Effect of Chromium on Mechanical Properties of Carbon Nanotube Reinforced Copper-Chromium Composite

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Dedication

Dedicated to my honored parents and family members whose immense support and cooperation led me to this wonderful accomplishment.

Acknowledgments

I am thankful to Almighty Allah for guiding me throughout this work at every moment, which makes it possible to accomplish this task.

I am highly grateful to my parents who supported me financially and emotionally in fulfilling this degree. Their support was of utmost importance to me. At the same time, I would present my special thanks to my supervisor Dr. -Ing. Farhan Javaid for his motivation and assistance in pursuing my research work. I also want to thank my GEC members Dr. Malik Adeel Umer and Dr. Muhammad Shahid for giving me their valuable suggestions, continuous encouragement, and support to carry out my research work. I express my deep gratitude to Dr. Amir Azam Khan (Principal SCME) and Dr. Khurram Yaqoob (HoD ME) for providing such a good platform for study and research.

I am also very thankful to all my friends and lab attendants for their support and help in completing this research.

Sincerely,
Waseem israr

Abstract

In the present work, Cu-0.5wt.%CNT and Cu-0.5wt.%CNT-1wt.%Cr composites were prepared via the conventional powder metallurgical route. For Cu-0.5wt.%CNT composite, the CNTs were sonicated in 10 mL ethanol first for better dispersion and later for 5 hours wet ball milling was performed. For Cu-0.5wt.%CNT-1wt.%Cr composite, first Cu and Cr powders were dry milled for 20 hours and later wet milling was done for 5 hours by adding sonicated CNTs. The powders obtained were dried in a vacuum oven at 40 °C for 2 hours. After drying, the pellets of 6.5mm diameter were obtained via uniaxial pressing and cold isostatic pressing. The samples were sintered at 950 °C in a tube furnace (under an inert environment) for 5 hours. The densification of pure copper and composites were measured by using a densitometer. The density of Cu, Cu-0.5wt.%CNT and Cu-0.5wt.%CNT-1wt.%Cr was found to be 90%, 90.56% and 86.81%, respectively. Scanning electron microscopy was used to study the topography of the prepared pallets, which shows the denser microstructure of sintered pallets as compared to non-sintered pallets. A micro-Vickers hardness tester was used to measure the hardness of the pure copper and the composite samples. The hardness of Cu, Cu-0.5wt.%CNT and Cu-0.5wt.%CNT-1wt.%Cr was calculated to be 54 HV, 84 HV and 74 HV, respectively. A Universal Testing Machine was used for finding the young modulus and yield point of the pure copper and composites. For Cu-0.5wt.%CNT composite, the young modulus and yield point were found to be higher as compared to both pure copper and Cu-0.5wt.%CNT-1wt.%Cr composite.

Table of Contents

List of Figures

List Of Tables

List of Abbreviations & Acronyms

Acronym	Meaning
Cu	Copper
CNTs	Carbon Nano Tubes
CTE	Coefficient of Thermal Expansion
Cr	Chromium
C.I.P	Cold isostatic Pressing
CVD	Chemical Vapor Deposition
DSC	Differential Scanning Calorimetry
GPa	Giga Pascal
H.I.P	Hot Isostatic Pressing
HV	Vickers Hardness
MMC	Metal Matrix Composite
MPa	Mega Pascal
MWCNT	Multi Walled Carbon Nano Tube
PM	Powder Metallurgy
SEM	Scanning Electron Microscopy
SWCNT	Single Wall Carbon Nano Tube
TEM	Transmission Electron Microscope
UTM	Universal Testing Machine
UTS	Ultimate Tensile Strength
XRD	X-Ray Diffraction
Y.P	Yield Point

Chapter 1

Introduction

1.1 Background

Copper is extensively used in our daily life equipment's such as electric wires and electronics. Copper has the best conducting capability, high thermal conductivity, cheap and good corrosion resistant, which makes it best choice to widely used in a range of electric applications. However, copper has certain drawbacks due to which it does not fulfill all the required goals such as copper breakup in certain electronic devices at high current and melt down due to high heat accumulation. Also, due to low strength and heavy weight it cannot be used in high transmission line and automobile sector. In view of these discussion, the modern technology equipment's need to replace copper with another metal or composite which can fulfill all the desired requirements.

Carbon nanotubes are the allotropic form of carbon and appears like cylindrical shape mostly prepared by chemical vapor deposition process. CNTs are of two types i-e multi walled carbon nanotube (MWNTs) and single walled carbon nanotube (SWNTs). In SWNTs, the walled structure looks like single graphite sheet enclosed in a tubular like structure while in MWNTs it appears like several graphite sheets that have been folded into a tube shape and stacked on top of one another shown in figure 1.1. CNTs are appropriate nanofillers for polymer composites because they have strong thermal and electrical properties, as well as a low density and a high Young's modulus. CNTs are considered as very special due to their size and nano-dimensions, remarkable strength, and unique properties. CNTs are tightly bound in nature by the van der Waals force between them and the weak interplanar contacts of graphene sheets. Due to which the CNTs aggregation and solvent chemistry control their structure morphology.

The MWNTs as mechanical reinforcing agents has grown significantly in recent years. However, the restricted accessible contact area in composites has

significantly impeded the improvement of mechanical properties. CNTs possess exceptional thermal and electrical properties in addition to their mechanical qualities which makes it perfect reinforcement in metal matrix [1]. CNTs have been extensively used as reinforcement in various polymer matrices [2]. However, due to the stringent production requirements, relatively limited literature is available for CNTs [3, 4].

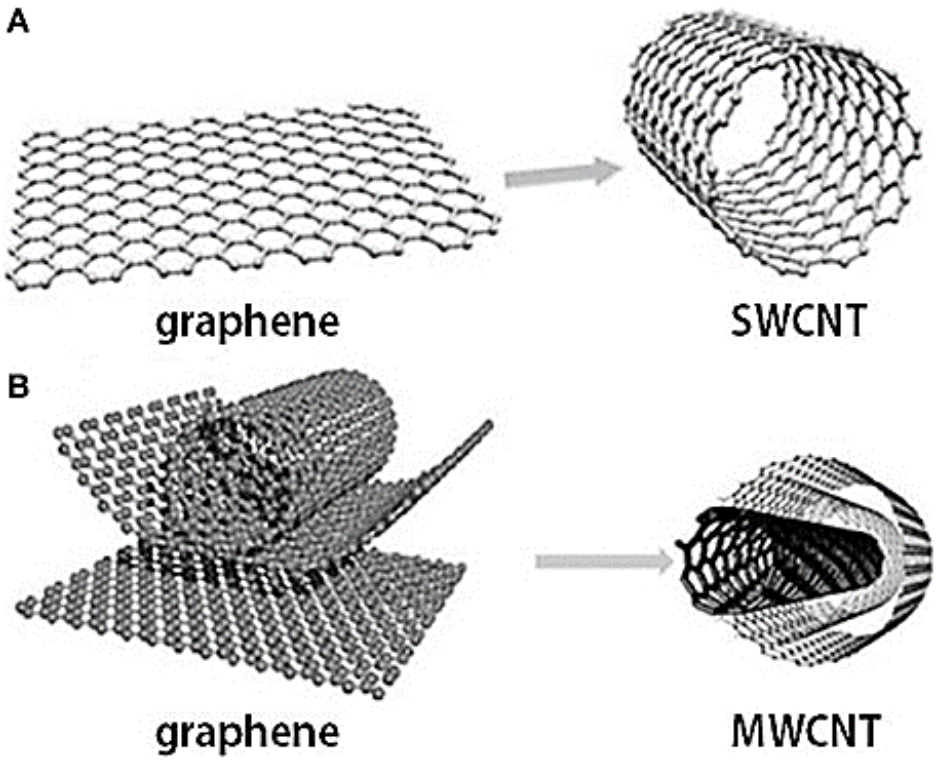

Figure 1.1: Schematic Illustration of SWCNT and MWCNT [62]

There are two key hurdles in the creation of highly effective CNT and metal composites [5]. One is the surface-to-surface bonding between the CNTs, and the other is the dispersion of CNTs in the matrix [6, 7]. To successfully boost the material characteristics of composites including CNTs, it is important to solve two key hurdles in the creation of high-performance CNT/metal composites.

To create efficient surface to surface bonding between CNTs and the matrix, the first step is to guarantee adequate dispersion of CNTs inside the matrix. As a mechanical dispersion approach, ball milling has gained the most interest and been proved to be a feasible way for dispersing CNTs in the metal matrix [3, 8]. Throughout the past five years, numerous novel techniques have been researched and

are constantly appearing [9, 10]. Less focus is paid to research on approaches to solve the issue of CNT/metal composite interfaces. Copper is innately non-wetting with CNTs hence normal CNT/Cu composites have a weak interaction between CNT and the pure copper matrix [7, 11]. Attempts have been made to minimize the interface energy between copper matrix and CNTs utilizing metal-coated nanotubes, which might enhance the load transfer performance of CNT/Cu composites.

Recently, the interfacial bonding of CNT/Cu composite materials with exceptional mechanical characteristics has been enhanced by coating CNTs with metals such as Cu [7], Ni [12], and Mo [13]. However, the ensuing densification process may weaken or even rupture the CNT-metal matrix link, resulting in a substantial reduction in composite characteristics. In addition, the production process for coating methods often involves a number of complex processing steps, resulting in substantial expenses.

Coated CNT/Cu composites have been the subject of several investigations [14, 15] whereas matrix-alloy CNT/Cu composites have been the subject of relatively few [16, 17].

1.2 Motivation

In the contemporary industrial period, the area of material composites is seen as a developing one. Chromium is one of the least examined and researched elements in the realm of reinforcement. On the other hand, chromium's qualities are regarded as important and current research indicates that it will contribute to the advancement of this sector. Current literature does not give sufficient information on chromium element and its reinforcing outcomes with Carbon Nanotubes. Therefore, in the present work, Cu-CNT and Cu-Cr-CNT composites were prepared via powder metallurgy and different characterization techniques apply to see Cr behavior. This study's primary objective is to examine the outcomes and empirical findings of chromium reinforcement using carbon nanotubes.

1.3 Objectives

This research work has the following objectives:

- Employing powder metallurgy route for the synthesis of Cu-CNT and Cu-Cr-CNT.
- Characterization of the synthesized composites using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Densitometer, Micro Vickers hardness tester and Universal Testing Machine (UTM).
- Comparison of mechanical properties of Cu, Cu-CNT and Cu-Cr-CNT.

Chapter 2

Literature Review

2.1 Carbon Nanotubes (CNTs)

Sumio Lizima made the discovery of CNTs in 1991. He was employed by the NEC Company in Tsukuba, Japan, where he was doing research and development work. He found a unique concentric carbon tube structure within each other known as MWCNTs (Figure 2.1) [18].

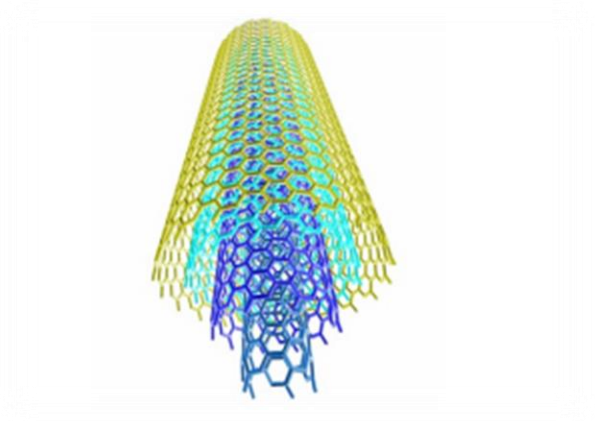

Figure 2.1: Multi walled carbon Nanotube schematic drawing [18]

Single Wall Carbon Nanotubes were discovered after two years later. SWCNT is a one-dimensional in which the walled structure looks like single graphite sheet enclosed in a tubular like structure. The MWCNT aspect ratio is lower than the SWCNT. Both forms of CNTs have different electrical and mechanical properties. CNTs appear like rolled graphene sheet that has been coiled into a tube while MWCNT is composed of many sheets stacked on top of one another. The electrical conductivity of CNTs is like that of copper while their thermal conductivity is comparable to that of diamond and their mechanical qualities are remarkable [19]. Depending on their chirality, CNTs may be classified as zigzag, armchair, or chiral-shaped. The final shape of CNT is determined by the graphite sheet which can be seen in figure 2.2.

