

# **Development of Copper-Diamond-CNT Composites via Powder Metallurgical Route for Enhanced Strength and Thermal Conductivity**



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# **Development of Copper-Diamond-CNT Composites via Powder Metallurgical Route for Enhanced Strength and Thermal Conductivity**



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## **Dedication**

*Dedicated to my proud parents and family members whose  
tremendous support and cooperation led me to this wonderful  
accomplishment*

## **Abstract**

The diamond-copper composite system has emerged as the most attractive material in the development of novel materials for thermal management applications. Due to the superior thermal conductivity of diamond/copper composite, the issue of heat dissipation in high heat flux situation is anticipated to be resolved in the future. In this study, the copper matrix composites reinforced with 0.5% Carbon Nanotubes (CNTs) and 3% diamond (D) particles were prepared via route of powder metallurgy. Diamond particles and CNTs were used as reinforcement. The chromium (Cr) powder was used to improve the interfacial bonding between the copper matrix and the diamond particle reinforcement. The sintering was conducted for all samples in a tube furnace having an argon gas environment. For Cr-D-CNT-Cr composites, the thermal conductivity was found to be 310 W/m K, which was higher as compared to Cu-D-Cr composite with an average value of 285 W/m K. Similarly, the Cr-D-CNT-Cr composites show 6 % higher compression and 10 % higher bending strength as compared to Cu-D-Cr composites, respectively.

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## List of Abbreviations and Acronyms

<b>Acronym</b>	<b>Meaning</b>
<b>Al</b>	Aluminum
<b>C</b>	Carbon
<b>Cu</b>	Copper
<b>CNTs</b>	Carbon Nano Tubes
<b>CTE</b>	Coefficient of Thermal Expansion
<b>Cr</b>	Chromium
<b>C.I.P</b>	Cold isostatic Pressing
<b>D</b>	Diamond
<b>DSC</b>	Differential Scanning Calorimetry
<b>FTIR</b>	Fourier Transform Infrared
<b>GPa</b>	Giga Pascal
<b>H.I.P</b>	Hot Isostatic Pressing
<b>MPa</b>	Mega Pascal
<b>SEM</b>	Scanning Electron Microscope
<b>UTM</b>	Universal Testing Machine
<b>UTS</b>	Ultimate Tensile Strength
<b>XRD</b>	X-Ray-Diffraction
<b>Y.P</b>	Yield Point
<b>Zr</b>	Zirconium

# Chapter 1

## Introduction

### 1.1 Background

Modern technologies demand materials with unusual properties that can't be provided by common metals, alloys, ceramics, and polymeric materials. The materials utilized in cutting-edge machinery for the aerospace, high-temperature, underwater, corrosive environments, and transportation industries all fit this description. For these purposes, specialized materials with superior combinations of various properties are needed. [1].

A composite material is a special type of material that is described as a multiphase material with a distinct interface between the phases and considerable amounts of both phases' characteristics. The reinforcing materials are often soft in the matrix phase, but the reinforcements are typically hard and brittle. The reinforcement primarily carries the entire load, while the matrix phase transfers the load from the reinforcement to the matrix. The phase of reinforcement may consist of fibers or particles. [2].

Metal-diamond composite materials have attracted a lot of attention in the field of thermal management due to their capacity to exhibit thermal conductivities that are significantly higher than those of conventional heat sink materials like aluminum and copper. It is impossible to exaggerate the importance of heat sink materials with high thermal conductivity. Diamond is considered to be the strongest competitor in this field due to its outstanding heat conductivity. By combining the benefits of diamond and copper with exceptional thermal conductivity and excellent mechanical properties, the researchers were able to generate diamond/copper composite materials with high thermal conductivity and adjustable coefficient of thermal expansion. However, only relatively specialized applications have used diamond plates as heat sinks due to their prohibitive cost. Because synthetic diamond particles are significantly more commercially viable than diamond plates, there have been various attempts to incorporate them into metal matrices [3].

The composite materials can be made using a variety of fabrication processes. Powder metallurgy, for example, is a unique manufacturing technology in that it can create high-quality, complicated products with tight tolerances at a low cost [4]. The study of metal powder processing, including manufacturing, characterization, and conversion of metal powders into useful components, is known as powder metallurgy. It is a method that can create a variety of materials, microstructures, and characteristics [5].

## **1.2 Motivation:**

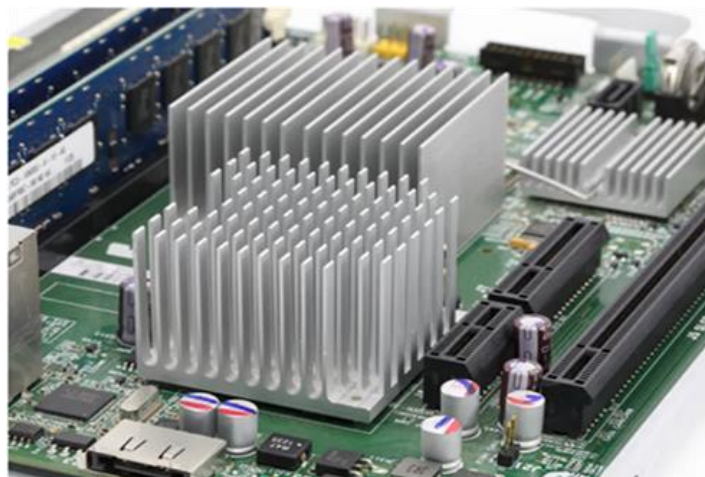
The requirements of high-power and component miniaturization with the advancement of microelectronic integration technology make the heat dissipation of heat sink materials crucial to ensure their dependability and endurance. [6].

A 10 °C rise in chip temperature results in increase in the chance of device failure. Improving the heat dissipation of heat sink materials as shown in figure 1.1 is an efficient technique to overcome this problem. Because of exceptionally high heat conductivity (2200 W/m k), diamond has gained a lot of interest for use in such devices as well as hardness. Similarly, Carbon Nano Tubes has also high thermal conductivity of 2700–6000 W/m K [7]. It is the best heat sink packaging material because of its excellent thermal qualities as well as the good mechanical capabilities of diamond and CNTs. The thermal and mechanical properties of copper and diamond can be combined to produce Cu/D composite heat-spreaders with customized thermal conductivity and CTE depending on the kind and volume fraction of diamond reinforcements [8].

Diamond reinforced copper matrix composites are regarded as particularly promising materials for heat dissipation systems due to their several advantages over copper, including reduced density, enhanced thermal conductivity, and decreased CTE. The filler-matrix interface determines the thermal and mechanical properties of the composite (thermal resistance of the interphase boundary, adhesion at the interface), so the composite's thermal conductivity and strength are interrelated. Despite the fact that mechanical properties are not functional targets for composites with high thermal conductivity, they are essential in (assemblies in electronic modules, etc.) [9].

Cu/diamond composites and Cu/diamond CNTs composite qualities are influenced by the internal matrix and reinforcement phase parameters, volume of the reinforcement phase, and interface quality. The interface's function is widely acknowledged. These components all have a significant role in the composites. Because copper does not moisten with diamond and there is no chemical reaction, sintering Cu-diamond and Cu-diamond-CNT composites is challenging. As a result, pure copper and diamond composite sintered without high pressure have a lower heat conductivity than pure copper. [10]

The interface plays a crucial role in determining the heat conductivity, CTE, and mechanical properties of a composite made of diamond particles implanted in a copper matrix. Strong adhesion and less thermal boundary resistance are desirable qualities for a contact. Pure liquid copper does not wet diamond, and interfacial adhesion in Cu-diamond composites made by powder metallurgy has been shown to be weak [11]. A appropriate connection between copper and diamond can be made, though, by adding a carbide-producing element to the copper, like boron or cr. The phonon channel between D and Cu is produced by adding a graphene layer between them to lower the interfacial thermal resistance. As a result of these components diffusing to the diamond's surface during the sintering process, an interface is created.



**Figure 1.1** Heat Dissipation in Electronic Circuits

### **1.3 Objectives:**

- Synthesis of Cu-D-Cr composite at concentrations (Cu= 96.2%, D= 3%, Cr= 0.8%) and Cu-D-CNT-Cr composite at concentrations (Cu= 95.7%, D= 3%, CNT= 0.8%, Cr= 0.8%) through powder metallurgy route.
- Characterization of the synthesized materials using Scanning Electron Microscopy (SEM), Densitometer, Universal Testing Machine (U.T.M) and Thermal Conductivity Meter.
- Development of Cu-D and Cu-D-CNTs composites with enhanced strength and thermal conductivity.
- Comparison of mechanical and thermal properties of Cu, Cu-D-Cr and Cu-D-CNT-Cr.

## **Chapter 2**

### **Literature Review**

The growing use of composites in a variety of applications stresses their importance in the mechanical and thermal qualities of a system. Since last two decades significant research is done on monolithic to improve their mechanical and physical properties by addition of ceramic reinforcement. Simultaneously there is remarkable increase in industrial application of Metal matrix composites [11]. Usage industry of MMC include aerospace, automotive, sport and defense application [12]. Metal matrix composites have superior mechanical properties which entail their high strength, high wear resistance, high stiffness and high temperature properties. These properties can be adjusted for specific application [13]. Previously metal matrix composites research activities were more aligned towards the reinforcement of fiber in the matrix phase. But due to their complex fabrication and simultaneously their reinforcement was a gigantic and complex process [14] So, these underlined difficulties impelled the technology toward particle-based reinforcement. Copper based Metal Matrix Composite have some exceptional properties like high strength , hardness and better thermal properties results in wide ranging applications [15]. The goal is to achieve a blended property of both ceramic and metal. As we know high strength and modulus due to addition of ceramic reinforcement, we can get mechanical properties of sample as hard and stiff as ceramic and as tougher and ductile as metal.

