MWCNT REINFORCED METAL MATRIX COMPOSITES USING LENS™: CASE STUDIES ON MWCNT-BRONZE AND MWCNT-Al-12%Si

By

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Abstract

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Laser engineered net shaping (LENS™) was used to fabricate Carbon nanotube reinforced metal matrix composites using metal powders mechanically alloyed with different contents of multi-walled carbon nanotubes (CNTs) as feedstock. Two different metal matrices, Bronze and Al-Si, were reinforced to fabricate free standing bulk structures and coatings respectively.

Microstructural observations of the CNT-Bronze composites showed that CNTs were retained in the composite matrix after laser processing. The addition of CNTs showed an enhancement in yield strength, elastic modulus, hardness and strain hardening rate of the composites. Yield strength was compared with predictions of theoretical models, which indicated the presence of load transfer to reinforcements, thermal mismatch and Orowan looping in the composites. Thermal conductivity increased linearly with increase in CNT volume fraction. The mechanical and thermal properties of these composites can be further improved by optimizing the LENS™ processing parameters. The composites prepared in this study were not completely dense which affected their properties negatively.
The tribological properties of Al-12Si improved with the addition of CNTs in the Al-Si matrix. The friction and wear behaviors of the composite were investigated using a pin-on-disk wear tester under dry condition. The tests were conducted at a sliding speed of 40 mm/s under an applied load of 1 N. The experimental results indicated that the friction coefficient of the composite decreased with the addition of CNTs due to the self-lubrication and unique topological structure of CNTs. The volumetric wear rate showed a drastic reduction with the addition of CNTs. Thermal properties showed a significant improvement with CNT addition. The thermal conductivity of Al-Si coated Al-2024 improved by 31 % after 8 vol% addition of CNTs. Thermal properties are a better indicator of the presence of CNTs in the Al-Si matrix. However, any hard evidence of the presence of CNTs in the Al-Si matrix was not obtained.
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Chapter 1

Introduction

Metals and alloys are popular as structural materials. Some metals and metal alloys possess high structural strength per unit mass, making them useful materials for carrying large loads or resisting impact damage. Metal alloys can also be engineered to have high resistance to shear, torque and deformation. The strength of metals and metal alloys can be improved by heat treatment up to a certain limit. The desire for further improvement of the strength and stiffness of metal has led to the development of metal matrix composites (MMCs). In MMCs the strength and ductility is provided by the metal matrix and further improvement in strength and/or stiffness is provided by a reinforcement which is either a ceramic or a high stiffness metal based particulate or fiber. Metal matrix composites can be designed to possess qualities such as low coefficient of thermal expansion and high thermal conductivity which make them suitable for variety of applications including electronic packaging.

The excellent physical properties of multi-walled carbon nanotubes (here after referred to as MWCNTs, unless mentioned) make them an attractive candidate for use as reinforcements in metal matrix composites. However, compared to polymer based nanocomposites, there hasn’t been much progress in this field [1]. This can be attributed to relative ease with which polymer based composites can be processed, which often does not require high processing temperatures. In recent years different research groups have begun to focus on processing of MWCNT reinforced MMCs. These composites are being projected for use in structural applications for their high specific strength as well as functional materials for their exciting thermal properties.
The focus of my MS thesis is MWCNT reinforced MMCs. This thesis consists in six chapters. In Chapter 1, the aim of the work is described. Brief review of conventional metal matrix composites and laser engineered net shaping is also presented in this chapter. In Chapter 2, a summary of carbon nanotubes and the advantages and challenges of the MWCNT applications in MMCs industry are discussed. Various processing methods, which have been reported in literature, for fabricating MWCNT-reinforced MMCs and the enhancement in the physical properties due to MWCNT addition are discussed as well. In Chapter 3, the methodology applied for processing and characterization are discussed for both MWCNT reinforced Bronze free standing bulk structures and MWCNT reinforced Al-Si composite coatings. In Chapter 4, experimental results obtained for MWCNT-Bronze bulk structures are presented and discussed. In Chapter 5, experimental results obtained for MWCNT-Al-Si composites coatings on Al-2024 substrate are presented and discussed. The conclusion of this thesis and proposal for future work is given in chapter 6.

1.1 Aim

This study focuses on use of Laser Engineered Net Shaping (here after referred as LENS™) for MWCNT-MMC fabrication. Lasers are attractive processing tools since they offer several unique advantages namely, high productivity, automation worthiness, non-contact processing, elimination of finishing operation, reduced processing cost, improved product quality, greater material utilization and minimum heat affected zone [2]. Laser processing technology can be used to deposit metals and alloys with fine grain microstructure by using appropriate operation parameters [3]. This can be used to build parts with good mechanical properties. It has been demonstrated that direct fabrication of metal–matrix composites using LENS™ process can lead to refined and homogeneous distribution of the reinforcement phase [4].
There is only one study which reports the fabrication of MWCNT-MMCs using lasers. Hwang et al. [5] have reported fabrication of 10 vol. % MWCNT-Ni composite using LENS™ after roller mixing of MWCNT and Ni powder. Although the process incurs very high temperatures, still MWCNTs were retained. The study also claimed wetting of MWCNT by Ni and no interfacial compound formation. However, the mechanical and thermal properties of the composite were not reported.

The motivation of this study was to explore the possibility of processing MWCNT-MMCs using LENS™. The combination of LENS™ processing with MWCNT reinforcements can help in development of high performance engineering materials. In this study we used MWCNTs to reinforce Bronze (Cu-90, Sn-10) and Al-12Si alloy. Bulk structures were made out of MWCNT-Bronze composites, while coatings were made out of MWCNT-Al-12Si composites. The microstructure and some physical properties like thermal and mechanical properties of these composites were studied.

1.2 Background Information

1.2.1 Conventional Metal Matrix Composites

A composite material is a mixture of two or more separate phases, matrix and reinforcements, which have been intimately bound together. The advantage is the combination of those different phases, providing a potential for tailoring material properties to meet specific and challenging requirements. The balance of the properties can be altered by the choice of the matrix and the level of reinforcement. Composites offer the only pathway for producing advanced “designer” materials. Most composites exploited in sport, aerospace and automotive industries consist of a reinforcing phase, such as glass or carbon fibers, and a polymeric matrix [1]. Polymers are
chosen for matrix materials because of their low density, low cost, and easy procedure in composite processing. However, compared with polymers, metals have other advantages, which are wanted in diverse applications, such that they combine strength and toughness, which can be maintained even at elevated temperature, do not absorb humidity, are not degraded by radiation, do not outgas in space, generally do not burn, but can conduct heat and electricity. With all of these desirable and interesting physical properties, metals were considered as matrices in composites although it would be significantly more difficult to process metal matrix composites (MMCs) than to produce polymer matrix composites.

