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

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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.***

Keywords: Diamond; CNTs; Heat Sink; Composites; Thermal Conductivity; Compressive Strength

1. Introduction

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. Usage industry of MMC include aerospace, automotive, sport and defense application. Metal matrix composites have superior mechanical properties which entail their high strength, high wear resistance, high stiffness, and high temperature properties [1]. These properties can be adjusted for specific application. 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 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 [2]. 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.

In MMCs with a high filler content, diamond - metal composites with a high thermal conductivity are uncommon. Because diamond is an isotropic material with a record thermal conductivity (up to 2200 W/ m K) for pure diamond, it was chosen as a filler. The matrix is made of metals with the highest conductivity, such as copper (390W/m K) or aluminum (230 W/ m K) Mechanical qualities aren't a functional goal for composites they're nevertheless important. Despite their high thermal conductivity, they perform a significant role because 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); as a result, the composite's thermal conductivity and its mechanical properties are determined by the state of the interface between the filler and the matrix.

Due to its appealing thermophysical and mechanical characteristics, metal matrix composites have recently been developed for electronic packaging applications. The capacity of metal matrix composites to change the volume fraction of reinforcement to change the thermal conductivity and coefficient of thermal expansion (CTE) is their most remarkable property. The diamond/Cu composite, one of the metal matrix composites, appears to have the potential to satisfy the rising need for heat sink materials and high - performance packages in the future. Studies have shown that the thermal conductivity, coefficient of thermal expansion, and mechanical properties of diamonds are all significantly influenced by the interface between the diamond and the copper matrix. Diamond and liquid copper cannot moisten each other, which leads to weak interfacial bonding. As a solution to overcome the weakness of interfacial bonding, the carbide - forming elements (e. g., Cr, Ti, Zr, and B) are incorporated into the copper matrix to react with diamond during the infiltration process [4].

2. Materials and Methods

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 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

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contains Cu, Diamond, CNTs and Cr Powder. Diamond and CNTs powder were used as reinforcement. Using analytical balance, Compositions described below in table 1 and table 2 were taken and put into wash bottle for mixing.

Table 1: Copper - Diamond - Cr

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

Table 2: Copper - Diamond - Cr - CNT

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

Wise Mix ball milling apparatus was used. 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. Powder mixed in ball milling was then pressed by using Hydraulic Press and Cold Isostatic Press. Following procedure was followed to carry out pressing. The powder mixed was weighed in Analytic balance and then below procedure was followed.

The die was then filled with powder according to the sample size required. Powder of 1.9 gm for each sample is taken. Each composition 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 sample pressed have 11 mm height and 6.5 mm diameter The green compact of each sample was then pressed again in Cold Isostatic Press for better densification. The fluid used in Cold Isostatic Press is oil. To apply liquid pressure, materials are 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. Samples are then removed from the apparatus for further process.

The Green Compact was then sintered. For sintering the samples are placed in quartz glass tube in Protherm tube furnace. environment used in the tube is 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. Density of the sintered pellets was measured using Archimedes principle. Sintered Samples are then grinded for analysis. Polishing was done after grinding for better surface finish. Surface of the pellet was properly cleaned with water after polishing each particle number. The surface was then dried, and its surface was analyzed in a microscope. Etching was performed then. Solution of following etchants were used to produce grain boundaries: Distilled water or Ethanol (100 - 120 ml) + Hydrochloric acid (25 - 50 ml) + Ferric chloride (5 - 10 g).

Scanning electron microscopy along with EDX was performed using Jeol 6490 LV which is a high - performance Scanning Electron Microscope. After that X - ray diffraction tests of the samples were performed. To study the mechanical behavior of the nanocomposites, compression test and bend test was performed on the Universal Testing Machine SHIMADZU AGX Plus instrument Thermal measurement apparatus was used for measurement of thermal conductivity of samples. Temperature on one side was 50 °C and on the other side it was 38 °C. A thermal analysis technique examines the heat flow and temperature connected to a material's thermal transitions.

3. Results & Discussion

3.1. SEM Analysis

The characterization was done using Jeol 6490 LV which is a high - performance Scanning Electron Microscope.

3.1.1. Copper Powder:

Scanning electron microscope images of pure copper powder in figure 4.1 shows that the particles are in the form of agglomerates. Their size ranges from 10 µ - m to 30 µ - m. Their shape is irregular.