#### **2.1 Composites**

Composite materials are constituted of two or more materials that forms a single component, they remain separate and distinct. The constituent phases have different properties from each other, and they should be properly mixed and combined to give the resultant composite material. The properties of the composite are designed to be superior to those of constituents acting independently [16].

## 2.2 Constituents of a Composite

Following are constituents of composite.

### I. Matrix

- It holds the reinforcement and distributes the load in the composite
- Matrix Forms a continuous phase throughout the composite.

### II. Reinforcement

- The reinforcement provides the strength and stiffness to the composite material.
- They may be in the form of fibers, particles, flakes, whiskers. It is shown in figure 2.1 below.

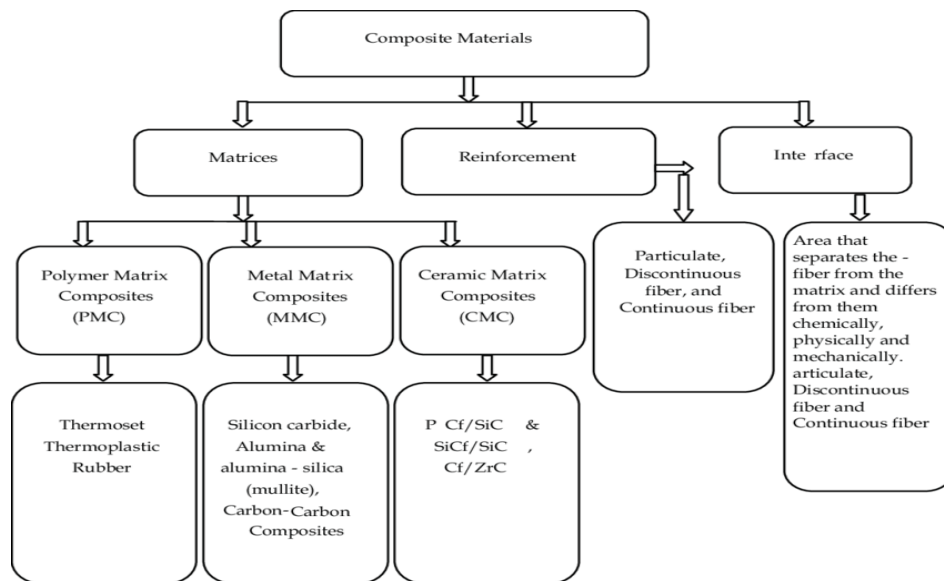


Figure 2.1 Constituents of Composite Materials [33]

## 2.3 Main Types of Composites

Based on matrix materials, composites are categorized into three major parts.



### **I. Polymer Matrix Composites (PMC's):**

- In Polymer Matrix Composites (PMC's), Polymer based material is used as a matrix and a variety of fibers like glass, aramid, carbon or natural fiber as reinforcement.
- They can be classified into thermosetting, thermoplastics or rubber composite based on their matrix.

### **II. Metal Matrix Composites (MMC's):**

- Matrix in these MMC's is constituted of metals such as aluminum
- The reinforcement in it is constituted of fibers or particles of boron, alumina, or silicon carbide. Their major use is in the automotive industry.

### **III. Ceramic Matrix Composites (CMC's):**

- Matrix in these materials is composed of ceramics and reinforcement is composed of short fibers or whiskers made of silicon carbide or boron nitride. and boron nitride whiskers.
- Major applications OF CMC's are high temperature environments

### **2.4 Metal Matrix Composites (MMC's):**

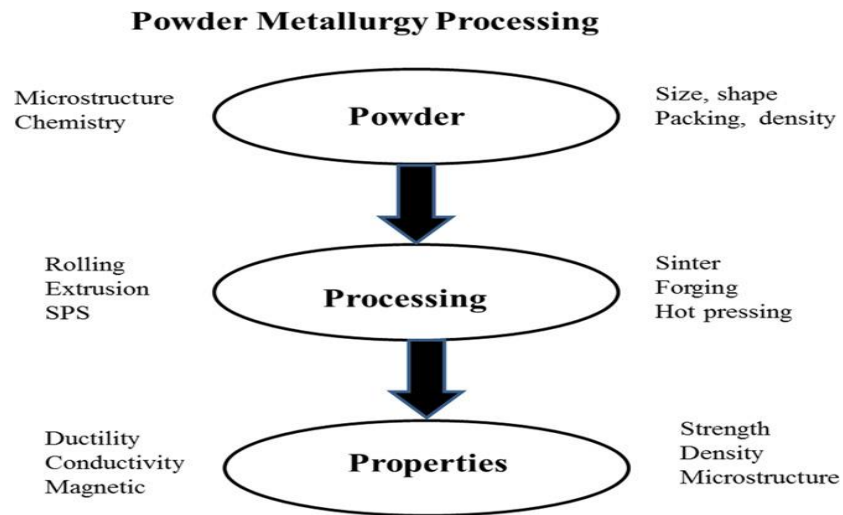
- In general, the metal alloy name of the matrix and the material type, volume fraction, and form of the ceramic reinforcement serve as the sole identifiers of a metal matrix composite system. [17].
- Metals are a substance with several uses. By choosing the right alloy composition and processing techniques, a metallic material can display a wide range of controlled qualities. The widespread usage of metallic alloys in engineering demonstrates not just their durability and strength but also how simple and inexpensive it is to manufacture engineering components using a variety of

methods. Beyond what is feasible with monolithic metals alone, combinations of attributes are now possible thanks to the creation of MMCs. Composites created by adding reinforcements to a metal can have greater stiffness together with better fatigue and wear resistance or increased specific strength along with desirable thermal properties [18].

- In many MMC applications, the cost of making desired property improvements still poses a significant problem. In many aspects, MMCs are different from other composite materials. Here are some examples of these distinctions:
- Higher ductility
- Higher toughness than ceramics.
- High Temperature Capability.
- Good Wear Resistance

## **2.5 Powder Metallurgy:**

The fabrication procedures used to create the composite materials are depicted in figure 2.2. A manufacturing technique called powder metallurgy can produce intricate goods of excellent quality and at a reasonable cost. Powder metallurgy is the study of metal powder processing, encompassing the creation, characterisation, and conversion of metal powders into useful engineering components. This versatile manufacturing method can produce a huge range of materials, microstructures, and properties. It may also directly create intricate geometric structures in order to maintain accurate dimensional control in sintered items. Powder manufacturing, blending/mixing, compacting, and compact sintering are the key operations in powder metallurgy. [19].



**Figure 2.2** Powder Metallurgy Processing [11]

## 2.6 Milling and alloying:

One method of manufacturing powder is by impacting and attrition of powder using balls in a jar. Mechanical alloying occurs when two or more elements are alloyed during the milling process. Milling and mechanical alloying are both complicated processes that include several variables. The following are the parameters:

- (I) Ball to powder weight ratio
- (ii) Milling speed (BPR)
- (iii) Filling the vials
- (iv) Milling temperature
- (v) Milling environment
- (vi) Grinding (wet/dry)
- (viii) Contamination issue

## **2.7 Processing Techniques:**

Due to the high interface energy between diamond and metals, copper and diamond are not wetted with one another, and the interface bonding is poor. As a result, to eliminate interface faults while making diamond and copper composites, first offer the sintering by pressure and temperature, then metalize the diamond surface or alloy the copper matrix. The following are two methods of interface change.

- 1) Diamond surface metallization
- 2) Copper matrix alloying

### **2.7.1 Diamond surface metallization**

Ti, W, Cr, Mo, and other active elements are plated on top of diamond particles during diamond surface pre-metallization. The diamond surface has a strong chemical connection with these active components, and copper is well wettable by the carbides created during the sintering process. Electroless plating, magnetron sputtering coating, salt bath coating, and powder coated sintering are a few of the common techniques.

### **2.7.2 Copper Matrix Alloying:**

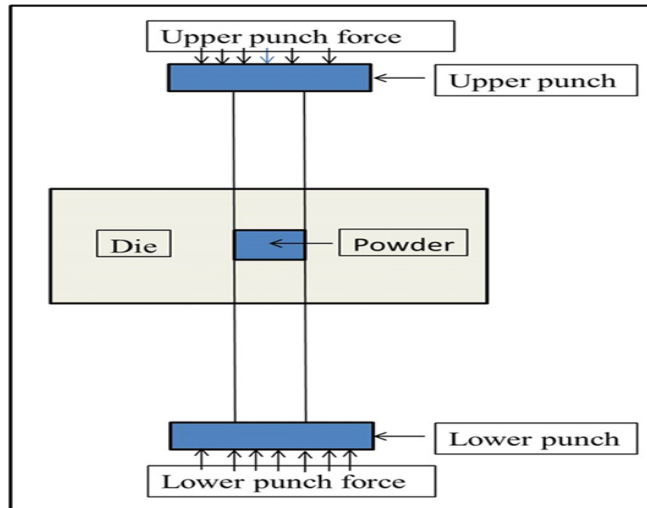
Doping different active elements into the copper matrix is known as copper matrix alloying. A carbide layer forms between the diamond/copper contact during sintering, and alloying can minimize the wetting angle between the two materials. The thermal conductivity of the composite and the interface between the diamond/copper composite are both improved. Ti, Cr, B, and Zr are some of the active elements utilised in alloying. Alloy melting and gas atomization are the processes used in copper matrix alloying

## **2.8 Powder Compaction**

After mixing of the powder with lubricants or additives, the powder is compacted. The density of loose powder particles cannot be increased with pressing. External pressure is required to increase density of the mixed powder. With the application of pressure, the initial densification rate is considerable. When pressure is applied, the particles are initially rearranged with big pores being filled, which results in a higher packing coordination. As the compaction process moves along and the pressure builds, the contact area and number of contacts expand. At the contact points, elastic deformation takes place, and the compact sites are where elastic energy is stored. High pressure increases density by causing contact enlargement and plastic deformation. As pressure increases, homogenous plastic flow propagates from the connectors and hardens the entire particle. Particle shape and size have an impact on the compaction behavior as well. Due to higher interparticle friction and particle work hardening rate, tiny particle size and irregular particles have an impact on compaction [20]. Here are a few methods for compacting powder.