At present, a variety of metallic matrices, metals and their alloys, are employed in MMC industry. Examples include Al, Ti, Mg, Fe, Cu, Ni, W, Ag, Ni, Mo, Be, NiAl, AlCu, AlCuMg, Al-4%wtCu, Al-4%Cu-1%Mg-0.5%Ag for numerous application. With their superior mechanical properties such as light weight, excellent strength, toughness and resistance to corrosion, which are critically important in aerospace and automotive applications, aluminum and aluminum alloys predominate as metallic matrices in the MMC industry.

In the most common metal matrix composites, the reinforcements are ceramics. The primary interests are in lighter ones such as SiC, Al₂O₃ (for instance SAFFIL), B₄C, TiB₂, TiC, among which SiC and Al₂O₃ are dominant. Other ceramic such as Si, TiB and Cr₃C₂ are also used [2]. The ceramic reinforcements can take various forms in composites: particulates, whiskers, filaments, short fibers (also called chopped fibers or staple fibers) or continuous fibers, depending on the demands, such as design properties or cost. Although particulate reinforcements provide inferior improvement in mechanical properties for metal matrix composites, the benefits from ceramic particulate reinforcements, including enhanced wear and erosion resistance, increased stiffness, higher damping and reduced thermal expansion, offer very
interesting advantages with respect to the un-reinforced matrix. These composites can still retain the advantages of the matrix (metals and alloys) in terms of cost, processing and some other properties such as the ultimate tensile strength.

Short fiber and whisker reinforced metals display characteristics and advantages similar to those of metals reinforced with particulates, the greater capacity of elongated reinforcements to carry load transferred from the matrix and the inherently stronger nature of whiskers enable short fiber and whisker reinforced metals to exhibit superior properties than an equivalent particulate reinforced metal. Moreover, anisotropy, which is not evident in particulate reinforced metals, is microscopically apparent in short fiber and whisker reinforced metals. The dominant applications of MMCs focus on three sectors: (i) automotive and ground transportation, (ii) aerospace and defense, (iii) thermal management for electronics. In the sector of automotive and ground transportation, metal matrix composites are used for their specific stiffness, high temperature strength and excellent wear properties. In aerospace applications, metal matrix composites satisfy the principal requirements such as low thermal expansion coefficient, low density, high stiffness, high strength and dimensional stability. In order to obtain the specific properties of a metal matrix composite, a number of variables should be taken into account: the choice of the matrix, the type and the level of the reinforcement, and the composite processing route.

1.2.2 Laser Engineered Net Shaping (LENS™)

Laser engineered net shaping is a solid freeform fabrication techniques which is capable of producing parts which are near net shape and require little post processing or machining. The LENS™ (Figure 1-1) consists of a continuous wave Nd:YAG laser, a controlled atmosphere glovebox, a x-y-axis computer controlled positioning system and a powder feed unit/units. The
Positioning stage is mounted inside the argon filled glovebox operating at a nominal oxygen level of 2-3 parts per million. The laser beam is brought into the glovebox through a window mounted on the top of the glovebox and directed to the deposition region using a plano-convex lens. The powders (of materials being deposited) are fed into the powder feed unit/units attached to the machine and are delivered through argon flowing through a multi-nozzle assembly. The nozzle assembly is designed such that the powder streams converge at the same point on the laser beam focused on a substrate placed on the positioning system.

![Diagram of LENS™ process setup](image)

Figure 1-1: A typical LENS™ process setup

The lens and powder nozzle assembly move as an integral unit and are sometimes referred to as deposition head.

LENSTM involves the use of a CAD design file of the 3-D component which is sliced into a series of 2-D layers during post-processing. A Nd:YAG laser beam, up to 2 kW power, is focused onto a metal substrate to create a molten metal pool on the substrate. Metal powder is
injected into the metal pool, which melts and solidifies. The substrate is then scanned relative to the deposition head to write a metal line with a finite width and thickness. Rastering of the part back and forth to create a pattern and fill material in the desired area allows a layer of material to be deposited. Finally, this procedure is repeated many times along the Z-direction, i.e., height, until the entire object represented in the three-dimensional CAD model is produced on the substrate. A variety of metals and alloys have been deposited using LENS™ from pre-alloyed as well as elemental powders [6,7].

1.3.2.1 Factors influencing LENS™ Processing

Processing parameters in LENS™ are laser power level, powder feed rate, scan speed and hatch/raster spacing [8]. These process parameters are changed according to the material being deposited. For example laser power is lowered while depositing materials with high laser absorptivity but higher laser power level is desired for materials having low laser absorptivity. Choice of the substrate is also important since it influences the bonding between the deposited part and the substrate. Powder flowability is a very crucial and good flowability is desired for LENS™ processing. Poor powder flowability can lead to clogging in the powder delivery system. Selection of proper process parameters allows control over properties like microstructure, surface finish, hardness and size.

1.3.2.2 LENS™ Processing of Metal Matrix Composites

There are several studies which report the use of LENS™ for processing of metal matrix composites. TiB reinforced Ti matrix composites have been manufactured by Banerjee et al. [9] and A. Genç [10]. Both of these studies reported a homogeneous distribution of reinforcement phase in the metal matrix. Similar studies have been reported for the fabrication of TiC-Ni
composites [11] and carbide reinforced TiAl composites. Apart from the aforementioned composites LENS\textsuperscript{TM} has been used to deposit WC-Co composites [12] as well.

Since LENS\textsuperscript{TM} process involves rapid solidification of molten metal, it is possible to achieve a fine grained microstructure in the deposited parts. Hence, better mechanical properties can be achieved as compared to conventional melting and solidification routes as predicted by Hall-Petch strengthening. The processing conditions can be varied in order to select different microstructures and all the benefits of metastable microstructures can be exploited. Since the deposition is carried out in argon atmosphere, problems related to oxidation during processing can be eliminated. An important feature of LENS\textsuperscript{TM} is its ability to process compositionally and functionally graded materials. This process can create metallic structures directly from CAD files which significantly reduces the processing time and possibility of human error. In conclusion, LENS\textsuperscript{TM} offers the advantages of producing complex near net shape structures which may require surface finishing [13].

