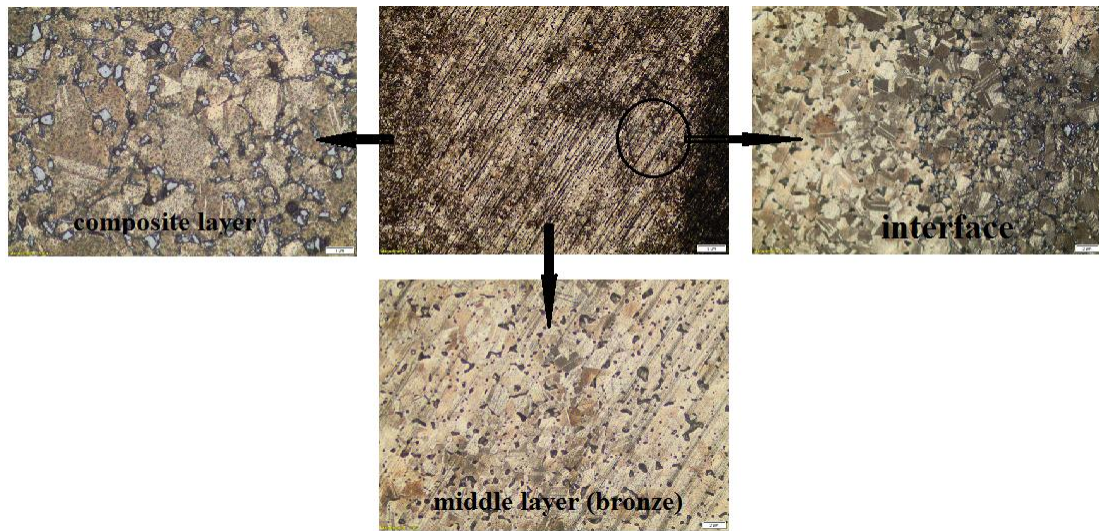


Photo 8.8. Optical microscope images of TiC reinforced bronze matrix FGM composite

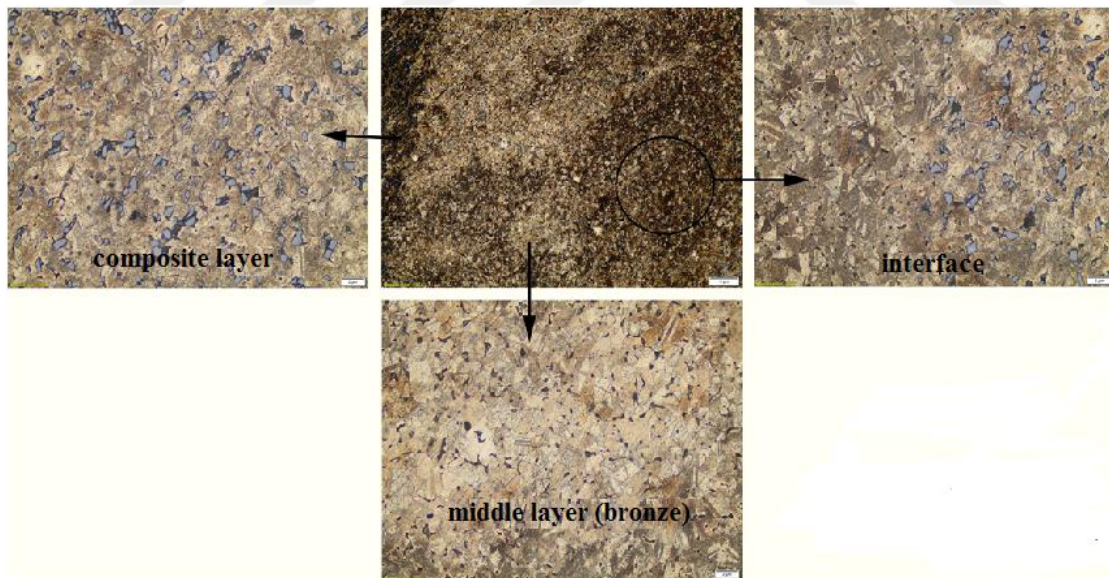


Photo 8.9. Optical microscope images of SiC reinforced bronze matrix FGM composite

The matrix and reinforcement of the samples of functionally graded bronze matrix ceramic reinforced composite materials have been analyzed using EDS (Energy-Dispersive Spectrometry) technique to determine and confirm its chemical compositions. After selecting different points in the matrices and reinforcements as shown in photos from Photo 8.10 to Photo 8.13 and graphs from Graph 8.1 to Graph 8.8. The basic element of FGM materials is Cu and Sn. The other elements are B, Mo, Ti, Si and C. It is clear from this analysis that boron carbide, molybdenum carbide, titanium carbide and silicon carbide grains are distributed uniformly. Furthermore, the EDS analysis showed that there is no agglomeration of the ceramic microparticles found in the composite layers. The homogeneous distribution of the elements in the material has a positive effect on the physical, chemical and mechanical properties of the material.