### **2.8.1 Conventional compaction**

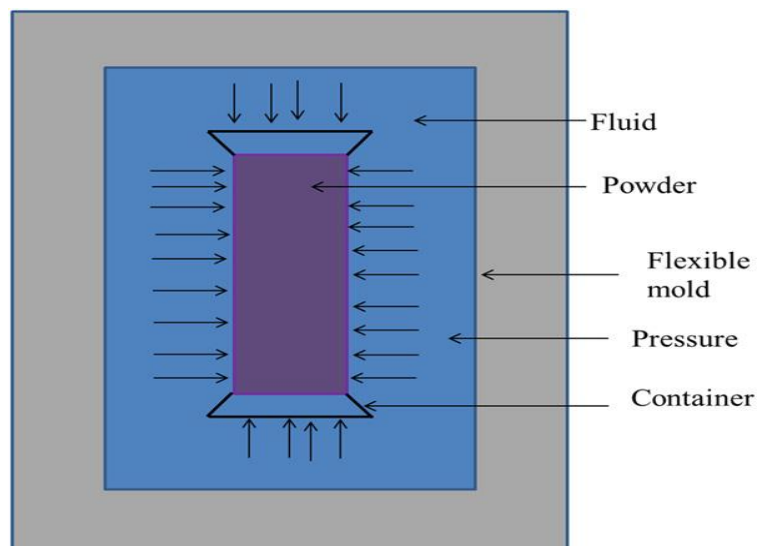
Cylindrical dies and punches have historically been used for compaction (upper and lower punches). With this technique, a lower punch is inserted into the die before being filled with powder. Next, the top of the die is placed on the upper punch. The die and punch assembly is pressed lastly during uniaxial compaction. The upper punch is removed from the die after exerting pressure on it for a predetermined period of time, and the lower punch is then used to remove the compact. Traditional die compaction is depicted schematically in Figure 2.3.



**Figure 2.3** Conventional Pressing [12]

### 2.8.2 Cold isostatic pressing (CIP)

For complex designs, huge length to diameter ratios, homogenous density, and strength, CIP is a viable technology. A fluid such as oil or water is used to isostatically apply pressure to a flexible mold that has been filled with powder. Applying pressure in all directions results in higher density when compared to conventional die compaction. Figure 2.4 displays the CIP's schematic diagram. [20].



**Figure 2.4** Cold Isostatic Pressing [11]

## **2.9 Sintering**

After improving the wetting between diamond and copper and interface bonding, the forming process is started. Sintering is the process of particles joining together at a higher temperature. Solid state sintering can occur below the melting point (0.7–0.8 of melting temperature). The creation of a liquid phase is also a part of the sintering process. The reduction in surface energy is the main reason behind sintering. Smaller particles have a larger surface area and sinter more quickly than larger particles. Sintering can occur either in a solid or a liquid state. For solid state sintering, surface energy is usually a minor driving force. A low melting phase is created during liquid phase sintering, and this liquid phase may allow for quick transport. All sintering parameters must be tuned to provide enhanced sintered characteristics. Greater strength, density, contact size, and dimensional control are produced after sintering by compaction at a higher pressure. Fabrication of composite materials can be done in a variety of ways. Fabrication procedures are determined by the component's material system and required qualities. [21]

### **2.9.1 Sintering Mechanism:**

In sintering, there are two types of transport mechanisms: surface transport and bulk transport. Sintering between two particles results in the formation of a neck. Because material originates and terminates at the surface, there is no shrinkage or densification in the surface transport process. The two most essential contributors during the process are surface diffusion and evaporation-condensation. Sintering was regulated through surface transport. Surface diffusion is dominant during metal sintering at low temperatures. On the contrary, Shrinkage or densification occurs because of bulk transport. The mass begins in the interior of the particle and is deposited at the neck. Examples of mechanisms include the transport of bulk materials, volume diffusion, grain boundary diffusion, plastic flow, and viscous flow. Although bulk transport activities also result in bulk shrinkage or densification, both surface and bulk transport methods promote neck growth. Typically, bulk transportation takes place in a hot environment [22]

### **2.9.2 Liquid and Solid-State Sintering:**

Sintering can take place in a liquid or solid form. Solid state sintering is frequently driven by modest amounts of surface energy. Sintering is frequently improved to generate material with a higher density and strength. The appearance of a liquid phase, the application of external stress (pressure aided sintering), and the addition of additives all improve sintering (activated sintering). During phase sintering, a liquid state low melting phase is produced, and this liquid phase may enable fast transfer. Several conditions must be satisfied for liquid phase sintering. Wetting is the first of these elements. There needs to be good wettability between the solid and liquid phases. Good wettability is ensured by a low contact angle between the solid and liquid phases because liquid spreads across the solid surface. [23] .

### **2.9.3 Sintering Methods**

Following are some of the most common Sintering or Forming Methods.

- (1) Sintering Without Pressure (Conventional)
- (2) Hot Pressing Sintering:
- (3) Spark plasma sintering
- (4) High Temperature and High-Pressure Sintering
- (5) Infiltration Process

#### **I. Sintering Without Pressure (Conventional)**

The composite powder combination is first compacted with a die, and the green compact is subsequently sintered in a furnace. Depending on the materials system, different atmospheres, including Ar, N<sub>2</sub>, H<sub>2</sub>, and NH<sub>3</sub>, are employed during sintering. It is possible to sinter green compacts in either a solid or a liquid state. External additives are occasionally employed to aid in the production of the liquid phase in solid state sintering because the rate of densification is slower. Usually, the sintering temperature is between 0.7 and 0.8 of the selected melting point.



## II. Hot Pressing Sintering:

A popular powder metallurgy procedure is hot pressing sintering, which is shown in figure 2.4. This procedure involves pouring a mixture of diamond and copper powder into a mold, which is then heated and pressed simultaneously in a vacuum hot-press furnace. To maximize the interface bonding between the copper and diamond, the technique relies on the management of sintering settings and the insertion of active materials.

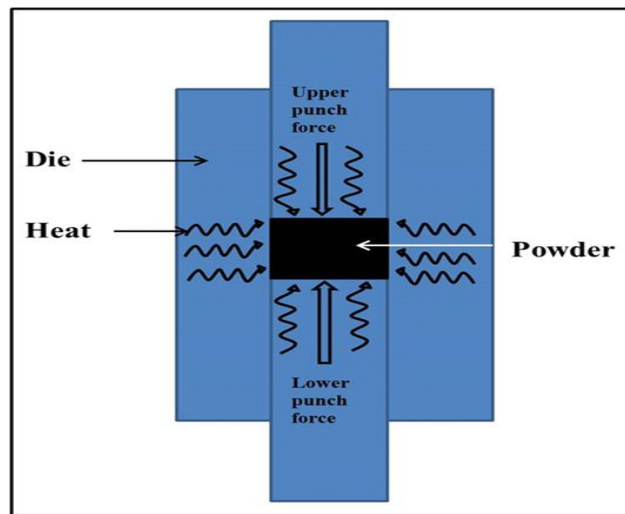


Figure 2.5 Hot Isostatic Press [11]

## III. High Temperature and High-Pressure Sintering:

To create composite materials with a high density and good performance, the high temperature and pressure sintering method involves sintering a mixture of diamond and copper powder at high temperatures and high pressure. The cavity is often pressurized in several directions throughout this process using a hexahedral press, and the sintering pressure is significantly higher than the hot-pressing pressure. High density and great efficiency are its benefits. This process produces materials with exceptional qualities, but it is expensive and requires complicated equipment.

#### IV. **Spark plasma sintering (SPS)**

In recent years, the spark plasma sintering (SPS) technology has been developed, which densifies powder particles rapidly at temperatures below the melting point. Pulse current and pressure are delivered to the powder particles in this process, which eats the particles uniformly through the plasma formed at the time of the spark discharge, activating the particle surface, and allowing for quick densification sintering. Fast sintering speed, rapid temperature rises or decreases, low sintering temperature, energy savings, and environmental protection are all advantages.

#### V. **Infiltration Process:**

Copper is heated to a liquid or molten state during the infiltration process in order to pass through the diamond particle gap and produce high-performance composite materials. Pressure infiltration and pressure less infiltration are two different types of infiltration tactics. Pressured infiltration, on the other hand, takes place when an external force is applied to promote infiltration in the process of infiltration, which is widely used and yields satisfactory results. Pressure less infiltration takes place when no external force is applied, during which molten copper or copper alloy primarily infiltrates into the pores of diamond preforms to produce composite materials. Regular pressure infiltration and ultra-high-pressure infiltration are the two categories into which pressure infiltration may be divided.

#### **2.10 Diamond Based Composites:**

Diamond-metal composites with a high heat conductivity are rare in MMCs with a high filler percentage. Diamond was chosen as a filler because it is an isotropic material with a record thermal conductivity (up to 2200 W/ m K for pure diamond). The matrix is constructed of metals with the highest conductivities, such as copper (390 W/m K) or aluminum (230 W/m K), and, less frequently, silver (420 W/m K), due to its higher melting point, expense, and rarity. Although they are not a functional purpose for composites, mechanical properties are nonetheless significant. The state of the interface between the filler and the matrix determines the composite's thermal and mechanical properties (interphase boundary thermal resistance, interface

adhesion), despite the fact that they have a high thermal conductivity. As a result, they play a significant role in both the thermal conductivity and the mechanical properties of the composite. For the creation and use of products, excellent mechanical properties are essential for thermal applications from composites (assemblies in electronic modules, etc.) [24].