Since the molten metal pool created in LENS\textsuperscript{TM} process solidifies rapidly, the interaction time between the molten metal pool and reinforcements is very small, thus minimizing the formation of any reaction products. The properties of the materials fabricated by LENS\textsuperscript{TM} are tailorable and can be controlled by controlling the processing parameters. Another important feature of LENS\textsuperscript{TM} is its versatility, i.e. the ability to make structures out of various materials.
2.1 Carbon Nanotubes (CNTs)

In nature, carbon exists as solids in two basic forms: transparent diamond and black graphite (Figure 2-1). Diamond exhibits a very rigid, stable and hard configuration, where each carbon atom has four nearest neighbors arranged in a tetrahedron and the carbon atoms are in \( sp^3 \) hybridized orbits. Whereas, graphite, with different atomic orbital state (\( sp^2 \) hybridisation), consists of planar layers, called graphene layers, which are composed of carbon atoms in hexagonal structure and each carbon atom has three nearest neighbors. Thus the bonding in the plane is very strong, but it is weak between the layers because the binding forces between layers are the relatively weak Van der Waals forces. Carbon nanotubes (Figure 2-2) (MWCNTs) are allotropes of carbon with a cylindrical nanostructure which are made by rolling a sheet of graphite into itself [14]. Carbon nanotubes have a very high aspect ratio which means that they can be considered as one dimensional material. Carbon nanotubes can be chiefly classified into two categories: single walled carbon nanotubes and multi-walled carbon nanotubes. Most single-walled nanotubes (SWNT) have a diameter of close to 1 nanometer, with a tube length that can be many millions of times longer. The structure of a SWNT can be conceptualized by wrapping a one-atom-thick
layer of graphite called graphene into a seamless cylinder. Single-walled nanotubes (SWCNTs) are an important variety of carbon nanotube because they exhibit electric properties that are not shared by the multi-walled carbon nanotube (MWCNT) variants. SWCNTs are very expensive compared to MWCNTs [1]. Multi-walled nanotubes are made by rolling several sheets of graphite into concentric cylinders. The typical diameter of multiwalled carbon nanotubes (MWCNTs) available commercially lies between 20nm-60nm [15].

2.2 Properties of Carbon Nanotubes

MWCNTs have been focus of considerable interest due to their excellent physical properties. Experiments and simulations have have shown that MWCNTs have a very high stiffness of ~1000 GPa and yield strength of the order of 100 GPa along the direction of the tube length [16]. Even though MWCNTs have a high stiffness and tensile strength, their density is very low which means that they can be used in applications which require light weight high strength materials, e.g. in components for aerospace applications. The thermal conductivity of MWCNTs is 3000W/m-K to 6000 W/m-K in the direction of tube axis and they have a negligible coefficient of thermal expansion (~0x10^-6) [17]. In vacuum, MWCNTs are thermally stable upto 2800°C [18]. These qualities make MWCNTs a sought after material for thermal management applications. However, the thermal conductivity across the cross section is poor [19]. Hence the alignment of MWCNTs in a matrix affects the thermal conductivity enhancement of the

Figure 2-2: Schematic representation of MWCNTs
composite over unreinforced matrix. Similarly, MWCNTs show high electrical conductivity along the tube axis owing to ballistic electron transport [20] and depends of the alignment of MWCNTs. The laser absorptivity of MWCNTs is very high (~ 0.99 for a MWCNT forest) [21], which means that they are able to absorb most of the radiations incident on them. A strong heat absorption by carbon nanotubes from light has also been observed by Ajayan and co-workers who observed the ignition of MWCNT due to flash light [22].

2.3 Advantages and Challenges of Using MWCNTs in MMCs

Because of their outstanding properties, carbon nanotubes have been proposed for many potential applications. In particular, their high stiffness and ultimate strength and excellent resilience make them excellent candidates as reinforcements in composites. MWCNTs have been used to reinforce polymers, ceramics and metals and enhancements in the physical properties of the respective matrices have been reported [23,24,25]. Incorporation of carbon nanotubes into metal matrix could potentially provide structural materials with increased Young’s modulus and strength. This indicates that this new type of materials could meet higher requirements in mechanical properties demanded for some applications. Metal reinforced with MWCNTs composites, with excellent mechanical properties, could find wide applications in aerospace, automotive industry and microtechnology, replacing conventional materials: alloys or conventional composites.

Major challenge in fabrication of MWCNT-MMCs is to obtain a homogenous dispersion of the MWCNTs through the desired matrix material. MWCNTs have very high surface area (~200m²/g) and a very high aspect ratio (~10⁴ normally) which leads to agglomeration due to the presence of attractive Van der Waals forces. Also, in order to take full advantage of MWCNTs as
reinforcements it is important to establish a strong interfacial bond between MWCNTs and the surrounding matrix.

2.4 Processing Methods

MWCNT reinforced metal matrix composites are prepared through a variety of methods. Powder metallurgy route is the most widely used since it is easy. Apart from powder metallurgy, processing methods like electrodeposition, electroless deposition, casting and vapor deposition have been used. Irrespective of the processing method used for MWCNT-MMC processing, main focus is always on obtaining good reinforcement by achieving homogenous dispersion and good bonding at MWCNT-metal interface. In this section processing methods for MWCNT-MMC bulk structures as well as coatings will be discussed.

2.4.1 Dispersion of MWCNTs in Metal Matrices

Use of ball milling as a mechanical dispersion technique receives the most attention and has been proven for dispersing MWCNTs in metal powders [26,27]. These metal powders can be used for fabrication of MWCNT/MMCs. Several studies show that the dispersion of MWCNTs in metal matrix can be improved by increasing time of milling and using proper control agents [28,29]. In order to achieve better interfacial bond strength between MWCNTs and metal matrix, a few researchers have coated MWCNTs with metals like Ni and Co [30,31]. Milling/mechanical alloying has been used in combination with hot pressing, sintering and deformation routes such as rolling and hot extrusion of the MWCNT-metal matrix powder compacts. Although, mechanical alloying is the most popular technique for mixing MWCNT-metal composite powder, it has many disadvantages as well. For example, during mechanical alloying MWCNTs can be broken and deformed which can reduce the effect of MWCNT reinforcements in the
metal matrix. Also, mechanical alloying does not ensure homogeneous dispersion in the metal powders. Some studies have reported the formation of MWCNT clusters after milling. In order to preserve the features of MWCNTs and improve their dispersion in metal powders some novel processing routes have been invented. Molecular level mixing and nano-scale dispersion are two novel processing routes which have been used to produce uniform dispersion of nanotubes in metal powders to be used as feedstock. The details of these techniques can be found elsewhere [32,33].