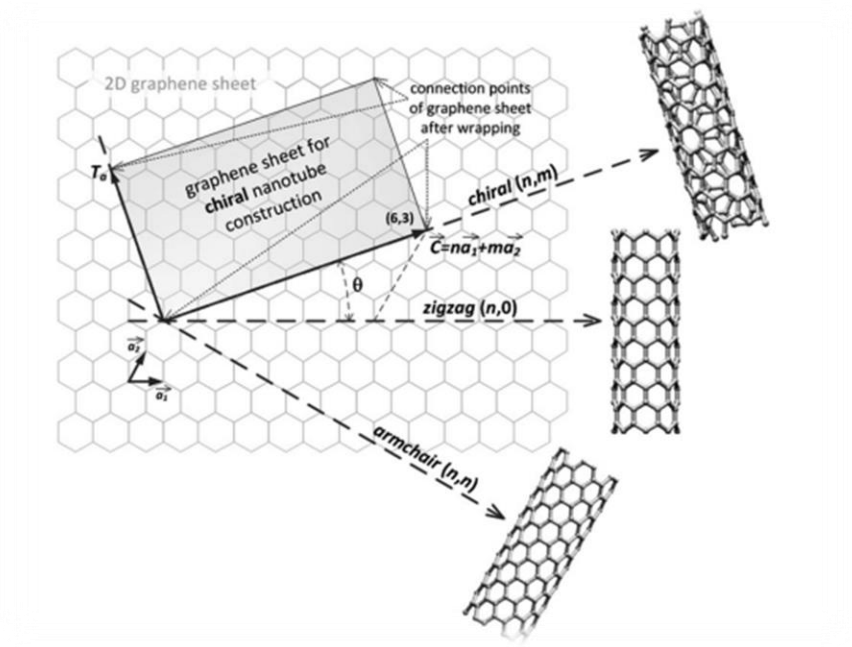

Figure 2.2: Forms of CNTs [63]

Many researchers throughout the world were drawn to the material's mechanical qualities, particularly its amazing elasticity owing to its high aspect ratio. Nanotubes may currently be manufactured using a variety of methods. CNT attributes are directly influenced by the technique of their production. In figure 2.3 brief history of CNT is illustrated.

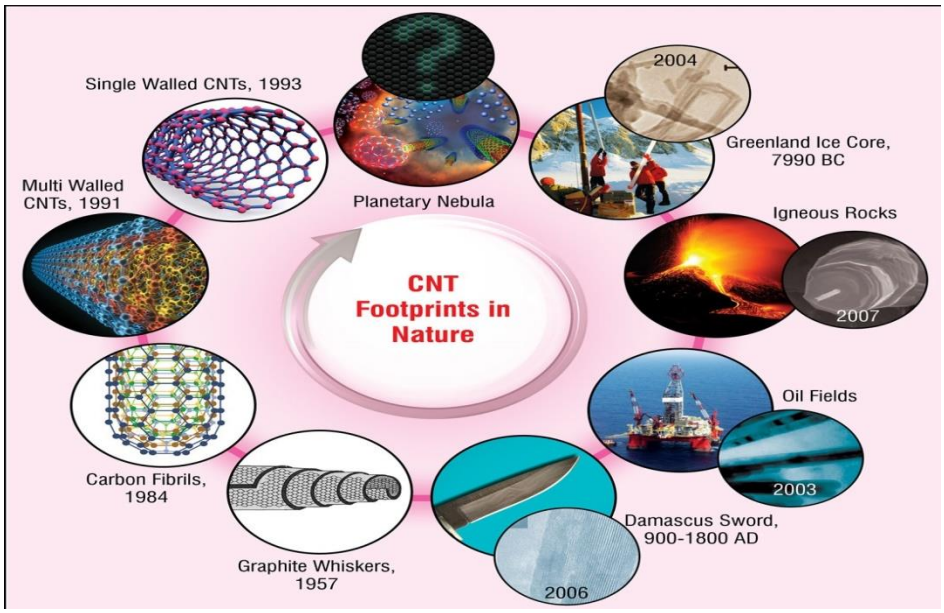

Figure 2.3: CNT history in nature

2.2 Carbon Nanotubes Synthesis Techniques

There are three potential techniques for creating CNTs which are:

2.2.1 Arc discharge method

Both MWCNTs and SWCNTs may be produced by arc discharge method. A direct current flows between two graphite electrodes that are mounted in a water-cooled chamber filled with helium in the case of MWCNTs while in case of SWCNTs, metal and graphite mixture is evaporated anode. To produce these structures, graphite and metal are introduced into a hole in the graphite anode. Useable metals include Fe, Co and Ni [20].

2.2.2 Laser ablation method

Second technique, the laser ablation of a carbon metal target generates only SWCNT by evaporating carbon metal on a composite target through laser pulse.

2.2.3 Chemical vapor deposition

Third technique is a chemical vapor deposition which uses a quartz tube put within a furnace and the substrate is inserted into the tube. Until the furnace temperature reaches the desired limit, a flow of CO, methane, or ethane gas is supplied within the tube together with an inert gas. At that point, the flow of the inert gas is stopped. The inert gas is reintroduced at the end of the procedure until the temperature reaches 300°C, at that point the CNT can be exposed into air [21].

The expensive cost of carbon nanotubes is justified by their exceptional mechanical and electrical capabilities.

Comparison between synthesis technique of carbon nanotube is presented in table 2.1.

Table 2.1: comparison of processing methods of sintering

Method	Description	Temperature and pressure	Advantages	Disadvantages
Arc discharge	CNT formed on electrodes during quenching	> 3000°C. 50-7600 Torr Under vacuum	Best quality	Difficult to scale up
Laser ablation	CNT formed on receiver during quenching	> 3000°C. 200-750 Torr under vacuum	Best quality, SWCNT formed confirmation	Difficult to scale up and costly
Chemical vapor deposition process	Hydrocarbon decomposition over transition metal catalyst	< 1200°C 760-7600 Torr	Easy scale up	Quality not good

2.2.4 CNT Applications

The primary commercial uses for using Cu/CNT to replace Cu are

(a) Medical purposes such as tumor of breast cancer is eliminated through use of nanotubes. They are engaged with the antibodies and cancer cells in the body attract the antibody and nanotubes to the proteins, and nanotubes absorb the laser beam, killing the tumor-causing bacteria.

(b)Wind generator blades are made of CNTs composites, and which helps in producing more electricity in small time at faster rate.

(c) CNTs can be used in aerospace application due to its light weight which reduces overall weight of aircraft.

(d) CNTs acts as a nano cylinder in which hazardous gases like H_2 can be stored easily.

(e) used in transistors and capacitor wires as interconnects.

(d) Used in quantum wires as interconnects.

(e) Used in flat panel displays.

(f) Used in TH_2 oscillator.

2.3 Carbon Nanotubes Metal-Matrix Composites (CNT-MMCs)

CNTs offer very high mechanical and electrical strength, making them perfect for usage as composite reinforcement. By incorporating carbon nanotubes into their creation, Metal Matrix-Nanotube products might be made lighter, stronger, and more rigid. Creating a homogenous and uniform dispersion of CNT in the matrix and developing a strong bond between CNT-metal contact sites are two of the most significant challenges CNT-reinforced composite scientists and researchers confront [22]. Extensive research has been conducted on dispersion and some researchers have developed strategies to cope with it but no study has yet shown how to enhance the binding between CNT and their matrix.

2.4 Composites

A composite material is created when two materials with different physical and chemical properties are combined. Together, they create a substance that is specifically created to do a particular function, such as growing stronger, lighter, or electrically resistant. Because they enhance the qualities of their basic materials, they are preferred over conventional materials [23].

2.4.1 Constituents of a Composite

I. Matrix

- Continuous phase in the composite is known as Matrix.
- It distributes the load throughout the composite while holding the reinforcement.

II. Reinforcement

- Reinforcement gives the composite material strength and rigidity.
- Reinforcement can be in various shapes such as of fibers, particles, flakes and whiskers.

2.4.2 Types of Composites

Composites are classified into three major types based on matrix materials which are given below:

I. Polymer Matrix Composites (PMC's):

In PMC's, various fibers including glass, carbon, aramid, or natural fiber acts as reinforcement while polymer-based materials serve as a matrix. PMC's are ideal matrix materials because it can be processed easily into desired shape, have low density and shows good mechanical characteristics. The two major types of polymers are thermoset and thermoplastic.

II. Metal Matrix Composites (MMC's):

In MMC's, matrix is composed of metals such as copper, aluminum or steel and reinforcement is usually made of ceramics such as alumina. MMCs are frequently employed in demanding applications because they can have substantially better strength-to-weight ratios, stiffness, and ductility.

III. Ceramic Matrix Composites (CMC's):

In CMC's, matrix usually consist of ceramics and reinforcements are usually short fibers, particles, and whiskers. CMC's are used in energy sector and aerospace applications.

2.4.3 Metal Matrix Composites (MMCs)

At least fifty percent of the volume of a metal matrix composite (MMC) consists of a reinforcing metal, ceramic, or organic compound. Frequently utilized matrix components include Chromium, magnesium, copper, titanium, Cr-lithium, and super alloys [24]. Due to its low density, high specific stiffness, and wear resistance, Cr-based (MMC) are extensively used and needed in a variety of industries. To make MMCs, reinforcing elements with various physical properties such as oxides, carbides, and nitrides, may be dispersed throughout a Cr matrix. The composite transfers load from matrix to reinforcement. Manufacturing MMCs has been a tremendous success because it permits the development of composites with features that combine those of their constituent materials [23]. Changing the composite's composition to get the needed qualities is easy and uncomplicated.

There are many approaches that fall into the following categories for producing MMCs: First, there is the solid-state method, which is a PM technique in which the solid form of the components is addressed. The liquid state technique may be employed when one or more components are treated in a liquid state such as

during stir casting, spray casting or electroplating. Vapor deposition is the third approach [24].

Advantageous matrix composites are not limited to MMCs. MMCs exceed polymer matrices in terms of elastic modulus, temperature resistance, moisture absorption resistance, toughness, and ductility [23]. The segregation issue may be eliminated by employing a proper consolidation process and equally spreading the reinforcing material. Because the qualities of a single MMC may be readily tweaked by modifying the composite's constituents or even the production method, materials scientists are able to create new materials with superior properties across the board [24].

MMCs may be manufactured via powder metallurgy, which is now the topic of intensive research. The following sections will explain some of the restrictions and criteria that govern the powder metallurgy process and have a significant impact on the features of the final output. Figure 2.4 illustrate schematic diagram of types of composites.

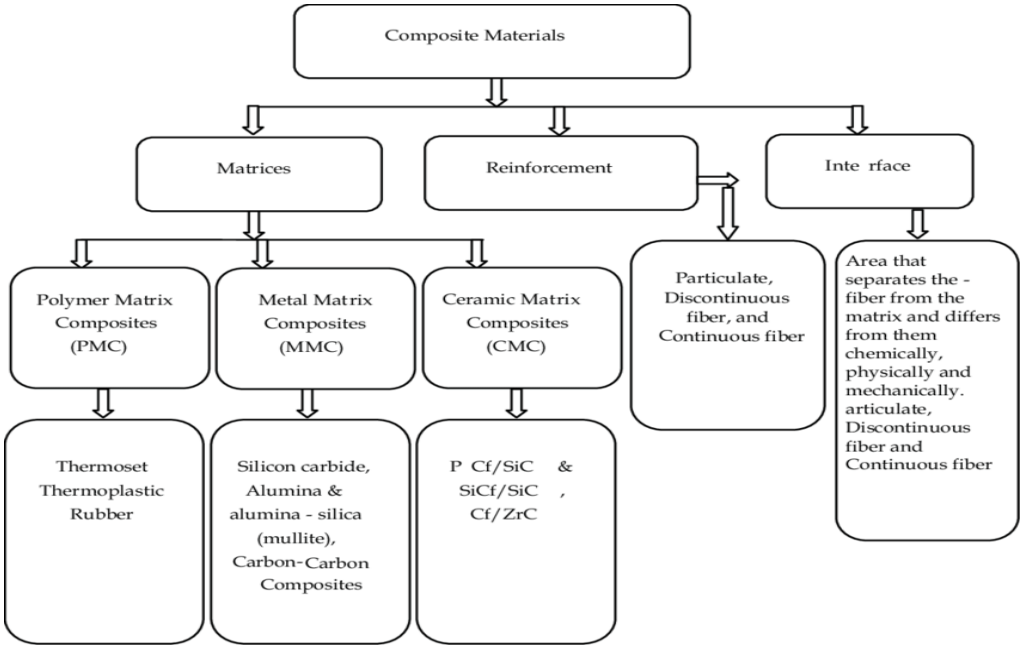

Figure 2.4: Types of composites [25].

2.5 Powder Metallurgy (PM)

Powder Metallurgy is all about converting powders into bulk materials. The capacity to treat a broad variety of materials is the driving factor for the widespread usage and acceptance of PM technology in several sectors, ranging from consumer

products and vehicles to aerospace. Figure 2.5 shows the goods that PM has processed [26].