### **2.11 Heat Sink Application:**

Metal matrix composites have lately been developed for electronic packaging applications due to their appealing thermophysical and mechanical properties. The most striking attribute of metal matrix composites is their ability to modify the volume fraction of reinforcement to modify the thermal conductivity and coefficient of thermal expansion (CTE). One of the metal matrix composites, the diamond/Cu composite, looks to have the ability to eventually meet the growing demand for heat sink materials and high-performance packaging. Studies have demonstrated that the interface between the diamond and the copper matrix has a substantial impact on the thermal conductivity, coefficient of thermal expansion, and mechanical properties of diamonds. Due to their inability to wet one another, diamond and liquid copper have weak interfacial bonds. [25].

There are numerous papers on the above-mentioned features of composites in the literature, as well as several publications on the properties of nanocomposites [26]. Wide ranges of research have validated its useful properties which are underlined in next section.

### **2.12 Literature Background**

Hybrid composites perform very good function due to its improved properties. The prime objective is to enhance its mechanical properties and thermal conductivity [27]. Several researchers have confirmed the effect of reinforcement on copper-based matrix and have published their result.

### **1. Luhua Wang [3]**

The goal of this research is to create a homogeneous and dense carbide layer on the diamond surface, which will improve the interfacial reaction. To adjust the thickness of the interfacial carbide layer, the Cr content in the Cu-Cr alloy matrix was varied. By doing so, the Cu-0.5 wt% Cr/Cr-diamond composite achieves a maximum thermal conductivity of  $810 \text{ W m}^{-1} \text{ K}^{-1}$ , the highest value ever reported for Cr-modified Cu/Diamond composites. This research presents a unique way for altering the interface bonding of diamond/copper composites and increasing thermal conductivity.

### **2. Jing Sun [10]**

In the current study, mechanical alloying was successfully used to deposit Ti-coated diamond/copper composite coatings on T2 Cu matrix. On the coatings, the effects of milling time and diamond content were examined. The results showed that mechanical alloying on a diamond surface with Ti powder could enhance the wettability between copper and diamond. Additionally, pre-refinement of the diamond particles was used, which contributed to the creation of coatings with uniform diamond distributions and improved properties.

### **3. Hai Jun Cho [28]**

Thermal conductivities of materials electrodeposited in this study were measured. At 68.2 vol percent diamond, the greatest thermal conductivity ever measured was  $454 \text{ W/mK}$ . Titanium carbide (Tic) coatings were applied to the diamond particles to boost heat conductivity even more. The thermal conductivity of the electrodeposited copper matrix was increased to  $557 \text{ W/mK}$  at 34.7 vol% due to the presence of Tic-coated diamond particles. The new value is 40% higher than the previous one. For pure copper, the value is  $400 \text{ W/mK}$ . These findings imply that electrodeposition might be employed as an alternate method for creating copper-diamond composite materials for thermal management. Nonetheless, the microstructure altered after electrodeposition.

#### **4. Shugang Dai [21]**

This study observed the thermal conductivity of a composite diamond/copper material. The theoretical framework, production process, and early application of the research on diamond/copper composite materials are outlined in this article. The current study examines the factors that affect high thermal conductivity, including molding technology, composition parameters, interface thickness, interface modification methods, and active element selection. Theoretical model modification, interface modification improvements, the use of aggregated diamond to generate high heat conduction channels, and near net forming technology should be the main focus of future study in this field.

#### **5. Muhammad Zain-ul-abdein [9]**

This paper investigates the interfacial debonding of Cu/D composites under steady-state and short heat cycle loading. From a SEM image, a micro-scale finite element model of the Cu/20 vol percent diamond composite sample was created. Regarding the movement of heat and the interactions at the borders between diamonds made of copper and those coated with chromium. Different debonding tendencies have been observed as a result of the variations in the coefficients of thermal expansion (CTEs) of Cu, diamond, and Cr. The separation of surfaces also had an immediate effect on the equivalent stress state of the Cu-matrix since diamond particles can only deform elastically. Due to repeated heating and cooling cycles, FE analysis revealed that the Cu-matrix along the diamond interface was under extremely high stress. The numerical analysis of these stresses can be utilized to forecast the service life of heat sinks for a certain application in advance since they lead to interfacial debonding.

#### **6. Katsuhito Yoshida [33]**

In this study, a novel composite material consisting of copper and diamond was successfully created utilising high pressure and high temperature to suit the demands for a high-performance material for heat spreader materials and packaging. The effects of diamond particle sizes and volume fractions on thermal conductivity and the coefficient of thermal expansion were examined (CTE). While the thermal

conductivity of the composite material was influenced by both particle size and diamond volume fraction, the CTE was primarily determined by diamond volume fraction. The empirically obtained thermal conductivities of the composite materials exceeded the theoretically predicted values at larger diamond volume%, while the CTE was calculated experimentally and lay between the two theoretical Kerner lines. Due to its high thermal conductivity and capacity to adjust its coefficient of thermal expansion to a semiconductor material of electronics devices, the diamond-copper composite has the potential to be a heat spreading substrate with good performance and high reliability..

## **7. Congxu Zhu [42]**

This paper offers a novel molten salt method for producing surface-modified diamond particles in situ. Metal-based (copper or magnesium) composites with surface-modified diamond particle reinforcement were created via spark plasma sintering. Field-emission scanning electron microscopy was used to examine the surface morphologies of the surface-modified diamond samples as well as the interfacial bonding of the diamond-metal composite materials. The elemental distributions of the surface-modified diamond particles were evaluated using energy-dispersive X-ray spectroscopy, and the phase compositions of the samples were examined using X-ray diffraction. X-ray photoelectron and laser Raman spectroscopy were used to investigate the surface bonding and graphitization of the surface-modified diamond particles further. The results showed that the thickness of the modification layer on the diamond surface gradually increased as holding time was increased. The surface-modified diamond particle reinforced metal-based composite materials had high heat conductivities..

## **8. Seungchan Cho et al [56]**

This study used spark plasma sintering and hot extrusion to produce a multi-walled carbon nanotube reinforced copper matrix with chromium at the Cu-CNT Nano-composite interface. According to this study, increasing the number of CNTs in a composite increases its tensile strength. The potential load-transfer mechanisms of the

interfacial Cr carbide nanostructures can be ascribed to the improved tensile strength of MWCNT/CuCr composites.

#### **9. M. Masroor et al [59]**

The author explored the influence of milling energy in two distinct media on CNT dispersion and nanocomposite manufacture in this work. To create a Cu-Cr/carbon nanotube (CNT) hybrid nanocomposite, wet and dry milling techniques with three distinct degrees of milling energy were used. The structural morphology was investigated using the x-ray diffraction method. SEM was used to analyse the microstructure of the composite. Mechanical characteristics were determined using microhardness and ultimate tensile testing. The crystallite size varied from 20 to 63 nm. Milling energy has an influence on dispersion, and it has been observed that wet milling at higher milling energy is more successful at dispersing Nanocomposite.

#### **10. Choi, H et al [58]**

Focused their attention on the mechanical properties of composites made of Cr-CNT as well as the effect of CNTs and variations in grain size. In a ball mill with a BPR ratio of 15:1, the grinding of pure Cr and Cr-CNT containing 4 vol. percent took six and twelve hours, respectively. After being vacuum-sealed, compressed, and sintered at 470 degrees Celsius, the samples were then subjected to a process known as hot extrusion at a ratio of 15:1. An analysis of TEM images revealed that the grain size of pure Cr powder reduced to 200 nm after six hours of milling and to 70 nm after 12 hours of milling. On the other hand, the grain size of composite powder was comparable to that of pure Cr at the same milling durations. Following the extrusion process, the grain size of both the pure and composite samples was essentially unaffected in any way. The results of the compression tests carried out on both pure and composite materials. It is clear from the compression data that the addition of CNT to the sample that was milled for 6 hours resulted to a considerable improvement. Samples that had been treated for a period of 12 hours demonstrated no influence from CNTs because of the very small particle size and the material's hardening [39].

The author asserts in his conclusion that the CNTs were aligned in the direction of extrusion without any clustering and that the sintering and extrusion temperatures are relatively low (470 degrees Celsius), which, in his opinion, prevented the formation of chromium carbide.

#### **11. Kuzumaki et al [57]**

Employed CNTs created by arc discharge in this study. He blended 5 and 10 percent volume CNT with pure Cr and ethanol for a half hour to disperse 26 CNT. Next, the mixture was dried and placed in a Cr case for storing. After heating and compressing the case in a steel die to 773 K, the case was extruded at 773 K. The tensile strength and elongation % tests vs annealing time yielded the most notable findings, despite the use of several characterization methods. The addition of 5 and 10 percent vol. CNT to the annealing process prevents a decrease in tensile strength as well as an increase in percentage elongation. Using SWCNTs in conjunction with 50-nm Cr powder, Zhong et al. reported on the results five years later. However, unlike Kuzumaki et al., the sintered compact was not extruded from the sintered powder. Al with no reinforcement was found to have an expansion coefficient that was 65 percent lower than that of CNTs with a 15% volume. In addition, the composite's hardness was much higher than that of the unreinforced sample.



## Chapter 3

# EXPERIMENTAL WORK

### 3.1 Materials

Copper powder of 200 mesh (74 micron) and 99.9 % purity was used as a matrix. The powder is supplied by 'Uni-Chem Chemical Reagents'. Chromium powder was of 45 micron and purity of 99%. The powder was supplied by 'Sigma-Aldrich Germany'. The diamond particles are regular cube-octahedral shape. Two different compositions of powder were prepared. First composition contains Cu, Diamond, and Cr Powder while second composition contains Cu, Diamond, CNTs and Cr Powder. Diamond and CNTs powder were used as reinforcement. Using analytical balance, Compositions described below in table 3.1 and table 3.2 were taken and put into wash bottle for mixing.