2.4.2 MWCNT-MMC Bulk Structures

2.4.2.1 Powder Metallurgy Route

Conventional sintering, hot pressing and deformation routes such as rolling and hot extrusion have been used for consolidation of mechanically alloyed MWCNT-metal powders. MWCNT reinforced MMCs with Cu [34], Al [35] and Mg [36] have been fabricated in using conventional sintering while hot extrusion and rolling have been mainly confined to MWCNT-Cu [37] and MWCNT-Al [38] composites, although some studies have also been done on MWCNT-Mg [39]. The main advantage of using deformation routes like extrusion is that it is easier to align the MWCNTs into one direction e.g. extrusion direction. Instead of sintering, some researchers have used hot pressing consolidation of powder mixtures. Kuzumaki et al. [40] optimized milling time for mechanical mixing at 5 h to avoid damage to MWCNTs and fabricated Ti-MWCNT composite by hot pressing. Mg-MWCNT composites [41], Al-MWCNT [41] and Fe3Al-MWCNT composites synthesized via hot-pressing [42] have shown improved mechanical properties (hardness, compressive strength and bend strength) due to uniform distribution of MWCNTs. The enhancement in the mechanical properties was attributed to grain growth
inhibition caused by interlocking nanotubes [42]. Hot pressing route has also been explored for processing MWCNT-reinforced Ti-based bulk metallic glass (BMG) composite [43]. Addition of MWCNT has been shown to increase in the glass transition and crystallization temperature in this composite which further assisted in decreasing the required cooling rate for glass formation, thus assisting BMG formation.

Novel powder metallurgy techniques like spark plasma sintering have also been used to make MWCNT-MMC. This method has been used to process MWCNT-Cu [44], MWCNT-Al[45] and MWCNT reinforced Ni-Ti based alloys [46]. In this process, a pulsed direct current is passed through a die and the powder, producing rapid heating and thus greatly enhancing the sintering rate [47]. Efficient densification of powder can be achieved in this process through spark impact pressure, joule heating and electrical field diffusion. This method is, generally, suitable for consolidation of nano powders, without allowing sufficient time for grain growth. SPS being a high temperature and pressure process, results in dense composites with minimum porosities.

The conventional sintering techniques lead to agglomeration of MWCNTs during consolidation stages. This can be prevented by the use of spark plama sintering and post sintering deformation. However, post sintering deformation can damage MWCNTs and lead to the formation interfacial compounds.

2.4.2.2 Melting and Solidification Routes

Melting and solidification is the oldest and most conventional method for processing metals. It has been used to process metal matrix composites and up to some degree in the processing of MWCNT- MMC. Since the processing temperatures are high, MWCNTs can get damaged or react with the matrix material to form reaction products. Hence this route is normally used for
low melting point matrices. Another challenge is the agglomeration of MWCNTs due to surface tension forces. Mg, being a low melting point metal, has been suitably processed through melting and casting route [48]. The MWCNTs can be plated with Ni plated to improve wettability with the matrix [49] which can result in mechanical property enhancement from addition of smaller quantities of MWCNTs to the matrix.

In order to ensure homogeneous distribution of MWCNTs in Mg, Yang and Schaller [36] used melt infiltration technique. Melt infiltration techniques uses a solid porous structure in which MWCNTs are dispersed. The molten metal (matrix) is then infiltrated into the pores and allowed to solidify. Due to the high temperature of the molten metal, the solid perform can melt leading to agglomeration of MWCNTs. Also the time required to fill the porous solid perform and efficiency of the process are other critical factors that decide the final properties of the composite in this case. However, improved dispersion has been reported for Al-MWCNT [50] and Mg-MWCNT composites.

The melting techniques should ideally produce much denser composites compared to powder metallurgy. The interfacial bonding would depend on the wettability of MWCNTs with the matrix. Formation of MWCNT clusters and interfacial compound formation should be preventable by using rapid solidification techniques.

### 2.4.3 MWCNT-MMC Coatings

#### 2.4.3.1 Electrochemical Methods

Electrochemical methods are very popular coating deposition methods. They have been used for thin film deposition [51], corrosion resistant coatings [51] etc for metals. Electrochemical deposition techniques are mainly of two types: electrodeposition and and electroless deposition.
Electrodeposition requires electrochemical cells in which a film is deposited by current flow between cathode and anode. On the other hand electroless deposition does not require any external energy sources and is primarily a chemical process. Both electrodeposition and electroless deposition have been used for MWCNT-MMC coating deposition. Electrodeposition techniques have been used for making MWCNT-Ni and MWCNT-Cu composites. Chen et al. [52] have reported co-deposition of a 14% MWCNT-Ni coating from an electrolytic bath at a current density of 15 A/dm² and MWCNT concentration of 2g/L. The MWCNT content in the coating increased with the MWCNT content of the bath.

Electroless deposition is basically a chemical technique in which a metal or its alloy is decomposed by catalytic action and deposited onto a surface without application of any current. The mechanism of deposition in electroless process is based on thermochemistry of the system. Hence, the bath temperature and pH value plays a very critical role in the coating composition and morphology. This method has been employed for MWCNT-Ni alloys [53] and MWCNT-Co systems. In electrochemical methods the key factor for getting coatings with homogeneous distribution MWCNTs is uniform distribution of MWCNTs in the bath and good suspension. Ultrasonication and magnetic stirring have been used to maintain good suspension of MWCNTs in the electrolytic bath [54,55]. Addition of surfactants has also been used to improve the suspension of MWCNTs. Increasing the MWCNT content in the bath beyond a particular concentration reduces the MWCNT content in the coatings due to agglomeration [56].

**2.4.3.2 Thermal Spray**

Thermal spraying has been used for coating metal substrates with MWCNT-MMCs. Plasma spraying [57], HVOF spraying [58], and cold spraying [59] have been successfully demonstrated
for the fabrication of MWCNT-reinforced MMC coatings. Laha et al. have studied the feasibility of spraying MWCNTs with Al powders to form composite coatings [57]. Thermal spray techniques are mainly used for depositing coatings. However there are a few instances where thermal spraying was used to fabricate bulk structures as well. Hollow cylinders made of MWCNT reinforced Al-23 wt % Si alloy have been fabricated by spraying (plasma spray and HVOF) by Laha et al. [60]. The thickness of these hollows cylinders was restricted by the poor flowability of the blended powders. Bulk MWCNT-Al cylinders have also been made by using spray dried powder [61].

Cold spraying is a relatively new process in which particles are accelerated to very high velocities at low temperature (470-770 K) and made to impact on a substrate. The particles undergo severe plastic deformation on impact and form splats that stick to each other. Since the temperature of the particles is below the melting point, oxidation and phase transformations can be avoided. Cold spraying has been successfully used in the fabrication of MWCNT-reinforced aluminum composites coatings [59]. Addition of MWCNTs could lead to improvement in the wear resistance and thermal conductivity of the coatings. Also possibilities of rapid prototyping exist with thermal spray methods.