Figure 2.5: Products made by PM techniques

The precision of the processing method utilized in all PM-produced components and the secondary processes performed to the product have a substantial effect on the quality of the final PM-processed product. The following are the key processes that contribute in the production of polymer (PM): The sintering process includes powder preparation and manufacture, powder mixing, powder compression, and compact sintering. Extrusion, forging, rolling, etc. may be required if the final product is to be used in a certain manner or has a particular structure.

PM process usually involves the following four steps:

1) Fabrication of powders.
2) Blending.
3) Compaction.
4) Sintering.

2.5.1 Fabrication of metal powders

Metal powders may be produced using a variety of techniques, depending on the actual use and quality of the finished product. Most metal powders can be processed, and new technologies are always being developed to make production processes more efficient and to produce powders of higher quality. Carbon or hydrogen oxide reduction, the thermal breakdown of a chemical, electrolysis and metal precipitation are a few of the methods for producing powder. Through powder

characterization physical parameters such as specific surface area and compressibility may be determined. Based on the particle size, the powder is subsequently separated into many batches. As a precaution against the formation of oxides, oxygen levels are also decreased. Atomization, one of the most common powder production processes, was employed to manufacture the pure Cr powder used in this study [27].

2.5.2 Powder Blending

Attaining consistent particle size and refining particle size are two of the goals of this stage. Blending may be used to combine many powders into a single product. To prevent particles from cold welding together and creating agglomeration, lubricant must be used [26].

Following are the parameters on which blending depends:

I. Ball to weight ratio.
II. Milling time.
III. Milling speed.
IV. Feed size.

2.5.3 Powder Compaction

In this phase, powder particles are melted together to create compacted sample. It is the most important step in the process. This step may be accomplished using cold and hot unidirectional compaction, cold and hot isotactic pressing, or rolling [29]. For the course of the project, the main technique of compaction will be cold unidirectional pressing. Due to the applied force, particles may be rearranged by deformation during compaction, resulting in an improvement in volumetric efficiency. During the process of compaction, particles undergo reorganization and plastic deformation. Due to high and unnecessary pressures, there is a danger of stress concentration in certain locations [26].

Compression via unidirectional pressing is an established and time-honored technique. The outcome of compression is referred to as a "green compact" or "preform" since it comes from the die intact. After compaction, densities of up to 90 percent may be attained. In this experiment, powder particles get pressure from the punching plunger through a circular die chamber. As a response to the imparted vertical pressure, the plunger transmits pressure axially and laterally through the die

walls. To ensure that the applied pressure reaches the lowest regions of the compact, it is necessary to maintain an acceptable height-to-diameter ratio. Inter-particle friction and friction between the die walls and powder particles create pressure fluctuations [28]. As seen in Figure 2.6, lubrication may have a substantial effect on compaction, and it is essential to keep this in mind [30, 31].

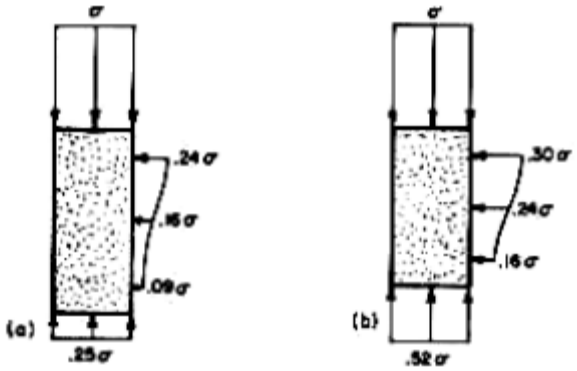

Figure 2.6: Representation of pressure changes in a uniaxial pressing die (a) without and (b) with oil [29]

Following are two methods of compaction.

- **Conventional Pressing:**

It consists of punches with a die in which powders are placed which we want to compact. Lower punch presses the powders in the die and pressure is applied for some time with the help of hydraulic oil. After that pressure is released the punch moves to its original position and die is ejected. Conventional press can be seen in figure 2.7.

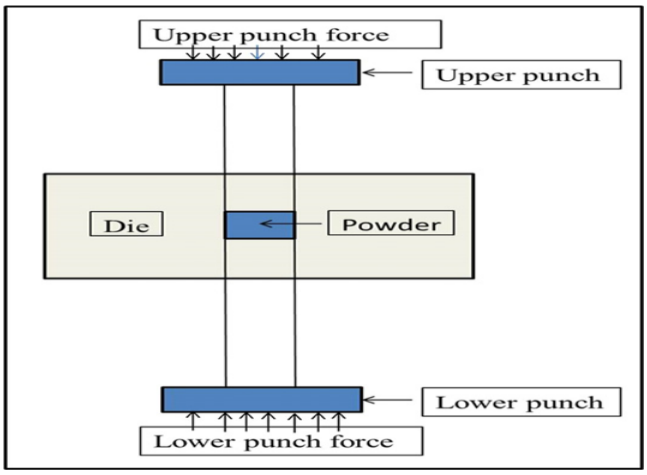

Figure 2.7: schematic representation of Conventional press [26].

- **Cold isostatic pressing (CIP):**

CIP is a technology that has great potential for complicated designs, huge length to diameter ratios and homogenous density and strength. In this type of press, the container is filled up with oil in which the sample is placed in a flexible mold. Molds are usually of rubber type because of its low deformation resistance. In CIP pressure is applied from all sides which give the sample uniform shape and density. Figure 2.8 shows schematic diagram of CIP.

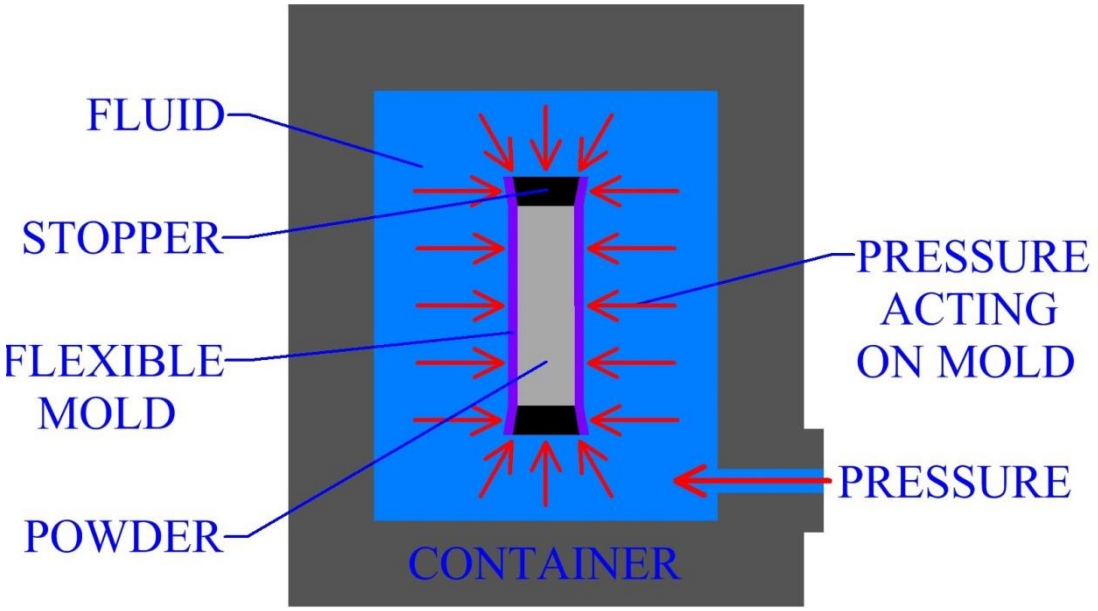

Figure 2.8: Schematic diagram of CIP [32].

2.5.4 Sintering

Sintering is the last step in a process in which metal particles are combined. In order to melt the previously formed compact, temperatures between 0.7 and 0.9 degrees Celsius must be applied [27, 33]. Prior to sintering, the green strength of the compact is low and it is brittle. Regarding the kind and strength of particle bonding and the final sintered product, a number of aspects must be considered. Plastic flow is influenced by diffusion processes, the evaporation of volatile chemicals from the solid during solidification, recrystallization, grain expansion and pore contraction [27].

Temperature, time, and the furnace environment are all crucial while sintering. To begin with, there are both solid-state and liquid-phase methods for sintering. Figure 2.9 depicts solid-state bonding as the diffusion of two neighboring particles. As a consequence of this method, the mechanical and thermal qualities of the

compact may be enhanced. In liquid-phase sintering, when alloying occurs at this interface, one of the particles shown in Figure 2.9(b) melts and surrounds and encircles the un-melted particle. This technique is effective for producing denser and more robust components. Because gravity tends to concentrate heavier metals at the bottom of a melt, segregation is a typical occurrence during the sintering process. As with other sintering processes, the provided heat reduces the system's energy while reducing the particle's surface area. Sintering is a three-step process that may be broken down into three distinct stages [27]:

- The formation of initial contact between particles.
- Neck growth, which happens at the particle boundaries.
- The particles coalescing together.

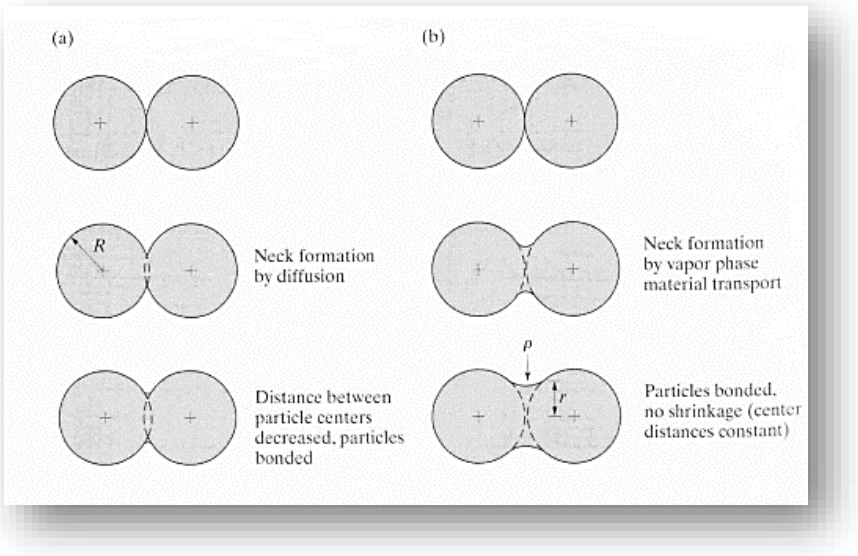

Figure 2.9: Sintering based on solid state bonding (b) sintering based on liquid-phase bonding [27]

Since heat reduces the pressure required for plastic deformation, hot compression may be used to complete both the compression and sintering operations in a single step. Spark sintering is now under research as a technology. Metal powder is deposited into a graphite mold, which is then heated and crushed simultaneously. By removing impurities and oxide coatings from the surface of Cr particles with a fast discharge, the adhesion between particles is strengthened [27].

2.5.5 Sintering methods

1) **Conventional sintering**

Powders to be sintered are first compacted and the obtained pellet is subsequently sintered in the furnace. Inert atmosphere such as Ar, H_2, N_2 and NH_3 is provided during sintering process. It is possible to sinter the pellet in either a solid or a liquid state. External additives are occasionally employed so that the process goes into liquid phase because the rate of densification is slower in solid state sintering. Usually, the sintering temperature is between 0.7 and 0.8 of the selected melting point [33].

2) **Hot pressing sintering**

In hot pressing, powders undergo a simultaneous chemical reaction and densification while being subjected to pressure and heat [34]. In this process, the powder to be sintered is placed in a mold which is then heated and pressed simultaneously in a vacuum hot-pressing furnace. The Hot Pressing is widely used to create composite materials based on ceramics. Hot press can be seen in figure 2.10.

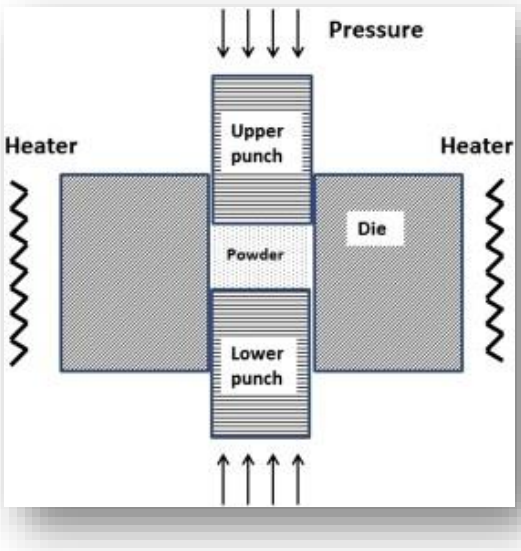

Figure 2.10: Hot isostatic press [34]

3) **Spark plasma sintering**

In spark plasma sintering the powder samples are put in an electrically conducting die and sintered under a uniaxial pressure which is assisted by pulsed-current. SPS is modified form of hot press sintering in which the

furnace replaced by mold and the current flows through the mold in which the sample is also heated. Due to its extraordinary efficacy, which makes it possible to achieve quick sintering and densification, SPS has attracted increasing interest. Very hard material such as refractory material, Nano materials can be sintered very easily through SPS [35].