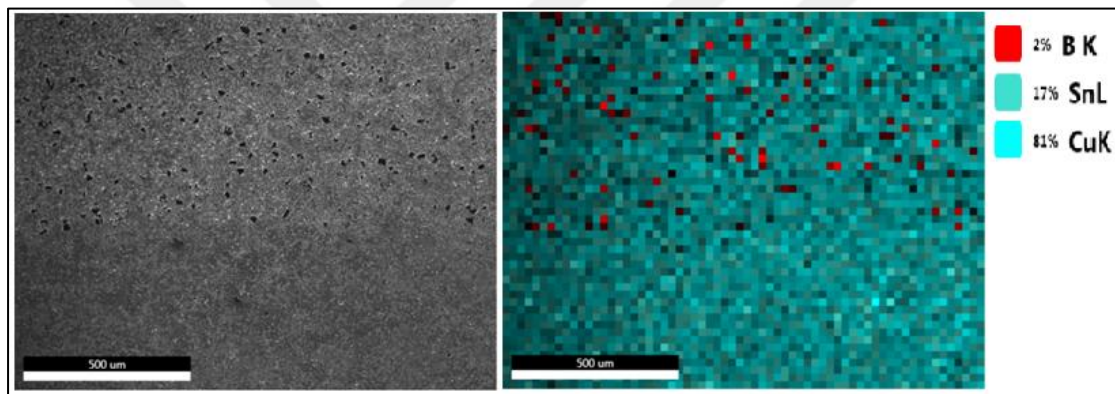
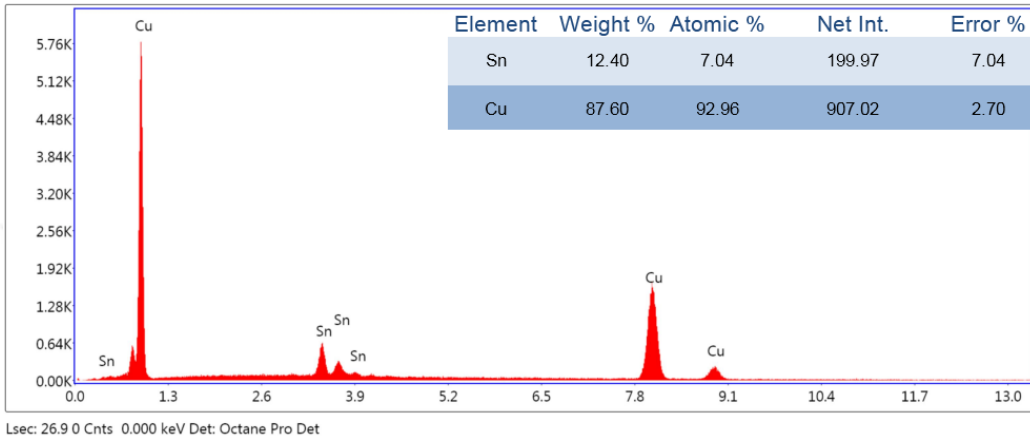
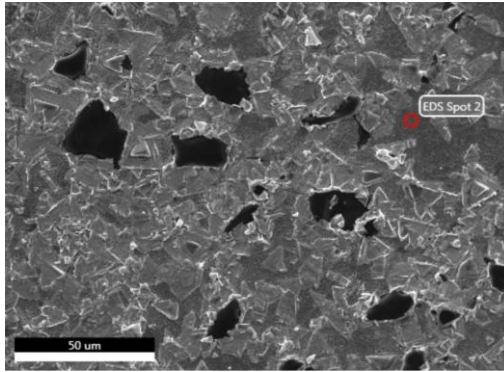
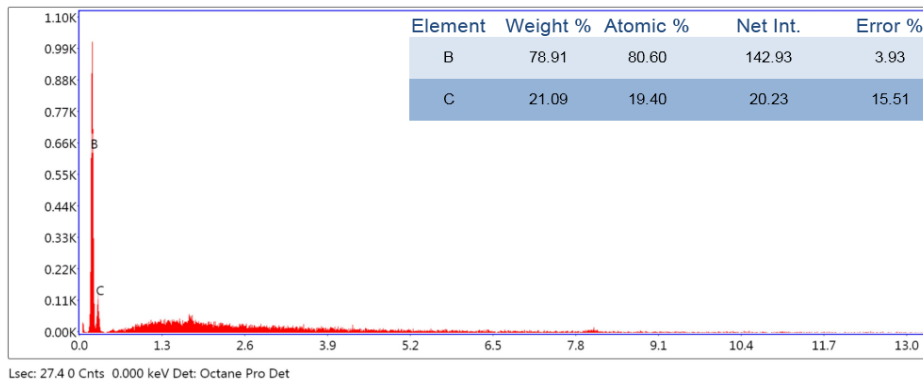
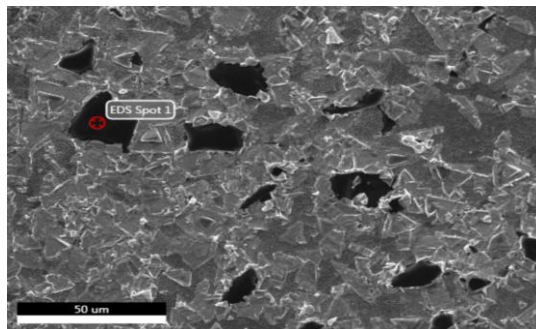


Photo 8.10. EDS analysis of B<sub>4</sub>C reinforced bronze matrix FGM composite



Graph 8.1. EDS analysis of the matrix in B<sub>4</sub>C reinforced bronze matrix FGM composite



Graph 8.2. EDS analysis of the reinforcement in B<sub>4</sub>C reinforced bronze matrix FGM composite