2.5 Mechanical Properties

Many researchers have observed improvement in the mechanical properties of the MWCNT reinforced MMC over unreinforced metals. Enhancement in hardness has been observed in conventionally sintered MWCNT-Al and MWCNT-Mg [36] composites. The hardness of Ti bulk metallic glass was reportedly increased by 30% with addition of 10 vol% MWCNTs. An improvement in shear modulus by 20% was also observed for MWCNT-Mg composites. Hot
extrusion of MWCNT-Mg composites lead to the formation of high density composites which had higher hardness and strength compared to pure Mg [36]. Similar enhancements have also been observed for hot pressed MWCNT-Mg composites, where the addition of only 2wt% MWCNT to the Mg improved its Young’s modulus by 9% [41]. However, no change in the yield strength or ultimate tensile strength was reported. Al-MWCNT composites manufactured by mechanical mixing and post sintering deformation by Kwon [45] were twice as hard has pure Al manufactured using same method. They also reported a 3 fold increase in the yield strength. The increase in strength was attributed to the presence of MWCNTs as well as Al$_4$C$_3$ in the composite. Esawi et al. reinforced Al strips with carbon nanotubes by a powder can rolling technique [62]. The Young’s modulus of the composites was increased by 20% after adding 0.5 wt% carbon nanotubes. Y. Feng et al. reported an increase of 27% in hardness and 9% in bend strength due to 8 vol % MWCNT addition to the silver matrix.

However, most of the studies report a loss in the mechanical properties when the volume fraction of MWCNTs added to the metal matrix exceeds a particular value. This is due to the clustering of MWCNTs which leads to a reduction in density of the metal matrix composite and formation of pores.

Various theoretical models have been used to relate the volume fraction MWCNTs with the enhancement in the yield strength of the composite. Halpin Tsai equation, which has been used to determine the properties of fiber reinforced composites are most widely used in this respect. A special case of this equation relates the properties of whisker reinforced composites with the volume fraction of whiskers. This is the most important of all, since whiskers are closest to MWCNTs in terms of size and geometry. Halpin Tsai equation has been used to obtain elastic modulus of a composite with randomly oriented nanotubes using [63];
\[
\frac{E_c}{E_M} = \frac{3}{8} \left[ \frac{1+(2l/D)\eta_L V_f}{1-\eta_L V_f} \right] + \frac{5}{8} \left[ \frac{1+2\eta_T V_f}{1-\eta_T V_f} \right] \tag{1}
\]

Where, \( E_c \) = elastic modulus of the composite, \( E_M \) = elastic modulus of the matrix, \( l \) = length of the nanotube, \( D \) = diameter of the nanotube and \( V_f \) is the volume fraction of the reinforcements.

\( \eta_L \) and \( \eta_T \) are constants which can be determined using:

\[
\eta_L = \frac{E_f/E_M - 1}{E_f/E_M + 2l/D} \quad \text{and} \quad \eta_T = \frac{E_f/E_M - 1}{E_f/E_M + 2}
\]

Halpin Tsai equations have also been used by Yeh et al. to determine yield strength in MWCNT reinforced phenolic resins [64] from:

\[
\sigma_c = \frac{1+\xi \eta V_f}{1-\eta V_f} \sigma_M \tag{2}
\]

Where, \( \sigma_c \) is the yield strength of the composite, \( \sigma_M \) is the yield strength of the matrix and \( \sigma_M = \frac{\alpha(E_f/E_M) - 1}{\alpha(E_f/E_M) + \xi} \). \( \alpha \) and \( \xi \) are constants which are determined from the dispersion of the reinforcements and their geometry. For discontinuous and randomly oriented fibre reinforcements, \( \alpha = 1/6 \).

Apart from Halpin Tsai equations Cox model or shear lag model is used for predicting the elastic modulus of a fiber reinforced composites. George et al. have used shear lag model for their calculations of elastic modulus for MWCNT reinforced aluminum [65]. The shear lag model involves the transfer of load from the matrix to the reinforcements. In this model the stiffness of the nanotubes is directly utilized. The elastic modulus of the composite is given by:
Here, $\eta_2 = 1 - \frac{\tanh (\beta s)}{\beta s}$, $s = \frac{2l}{r}$ and

$$2 = \frac{2E_M}{E_f (1 + \nu_M) \ln(1/V_f)}$$

where $l$ and $r$ are the length and radius of the fibre reinforcements respectively. $E_C$ is the Young’s modulus of the composite, $E_f$ is the Young’s modulus of the reinforcements, $E_M$ is the Young’s modulus of the matrix and $\nu_M$ is the Poisson’s ratio of the matrix.

### 2.6 Thermal Properties

There are a very few studies on MWCNT-MMC which report the thermal properties of these composites, although there are many studies which report the improvement of thermal conductivity in MWCNT-Polymer composites. This is strange considering the fact that MWCNT-MMCs have been projected for use as materials for thermal management.

Recently Chu et al. [66] reported successful fabrication of MWCNT-Cu composites using molecular level mixing and spark plasma sintering. The thermal properties of these composites improved for 5 vol% MWCNT addition. However, the thermal conductivity decreased with further additions of MWCNTs. This was attributed to an increase in the interfacial thermal resistance between matrix and reinforcements due to processing induced defects. Similar decline in thermal conductivity was also reported by Cho et al. [67] who treated MWCNTs with acids to improve interfacial bonding between Cu-matrix and MWCNTs. In their case thermal conductivity declined after more than 3 vol% MWCNTs were added to the Cu-matrix. Kim et al. [31] coated single-walled nanotubes with Ni in order to decrease the interfacial thermal resistance between MWCNTs and Cu-matrix. However the results of their experiments were not fruitful either.
Thermal conductivity in MWCNTs is based on ballistic phonon transport along the tube length. The presence of a weak interface between MWCNTs and metal matrix leads to scattering of phonons in MWCNTs which leads to decrease in the overall thermal conductivity of the MWCNT-reinforced composites. In MWCNT reinforced polymers, fuctionalization of MWCNTs has been carried out to improve the interfacial bonding. The presence of a good interface is very effective in improving the thermal properties of the resulting composite [25].

2.7 Tribological Properties

It has been reported that presence of MWCNTs in composite matrix can drastically improve the wear resistance and decrease the coefficient of friction. It is postulated that the increase in surface fraction of MWCNTs reduces the direct contact between surface of the composite and abrasive medium. The reduction in coefficient of friction is attributed to the self-lubricating behavior of MWCNTs. Since the presence of MWCNTs reduces the coefficient of friction, a reduction in wear loss also occurs.