4) **High temperature and high pressure sintering**

This process of sintering is generally used for very hard materials such as refractory material because of their high melting point. The cavity is often pressurized in this procedure in all directions using a hexahedral press due to which the sintering pressure is significantly higher than the hot pressing pressure. A very dense and highly efficient result is obtained but the process is expensive and very complex [36].

5) **Infiltration sintering**

Infiltration is the process of utilizing a liquid metal or alloy with a lower melting point to fill pores and reduce porosity in a sintered pellet by penetrating the pore system via surface or capillary forces [37]. Infiltration sintering is of two type's i-e Pressure less infiltration and Pressured infiltration.

2.5.6 Forming of the sintered powders

If you're seeking for a certain form and set of attributes for your sintered product, you have a multitude of possibilities. Extrusion, rolling, and forging are examples of such processes. By removing holes and maybe any immaturity during the sintering process, the bulk material's mechanical and structural characteristics can be enhanced, which is why these activities are so crucial for shaping the sintered product into the appropriate form.

2.5.7 Advantages and disadvantages of PM

Following are the advantages and disadvantages of PM process presented in form of table:

Table 2.2: Advantages and disadvantages of powder metallurgy

Advantages	**Disadvantages**
1. Nano sized powder can be processed into desired shape.	Hazardous process for health.
2. PM process is cheap process.	Equipment cost is high
3. Product obtained has good quality.	Dense and uniform product cannot be produced
4. High performance materials can be easily processed into net shape	Metals have low melting point cannot be casted.

2.6 Using PM in Producing MMCs

As their strength, stiffness, toughness, and wear resistance rise, MMCs are lauded as a scientific breakthrough. To make MMCs, a reinforcing material with a concentration of less than 50 percent is disseminated throughout the metal matrix, therefore producing a composite material having the characteristics of both the metal and the reinforcing material. In conventional ingot metal working, segregation, which has a detrimental effect on the mechanical characteristics of MMCs, is one of the most difficult processing challenges. It's all about the material properties of the components themselves when it comes to separation. To optimize the bonding of MMC components, it is now possible to modify the particle size and form of materials produced by PM [24].

2.7 Mechanical Alloying via Ball Milling

Mechanical alloying is the word for this procedure. "A ball mill is used to grind together two or more metal particles. With each impact, the granules break away and fuse together, forming alloy particles". Due to the fact that all reactions occur in solid form in various media, this method is economical and unique (gas, vacuum, or liquid.) No melting occurs throughout the process, allowing us to deal with immiscible materials and novel forms of materials that do not fit into conventional phase diagrams. For instance, it may be used to decrease particle size (grind), harden the material under stress (strain), combine components (mixing), and alloy materials (mechanical alloying). The most typical technique for grinding

involves placing the powdered product in a container (such as steel agate) with or without grinding balls (steel or titanium carbide). This technology has been used well to disperse a broad range of reinforcements in a powdered composite matrix [38, 39].

Ball mills are divided into two main types which are:

- High energy ball mill.
- Low energy ball mill.

High energy ball mills are of different types such as planetary ball mill, attrition ball mill, vibratory ball mill and spex ball mill. Tumbling type of ball mill is generally known as low energy ball mill [40].

2.8 Literature Background

Ghorbani et al. [41] used mechanical alloying to create Cu-1wt. percent Cr and Cu-1wt. percent Cr/5wt. percent CNT Nano composite powders. The Nano composites were subsequently heated at 25,300,500°C for 30-60-90-120 seconds at pressures between 40 and 120MPa. X-ray diffraction, scanning electron microscopy (SEM), shear punch test, wear test, micro hardness and thermal stability tests were used to characterize these Nano composite materials. The hardness of a product may be increased by about 65 percent by increasing the pressing temperature. The link between relative density and pressing pressure was suggested to be quantifiable. It was also investigated how the addition of CNTs influenced the consolidation procedure and sample attributes. According to research, CNTs reduce a number of characteristics, including stiffness and elongation-to-failure. As a consequence, the Cu-1wt. % CNT/5wt. % CNT Nano composite exhibited 72 percent more wear resistance than the Cu-1wt. % Cr Nano composite with the same friction coefficient. In addition, the addition of 5% CNTs quadrupled the thermal stability of the material.

Ke Chu et al. [42] were able to successfully build a robust contact between the carbon nanotube (CNT) and the Cu matrix. High-resolution transmission electron microscopy (HRTEM), hardness, and tensile tests, respectively, are used to characterize the interface microstructure and mechanical characteristics of composites. CNT/CNT–Cr composites exhibit uniformly increased interfacial bonding and enhanced mechanical characteristics when compared to CNT/Cu

composites. This is because between the CNTs and the Cu-Cr matrix, a thin layer of Cr3C2 was formed.

Only a few studies have been produced on Cr-CNT composites in the scholarly literature. To create Cr-CNT composites, various different kinds and sizes of CNT have been synthesized employing the diverse processes outlined previously in this chapter. Processing Cr from its powder form using the PM technique is one of the most well-known ways for making a bulk material Cr-CNT composite owing to CNT's low vaporization temperature as a first stage, the matrix metal may be directly deposited onto the CNT, resulting in the composite. The second step is to mix the CNT with a solution of a different matrix metal. Another alternative is to utilize ball milling, turbulent mixing or sonication to blend the CNT powder with the metallic powder. This combination may later be processed into bulk material via PM methods. After the deposition is complete, the mixture powder may be removed from the substrate (the plasma spray forming process) (the plasma spray forming process).

Daoush et al. [7] in this study electroless Cu deposition on the multiwalled carbon nanotubes (CNTs) was used to create nanocomposite powders with varied CNT volume fractions. On the surface of the CNTs, copper was placed as a coating. Sintering was done by using spark plasma sintering. The microstructure of the composite was examined by SEM, HRTEM and XRD which shows the uniform distribution of CNT in Cu matrix with porosity less than 1% in case of 5% and 10% CNT, 2.9 in case of 15% and 3.5 in case of 20%. The electrical conductivity was decreased when CNT contents increased while hardness increased when CNT content were increased. Young modulus and elongation were find out by using compression test and it was noted that young modulus increased while elongation decreased by increasing CNT volume fraction.

Chai et al. [43] in this study CNT reinforced Cu is manufactured by electrochemical Copper deposition process. Because of excellent distribution of CNTs and bonding, mechanical properties are greatly improved. Yield strength and ultimate tensile strength was find out by offset method which were 75 MPa and 230 MPa which are justified with other literature [35]. Yield strength has value of five times more than pure copper and that of ultimate tensile strength is three times of pure copper which shows that mechanical characteristics are greatly improved by addition of CNTs.

Uddin et al. [44] in this study CNT reinforced Cu and bronze is manufactured via powder metallurgy by using spark plasma sintering. Powders are milled by using high energy ball mill at a speed of 200 rpm for 5 hours. Sintering temperature for Cu-CNT is 750°c and pressure of 40 MPa for 15 minutes while for Br-CNT temperature is 800°c and pressure is 40 MPa. Hardness is determined almost double (58 HB) to that of pure copper (35 HB) but hardness is decreased when CNT amount is increased. Electrical conductivity of Cu-CNT is found almost same to pure copper but in case of Br-CNT it has improved significantly upto 20%.

Kuzumaki et al. [45, 46] who employed CNTs created by arc discharge. 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.

George et al. [47] used ball milling for the first time in 2005 to mix Al-CNT particles. After 20 minutes of sonication in alcohol, George et al. used MWCNT generated by arc evaporation and ball milled it for 5 minutes with Cr powder. The longer the milling time, the more likely it was to damage the CNT, according to the author. K_2ZrF_6 was added to the composite samples. To compress the mixture, it was crushed in a cylindrical die with 120 KN of force. Before being extruded, the billet was sintered for 45 minutes at 580°C in a nitrogen atmosphere. There were no chemical reactions, and no carbides formed at the contact, according to the results of the Raman spectroscopy in figure 2.11.

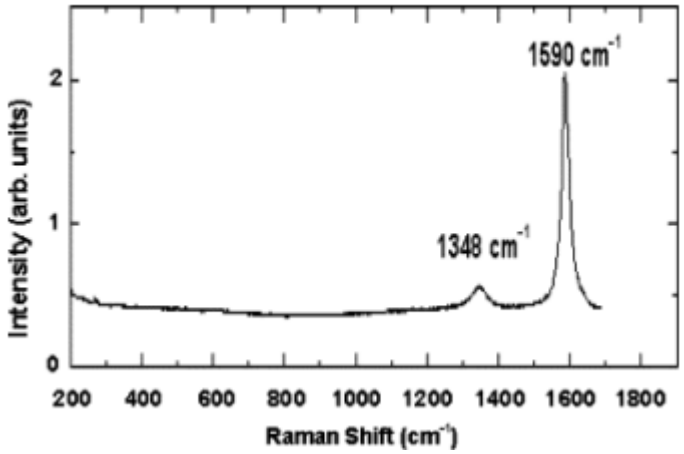

Figure 2.11: Raman Spectroscopy of MWCNT [38]

According to the study conducted by George et al., the use of K_2ZrF_6 as a wetting agent had a positive influence. In example, the addition of K_2ZrF_6 resulted in a notable increase in the ultimate tensile strength of the SWCNT composite. The author contends that UTS was increased by the effect on the surface of the CNTs by using K_2ZrF_6 as a wetting agent in his argument. The inclusion of a wetting agent had no influence on Young's modulus despite the fact that CNT concentration increased, which caused it to rise. These figures are quite close to the shear lag method's expected values, with just a very small margin of error separating them. Both the addition of a wetting agent and an increase in the CNT amount produced improvement in yield strength. This demonstrates how well the shear lag model represents the connection between CNT and matrix.

Wang et al. [48] in this study MWCNTs/Cu composite powders were successfully made by electro deposition, and they were then compacted by hot pressing and cold rolling. Prior to electro deposition, a functional MWCNTs solution was centrifuged to increase MWCNT dispersion in the acid copper sulphate electrolyte which strengthen the bonding of the Cu ions with the MWCNTs. Investigations were done to know how MWCNT content and powder microstructure were affected by the concentration of MWCNTs in the electrolyte. Additionally, the treatment of scraping powders during electro deposition greatly increased the uniformity of MWCNT distribution and created MWCNT network architecture. The resultant composites show improved tensile strength (451.57 MPa) and good

electrical conductivity because of uniform distribution of MWCNTs and robust surface to surface bonding between the reinforcements and Cu matrix.

B.J.Kim et al. [49] in this research, the poor wettability between the metal matrix and carbon nanotubes (CNTs) was improved using the mechanical alloying (MA) process using the ball milling method. Additionally, the CNTs were pre-coated to enhance the CNTs' aggregation with copper powder. The creation of Cu-CNT Nano composite powder utilizing the mechanical alloying and ball milling is the primary goal of this work. The dendritic copper powders as received gradually transform into flaky, disk-shaped particles, and then globular particles. Additionally, the milling Cu-Cu coated MWNTs powder showed a strong tendency to form globules and the grain size of the sintered Cu coated MWNTs specimen shrank more than that of the pure copper specimen. In this way, homogenous Cu-CNT composite was prepared with well dispersed CNT having dense grains.

Choi, H et al. [50] 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 there was no clustering due to fact of CNTs alignment and that the sintering and extrusion temperatures are relatively low (470 degrees Celsius), which halted the production of chromium carbide.

Tokunaga et al. [51] in this study other ways for producing Al/CNT composites are explained besides ball milling and hot extrusion include plasma spraying, high-pressure torsion, and spark plasma sintering and extrusion. These procedures may also be combined to produce the final product. According to Tokunaga et al., a carbide-forming interaction between aluminum and carbon nanotubes (CNT) happens in all of these methods for producing Al-CNT composites, in addition to a number of additional methods that include heating the mixture. In addition, he claims that the brittleness of the carbides would lead the composite to crack under bending stress. They developed a technique known as high pressure torsion, which they say aids in the development of carbide-free composites. This was made possible by the fact that the whole procedure is carried out at room temperature. In this method, Al that was 99.99 percent pure and had a particle size of 75 micrometers was combined with SWCNT that had a tube diameter of 1-2 nanometers. They used a process called sonication for five minutes on a CNT/Cr mixture that included five percent CNT. The process description is shown in Figure 2.12.