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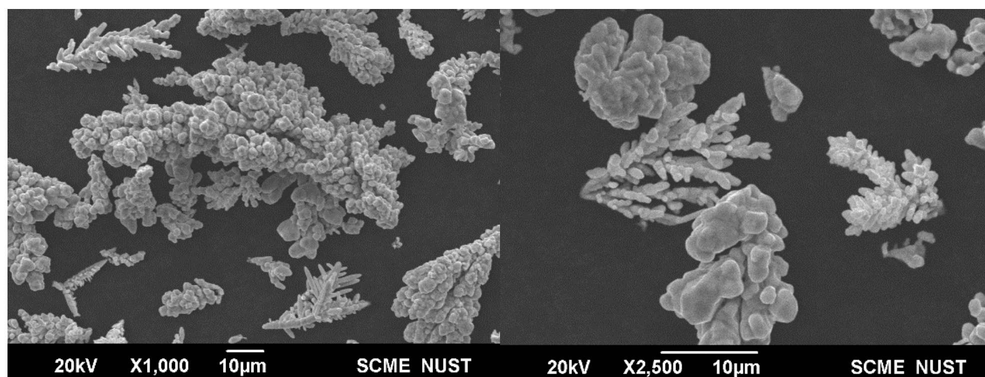

Figure 1: Copper powder

3.1.2. Diamond Powder:

Scanning electron microscope images of diamond powder in figure 2 (a) and figure 2 (b) shows that most of the diamond particles are single particles of diamond. A very small amount is in the form of clusters of a few diamond particles. Their size ranges from 100 µ - m to 200 µ - m.

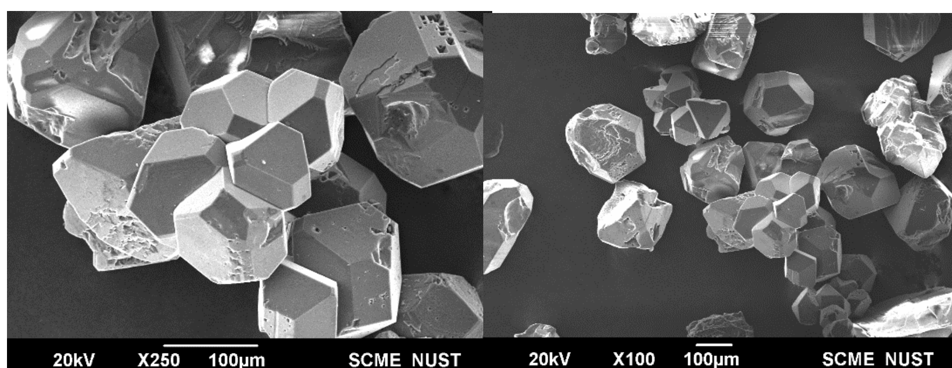

Figure 2 (a, b): SEM Micrograph of Diamond Powder

3.1.3. Cu - D - Cr:

Microstructure of composite in figure 3 (a) reveals even distribution of diamond powder in copper matrix and agglomeration of diamond particles in matrix has not occurred. The structure of matrix is not visible in these images because the sample could not be further grinded due to diamond grains on the surface. But it is clear from the smooth surface of the sample that the matrix is uniformly compacted. Figure 3 (b) is image of diamond powder in copper matrix. It shows that the matrix has tightly held the diamond grain i - e the bonding between matrix material and diamond grains is strong. Therefore, they will conduct heat at a faster rate.

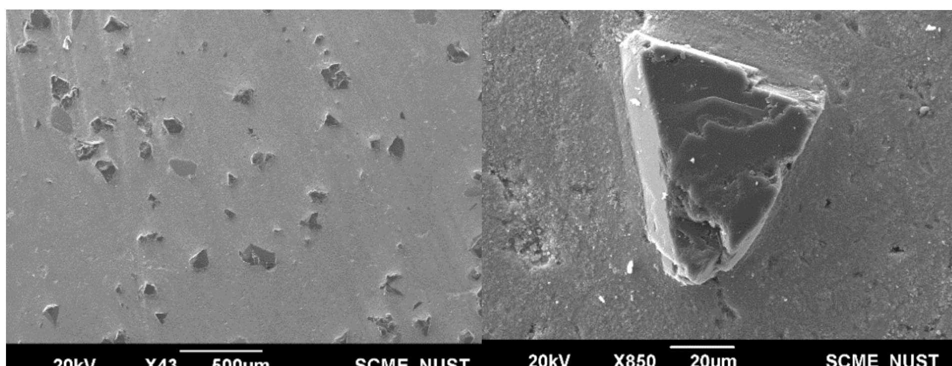

Figure 3 (a, b): SEM Micrograph of Copper - Diamond - Cr Composite

3.1.4. Cu - D - CNT - Cr:

Microstructure in figure 4 (a, b) shows 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 grains is in good contact with the diamond grains which will help in the conduction of heat through the sample.