Kim et al. [31] reported a decrease in wear loss in Cu-MWCNT composites fabricated using hot pressing method. Zhou et al. [50] reported a steady decrease in coefficient of friction as well wear rate with 0-20% vol% addition of MWCNTs to Al. Reduction in wear rate has also been reported for MWCNT-Cu composites fabricated by conventional sintering methods [34]. Chen [52] applied MWCNT-Ni coatings on carbon steel and observed a decrease in coefficient of friction and wear rate. The MWCNT-Ni coatings were deposited by electrodeposition in a Ni salt bath. It was claimed that the presence of MWCNTs decreased the plastic deformation by reinforcing the matrix and hence caused reduction in the wear rate of Ni coating.
In conclusion, there are a few methods which have been explored extensively for fabrication of MWCNT reinforced MMCs. Powder metallurgy route is the most popular route for processing MWCNT reinforced MMCs. Melting and solidification routes have been explored up to some extent and are usually more complicated than powder metallurgy routes. Also, there is a high possibility of reaction between MWCNTs and molten metal at high temperatures due to which only low melting point metals matrices have been used. Electrodeposition and thermal spraying are used to manufacture coatings and have been quite successfully employed for MWCNT-MMC coatings. Most of the studies report an improvement in the mechanical properties as expected, but very few report studies on thermal properties. Also, most of the studies on thermal properties have not yielded any fruitful results.

LENS\textsuperscript{TM} is basically a melting and solidification route for processing metals and MMCs. As mentioned earlier (Page5, 1.2.2), LENS\textsuperscript{TM} involves rapid solidification of melt pool. This gives the molten metal matrix little time to interact with the reinforcements and also prevents their agglomeration. This can be exploited for MWCNT-MMC processing as well. Also since this process is carried out in argon atmosphere oxidation of MWCNTs can be prevented. These features of LENS\textsuperscript{TM} make it an attractive option for processing of MWCNT-MMCs. High temperatures incurred during LENS\textsuperscript{TM} processing may lead to graphitization of MWCNTs. However, since this method hasn’t been explored in depth, there is a need to study LENS\textsuperscript{TM} process for fabrication of MWCNT-MMCs owing to its obvious advantages.
Chapter 3
Materials and Methods

3.1 MWCNT-Bronze Composites

3.1.1 Fabrication

3.1.1.1 Mechanical Alloying

Tin Bronze powder (99.9% pure, 200 mesh, Cu90-Sn10, melting point: 1150°C, supplied from Sigma-Aldrich®) and Multi-walled MWCNTs (95% pure, 30-50 nm outer diameter, ~10-20 µm length, supplied from Cheap Tubes Inc.) were used as starting materials for preparing MWCNT-Bronze composites. Ball milling was used for dispersing MWCNTs in Bronze powder. MWCNT-Bronze composites with four different compositions were prepared in this study: 2, 4,
8, 12, 20 vol. % MWCNTs with the balance in each case being Bronze. 250 g of Bronze powder with desired vol. % of MWCNTs was placed in a metallic container with 100 steel milling balls of 6 mm diameter each (giving an initial ball to powder ratio of 1: 2.5). This container was then placed on a ball mill and its contents were mixed for 24 hours at a speed of 60 rpm. The powders prepared were analyzed using scanning electron microscopy and then used as feedstock for LENS™ processing for fabrication of MWCNT-Bronze composites.

3.1.1.2 LENS Processing

Two cylinders of different dimensions (12 mm diameter, 12.5 mm height; 8 mm diameter, 12.5 mm height) were deposited on stainless steel (316SS) for each composition. Laser powers in the range of 250W – 500W were tried to deposit the cylindrical parts. Because of low laser absorptivity of bronze, complete melting of powder was achieved only at laser powers greater than 350 W. Parts processed at lower laser powers resulted in severe porosity. Similar observations were made when high scan speeds and high powder feed rates were used during deposition. The deposited parts were initially found to peel off at the first layer/substrate interface during second layer deposition at laser powers ≥450 W. It was found that laser deposition carried out at a laser power level of 400 W, scan speed of 15 mm/s and powder feed rate of 23.5 g/min was the most suitable for our composite samples. Laser deposition was carried in argon atmosphere in order to avoid loss of MWCNTs at high temperatures. During deposition it was observed that melt pool spreading increased with the addition MWCNTs. Melt pool spreading occurs when Argon flowing through the nozzles hits the molten metal pool. Spreading was severe in 20 vol% MWCNT-Bronze due to which good samples for further testing and characterization could not be obtained. Laser deposition was carried in argon atmosphere in order to avoid loss of MWCNTs at high temperatures. Pure Bronze cylinders of same sizes were
deposited for reference using same processing parameters. All the LENS™ processed cylinders were later machined to make samples to carry out measurements of compressive strength, hardness and thermal conductivity. Microstructural examination of the fabricated composite samples was carried out using scanning electron microscopy and optical microscopy. The samples were polished using standard metallographic techniques.

3.1.2 Hardness Test and Compression Test

Vickers microhardness measurements were performed on the samples using Shimadzu microhardness tester (HMV-2T series, Shimadzu Corporation, ASTM E-140) at 500g applied load for 15s. The hardness values were the average of twenty readings for each sample. Uniaxial compression test was performed on samples that were 5 mm in diameter and 8 mm in height (such that 1.5< L/D< 2.0). These samples were subjected to compression using AG-IS Autograph ® (Shimadzu Corporation) with a strain rate of .001 s⁻¹. The density of these samples was measured using Archimedes law. The samples were immersed in water and following relationship was used;

\[
\rho_A = \frac{W_a}{W_a + W_w - W_{water}}
\]

Where, \(\rho_A\) is the density of the composite material, in g/cm³, \(W_a\) is the weight of the specimen when hung in the air, \(W_w\) is the weight of the partly immersed wire holding the specimen and \(W_{water}\) is the weight of the specimen when immersed fully in distilled water, along with the partly immersed wire holding the specimen. The theoretical density of the composites was
calculated using rule of mixtures. The relative density was calculated from the ratio of $\rho_\text{rel}$ and theoretical density.