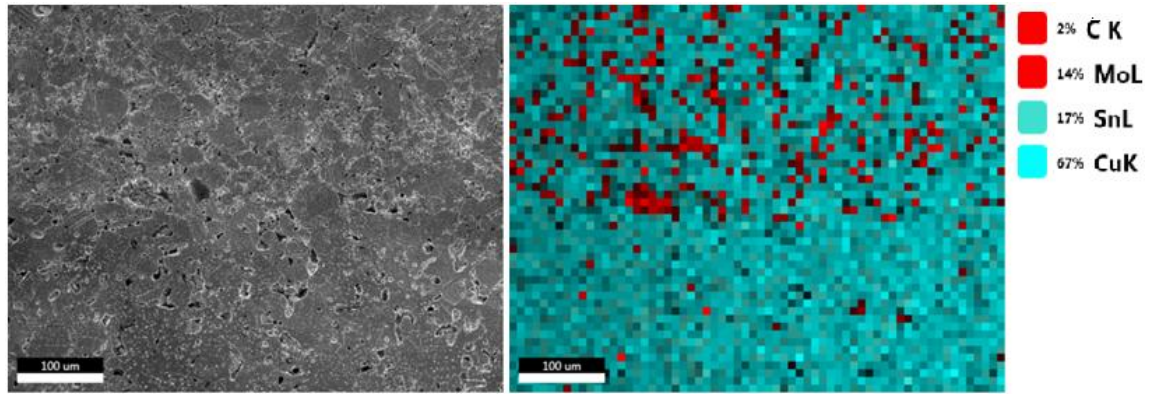
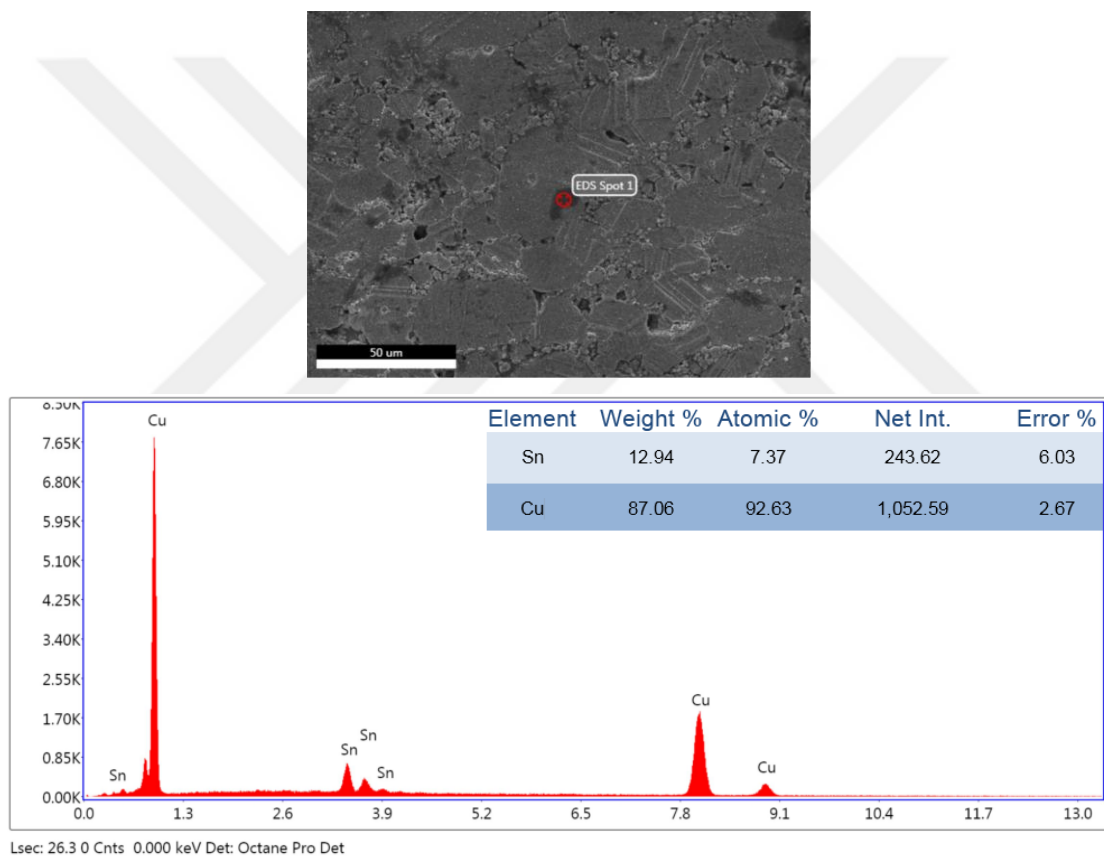
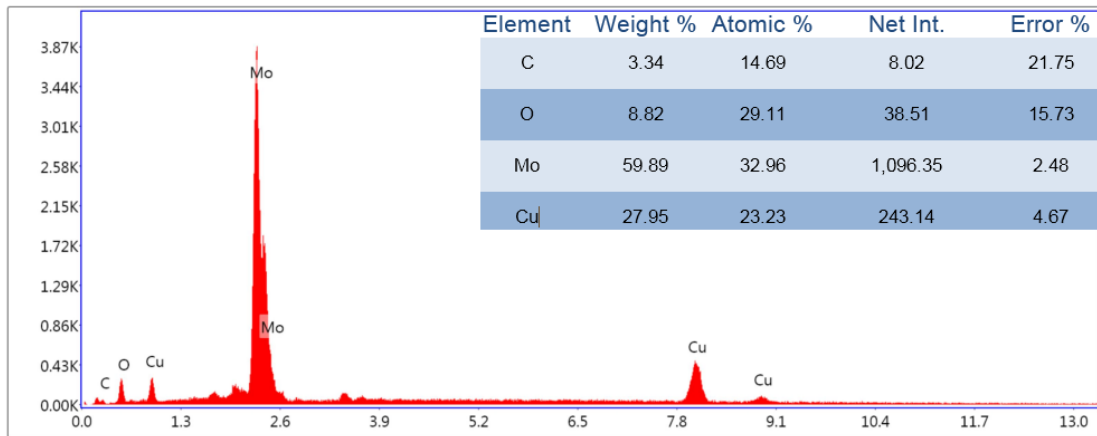
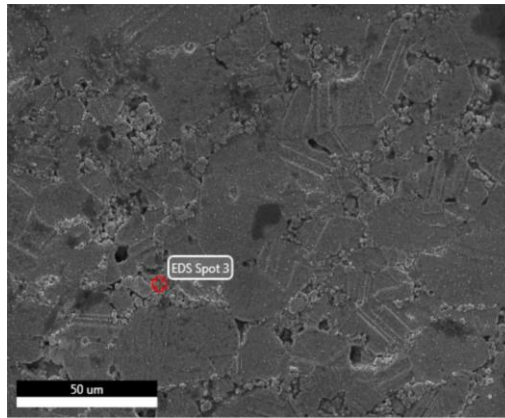


Photo 8.11. EDS analysis of Mo<sub>2</sub>C reinforced bronze matrix FGM composite



Graph 8.3. EDS analysis of the matrix in Mo<sub>2</sub>C reinforced bronze matrix FGM composite



Lsec: 27.4 0 Cnts 0.000 keV Det: Octane Pro Det

Graph 8.4. EDS analysis of the reinforcement in Mo<sub>2</sub>C reinforced bronze matrix FGM composite