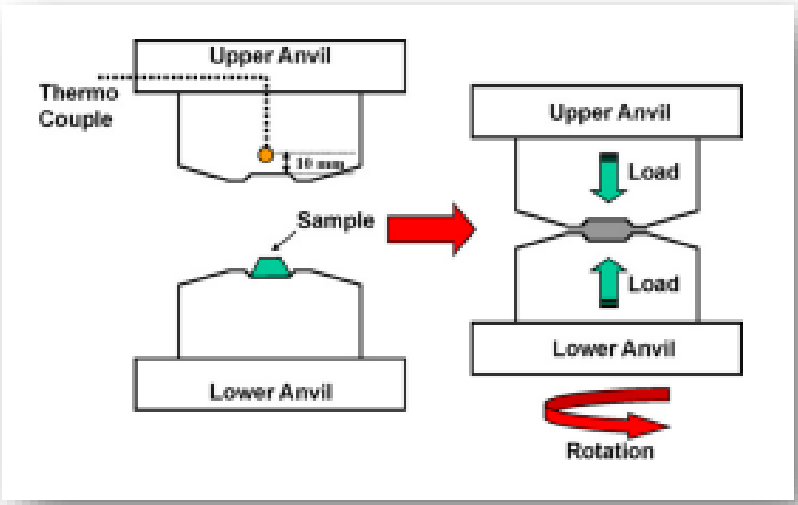

Figure 2.12: Illustration demonstrating the HPT test setting [51]

Al-CNT sample hardness increases considerably as we go away from the center, but that of Cr powder does not change at all. In the author's opinion, this is due to dislocation activity occurring inside grains and contact of dislocation and the grain boundary, because pure Al powder has reached prior in a stable state. Using

HPT leads CNT to crack and distort as we go away from the center, according to the author. When CNTs are closer together in the matrix, dislocations have more places to accumulate which is why hardness rises as we go away from the sample's Centre.

Wang et al. [52] in this study the author studied that the form and size of the carbon nanotubes employed in the composite had a significant impact on the particle size after milling. Notably, the researchers employed the same milling settings and CNT content as Esawi and Morsi when milling MWCNTs with curly structures of a 20-nm diameter. Esawy and Morsi observed a difference between the Al-CNT and pure Cu particle sizes. The size of pure Al particles rise from 29.3 microns to 106.0 microns, after 72 hours of milling., however there was no change in the particle size of Al-CNT. It took Esawi and Morsi 48 hours to mill the 2% Al-CNT composite to 1-2 mm diameter particle sizes. According to the author, the discrepancies in outcomes are attributable to the various sizes and architectures of the MWCNTs used in both experiments shown in figure 2.13.

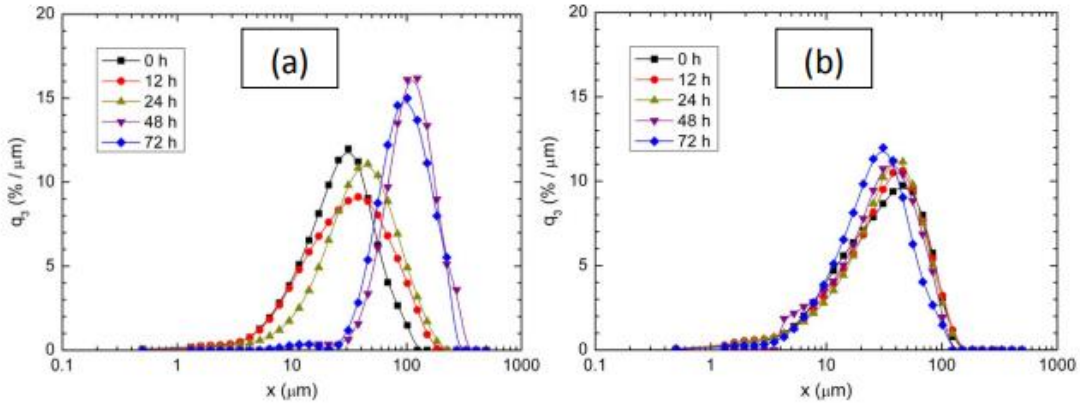

Figure 2.13: (a) Dispersion of Al, (b) Dispersion of Al-CNT mixture powders [52]

By utilizing smaller diameter CNTs boosts the overall surface area of CNTs in contact with Al. This is because there is less contact area between the Al particles during milling. This prevents cold welding of the Al particles. They used CNTs with a smaller diameter, which led to the CNTs being bent and trapped just under the Al particles surface. This led to the resistance against bending deformation and critical buckling stress being lower in their study than in Esawi and Morsi's [53].

Masroor et al. [54] the author in this research paper have examine the impact of milling energy in two different media on CNT dispersion and Nano-composite manufactured wet and dry milling methods at three different levels of

milling energy were used to create a Cu-Cr/carbon nanotube (CNT) hybrid nanocomposite. The x-ray diffraction technique was used to study the structure morphology. SEM was used to study the microstructure of the composite. Mechanical properties were measured by using micro hardness test and ultimate tensile testing. The crystallite size measured was 20-63 nm. Dispersion depends on the milling energy and it was studied that wet milling at higher milling energy is more efficient to disperse the Nano-composite.

Ashutosh et al. [55] they have studied the overview process and mechanical properties of Cu-CNT. They have used powder metallurgy along with spark plasma sintering to prepare Cu-CNT Nano-composite. According to authors view small amount of CNT improves composite characterization and mechanical properties and when the volume of CNT is increased properties such as hardness and density decreases due to the fact of formation of agglomerates. Also surface studies suggest that addition of CNTs convert the composite from brittle to ductile.

Seungchan et al. [56] in this study spark plasma sintering along with hot extrusion is used to prepare multi-Walled carbon nanotube reinforced Copper matrix which include chromium at the interface of Cu-CNT Nano-composite. This study suggests that by increasing CNT content volume increases the tensile strength of composite. The potential load-transfer mechanisms of the interfacial Cr carbide nanostructures cause the improved tensile strength of the MWCNT/Cu-Cr composites.

Lahiri et al. [57] in this study the author sprayed layers of pure Cr foil with ultrasonicated CNTs, each layer having a thickness of 40 m and a diameter of 60 nm. The layers were layered and then cold rolled a total of four times before being annealed for an hour at a temperature of 523 degrees Fahrenheit. The thickness of the sheet was reduced by seventy percent, reaching a value of 55mm, as a result of five further passes of cold rolling (mm). In order to analyze the elasticity and strength of the material, composites with varying amounts of carbon nanotube volume concentrations (2, 7.5 and 9) were used. In contrast to the surface of the 2.9 volume percent CNT sample, which had some clustering of CNTs, the 2.9 volume percent CNT sample that was subjected to Nano-indentation and tensile mechanical testing exhibited a wide range of fascinating results. The sample with 2 volume percent has the highest elastic modulus of any sample; nevertheless, the sample with 9 volume

percent has an ultimate tension stress value of 98 MPa, while the sample with 2 volume percent has an ultimate tension stress value of 72 MPa. It was determined that the only sample that exhibited an elastic modulus against which all of the Nano-indentation data could be compared was the one that contained 2 volume percent. The rule of mixing was valid for samples that had reinforcement that was evenly dispersed throughout them, but it was invalid for the 9 volume percent sample because it had clusters of CNTs on its surface, much as the 2 volume percent sample had. The elastic modulus of materials containing 7.5 percent and 9 percent by volume carbon nanotubes was lowered, which resulted in plastic deformation. This was caused by the presence of CNT agglomerates, which generated CNT-depleted patches. The theoretically predicted value for the elastic modulus was much higher than the value that was found for these two volume fractions. The author advanced the notion that CNT agglomerates constrain dislocation motion, which causes an increase in dislocation density as CNT concentration increases, in an attempt to provide an explanation for the UTS seen in the samples. Because of the impact of strain hardening, it has been given additional reinforcement.

Varol et al. [58] in this study flake powder metallurgy is used to prepare nano-graphite, graphene, and carbon nanotube. Content of CNT are varied to determine the impact on the microstructure, densification, electrical conductivity and hardness of Cu-based nano-composite. It was find out that average particle size at 5% reinforcement of graphene, nano-graphite and carbon nanotube was 94.9, 97.8 and 49.7 µm respectively. Density measured at Cu-0.5 wt.% nano-graphite was 8.78 g/cm^3 which is the highest value and for Cu-5 wt.% CNT it was 6.73 g/cm^3 which is the lowest density. It was noticed that when the amount of reinforcement is increased hardness is decreased for all the reinforcements.

2.9 Summary of Literature

The use of high-energy ball milling proved to be, without a shadow of a doubt, the most efficient and uncomplicated method for distributing CNTs throughout the Cr matrix. This method has been suggested by a great number of writers as a viable option for the production of a high-quality powder composite. In addition, recent studies have revealed that the composites that are made using this method are far more durable than those that are manufactured using other methods.

In addition, the destruction or amorphization of CNTs during milling has been called into doubt.

A similar debate surrounds the nature of the connection that exists between Cr and CNTs at the interface. It is very difficult to wet the surface of CNTs with Cr due to the significantly different surface tension values between CNTs and Cr. To manufacture bulk composite samples suitable for testing, the researchers used hot extrusion, SPS and SPE respectively. Numerous cases of carbide production occurred, particularly at high temperatures. There is also the possibility that carbides might form as a result of the CNT structure breaking down or becoming amorphous.

Chapter 3

Experimental Work

3.1 Materials

The 99% pure copper powder was supplied by 'Uni-Chem Chemical Reagents' of 200 meshes (74 micron). The 45 microns chromium was also of 99% purity and supplied by 'Sigma-Aldrich Germany'. Two distinct compositions were created. The first composition comprises copper, carbon nanotubes whereas the second contains copper, carbon nanotubes and chromium. Cur, Cr and CNTs powder were weighted by analytical balance and the compositions shown in Table 3.1 and 3.2 were obtained.

Table 3-1 Cu-CNT

Material	Weight %	Volume %
Copper	99.5	96.6%
Carbon Nanotube	0.5	3.4%

Table 3-2 Cu-Cr-CNT

Material	Weight %	Volume %
Copper	98.5	95.45%
Carbon Nanotube	0.5	3.34%
Chromium	1	1.2%

3.2 Milling and Mixing:

Milling was conducted using a low energy ball mill machine named 'Wise Mix Ball Mill' which can be seen in Figure 3.1. HDPE bottles (250 ml) 3 mm and 5 mm diameter stainless steel balls were used for mixing. Weights of 3 mm and 5 mm balls were 320 grams and 130 grams respectively. The mass ratio of ball to powders was 15:1 and speed was 300 RPM.

(a) For the preparation powders of Cu-CNT powders, sonicated wet CNTs were added to dry copper powder and mixed for 5 hours in ball mill. Powders were then sieved by using 80 mesh size sieve and then dried in vacuum oven at 40°C for 1 hour to evaporate ethanol.

(b) For obtaining powders of composition Cu-Cr-CNT, CNTs powders were sonicated in 10 mL ethanol in sonicator bath to break agglomerates. Sonicated wet CNTs were added to the mixture of Cu-Cr, which were dry mixed for 20 hour earlier and wet milled later 5 hours to obtain properly mixed Cu-Cr-CNT powders. After ball milling, steel balls and powder were adhered to each other. To remove powders from steel balls, sieving was done by using 80 mesh size sieves. The milled powder obtained were wet and dried in vacuum oven at 40°C for 1hours to evaporate ethanol.

Figure 3.1: Ball Mill*:*

3.3 Pressing

The mixed powder obtained after ball milling were pressed by using a Hydraulic Press and Cold Isostatic Press. The pressing method was carried out in accordance with the following steps.

3.3.1 Hydraulic Pressing

The powder was weighed using an analytical balance. A circular die of 6.5 mm diameter was used to press powder to prepare pellets. The die was filled with

powder in accordance with the specified sample size. Each sample contains 1.9 gm of powder. Each mixture stated in Tables 3.1 and 3.2 was then compressed in a 3 Ton hydraulic press. After 5 minutes of pressing the powder is transformed into pellet which measures 11 mm in height and 6.5 mm in diameter.

3.3.2 Cold Isostatic Pressing

Samples obtained after hydraulic pressing is repressed in a Cold Isostatic Press to enhance its density. In this type of press pressure is applied from every side which gives the sample uniform shape and uniform density. It contains oil which applies pressure in every direction. A flexible mold is used in which sample is enclosed and inserted into the container. Mold used are normally of rubber type which have low deformation resistance. Pressure exerted was 250 MPa for five minutes. Pressure is released and sample is extracted. Figure 3.2 below illustrates Cold Isostatic Press.