**Table 3.1** Copper-Diamond-Cr

Material	Weight %	Volume %
Copper	96.2	91.8
Diamond	3	7.3
Chromium	0.8	0.9

**Table 3.2** Copper-Diamond-CNT-Cr

Material	Weight %	Volume %
Copper	95.7	90
Diamond	3	7.3
CNT	0.5	1.8
Chromium	0.8	0.9

### 3.2 Milling and Mixing:

Wise Mix ball milling apparatus was used which is shown in figure 3.1. Stainless steel balls of 3 mm and 5 mm were used. 320 grams of 3mm and 130 grams of 5 mm balls were taken. The powder mixture and stainless-steel grinding balls were put into wash bottles of 250 ml, with the mass ratio of ball to powder at 15:1 (450 grams balls and 30 grams powder mixture). The mixing speed was 300 RPM. Powder of Copper and Chromium was mixed for 20 hours.

- Diamond powder of weight 3% was taken and blended in a wash bottle containing a mixture of copper and chromium. It was then milled for further 4 hours and dry mixed without using any fluid.
- Diamond and Carbon Nanotubes were wet mixed with Copper and Chromium powder that was already mixed for 20 hours. The wet mixing was done for 4 hours. Wet mixing was used instead of dry mixing because CNTs cannot be homogeneously mixed in dry form. In wet mixing ethanol (10 %) is also added. After mixing the powder was kept in the furnace for 4 hours at 400 °C. The powder was then separated from steel balls using a sieve of 80 mesh. The Mixed powder was then pressed.
- 



**Figure 3.1** Ball Mill

### **3.3 Sample Preparation:**

#### **3.3.1 Pressing:**

Powder mixed in ball milling was pressed by using Hydraulic Press and Cold Isostatic Press. Following procedure was followed to carry out pressing.

##### **a) Hydraulic Pressing:**

- The powder mixed was weighed in Analytic balance.
- Pellets of compression test were made by pressing powder using circular die which have 6.5 mm diameter.
- The die was then filled with powder according to the sample size required. Powder of 1.9 gm for each sample was taken. Each composition described in Table 3.1 and Table 3.2 was then pressed in Hydraulic Press at 3 Ton pressure.
- Pressing was done for 4 mins, which converts the powder into a green compact. The pressed sample have 11 mm height and 6.5 mm diameter

##### **b) Cold Isostatic Pressing:**

The uniaxially compressed green compact of each sample was then Cold Isostatically Pressed for the better densification. The fluid used in Cold Isostatic Press is oil. To apply liquid pressure, uniaxially compressed green compact materials was sealed in a forming mold with low deformation resistance, such as a rubber bag. Then, by conveying the liquid pressure, the rubber bag was crushed uniformly across its whole surface. Pressure applied was 250 MPa and time was 4 mins. Cold Isostatic Press is shown in figure 3.2 below.



**Figure 3.2** Cold Isostatic Press

### **3.3.2 Sintering:**

For sintering, a Protherm tube furnace was used (Figure 3.3). The samples were placed in a graphite boat and the same was placed in a quartz glass tube for heating in the Protherm tube furnace. After placing the samples, the tube was sealed using silicone gel to avoid leakage and oxidation of chromium. The environment used in the tube was Argon. The one side of the tube was used as input to argon gas while the other side as output of the gas. The temperature was set for 3 hours once it reaches 950 °C. It takes 2 hours for temperature to reach 950 °C as it is increased 10 °C per minute.



**Figure 3.3** Tube Furnace

### **3.4 Density:**

Density of the sintered pellets was measured using Archimedes principle. According to Archimedes' principle, the buoyant force exerted on an object is equal to the weight of the fluid that the water has displaced. In our case, we first measured the weight of the pellet in dry form and then dipped the pellet in water. From the difference of the weight, we calculated the density of the samples. The density measuring apparatus is shown in figure 3.4.



**Figure 3.4** Densitometer

### **3.5 Metallography:**

#### **3.5.1 Mounting & Grinding:**

Sintered samples were mounted using Bakelite powder. The emery Paper of different grit sizes were used for the grinding purpose. These sizes were for the grinding purpose. The emery papers with grit sizes of 180, 300, 400, 600, 800, 900, 1200 and 1500 were used. The water was continuously used during grinding. After grinding with each paper, it was checked in optical microscope.

#### **3.5.2 Polishing:**

After grinding the polishing was performed using a polishing cloth, alumina suspension and various diamond polishing pastes. Copper was polished using alumina as suspension. The Samples containing diamond powder were polished using diamond polishing paste. Polishing paste of different particle numbers was used. These particle numbers were W 10, W5, W 3, W 1. Surface of the pellet was properly cleaned with water after polishing. The surface was then dried, and its surface was analyzed in a optical microscope.

#### **3.5.3 Etching:**

For etching, the following etching solution was used.

- Distilled water or Ethanol 100-120 ml
- Hydrochloric acid 25-50 ml
- Ferric chloride 5-10 gm

### **3.6 Characterization Techniques:**

#### **3.6.1 SEM Analysis:**

SEM is an important technique to demonstrate the size, microstructures, form, and morphology of objects. The principle of SEM operation is that it uses a high-energy electron beam from an electron source (Gun) to generate a variety of signals at the sample. The images obtained contain external texture and crystalline structure. A sample of 1cm to 5 microns in size could be seen with magnifications ranging from 20X to 30,000X. The characterization was done using Jeol 6490 LV which is a high-performance Scanning Electron Microscope shown in figure 3.5.



**Figure 3.5** Scanning Electron Microscope Jeol 6490 LV [11]

### **3.6.2 X-Ray Diffraction (XRD)**

XRD is widely used for obtaining information on the crystallographic structure of samples. The peaks are shown for crystalline samples and hump for an amorphous sample. In its working in the x-ray tube rays are generated and collimated towards the sample. With the satisfaction of brag's law, the interaction of rays on a sample produces interference. The results are revealed in the form of intensity versus angle graphs. The confirmed identification of XRD patterns is done by matching them with by matching them with standard reference through software. By using Xpert's PRO PAN analytical X-ray diffractometer sample's pattern was obtained.

### **3.6.3 Vickers Hardness Test:**

Vickers hardness is a micro hardness testing used to determine the material hardness at microscopic level. In this test, a square indentation is produced in the sample using a  $136^\circ$  pyramidal diamond indenter. For 10 to 15 seconds, the load is applied. Based on a calibration for various kilogram loads, the two axes of the diamond-shaped indentation are averaged (to obtain the dimension d), and the

hardness is calculated (P). First Hardness of Pure copper was measured with Vickers. Then the hardness of composite materials was measured and compared with the pure Copper to check its improvement.



**Figure 3.6** Vickers Hardness Test

#### **3.6.4 Compression Strength:**

To study the mechanical behavior of the nanocomposites, compression test was performed using a tensile testing machine as shown in figure 3.7. A compression testing machine is a universal testing machine (UTM) configured to determine material's strength and deformation behavior under compressive (pressing) load. Three types of cylindrical samples of each composition were prepared for the Compression test which was carried at a strain rate of 0.05mm/sec.

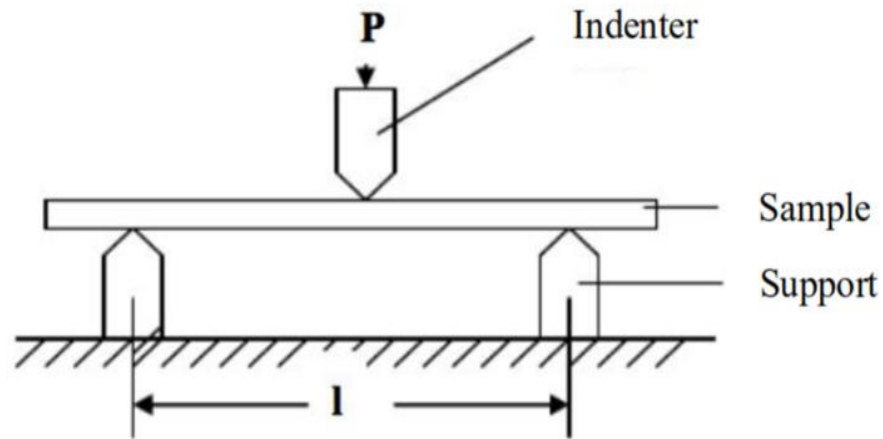




**Figure 3.7** Universal Testing Machine SHIMADZU

### **3.6.5 Bend Test:**

Bending strength (also known as flexural strength) is a critical index in the mechanical properties of cutting tool materials. To assess the bending strength of cutting tool materials, the three-point bending loading method is commonly employed. Rectangular samples were prepared for flexural strength and the test was carried at 1mm/min. To prevent surface microcracks from affecting the test results, the surface of the test sample was polished. The spread between the two fulcrums of the support was altered when clamping the sample in accordance with the sample size, The test schematic is shown in figure 3.8.



**Figure 3.8** Schematic of Bend Test [15]

### **3.6.6 Thermal Conductivity:**

The thermal conductivity measurements of the samples were measured using a thermal conductivity meter. These tests were performed at the Institute of Space & Technology (IST), Islamabad, Pakistan. A thermal conductivity meter is based on a thermal analysis technique, which examines the heat flow and temperature connected to a material's thermal transitions. For the present work experiments, the temperature on one side was 50 °C and on the other side was 38 °C. The obtained results are discussed in the preceding sections.