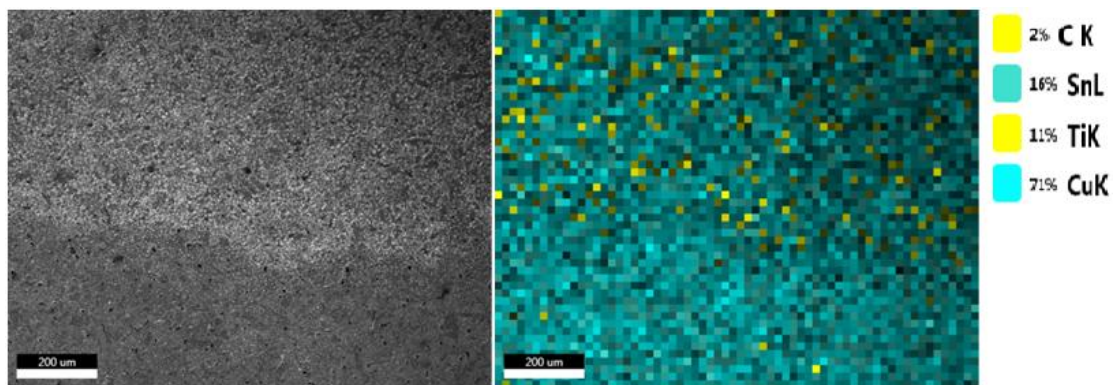
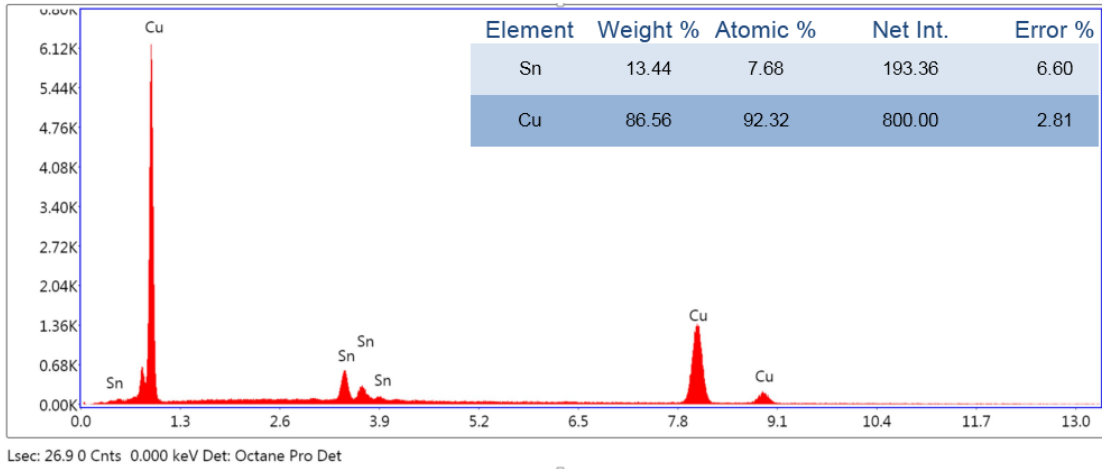
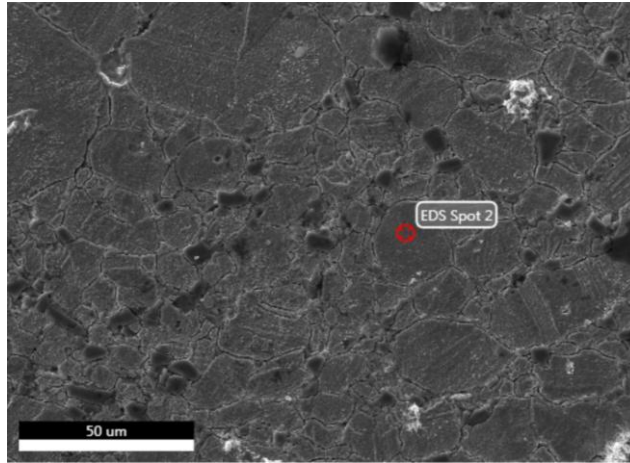
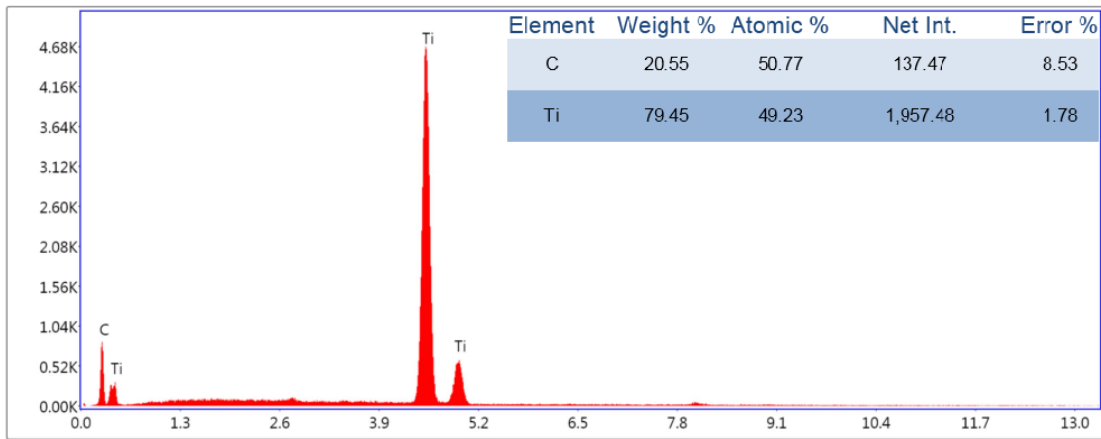
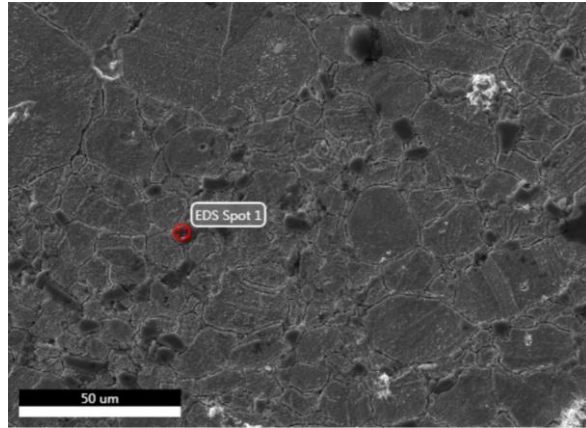


Photo 8.12. EDS analysis of TiC reinforced bronze matrix FGM composite





Graph 8.5. EDS analysis of the matrix in TiC reinforced bronze matrix FGM composite



Graph 8.6. EDS analysis of the reinforcement in TiC reinforced bronze matrix FGM composite