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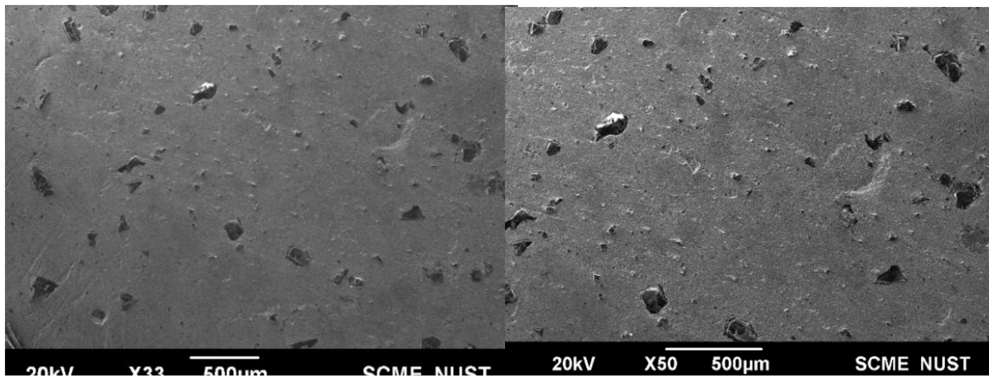

Figure 4 (a, b): SEM Micrograph of Diamond in Copper - CNT - Cr Matrix

3.2. 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:

3.2.1. XRD Analysis:

The XRD Patterns of the Cu - D - Cr - and Cu - D - CNT - Cr are shown in figures 5 (a) and figure 5 (b) respectively. Copper 2θ peak position is at (43.64, 50.80, 74.42) and d spacing of (2.073, 1.796 1.274) which corresponds with pattern of copper (JCPDS Card No 00 - 002 - 1225), diamond and carbon 2θ peak position is at (43.99, 75.41, 91.64) and d spacing of (2.068, 1.267 1.081) which corresponds with diamond (JCPDS Card No (96 - 901 - 2291) and carbon (JCPDS Card No 0 - 001 - 1242). The XRD patterns of copper pellet, Diamond pellet. Cu - D - CNT pellet and Cu - D - Cr - CNTs pellet matched with their respective patterns confirming the compositions of the samples.

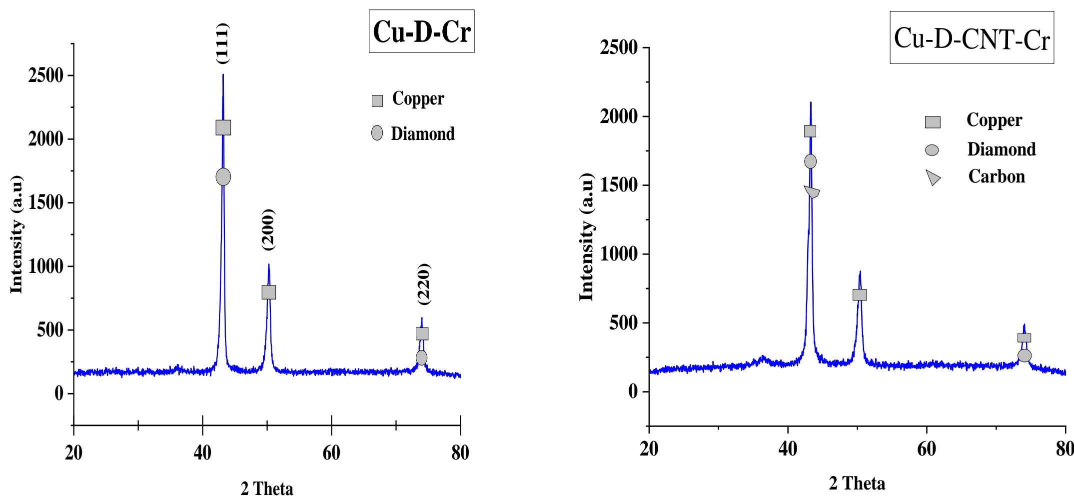

Figure 5: XRD Pattern of (a) Cu - D - Cr and (b) Cu - D - CNT - Cr

3.3. Density

Density of samples was measured using Archimedes Principle. 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: Density of Pure Cu sample and composite samples