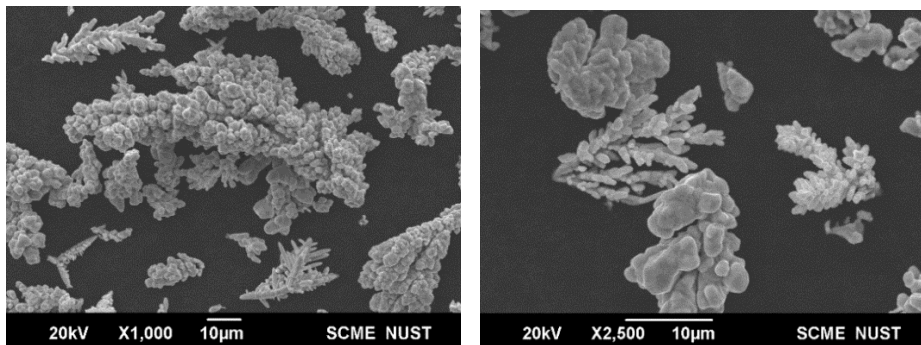
# Chapter 4

## Results and Discussion

### 4.1 SEM Analysis:

#### 4.1.1 Copper Powder:

Scanning electron microscope images of the pure copper powder are figure 4.1.

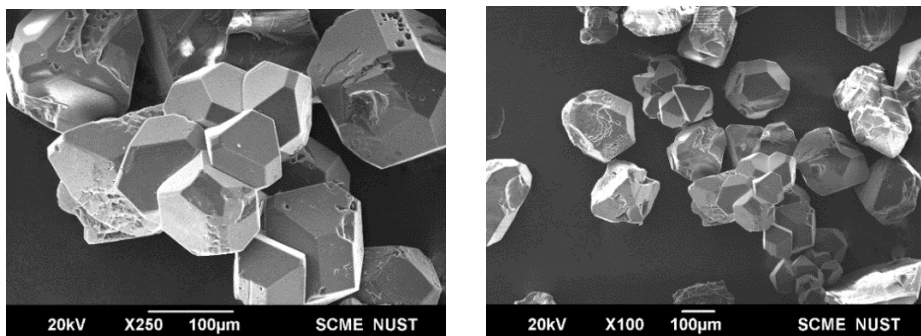


**Figure 4.1** Copper Powder

Figure 4.1 clearly shows that the copper particles are in the form of agglomerates and their shape is also irregular. Their size ranges from 10 µm to 30 µm.

#### 4.1.2 Diamond Powder:

Figure 4.2 show the SEM images of the diamond particles used in the present study



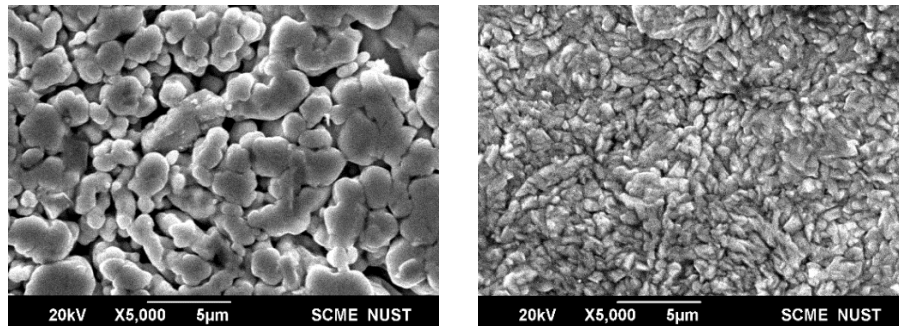
**Figure 4.2** Scanning Electron Micrograph of Diamond Powder

It is evident from figure 4.2 that the some of the diamond particles are in also in the form agglomerates. Therefore, the ball milling was conducted, which helps in

breaking of the agglomerates / cluster. From some isolated diamond particles, the size range was estimated to be from 100  $\mu\text{m}$  to 200  $\mu\text{m}$  .

#### 4.1.3 Copper Pellet:

Microstructure of non-Sintered and sintered copper Pellet is shown in figure 4.3

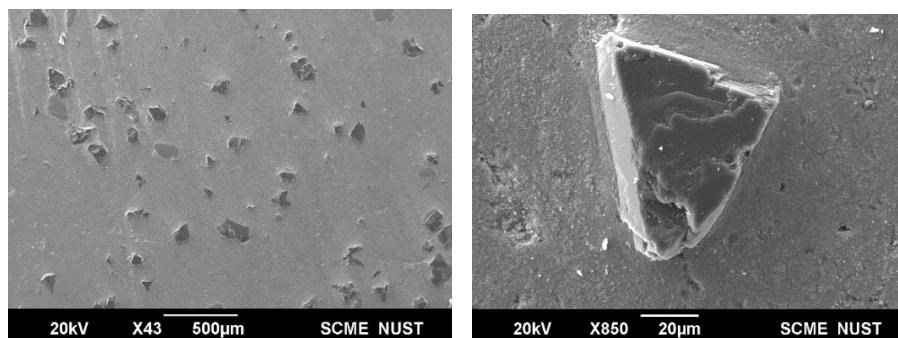


**Figure 4.3** Scanning Electron Micrograph of non-Sintered Copper Pellet (left) and Sintered Copper Pellet (right).

For the non-sintered pellet, large number of pores can be clearly seen in Figure 4.3 (left). In the figure 4.3 (right), we can see that the pores are now in small number and of small size. This is the effect of sintering on the copper pellet, which has reduced its porosity.

#### 4.1.4 Cu-D-Cr:

Figure 4.4 shows the SEM images of the sintered Cu-D-Cr composite.

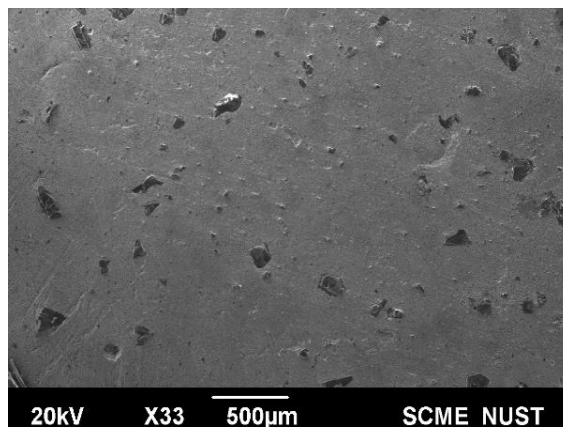


**Figure 4.4** Scanning Electron Micrograph of Copper-Diamond-Cr Composite

The figure 4.4 (left) reveals even the distribution of diamond powder in copper matrix and agglomeration of diamond particles has not occurred. It is also clear from the same image that the composite has smooth surface. Figure 4.4 (right) shows the image of the diamond powder in copper matrix. It shows that the matrix has tightly held the diamond particles, therefore, they will conduct heat at a faster rate.

#### 4.1.5 Cu-D-CNT-Cr

The SEM image of the sintered Cu-D-CNT-Cr composite is shown in figure 4.5



**Figure 4.5** Scanning Electron Micrograph of Diamond in Copper-CNT-Cr Matrix

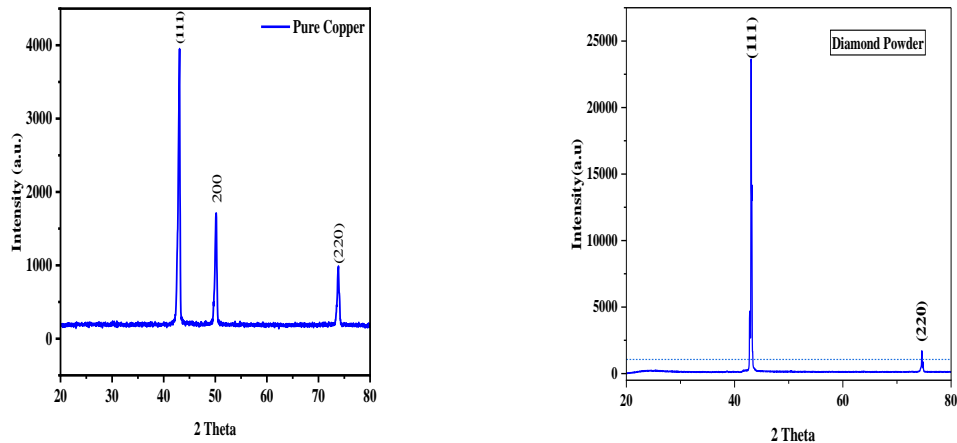
Figure 4.5 clearly shows the even distribution of diamond powder in copper matrix and agglomeration of diamond particles in matrix has not occurred in Copper-CNT-Cr matrix. The matrix material around the diamond particles is in good contact with the diamond grains, which will help in the conduction of heat through the sample.

## 4.2 X-RAY Diffraction (XRD):

Using an X-ray diffractometer model JEOL-JDX-9C, the XRD analysis was carried out. The major findings from the XRD analysis are discussed below:

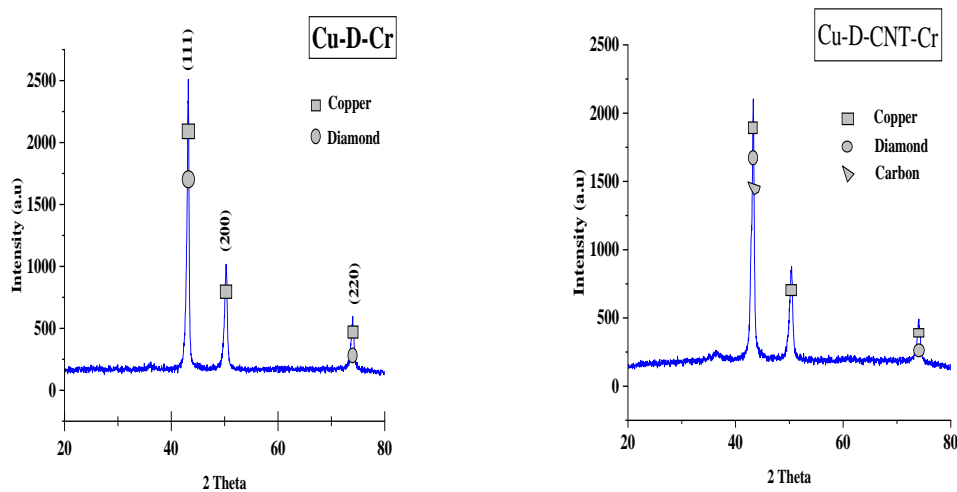
#### 4.2.1 XRD Analysis Pure Powder and Composite:

The XRD Patterns of the pure copper, pure diamond, Cu-D-Cr -and Cu-DCNT-Cr are shown in Fig. 4.6 (a. b) and Fig 4.7 (a, b), respectively.