Figure 3.2: Cold Isostatic Press

3.4 Sintering

Sintering was done by using Protherm Tube Furnace. Samples obtained after pressing were placed in a ceramic boat crucible and then the crucibles were inserted

in quartz glass tube. After inserting the crucibles, the quartz glass tube was sealed with both ends using silicon gel to avoid gas leakage and oxidation. Argon gas is supplied continuously to keep the atmosphere inert. One side of the tube acts as argon gas inlet and the other side acts as outlet which is then supplied to a beaker containing water. Sintering temperature sets as 950 ºC for three hours and the furnace taken two hours to reach the temperature 950 ºC at a rate of 10 ºC per minute. The sintering furnace can be seen in Figure 3.3.

Figure 3.3: Protherm Tube Furnace

3.5 Metallography

The metallographic specimen's surfaces were prepared using the grinding, polishing, and etching techniques.

3.5.1 Grinding:

Samples after sintering were grinded by using different grit sizes paper. Before grinding samples were mounted for effective grinding by using Bakelite powder. Emery paper of various grit sizes 300, 400, 600, 800, 900, 1200, 1500 and 2000 were used for grinding. Samples were grinded in presence of continuous water supplying. During grinding samples were examined under optical microscope to see whether the samples properly grinded.

3.5.2 Polishing

After grinding, the surface was polished to improve the appearance of samples to clearly see the internal microstructure. Polishing done by using two types

of Alumina paste in which the powder particle size was 0.5 and 1 µm. After polishing samples surfaces were cleaned carefully by using water and then dried with the help of heat gun. Samples were examined under optical microscope to see the surface morphology.

3.5.3 Etching

Etching was done by forming a solution of following etchants to produce grain boundaries.

- Ethanol 100 ml
- Hydrochloric acid 30 ml
- Ferric chloride 10 gm

3.6 Characterization Techniques:

The prepared samples were characterized using following techniques:

I. Densification (via Densitometer)
II. X-Ray Diffraction
III. SEM
IV. Vickers Hardness tester
V. Compression Testing Machine

3.6.1 Density

Density of the samples was measured by using Archimedes principle. Dry weight of the pellet is first noted before dipping it in water. Then the pellet is placed in a tray and it is depth in water. Density of the wet pellet is noted, and the densities of the samples were calculated by finding the difference in wet and dry weight sample in Archimedes' principle asserts that the buoyant force exerted by water [57]. While the liquid used in the beaker was distilled water. Formula used for finding density is given below. The device for measuring density is seen in Figure 3.4.

$$\rho_S = \frac{Ma\rho_1}{Ma-M1}$$

ρ_s is the density of the sample, ρ_1 is the density of the auxiliary liquid, Ma is sample mass in air and Ml is sample mass in the auxiliary liquid.

Figure 3.4 shows densitometer apparatus used for measuring densities.

Figure 3.4: Densitometer

3.6.2 X-Ray Diffraction (XRD)

The X-ray diffraction technique is commonly used to determine the crystallographic structure of materials. The peaks for crystalline samples and the hump for amorphous samples are shown. Brag's law is satisfied when the interaction of photons on a sample creates interference. The data are shown as graphs of intensity versus angle. XRD patterns are positively identified by comparing them with conventional references using software. Using Xpert's PRO PAN analytical X-ray diffractometer, the pattern of a sample was determined. To find the crystallite size, sherrer equation was used which is given below [58].

$$\beta \cos\theta = \frac{K\lambda}{D}$$

Where: β = Full Width at Half Maximum

θ = Diffraction angle

λ = Wavelength

D = Particle (crystallite) size

K = 0.91 (Scherrer constant)

3.6.3 SEM Analysis

SEM is an important instrument for revealing the size, microstructures, shape and morphology of objects. Utilizing a high-energy electron beam from an electron

source (Gun) to create a variety of signals at the sample is the basis of SEM operation. The produced pictures have an exterior texture and crystal structure. An object of size 1 cm to 5 micron sized can be seen to a magnification level of 20x to 30,000x can be easily seen. Figure 3.5 shows Scanning Electron Microscope Jeol 6490 LV.

Figure 3.5: Scanning Electron Microscope Jeol 6490 L

3.6.4 Vickers Hardness Test

Vickers hardness is a micro hardness test that measures the surface hardness of a substance at microscopic level. In this test, a 136-degree pyramidal diamond indenter produces a square depression in the sample. The duration of the load is 5 to 15 seconds. The two axes of the diamond-shaped indentation are averaged (giving the dimension d). Firstly, hardness of the reference element is calculated and then the hardness of the composite is calculated which is compared to the reference element. 8 indents were made at different places in each sample and average was taken as final result. Figure 3.6 Illustrate micro-Vickers hardness tester.

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Figure 3.6: Vickers Hardness Test

3.6.5 Compression test

To study the mechanical behavior of the nanocomposites, compression test was performed using a universal testing machine from SHIMADZU AGX Plus instrument as shown in figure 3.7. A universal testing machine (UTM) is used to apply tensile, compressive, or transverse stresses to test a specimen to determine its mechanical characteristics (tension, compression, etc.). The machine's name refers to the variety of tests it can run on various types of materials. It has two main parts i-e loading unit and control unit. Specimen placement and load is applied with the help of loading unit. Control unit is responsible to varies load and to give the corresponding results. UTM gives the load value in the Y-axis and displacement in the X-axis. Load vs displacement graph give us the stress-strain analysis, modulus of elasticity, yield strength etc. Following tests can be performed on UTM.

1. Tensile Test
2. Compression Test
3. Adhesion Tests
4. Pull-Out Tests
5. Bend Test
6. Hysteresis Test

We prepared three types of cylindrical samples of each composition were prepared for the Compression test which was carried at a strain rate of 0.05 mm/sec.

Figure 3.7: Universal Testing Machine SHIMADZU

Chapter 4

Results & Discussion

4.1 Density Measurement

Densities of all the samples were measured with densitometer using Archimedes principle. The measured densities of the samples are summarized in Table 4.1.

Table 4.1: Density measurements

Sample	**Actual Density**	**Theoretical Density**	**Relative Density (Densification)**
Copper	8.10	8.96	90 %
Cu-CNT	8.08	----	90.17 %
Cu-Cr-CNT	7.73	----	86.27%

4.1.1 Copper Density Measurement

For pure copper, theoretical density was calculated to be 8.10 g/cm^3, which is also good agreement with the literature value [40]. Moreover, relative density is calculated by dividing theoretical density over actual density which is 90%.

4.1.2 Cu-CNT and Cu-Cr-CNT Density Measurement

The actual density of Cu-CNT was calculated to be 8.08 g/cm^3. Relative density calculated by comparing the actual density of Cu-CNT with pure copper density, which is 90.17%. In the same way relative density of Cu-Cr-CNT was also find out whose value was 86.27%. From the above comparison it was concluded that the composite prepared had good density as compared to pure copper. There are some factors which have contributed in the density of composites which are Cold pressing, low energy ball milling, interfacial bonding, and wettability. Studies have shown that pellets prepared by ordinary cold pressing have relative density of more than 80% [41]. Also, because the shapes of our particles were irregular and secondly the pressing pressure that we used was small also contributed to lower the densities.

4.2 X-ray Diffraction

XRD was performed on JEOL-JDX-9C-X-ray diffractometer. Figure 4.1 and figure 4.2 shows the XRD patterns of pure copper and Cu-CNT composite. The XRD patterns were analyzed using the Xpert High score Plus software.

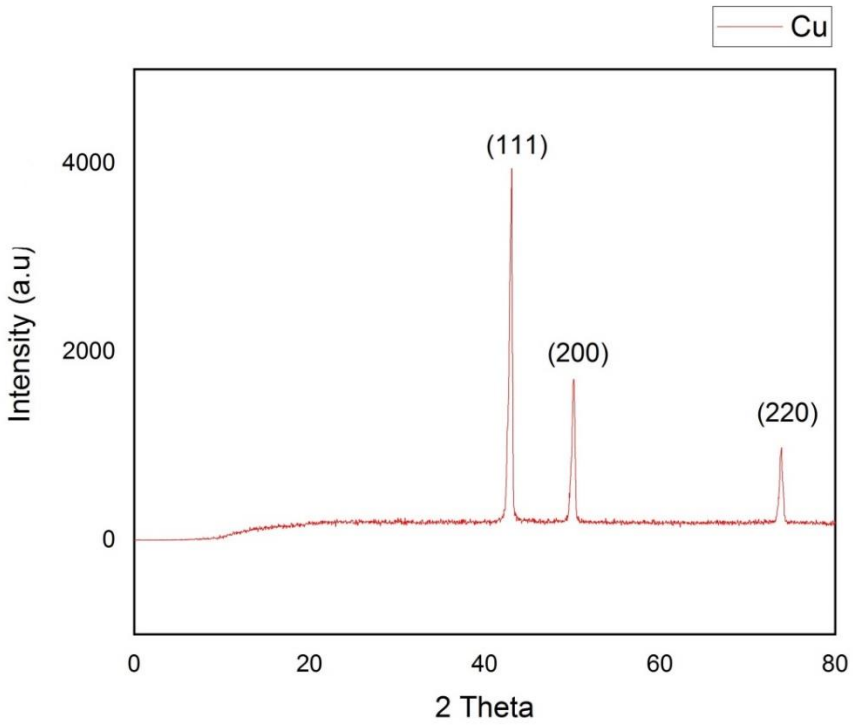

Figure 4.1: XRD of pure copper pellet

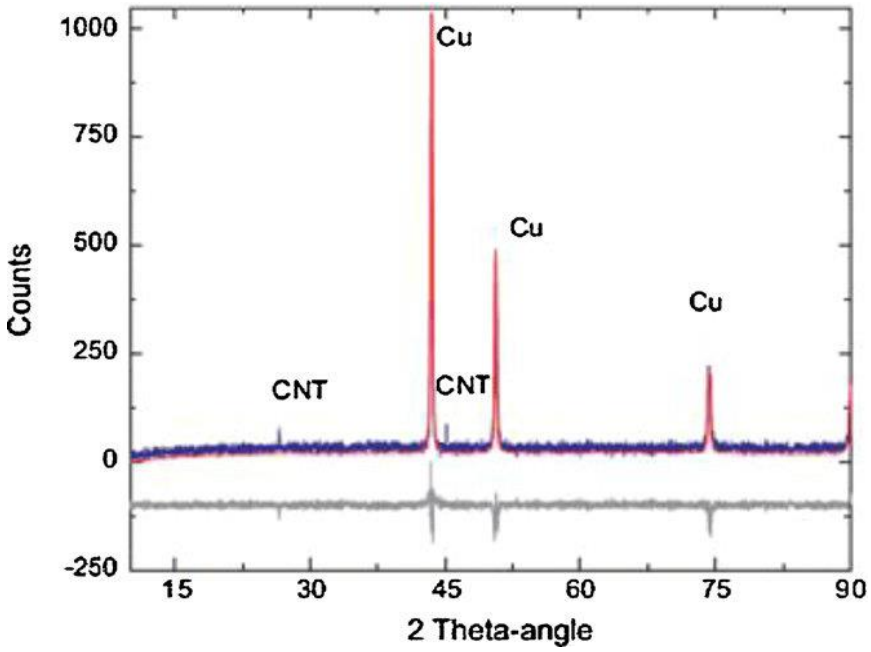

Figure 4.2: XRD of Cu-CNT composite

The XRD patterns were analyzed by comparing it with the card number JCPDS Card No. 00-002-1225 and JCPDS Card No. 0-001-1242 which confirm the composition of copper and Cu-CNT composite.

4.3 SEM analysis

4.3.1 Copper powder

Scanning electron microscope images of pure copper powder in figure 4.3 shows that the particles are in the form of agglomerates. Their size ranges from 10 μm to 30 μm. Their shape is irregular.