Elements	Density Measured	Relative Density
Cu	8.1 g/cm³	90 %
Cu - D	7.4 g/cm³	91 %
Cu - D - Cr - CNT	6.9 g/cm³	86 %

The Theoretical Density of Copper is 8.96 g/cm³ and the density of the pure sample measured was 8.11 g/cm³. The Relative Density was 90 % and was calculated by dividing theoretical density over measured density. 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

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increase in diffusion barriers and interfacial gaps, densification falls as the volume percent of diamond increases.

3.4. Compression Test:

Samples were tested for their compression properties on the Universal Testing Machine 'SHIMADZU AGX Plus instrument. Load speed was kept 0.5 mm /min and rod - shaped samples were used for testing. Pellet diameter is 6 mm and 10 mm is its Height. Compressed samples which have been tested are shown in Figure 4.14

Table 5: Compression Test Results of Samples

Material	Yield Point	Young Modulus
Cu	59 MPa ± 3	5.7 GPa
Cu - D	80 MPa± 2	11.2 GPa
Cu - D - CNT	84 MPa± 6	12GPa

3.4.2. Analysis of Cu - D - Cr &Cu - D - CNTs - Cr Compression test:

Yield Point of the C - D - Cr pellet tested by UTM was 79 MPa. Young modulus is 11.2 GPA. Yield Point of the pellet is 79 MPa and 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. Yield Point of the Cu - D - CNTs - Cr pellet is 84 MPa and is 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 can withstand larger strains before breaking and have high stiffness then pure copper

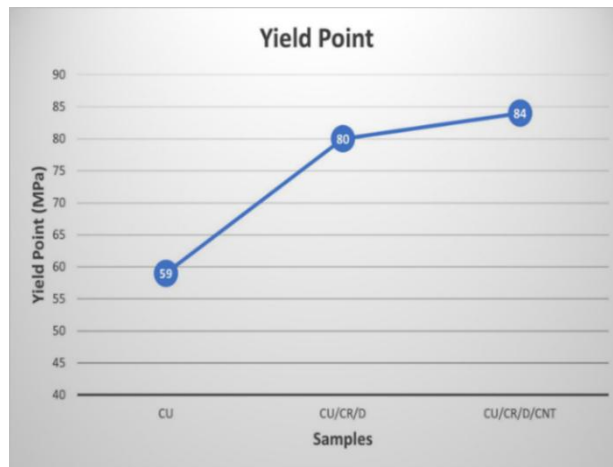

Figure 9: (a) Stress strain curve of Cu - D - CNT - Cr and (b) Yield point chart

3.5. Bend Test

This test was performed on a Universal testing machine 'SHIMADZU AGX Plus instrument' with a three - point bend fixture. The three - point bending loading method's test methodology was as follows: Make the test sample into a strip block shape. after that clamp it to the support, fasten it, and apply the load from top to bottom with the indenter. The test is finished when the sample is fully fractured.

3.5.1. 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 comparison of Cu - Diamond - CNT - Cr (figure 4.19) with Cu - Diamond - Cr (figure 4.20) shows increase in yield point and U. T. S.