**Fig 4.6** XRD Pattern of a) Copper Powder b) Diamond Powder

Copper 2 $\theta$  peak position is at (43.64, 50.80, 74.42) and d spacing of (2.07, 1.80 1.27) which corresponds with pattern of copper (JCPDS Card No 00-002-1225), diamond and carbon 2 $\theta$  peak position is at (43.99 ,75.41, 91.64) and d spacing of (2.07, 1.27 1.081) which corresponds with diamond (JCPDS Card No (96-901-2291) and carbon (JCPDS Card No 0-001-1242)



**Fig 4.7** XRD Pattern of a) Cu-D-Cr b) Cu-D-CNT-C

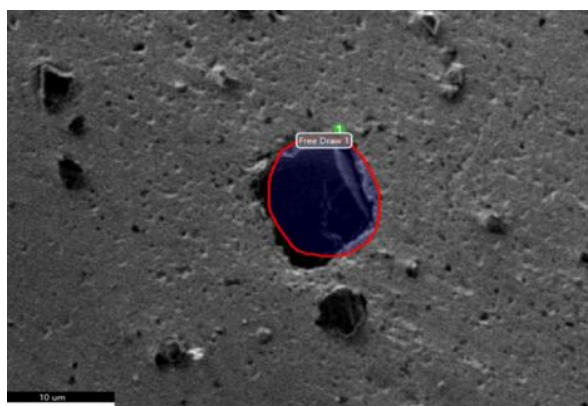
The XRD patterns Cu-D-CNT pellet and Cu-D-Cr-CNTs pellet matched with their respective patterns of Copper, Diamond, and CNT (as Carbon) shown in Figure 4.6 (a, b) confirming the compositions of the composite.

### 4.3 EDX:

In addition to SEM, energy dispersive X-ray analysis (EDX) was carried out to provide elemental identification and quantitative compositional information. Cu-Cr-D composite demonstrates how an adhesive interface form. The chromium-carbide bonding layer between the matrix and diamond particles is responsible for the adherent interface in the Cu-Cr-D composite. The unreacted chromium forms a diffusion bond with the carbide layer and the matrix during the sintering process. The carbide layer's chemical connection prevents the matrix from separating from the diamond particles during cooling [22]. The composites' interface-level EDX scan analyses are displayed in Figure 4.8. In Cu-Cr-D composites, the EDX scan reveals chromium deposition on diamond particles and its diffusion in the matrix.

**Table 4.1** Elemental Composition of Cu-D-Cr

<b>Elements</b>	<b>Weight %</b>	<b>MDL</b>	<b>Atomic %</b>	<b>Error %</b>
<b>C K</b>	87.3	0.01	97.3	9.4
<b>Cr K</b>	0.2	0.05	0.1	11.1
<b>Cu K</b>	12.6	0.1	2.7	2.7



**Figure 4.8** EDX Scan

## 4.4 Density:

Density of samples was measured using Archimedes Principle. In this process first dry weight and then wet weight of the sample is measured. After measuring the weights, dry weight value is subtracted from wet weight value. Difference is then divided on dry weight, which gives the value of sample. The density of copper/chromium/diamond composite is less than pure copper because of the small densities of chromium and diamond which decreases the overall density of the composite. Similarly, the density of copper/chromium/CNTs/diamond is the smallest than other samples due to the addition of CNTs which further decreases the overall density of the composite

**Table 4.2** Density of Pure Cu sample and composite samples.

Elements	Density Measured(gm/cm <sup>3</sup> )	Relative Density	Theoretical Density(gm/cm <sup>3</sup> )
Pure Cu	8.1	90 %	8.96
Cu-Diamond	7.40	91%	-
Cu-Diamond-Cr-CNT	6.9	86 %	-

### 4.4.1 Copper:

The Theoretical Density of Copper is 8.96 g/cm<sup>3</sup> [17] and the density of the pure sample measured was 8.11 g/cm<sup>3</sup>. The Relative Density was 90 % and was calculated by dividing theoretical density over measured density.

### 4.4.2 Cu-Cr-D & Cu-Cr-CNT-D

First Cu-Cr-D sample density was measured, and its value was 7.40 gm. The relative density calculated in comparison to pure sample which was 91 %. Then the Cu-Cr-CNT-D sample density was measured, and its value was 6.9 gm. The density



of second sample was 86% in comparison to pure copper. Relative density of composite in comparison with pure copper is 91 % and 86 %, which is acceptable. Studies shows that samples which are cold pressed have relative densities of more than 80 % [10]. As the volume percent of diamond rises, the densification of PM Cu decreases and is more than the densification of the other compositions. The reason for the decrease in densification as the volume percent of diamond increases is the strong restriction influence of hard diamond particles on the soft copper matrix, i.e., no deformation of the reinforcement during cold pressing. Additionally, as the diamond particles cool from the sintering temperature, they create air gaps at the interface and serve as diffusion barriers for the matrix particles throughout the sintering process. Due of an increase in diffusion barriers and interfacial gaps, densification falls as the volume percent of diamond increases [24].

#### **4.5 Compression Test:**

Compressed samples which have been tested are shown in Figure 4.9.



**Figure 4.9** Compressed Samples after Testing

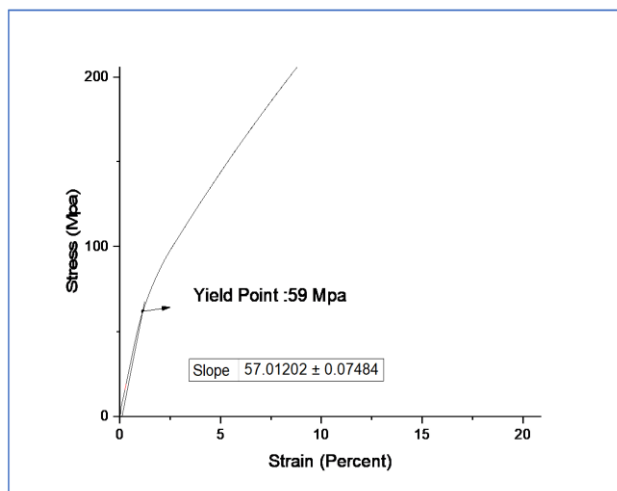
Yield point and Young Modulus values of Copper, Copper Diamond, and Copper-Diamond-CNT are shown in table 4.3 which shows increasing trend.

**Table 4.3** Compression Test Results of Samples

Material	Yield Point	Young Modulus
Copper	59 MPa $\pm$ 3	5.7 GPa
Copper-Diamond	80 MPa $\pm$ 2	11.2 GPa
Copper-Diamond-CNTs	84 MPa $\pm$ 6	10 GPa

#### 4.5.1 Analysis of Pure Copper Compression test

The yield point was calculated by using an off-set method and the straight region of the stress-strain curve was used for the estimation of the Young Modulus. For both, an Origin Lab software was used. Yield Point of the pellet tested by UTM is 59 MPa and Young modulus is 5.7 GPa as shown in figure 4.10.



**Figure 4.10** Pure Copper Stress strain graph

#### 4.5.2 Analysis of Cu- D-Cr Compression test:

Yield Point of the pellet tested by UTM is 79 MPa and Young modulus is 11.2 GPa as shown in figure 4.11. Yield Point of the Cu-D-Cr pellet is increased in comparison to copper which have Yield Point of 59 MPa due to presence of Diamond reinforcement Young Modulus of the composite is 11.2 GPa while copper have 5.7 GPa. The results are quite good as its properties have increased, and the composite material can withstand larger strains before breaking and have high stiffness then pure copper.