### 3.1.3 Thermal conductivity

Thermal diffusivity and specific heat were then measured between 25°C and 250°C using LFA 447 Nanoflash (NETZSCH) which uses flash method as per ASTM – E1461-07. In this method, the front side of a plane-parallel sample is heated by a short light pulse. The resulting temperature rise on the rear surface is measured using an infrared detector. By analysis of the resulting temperature versus time curve, the thermal diffusivity can be determined. 2 samples (12mm in diameter and 0.4mm thick) were tested for each composition. Samples were polished to ensure similar surface roughness and were coated with carbon using a carbon spray on the top and bottom surfaces to prevent the laser light and plasma generation at the surface. In order to obtain reliable results, five tests were performed on each sample and the mean value was chosen for calculations. Thermal conductivity was calculated using the relationship:

$$ k = \alpha \cdot C_p \cdot \rho $$  \hspace{1cm} (5)

where, $k$ is thermal conductivity, $\alpha$ is diffusivity, $C_p$ is the specific heat and $\rho$ is the density of the specimens. The bulk density ($\rho$) was measured from the mass and geometry of each sample.

### 3.2 MWCNT-Al-12Si Coatings

#### 3.2.1 Fabrication

Al-12Si powder (99.9% pure, -140+325 mesh, melting point ~ 650°C, supplied from PAC®) and Multi-walled MWCNTs (95% pure, 30-50 nm outer diameter, ~10-20 µm length, supplied from
Cheap Tubes Inc.) were used as starting materials for preparing MWCNT-Al-Si composites. Ball milling was used for dispersing MWCNTs in Al-12Si powder. 150g Al-12Si powder with 8 vol. % of MWCNTs was placed in a metallic container with 100 steel milling balls of 6 mm diameter each (giving an initial ball to powder ratio of 1: 1.5). Methanol (6 vol%) was added as control agent to prevent cold welding of MWCNTs on steel balls and the container. This container was then placed on a ball mill and its contents were mixed for 24 hours at a speed of 60 rpm.

Laser deposition carried out at two different laser power levels: 400 W and 300W on aluminum substrate (Al-2024, T-6). Scan speed (30 mm/s) and powder feed rate (4.75 g/min). Coatings with 12 mm and 15 mm diameter were deposited to perform wear test and thermal conductivity test respectively. The coating thickness was controlled by the number of layers deposited on the substrate and 0.3 mm thick coatings were obtained after grinding and polishing. Laser deposition was carried in argon atmosphere in order to avoid loss of MWCNTs at high temperatures. Deposition at 300W resulted in severe balling in the deposited surface and samples fabricated at this laser power level were not used for testing and analysis. Coatings deposited at 400W were polished to achieve good surface finish. Pure Al-12Si coatings were also deposited on Al-2024 substrate using same operation parameters. Microstructural examination of these coatings was carried out using scanning electron microscopy as well as optical microscopy. In order to reveal the microstructural features of the coatings, the polished samples were etched with a solution containing 2 ml of HF (40%), 3 ml of HCl (35%), 5 ml of HNO₃ (70%) and 190 ml of distilled water. Microstructural examinations were also performed on the cross section of the samples.
3.2.2 Hardness Profile

In order to track compositional changes, a series of indentations were made from coating onto the substrate through the interface. The indentations were made using Vicker’s hardness tester at a load of 200g applied for 10 seconds. The indentations were separated by a distance of 0.02mm. The hardness of the top surface was also measured at the same load and load application time. A total of 20 measurements were taken on two different samples.

3.2.3 Thermal Conductivity

Pure Al-12Si and 8vol% MWCNT-Al-12Si samples were polished so that they would have same surface roughness on the coating side as well as substrate side. Thermal diffusivity and specific heat were then measured between 25°C and 250°C using LFA 447 Nanoflash (NETZSCH) which uses flash method as per ASTM – E1461-07. Two samples were tested for each composition. First a single layer test was performed to determine the thermal conductivity of the substrate and coating as one integrated structure. The samples were coated with carbon using a carbon spray on the top and bottom surfaces to prevent the laser light and plasma generation at the surface. In order to obtain reliable results, five tests were performed on each sample and the mean value was chosen for calculations. Later a double layer test was performed to determine the thermal contact resistance at the interface and thermal conductivity of the coatings. In order to determine the thermal contact resistance Proteus LFA analysis software was fed with thermal diffusivity and specific heat capacity values for pure Al-12Si and Al-2024. These were determined by testing samples made of Al-12Si and Al-2024.
3.2.4 Wear Test

Rotating pin-on-disc wear testing, according to ASTM G133, was performed using a tribometer (NANOVEA, Microphotonics Inc., CA, USA) with 6 mm diameter crome steel ball rubbing against the test samples (unreinforced Al-12Si and 8 vol% MWCNT-Al-12Si coatings on Al-2024 substrate). The wear test samples with 15 mm diameter fabricated using LENS™ were polished to ensure a flat surface and good surface finish, following standard metallographic preparation steps. Two samples were prepared for each composition.

Two different test were preformed on each sample with wear track radii of 2mm and 4mm (full rotation represents 12.5mm and 25mm of travel respectively) at a speed of 2400 mm min$^{-1}$. The total distance travelled by the rotating pin for tests with wear track radius 2mm was 1000m and the total time taken was 7 hours. The total distance travelled and time taken was 3000m and 20 hours respectively for the wear tests performed with 4 mm wear track radius. Before each test, the samples and crome steel ball were cleaned with 100% ethanol to assure a clean surface. Wear tests were carried out in dry conditions at room temperature. A normal load of 1 N was used for all tests. Volumetric wear rate per unit path travelled was calculated using the following relationship:

$$Wear\ Volume = 2\pi r_b^2 \left(\frac{\theta - \sin\theta}{\sin\theta}\right) R_T$$

Where, $r_b$ is the radius of the steel ball, $\theta$ is in radians and is given by $\theta = 2\sin^{-1}(C/2r_b)$, $C$ is the width of the wear track, $R_T$ is the radius of the wear track, $P_A$ is the applied load and $D_p$ is the total distance travelled by the rotating ball. In order to measure wear track width accurately and determine standard deviation, 10 different measurements were performed on each wear track.
After performing the wear test, the samples were ultrasonicated for 15 minutes and then examined using SEM.
Chapter 4
MWCNT-Bronze composites

In this chapter various properties of LENS™ processed CNT-Bronze composites are discussed. The CNT-Bronze composites showed an improvement in yield strength, elastic modulus and thermal conductivity. Yield strength and elastic modulus were compared with theoretical models in order to understand the strengthening mechanisms involved. We also tried to quantify the thermal properties of our composites using a simple mathematical relationship.