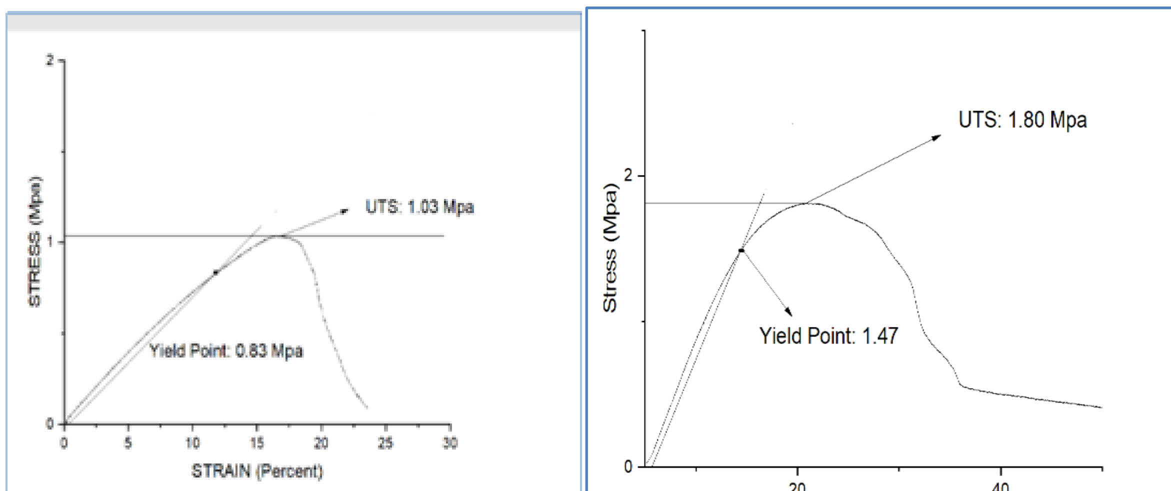

Figure 10: Bend Test of (a) Cu - D - Cr and (b) Cu - D - CNT - Cr

Table 6: 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 - CNT	1.47 MPa	1.80 MPa

3.6. Thermal Conductivity:

The thermal conductivity measurement apparatus was used for measurement of thermal conductivity of samples. Temperature on one side was 50 °C and on the other side it was 38 °C apparatus. According to published research, the

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lower thermal conductivity of PM Cu in comparison to pure copper is caused by persistent porosity, which is unavoidable in conventional pressure - less sintering. The densification and interface conditions in composites have a significant impact on heat conductivity. Porosity, whether in the form of interface separation or matrix pores, has a detrimental effect. When comparing Cu–D - Cr composites to Cu–D - CNT - Cr composites, Cu–D - CNT - Cr has higher thermal conductivity. Thermal conductivity of Cu - D - Cr is 285 W/m K while Cu–D - CNT - Cri s 310 W/m k.

The following factors contribute to the high thermal conductivity. First, compared to alternative techniques powder metallurgy produces thermal conductivities that are higher. The displacement of filler particles during the preparation process may be reduced by the uniform distribution of pressure, and the high temperature ensures that Cu is easily injected into the spaces between the diamond particles. Second, the interfacial carbide layer's thickness is increased. A thin and discontinuous carbide layer was unable to sufficiently lower the interfacial heat resistance because it could not enhance the bonding between the composite materials. Third, proper interfacial carbide morphology encourages heat transport across the interface. As a result, a thick and consistent carbide layer develops between diamond and copper. This facilitates heat flow over the diamond/matrix interface. Finally, the interface layer's appropriate crystallographic orientation encourages heat transport through the matrix/carbide/diamond interface. Besides the particle size, intrinsic thermal conductivity and volume content of diamond, the interfacial thermal resistance has a significant influence on the thermal conductivity of Diamond/Cu composites.

The thermal conductivities in this study are significantly lower for the same system than those described in the literature. This is attributed to the low densification values, which are the highest values obtained with Cold pressing and traditional pressure - less sintering are used. The findings are important for commercial purpose since traditional. Sintering processes are low - cost and have a high potential for mass manufacturing. Furthermore, this approach requires simple processing and low - cost equipment.

4. Conclusions

Cu - D - Cr and Cu - D - CNT - Cr composites containing 7.3 vol% of diamond and 1.8 vol% of CNT were prepared via powder metallurgy method with conventional sintering and pressing mechanism SEM was used to examine the microstructure and interface bonding process of composites made of diamond, carbon nanotubes, and copper. A universal testing machine was used to test the samples' strength. It is clear how the evolution of the interface structure affects the heat conductivity and strength of composite materials. The samples are best densified by cold compaction at pressures of 525 MPa and sintering for two hours at 900 °C. The results shows that composite was developed with uniform distribution of reinforced powder having good interface bonding. With the addition of diamond and CNT in the copper matrix, the tensile strength of increased from 59 MPa to 80 MPa and 84 MPa respectively. Increasing the interface layer thickness is helpful for enhancing the interface bonding strength since the strength of diamond/copper is highly related to the interfacial carbide structure. The physical properties like young modulus, yield strength, hardness and ultimate tensile strength has been greatly improved. Thermal conductivity has been increased due to reinforcement of diamond to the copper matrix. It further increased with addition of CNTs to the composite from 285W/m K to 310 W/m K.

Declaration of competing interest
None.

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