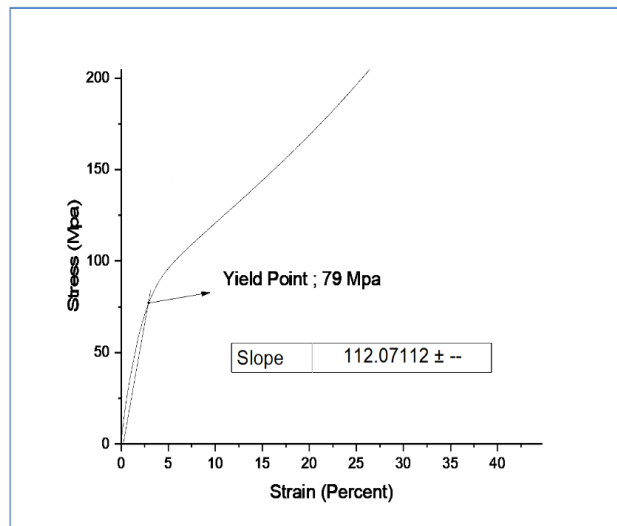
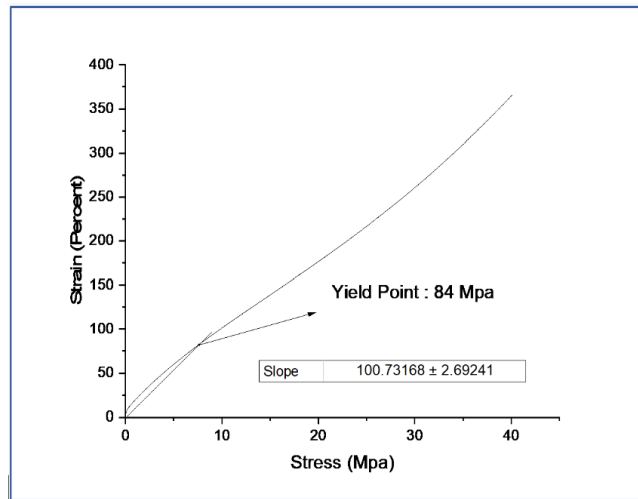


Figure 4.11 Cu- D-Cr Stress strain graph

#### 4.5.3 Analysis of Cu-D-CNTs-Cr Compression Test:

Yield Point of the Cu-D-CNT-Cr composite pellet is 84 MPa and increased in comparison to pure copper which have Yield Point of 59 MPa and Cu-D-Cr having yield point of 79 MPa due to presence of Diamond reinforcement and CNTs. Young Modulus of the composite is 10.07 GPa while copper have 5.7 GPa. The results are encouraging as its properties have improved, and the composite material is much stronger than pure copper and even Cu-D-Cr composite.



**Figure 4.12** Cu-D-CNT-Cr Stress strain graph

## 4.6 Bend Test:

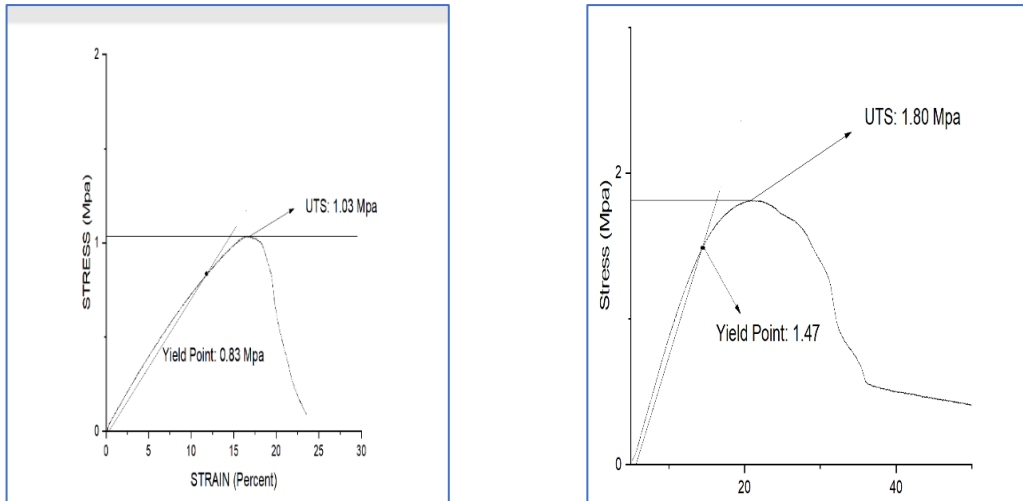
This test was conducted using a three-point bent fixture on a SHIMADZU AGX Plus instrument, a universal testing equipment. The test procedure for the three-point bending loading method was as follows: Create a strip-block shape out of the test sample. Then, using the indenter, apply the load from top to bottom while clamping it to the support and fastening it. When the sample has entirely shattered, the test is concluded.

### 4.6.1 Analysis of Cu-D-Cr & Cu-D-CNT-Cr Bend test:

Three-point bend test of Cu-Diamond-Cr gives results of U.T.S 1.03 MPa and Yield Point of 0.83 MPa, while Cu-Diamond-CNT-Cr have U.T.S of 1.80 MPa and Yield Point of 1.47. The obtained results are compiled in Table 4.3.

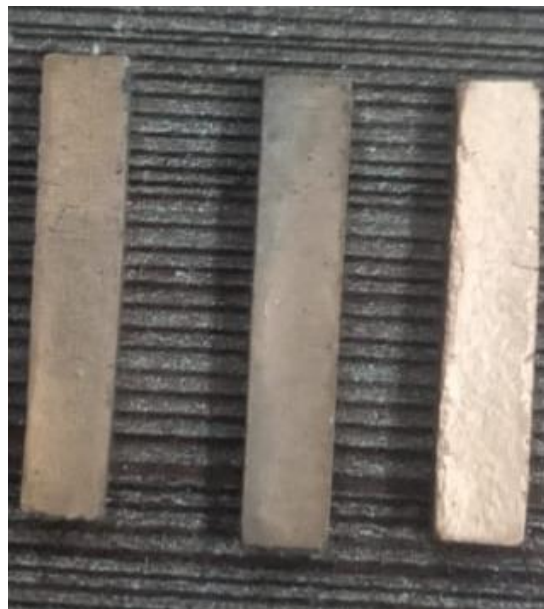
Table 4.3 Bend Test of Cu-D-Cr & Cu-D-Cr-CNTs

Material	Yield Point	U.T.S
Cu-D-Cr	0.83 MPa	1.03 MPa
Cu-D-Cr-CNTs	1.47 MPa	1.80 MPa



**Figure 4.13** Bend Test of Cu-D-Cr ( Left) & Cu-D-CNT-Cr (Right)

The stress-strain curves obtained for both of Cu-Diamond- CNT-Cr and Cu-Diamond-CNT-Cr are also shown in figure 4.13 (Left) and 4.13 (Right ). As discussed earlier, the presence of both CNTs and diamond particles enhanced the strength of the composites as compared to the Cu-D-Cr composite [19].



**Figure 4.14** Bend Test Samples

## 4.7 Thermal Conductivity:

The thermal conductivity of the Cu-D-Cr and Cu-D-Cr-CNT composite was measured to be 285 W/m K and 310 W/m k, respectively. Comparing Cu-D-Cr composites to Cu-D-CNT-Cr composites, Cu-D-CNT-Cr thermal conductivity was increased 9 percent. The Thermal conductivity meter was used for measurement of thermal conductivity of samples which is shown in figure 4.15. Temperature on one side was 50 °C and on the other side it was 38 °C apparatus. According to published research, the lower thermal conductivity of PM Cu in comparison to pure copper is caused by persistent porosity [13], which is unavoidable in conventional pressure-less sintering. The densification and interface conditions in composites have a significant impact on heat conductivity. The porosity, whether in the form of interface separation or matrix pores, has a detrimental effect. [10].

The thermal conductivity of diamond/Cu composites varies with the thickness of the contact layer. The thermal conductivity of Diamond/Cu composites first rises and then falls as the thickness of the Cr<sub>3</sub>C<sub>2</sub> interfacial layer is increased. The relationship between thermal conductivity and interfacial layer thickness of Diamond/Cu composites can be explained using the following justifications. Due to low chromium addition, direct contact between diamond and copper will result in a discontinuous surface. In the presence of defects or voids, the thermal conductivity of Diamond/Cu composites will be significantly lowered and the interfacial thermal resistance would rise.

The high thermal conductivity is influenced by the following elements. First, powder metallurgy yields thermal conductivities that are higher than those of competing methods. The homogeneous pressure distribution may lessen the displacement of filler particles during the preparation process, and the high temperature ensures that Cu is easily injected into the gaps between the diamond particles. The thickness of the interfacial carbide layer is also increased. Due to its inability to strengthen the bonding between the composite materials, a thin and discontinuous carbide layer was unable to significantly reduce the interfacial heat resistance. Thirdly, ideal carbide interfacial morphology promotes heat transfer across the interface. As a result, between diamond and copper, a substantial and persistent carbide layer form. Heat is better able to flow over the diamond/matrix interface as a

result. Finally, the proper crystallographic orientation of the interface layer promotes heat transfer through the matrix-carbide-diamond interface. The interfacial thermal resistance significantly affects the thermal conductivity of Diamond/Cu composites, in addition to the particle size, inherent thermal conductivity, and volume concentration of diamond. The thermal conductivities in this study are significantly lower for the same system than those described in the literature. This is explained by the low densification values, which are the greatest values attained with conventional pressure-free sintering and cold pressing, respectively. The findings are significant for traditional business purposes. Processes for sintering are inexpensive and have a great deal of potential for mass production. Additionally, this method calls for affordable equipment and straightforward processing.



**Figure 4.15** Thermal Conductivity Meter (I.S.T Islamabad)

## Conclusions

Cu-D-Cr and Cu-D-CNT-Cr composites containing 7.3 vol% of diamond and 1.8 vol% were prepared via powder metallurgy method with conventional sintering and pressing. The samples were compacted at a pressure of 525 MPa and sintering was performed under the argon atmosphere for two hours at 900 °C. The powders were characterized via XRD analysis. SEM was used to examine the powders and composite microstructures along with interfacial bonding of the diamond particles and matrix interfaces. SEM results confirms that the prepared composites were developed with uniform distribution of diamond particles and having good interface bonding with the matrix. A universal testing machine was used to study the young modulus, compression and bending strength of the composites. With the addition of diamond and CNT in the copper matrix, the compressive strength increased from 59 MPa to 80 MPa and 84 MPa, respectively. The comparison of Cu-D-CNT-Cr with Cu-D-Cr shows significant increase in yield point 0.83 MPa to 1.42 MPa and U.T.S. From 1.03 MPa to 1.60 MPa. Thermal conductivity of the composites was measured using a thermal conductivity meter, which was calculated to be 285 W/m K and 310 W/m k, for the Cu-D-Cr and Cu-D-Cr-CNT composite, respectively. It is evident that the thermal conductivity of Cu-D-Cr-CNT composite was increased by 9% as compared to Cu-D-Cr composite.



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