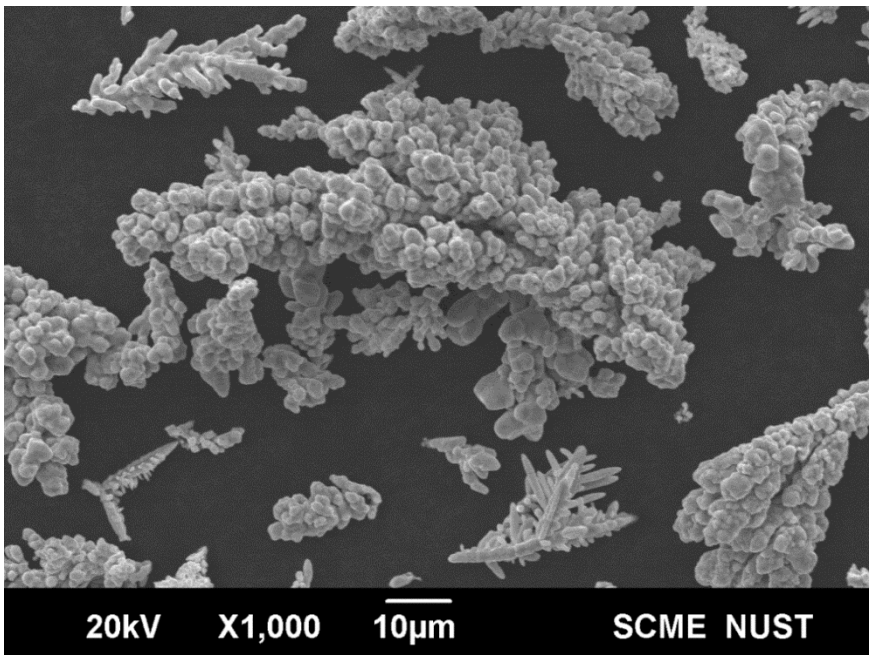

Figure 4.3: SEM of pure copper powder

4.3.2 CNT powder

Scanning electron microscope images of carbon nanotubes is shown in figure 4.4. The CNTs are found in the form of agglomerates, therefore sonication was performed later for their better dispersion.

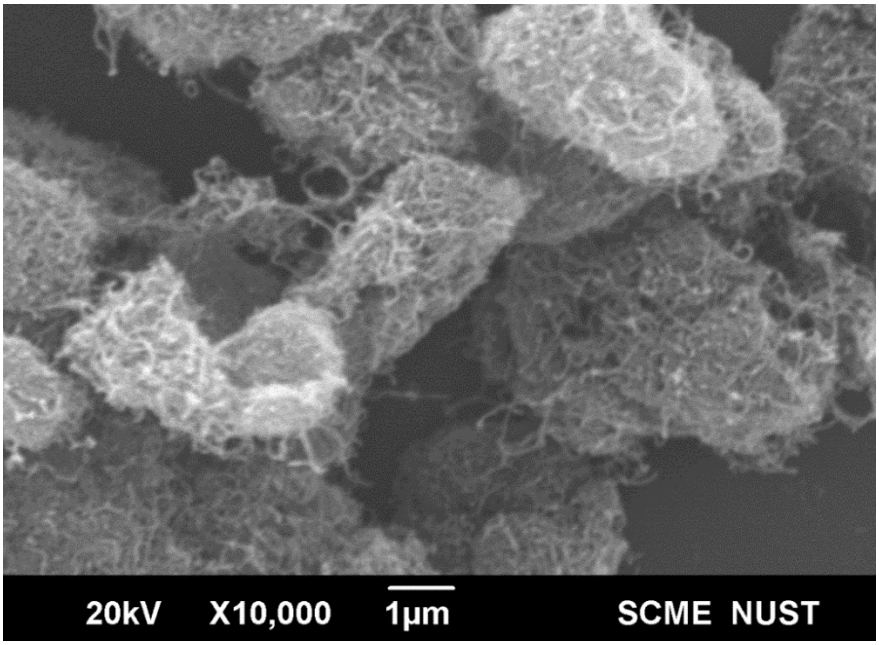

Figure 4.4: SEM of CNTs powder

4.3.3 Copper Pellet

Scanning electron microscope image of pure copper and pressed by cold isostatic pressing process in figure 4.5.

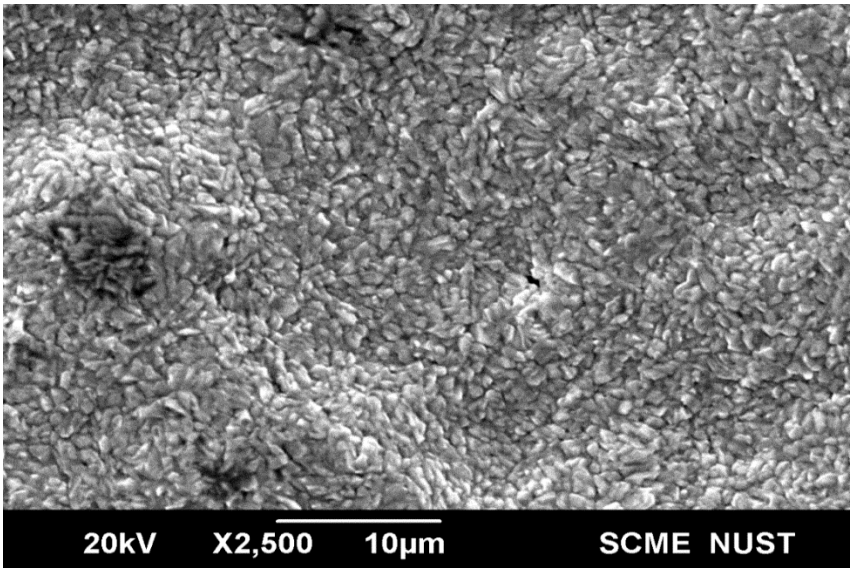

Figure 4.5: SEM of CIP pure copper pellet sintered

Figure 4.6 shows the SEM image of the same sintered pallet. As compared to non-sintered pallet (Figure 4.5), the sintered pallet shows more dense structure.

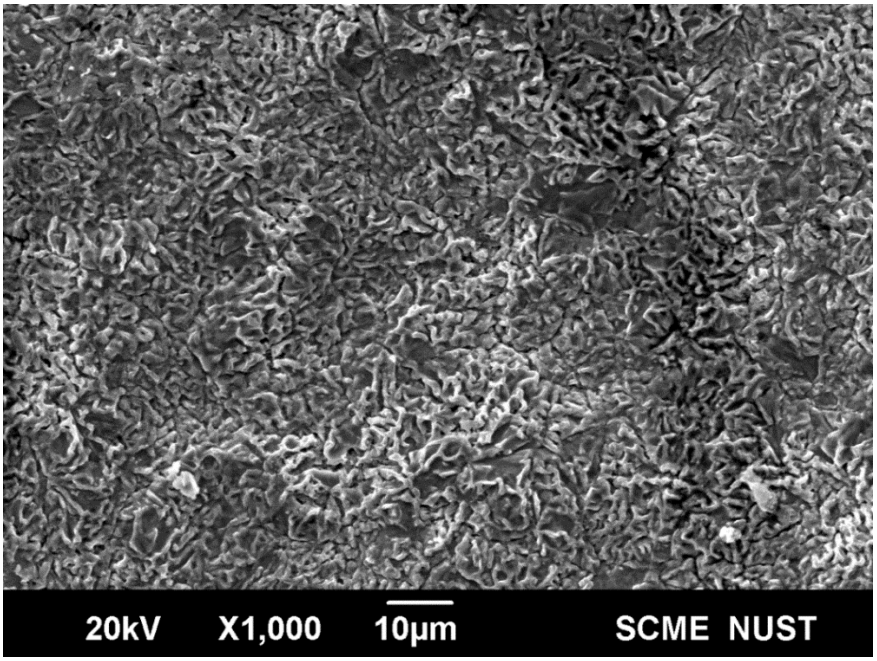

Figure 4.6: SEM of pure copper pellet (CIP and Uniaxial pressing)

4.3.4 Cu-CNT composite Pellet

Scanning electron microscope images of Cu-CNTs composite in figure 4.7 which shows the dense microstructure of the prepared Cu-CNT composite. Since the CNTs are in very small amount i-e 0.5 %, therefore they are not visible at even higher magnification.

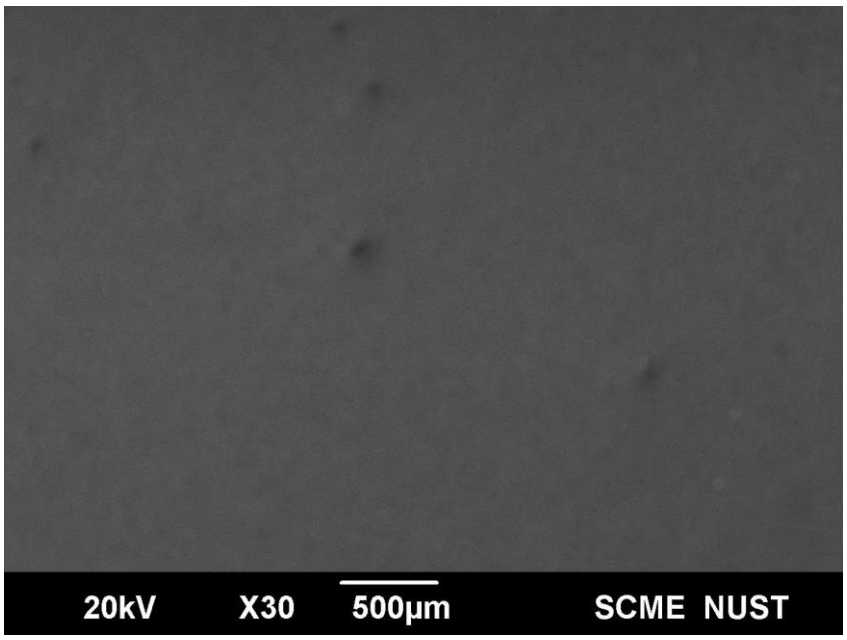

Figure 4.7: SEM of copper and CNTs composite pellet

4.4 EDX Analysis

The Energy Dispersive X-ray (EDX) is a method of analysis used to characterize a sample's chemical composition or elemental composition. It depends on examining how a source of X-ray excitation interacts with a material. EDX analysis of Cu-Cr-CNT composite was conducted in SEM and summarized in Table 4.2. The EDX results confirmed the presence of the Cu, Cr and CNTs. The EDX analysis shows the higher Carbon amount as expected. It is a normal phenomenon is EDX results that carbon is always in greater amount than the original. It is due to different factors like contamination of the machine etc.

Table 4.2: Elemental Composition of Cu-Cr-CNT

Elements	**Weight %**	**MDL**	**Atomic %**	**Error %**
C K	12	0.35	2.7	9.4
Cr K	0.7	0.15	0.1	11.1
Cu K	87.3	0.33	97.3	2.3

4.5 Hardness

Hardness was calculated by using micro-Vickers hardness tester. In Vickers hardness test, indenter tip indents into the surface of the sample with a specific load applied. The force applied may varies from 5 to 15 seconds. In our case load applied was 500g for 15 seconds. Hardness value of pure copper, Cu-CNT and Cu-Cr-CNT was calculated to be 54 HV, 84 HV and 74 HV, respectively. In figure 4.8 the results shows that hardness value of Cu-CNT composite pellet is greater than others. The reason is that Cu-CNT are more homogeneously distributed in each other, and their interaction is effective.

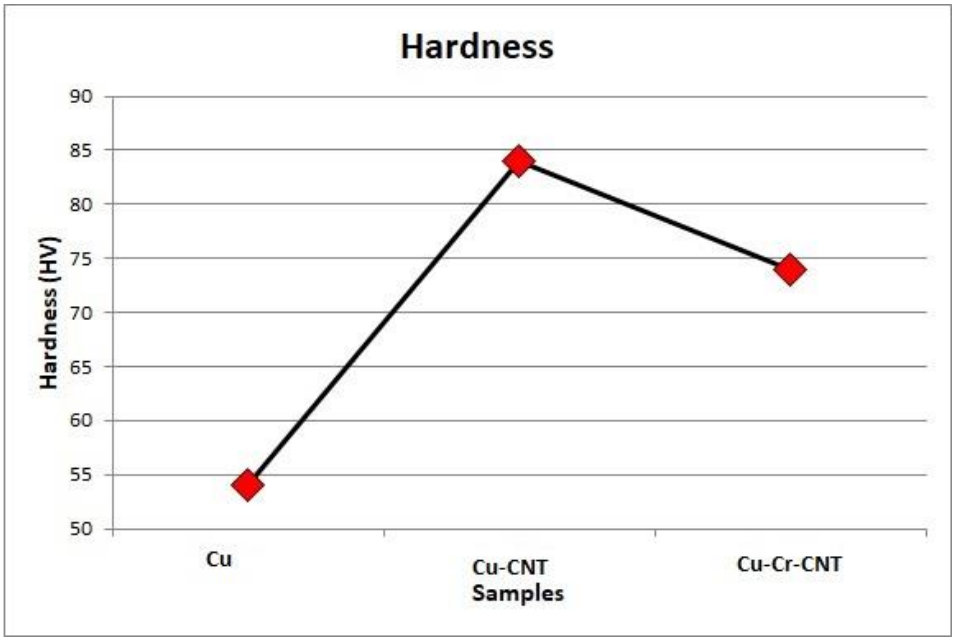

Figure 4.8: Hardness results and comparison

4.6 Compression Testing

The compression testing of samples was performed by using a UTS machine known as 'SHIMADZU AGX Plus'. Compression testing is a mechanical process where a material or product is subjected to forces that push, compress, squash, crush, and flatten the test specimen. Basic mechanical tests like tensile and bend tests are comparable in nature to compression tests. Compression tests identify the stiffness and strength of a material or product under crushing loads. Compressive testing allows for the determination of a material's compressive strength, yield strength, ultimate strength, elastic limit, and elastic modulus among other properties. If these various factors and the values associated with a particular material are understood, it is possible to assess whether the material is suitable for a given application or whether it will fail under the given stresses. The behavior of materials under a compressive load can be assessed using a compression test. Pellets to be tested were loaded between the two plates and a force was applied by bringing the crossheads together. The pellets were compressed, and deformation measured against the applied load. Pellets used were 6 mm in diameter, 10mm height and cylindrical shaped. Load speed was 0.5 mm/min throughout the entire process. Compressed sample after compression operation can be seen in figure 4.9.