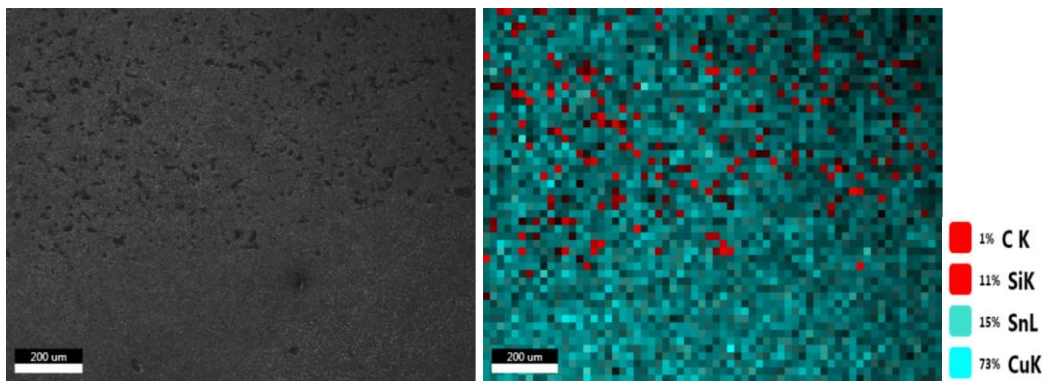
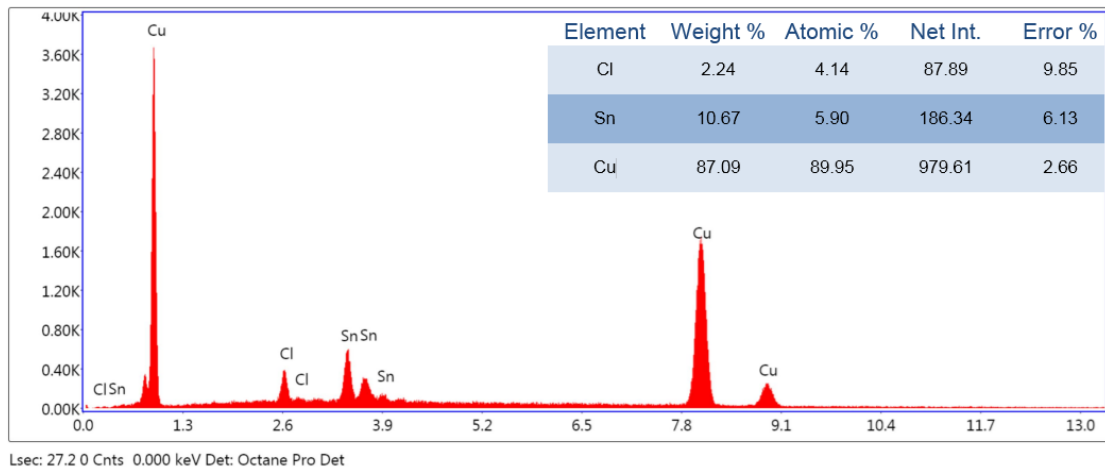
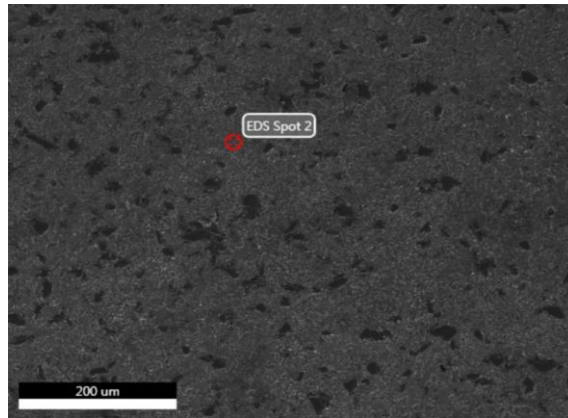
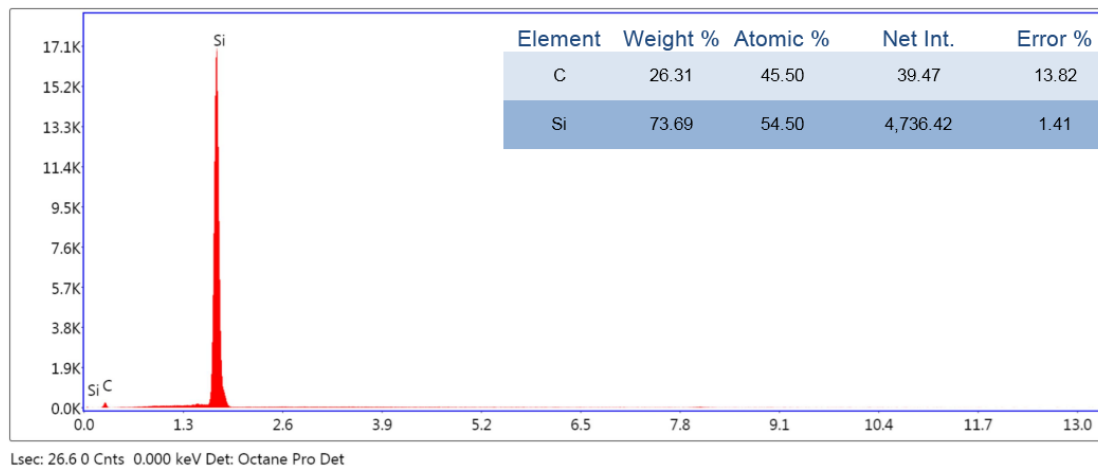
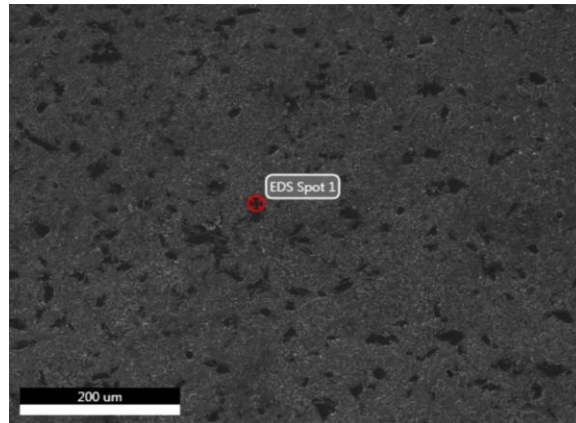


Photo 8.13. EDS analysis of SiC reinforced bronze matrix FGM composite



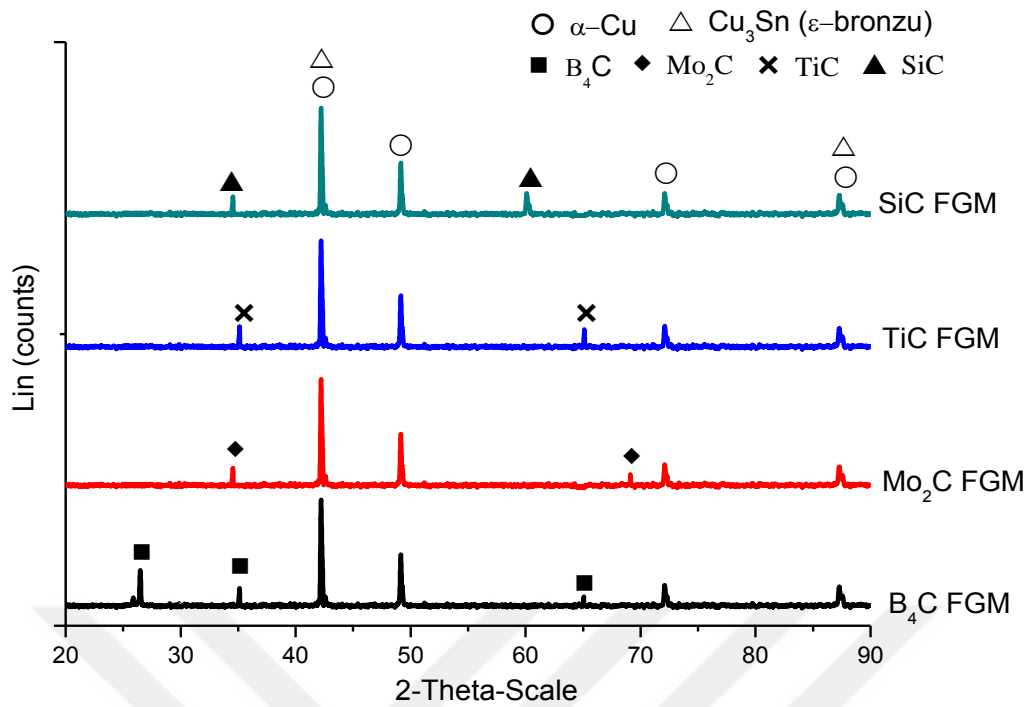
Graph 8.7. EDS analysis of the matrix in SiC reinforced bronze matrix FGM composite