Figure 4.9: Samples after compression testing

4.6.1 Pure Copper Pellet

Figure 4.10 shows the stress-strain curve of pure copper pellet obtained from the compression test. The yield point is the location on a stress-strain curve where elastic activity ends, and plastic behavior starts. Below yield point the material can return to its original shape when the applied force is removed. Yield point was calculated by offset method and found to be 87 MPa. Young modulus calculated by finding the slope of the linear region of the stress-strain graph and calculated to be 3.6 GPa.

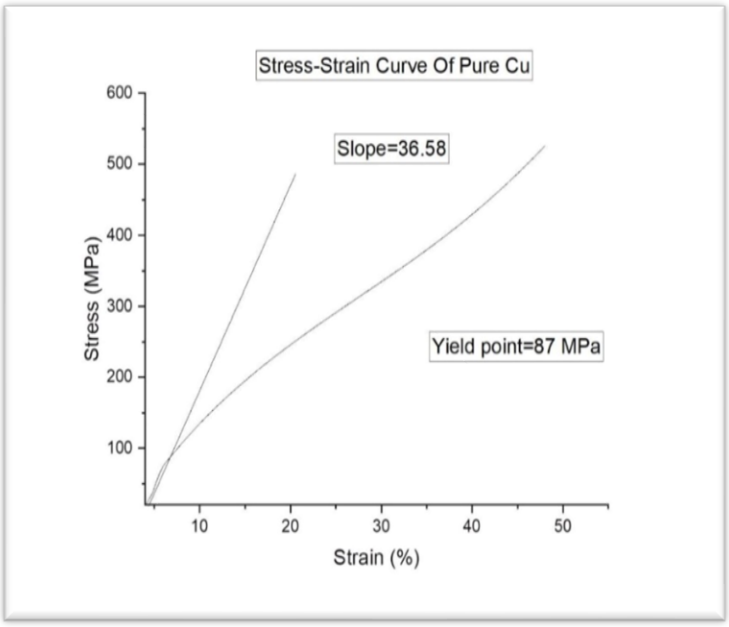

Figure 4.10: Stress-Strain Curve of Pure Copper

4.6.2 Cu-CNT Composite

The stress strain curve of Cu-CNT composite is shown in figure 4.11. Yield point of the pellet after compression testing was find out by offset method and its value was 164 MPa. From the slope of the graph young modulus was find whose value was 5.5 GPa. Due to the presence of CNT reinforcement, the yield point of the pellet is 164 MPa which is higher than copper's yield point which is 87 MPa. Also, the composite's Young Modulus is 5.5 GPa while copper's is 3.6 GPa.

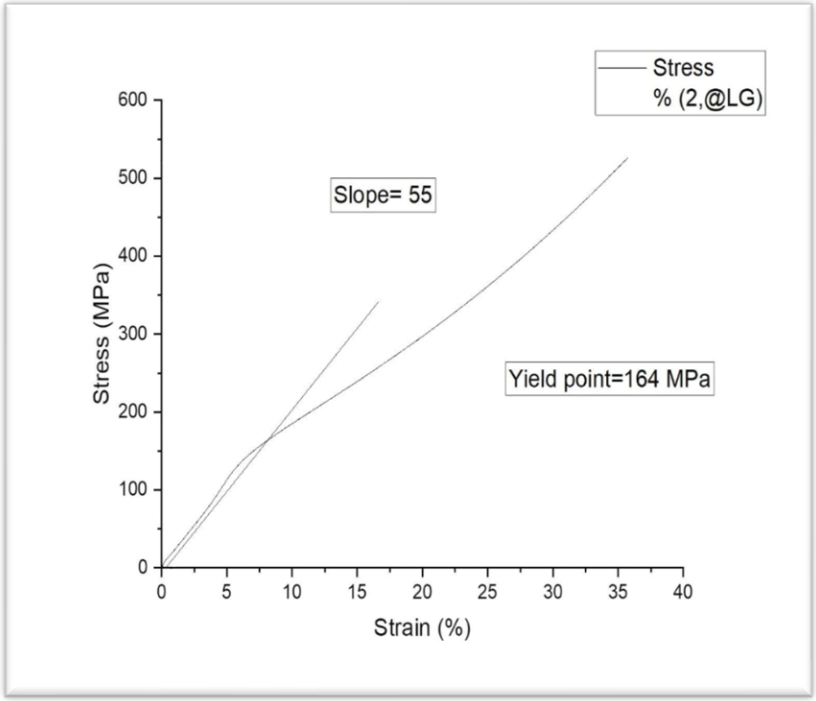

Figure 4.11: Stress Strain Curve of Cu-CNTs

4.6.3 Cu-Cr-CNT Composite

The compression testing of the Cu-Cr-CNT composite was conducted, and stress-strain curve is shown in figure 4.12.

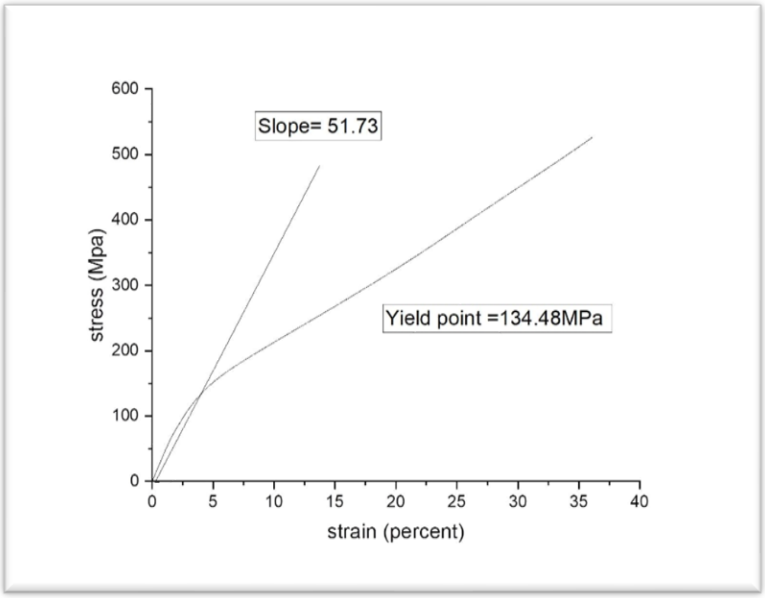

Figure 4.12: Stress- Strain Curve of Cu-Cr-CNTs

Yield point of Cu-Cr-CNT composite was found to be 135 MPa which is increased by 36% in comparison to pure copper (i.e., 87 MPa) but when compared with yield point of Cu-CNT (164 MPa), we see that its value is decreased by 18%. In figure 4.13 we can see the comparison of yield point between Cu and other composites.

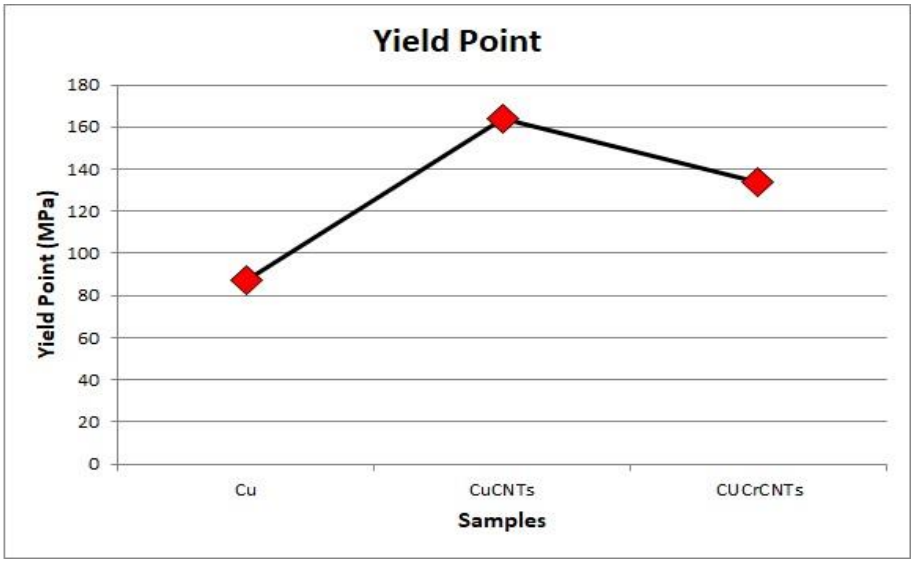

Figure: 4.13: Graph of yield point of all samples

Young modulus of the Cu-Cr-CNT composite was calculated to be 5.1 GPa which is increased by 30% when compared with pure copper but when compare with Cu-CNT, its value is decreased by 7% as shown in Fig 4.14.

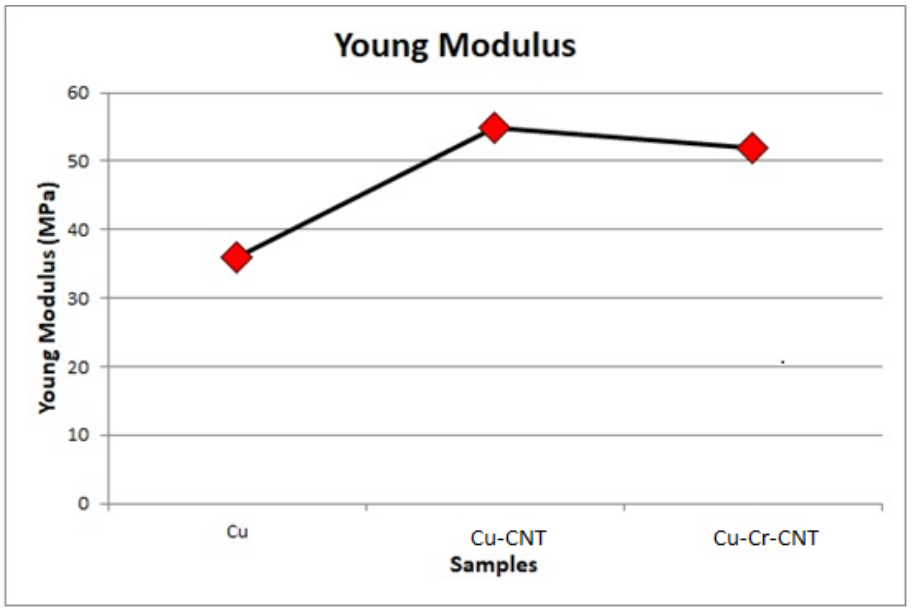

Figure 4.14: Graph of young modulus of all samples

Summary

In the present work, Cu-0.5wt.%CNT and Cu-1wt.%Cr/0.5wt.%CNT composites were prepared via powder metallurgical route. CNTs were first sonicated to break the agglomerates and homogenously disperse it. Then through ball milling process composite powders were mixed. The mixed powder obtained after ball milling were pressed and pellets of size of 6.5 mm diameter were obtained. The samples were sintered at 950 °C in a tube furnace (inert environment) for 5 hours. The characterization techniques were performed to know all about the composites prepared. The Densification of composites were measured by using densometer and the density of Cu, Cu-CNT and Cu-Cr-CNT were known as 90%, 90.56% and 86.81%, respectively. The SEM was used to study the topography of the prepared samples. Hardness test was performed by using micro-Vickers hardness tester to know about the increase in hardness of composite pellets and it was found that it is increased by 55.56 % in case of Cu-CNT while in Cu-Cr-CNT composite it is increased by 37.03 % when compared to copper. Universal testing machine was used to measure young modulus and yield strength. It was found out that in case of Cu-CNT, young modulus is increased by 52.78 % and yield strength by 88.50 % when compared to pure copper. Also, for Cu-Cr-CNT, young modulus increased by 41.67% and yield strength by 54.57 % when compared with Cu. It was concluded that the combination of Cu and CNTs is found to be an excellent composite for applications needing high mechanical properties.

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