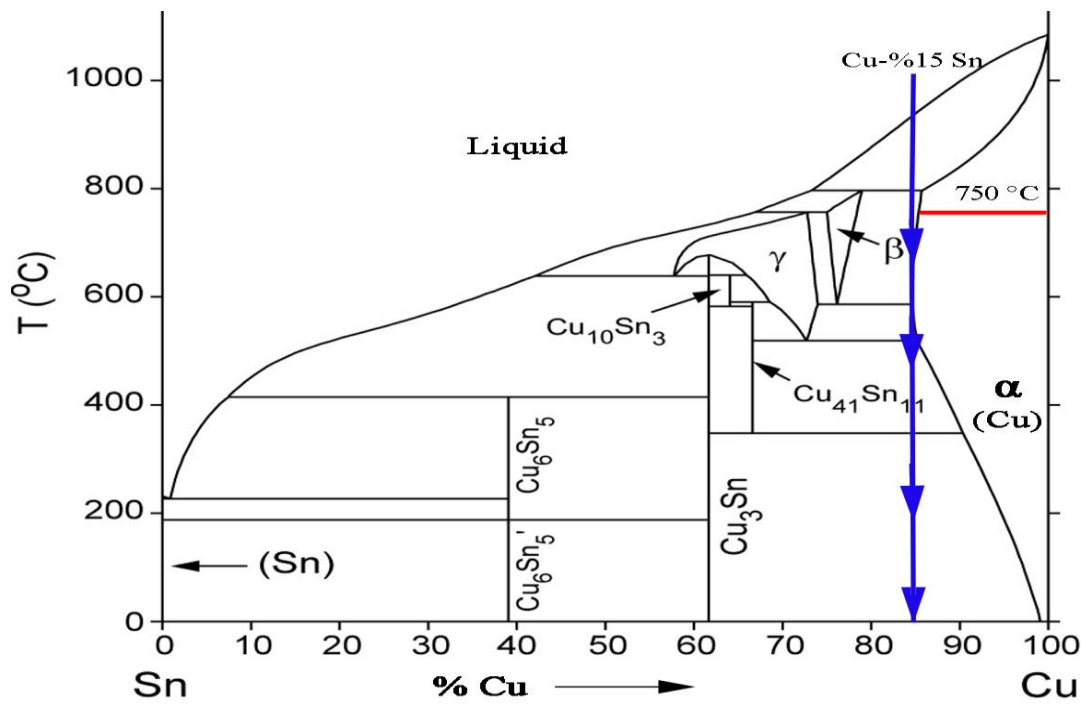
Graph 8.8. EDS analysis of the reinforcement in SiC reinforced bronze matrix FGM composite

## 8.2. XRD Results

XRD analysis was performed for each FGM composite to determine whether a phase that would bind the matrix and the carbide particles at the interface. XRD graphs of bronze matrix carbide reinforced FGM composites are given in Graph 8.9. XRD measurements were taken from the section containing three layers (composite layer - matrix layer - composite layer). No intermetallic compound formed between the carbide particles and the matrix. This is due to the absence of any chemical reaction between the matrix and the carbides. In the bronze matrix,  $\alpha$ -Cu and  $\text{Cu}_3\text{Sn}$  phases were formed as seen from XRD graphs. The Cu-Sn binary phase diagram in Graph 8.10 also supports this. In addition, carbide phases are clearly seen in XRD graphs.



Graph 8.9. XRD analysis of the FGM composite



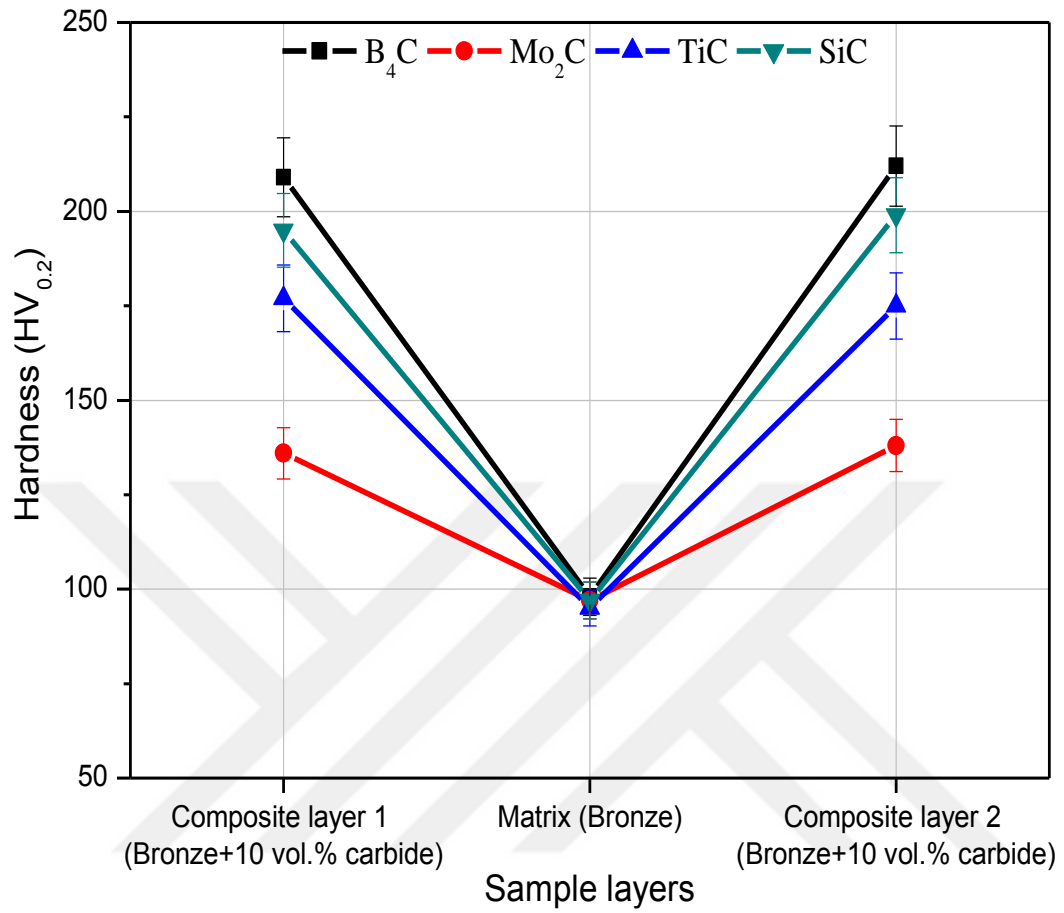
Graph 8.10. Cu-Sn binary phase diagram (Saunders and Miodownik, 1990)

### 8.3. Hardness Results

The hardness graphs of boron carbide, molybdenum carbide, titanium carbide, and silicon carbide reinforcement bronze matrix FGM composites are given in Figure 8. The hardness of the middle layer is about 95 HV<sub>0.2</sub>, while the hardness of composite layers are between 130 HV<sub>0.2</sub> for Mo<sub>2</sub>C and 210 HV<sub>0.2</sub> for B<sub>4</sub>C. The hardness of the composite layers has a very high hardness compared to the middle layer. This rate of increase is about 35 % in Mo<sub>2</sub>C additive, 100% in SiC additive, 75% in TiC additive and approximately 121% in B<sub>4</sub>C additive. There are several factors that cause hardness growth. These can be listed as the hardness of the composite elements, the dispersion strengthening effect and the effect of the hard particles on the movement of dislocations depending on the mixture rule.

Table8.1: *FGM's Hardness values*

Samples	Hardness (HV <sub>0.2</sub> )		
	Composite layer 1	Unreinforced layer	Composite layer 2
Bronze + 10% B <sub>4</sub> C (vol)	209	98	212
Bronze + 10% Mo <sub>2</sub> C (vol)	136	97	138
Bronze + 10% TiC (vol)	177	95	175
Bronze + 10% SiC (vol)	195	97	199



Graph 8.11. Hardness Test Results

## 9. GENERAL RESULTS

In this thesis study, the microstructure, hardness properties of bronze matrix B<sub>4</sub>C, Mo<sub>2</sub>C, TiC and SiC reinforced functionally graded material composites produced by powder metallurgy technique were investigated experimentally in detail.

- Bronze matrix B<sub>4</sub>C, Mo<sub>2</sub>C, TiC and SiC reinforcement FGM composites were successfully produced by using powder metallurgy method.
- Composite layers of ceramic particles from both optical photographs and SEM-MAP analyzes are homogeneously distributed. Microstructures were generally similar in all composites. The reinforcing particles were located at the contact points of the matrix grains and slightly embedded in the matrix.
- Proper powder mixing in 45 minutes at the speed of 20 rpm lead to uniform distribution of ceramic reinforcement powders in the bronze matrix Which in turn lead to improvement in microstructure and mechanical properties of resultant composites.
- Hardness of functionally graded bronze matrix ceramic reinforced composite materials showed an increase with reinforcements. While the hardness of matrix was about 95 HV<sub>0.2</sub>, maximum hardness was measured in CuSn - %10B<sub>4</sub>C composite as 212 HV<sub>0.2</sub>. The hardness of the other ceramic composites varies from 136 to199 HV<sub>0.2</sub> range. Hardness increased by the dispersion resistance effect created by reinforcing particles in the matrix and/or preventing the dispersion strengthening.
- Sintering temperature (750°C) and sintering time (90 min) were appropriate to improve the microstructure and mechanical properties of functionally graded bronze matrix ceramic reinforced composite materials.
- At the microstructure, little pore formation was observed.



## 10. RECOMMENDATIONS

Following recommendations can be made as a result of the study:

- Wear and corrosion resistance can be examined by performing wear and corrosion tests on samples.
- Different sintering temperatures can be applied to samples to determine the effect of sintering temperature on some properties.
- Hybrid composite layers can be designed to produce new FGM composites.

## REFERENCES

- Alaneme, K. K., & Bodunrin, M. O. (2011). Corrosion behavior of alumina reinforced aluminium (6063) metal matrix composites. *Journal of Minerals and Materials Characterization and Engineering*, 10(12), 1153.
- Ali, M., Suppiah, B., & Muayaduldeen, Z. (2016). Preparation and Corrosion Behavior of Bronze-40% w Composite. *Jordan Journal of Mechanical and Industrial Engineering*, 10(2), 141-147.
- Bannan, J., Temple, R. I., & Jones, R. (2003). In situ fabrication of titanium carbide reinforced copper MMC. *Materials science and technology*, 19(8), 1148-1150.
- Chawla, K. K. (2012). *Composite materials: science and engineering*. Springer Science & Business Media.
- Chen, Y., Zhang, H., Zhang, J., Ma, J., Ye, H., Qian, G., & Zhong, S. (2011). Facile synthesis and thermal stability of nanocrystalline molybdenum carbide. *Materials Sciences and Applications*, 2(09), 1313.
- Chumanov, I. V., Anikeev, A. N., & Chumanov, V. I. (2015). Fabrication of functionally graded materials by introducing wolframium carbide dispersed particles during centrifugal casting and examination of FGM's structure. *Procedia engineering*, 129, 816-820.
- Cui, G., Bi, Q., Zhu, S., Fu, L., Yang, J., Qiao, Z., & Liu, W. (2013). Synergistic effect of alumina and graphite on bronze matrix composites: tribological behaviors in sea water. *Wear*, 303(1-2), 216-224.
- Dantas, S. L., Lopes-Moriyama, A. L., & Souza, C. P. (2018). Synthesis and characterization of molybdenum carbide doped with nickel. *Materials Chemistry and Physics*, 216, 243-249.
- Gasik, M. M. (1998). Micromechanical modelling of functionally graded materials. *Computational Materials Science*, 13(1-3), 42-55.
- Gou, H. P., Zhang, G. H., & Chou, K. C. (2017). Preparation of Titanium Carbide Powder from Ilmenite Concentrate. *Chemical Industry & Chemical Engineering Quarterly*, 23(1).
- Gupta, A., & Talha, M. (2015). Recent development in modeling and analysis of functionally graded materials and structures. *Progress in Aerospace Sciences*, 79, 1-14.
- Hon, D., & Shiraishi (2001). *Wood and cellulose chemistry*, 2nd ed. (New York: Marcel Dekker).

- İpek, H., Cuvalci, H., & Celebi, C. (2017). Tribological properties of boron carbide reinforced copper based composites. *European Journal of Engineering and Natural Sciences*, 2(1), 102-107.
- Kato, K., Kurimoto, M., Shumiya, H., Adachi, H., Sakuma, S., & Okubo, H. (2006). Application of functionally graded material for solid insulator in gaseous insulation system. *IEEE Transactions on Dielectrics and Electrical Insulation*, 13(2), 362-372.
- Kieback, B., Neubrand, A., & Riedel, H. (2003). Processing techniques for functionally graded materials. *Materials Science and Engineering: A*, 362(1-2), 146-156.
- Kieback, B., Neubrand, A., & Riedel, H. (2003). Processing techniques for functionally graded materials. *Materials Science and Engineering: A*, 362(1-2), 203-210.
- Kieback, B., Neubrand, A., & Riedel, H. (2003). Processing techniques for functionally graded materials. *Materials Science and Engineering: A*, 362(1-2), 81-106.
- Kok, M. (2005). Production and mechanical properties of Al<sub>2</sub>O<sub>3</sub> particle-reinforced 2024 aluminium alloy composites. *Journal of Materials Processing Technology*, 161(3), 381-387.
- Mahamood, R. M., Akinlabi, E. T., Shukla, M., & Pityana, S. (2012). Functionally graded material: an overview.
- Miyamoto, Y. (1996). The applications of functionally graded materials in Japan. *Materials Technology*, 11(6), 230-236.
- Miyamoto, Y., Kaysser, W. A., Rabin, B. H., Kawasaki, A., & Ford, R. G. (Eds.). (2013). *Functionally graded materials: design, processing and applications* (Vol. 5). Springer Science & Business Media.
- Moore, S. (1993). New materials set endurance records. *Chemical Engineering*, 100(5), 39.
- Naebe, M., & Shirvanimoghaddam, K. (2016). Functionally graded materials: A review of fabrication and properties. *Applied Materials Today*, 5, 223-245.
- Pierson, H. O. (1996). *Handbook of Refractory Carbides & Nitrides: Properties, Characteristics, Processing and Apps*. William Andrew.
- Radhika, N., Thirumalini, S., & Shivashankar, A. (2018). Investigation on mechanical and adhesive wear behavior of centrifugally cast functionally graded copper/SiC metal matrix composite. *Transactions of the Indian Institute of Metals*, 71(6), 1311-1322.
- Rhee, R. S. (2007). *Multi-scale modeling of functionally graded materials (FGMs) using finite element methods*. University of Southern California.
- Rodríguez-Lorenzo, L. M., & Ferreira, J. M. F. (2004). Development of porous ceramic bodies for applications in tissue engineering and drug delivery systems. *Materials research bulletin*, 39(1), 83-91.

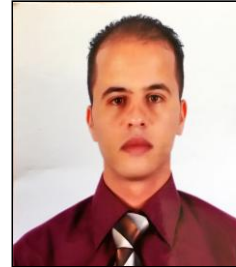
- Ryan K.R., et al., (2002). Tool Material Manufacturing. *Engineering Materials Production Reviews*, 2, 58-60.
- Saunders, N., Miodownik, A. P., 1990, Bull. Alloy Phase Diagrams, vol.11, pp. 278-87.
- Sharma, S. C., Satish, B. M., Girish, B. M., & Somashekar, D. R. (2001). Wear characteristics of phosphor-bronze/silicon carbide particulate composites. *Journal of materials processing technology*, 118(1-3), 65-68.
- Shumiya, H., Kato, K., & Okubo, H. (2004, October). Feasibility study on FGM (functionally graded materials) application for gas insulated equipment [solid insulators]. In *The 17th Annual Meeting of the IEEE Lasers and Electro-Optics Society, 2004. LEOS 2004*. (pp. 360-363). IEEE.
- Sobczak, J. J., & Drenchev, L. (2013). Metallic functionally graded materials: a specific class of advanced composites. *Journal of Materials Science & Technology*, 29(4), 297-316.
- Suk, M. J., Choi, S. I., Kim, J. S., Do Kim, Y., & Kwon, Y. S. (2003). Fabrication of a porous material with a porosity gradient by a pulsed electric current sintering process. *Metals and Materials International*, 9(6), 599-603.
- Tampieri, A., Celotti, G., Sprio, S., Delcogliano, A., & Franzese, S. (2001). Porosity-graded hydroxyapatite ceramics to replace natural bone. *Biomaterials*, 22(11), 1365-1370.
- Thieme, M., Wieters, K. P., Bergner, F., Scharnweber, D., Worch, H., Ndop, J., & Grill, W. (2001). Titanium powder sintering for preparation of a porous functionally graded material destined for orthopaedic implants. *Journal of materials science: materials in medicine*, 12(3), 225-231.
- Thorp, R. L. (2006). *China in the early Bronze Age: Shang civilization*. University of Pennsylvania Press.
- Tjong, S. C. (2014). Processing and deformation characteristics of metals reinforced with ceramic nanoparticles. In *Nanocrystalline Materials* (pp. 269-304). Elsevier.
- Toudehdeghan, A., Lim, J. W., Foo, K. E., Ma'arof, M. I. N., & Mathews, J. (2017). A brief review of functionally graded materials. In *MATEC Web Conferences* (Vol. 131). EDP Sciences.
- Udupa, G., Rao, S. S., & Gangadharan, K. V. (2014). Functionally graded composite materials: an overview. *Procedia Materials Science*, 5, 1291-1299.
- Uysal, M., Karslioglu, R., Akbulut, H., & Alp, A. (2013). Characteristics Bronze/Al<sub>2</sub>O<sub>3</sub> (Ni) Reinforcement Metal Matrix Composite Produced by Current Activated Sintering. *Acta Physica Polonica, A*, 123(2).

- Watanabe, Y. (2000). Microstructures and mechanical properties of functionally graded materials fabricated by a centrifugal method. *Rec. Res. Devel. Metal. Mater. Sci.*, 4, 51-93.
- Watanabe, Y., Yamanaka, N., & Fukui, Y. (1998). Control of composition gradient in a metal-ceramic functionally graded material manufactured by the centrifugal method. *Composites Part A: Applied Science and Manufacturing*, 29(5-6), 595-601.
- Xie, Y.-B., Hou, Y.-G., Li, W.-F., Huang, Q.-F., & Ding, Z.-J. (2017). Effect of Sintering Temperature on Properties and Microstructure of Ceramic/Bronze Composite Bond. *Rengong Jingti Xuebao/Journal of Synthetic Crystals*, 46(8), 1511–1516.



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