4.1 Microstructure

The investigation of dry-mixed powder was carried out using scanning electron microscopy. The SEM images of the dry mixed powders show that the MWCNTs were able to attach to the bronze powder. Figure 4-3 shows the SEM micrographs of the mixed powders containing (a) 2 vol% and (b) 12 vol % MWCNT in bronze powder. It is clear from Figure 4-3(b) that the MWCNTs are curled, kinked and some of them are highly twisted with each other to form the big MWCNT bundles because of the strong inter-tube Van der Waals attraction. The average length of the nanotubes after mechanical alloying was 1.7±0.9 µm. One notable feature of the dry mixed powder was that there was negligible change in the powder size and morphology which meant that the powder flowability was not affected by mechanical alloying. This proved beneficial since good powder flowability is required for LENS™ process. Figure 4-1 shows SEM micrographs of polished samples which were made using LENS™. After processing the final product seems to retain MWCNTs, however it is not known whether all the MWCNTs added to the bronze powder were retained in the final product or not. It was found that the MWCNTs were present at the grain boundaries (Figure 4-2).
**Figure 4-1:** SEM micrographs of polished surface of LENS\textsuperscript{TM} fabricated MWCNT-Bronze composites with (a) 4vol. % MWCNT (b) 12vol% MWCNT

**Figure 4-2:** SEM micrograph showing a MWCNT lying at the grain boundary

**Figure 4-3:** SEM micrographs of mechanically alloyed MWCNT-Bronze powders with (a) 2vol. % MWCNT (b) 12vol% MWCNT
The MWCNTs that are visible in the SEM micrographs are isolated from each other, however it is seen that their shape and dimensions have changed after processing and subsequent polishing of the samples. Melting and solidification routes used for fabrication of MWCNT-MMCs usually require mechanical stirring/ agitation of the melt pool to ensure homogeneous dispersion of MWCNTs because they tend to agglomerate [1].

LENS™ processing can solve this problem since molten metal pool is rapidly solidified, which would prevent the agglomeration of MWCNTs and formation of MWCNT clusters.
Table 1 shows the relative density of the composite samples with different volume fractions of MWCNTs and Figure 4-4 shows the optical micrographs of 12 vol % MWCNT-Bronze and 4 vol% MWCNT-Bronze composite samples. The difference in theoretical density and the bulk density of the samples is due to the presence of porosities, which is different in each sample.

<table>
<thead>
<tr>
<th>MWCNT vol%</th>
<th>Relative density</th>
<th>Grain size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>97.97</td>
<td>31.7±4.1</td>
</tr>
<tr>
<td>2</td>
<td>91.01</td>
<td>27.2±3.6</td>
</tr>
<tr>
<td>4</td>
<td>97.11</td>
<td>28±3</td>
</tr>
<tr>
<td>8</td>
<td>90.63</td>
<td>26±1.5</td>
</tr>
<tr>
<td>12</td>
<td>92.36</td>
<td>29.1±3.7</td>
</tr>
</tbody>
</table>

**Table 4-1: Relative Density and Grain Size of the MWCNT-Bronze Composites**

During fabrication melt pool spreading increased with an increase in MWCNT content. MWCNTs have a very high laser absorption coefficient due to which the overall laser absorption of the composite increases [68]. Hence the temperature attained by the composite surfaces due to interaction with Nd:YAG laser beam increases with the addition of MWCNTs. This leads to a decrease in the viscosity of the melt pool and increases spreading of the same. The spreading of melt pool during deposition led to formation of porosities which can be seen in the optical micrographs of the polished surface. In order to make completely dense sample, process parameters of LENS™ processing need to be optimized for each composition separately.
4.2 Mechanical properties

Figure 4-6 shows true stress-strain curves of one randomly chosen sample of each composition. The yield strength increased with the increase in MWCNT content. 12Vol% MWCNT-Bronze composites had the maximum yield strength (~ 188 MPa) which was 25% higher than pure bronze samples tested under the same conditions.

![Stress-Strain Curves](image)

**Figure 4-6:** True Stress Strain Curves for one randomly selected composite sample for each composition

The presence of MWCNTs in the bronze matrix also affected its elastic modulus which showed 82.2% enhancement in 12Vol% MWCNT-bronze compared to pure bronze. Yield strength and elastic modulus of 2 vol% MWCNT-Bronze increased slightly over those of pure Bronze.

The elastic modulus of the composite sample containing 4 vol% MWCNTs increased considerably compared the rest of the composite samples. This was due to higher densification
achieved during the fabrication of these composites, i.e., lesser porosities were present in the composites containing 4 vol% MWCNTs.

Figure 4-7: Vicker’s Hardness No. as a Function of MWCNT-Volume Fraction

Figure 4-8: Strain Hardening Curves for the MWCNT-Bronze composites
The presence of porosities can affect the elastic modulus and yield strength of a material because it reduces the effective load bearing area. Hardness increased with the increase in MWCNT content in the composite (Figure 4-7). The hardness of 12Vol% MWCNT-Bronze was 23% higher than pure bronze. The strain hardening behavior changed with the increase in MWCNT contents as shown in Figure 4-8. With the increase in MWCNT content the strain hardening rate increased. The improvement in mechanical properties was due to the reinforcing effect of MWCNTs.

According to George et al. [65] and Zheng [69] there are three different mechanisms which contribute to strengthening in metal matrix nano-composites: load transfer, thermal mismatch and Orowan looping. Bronze has a coefficient of thermal expansion of $\sim 10.2 \times 10^{-6}$ K$^{-1}$ which is higher compared to MWCNTs ($\sim 0$). The reinforcement and the matrix are in thermal equilibrium only at the processing temperature, i.e. at the temperature of the melt pool in LENS processing. As the melt cools and solidifies thermal stresses are generated around MWCNTs. These stresses reduce with increasing distance from the MWCNT-matrix interface and give rise to defects like dislocations. In Orowan looping, the motion of dislocations is inhibited by nanometer sized tubes, leading to bending of these dislocations. This strengthening mechanism has significant impact in case of MWCNT/MMCs since the size of reinforcements is smaller [65]. The third strengthening mechanism involves transfer of load from the matrix to the reinforcements by interfacial shear stress in which high stiffness and yield strength of carbon nanotubes are directly utilized. Strengthening due to this mechanism is mainly dependent on the aspect ratio of the reinforcements and the interfacial bonding between matrix and the reinforcements. There are several analytical models which include the effect of the above mentioned factors.
Ramakrishnan proposed an analytical model to predict yield strength of (micron size particulate reinforced) metal matrix composites [70] using:

\[ \sigma_c = \sigma_M(1 + f_1)(1 + f_d) \]  \hspace{1cm} (7)

where, \( \sigma_c \) is yield strength of the composite, \( \sigma_M \) is the yield strength of the matrix, \( f_1 \) and \( f_d \) are the improvement factors associated with load bearing effect of the reinforcements and dislocation density due to thermal mismatch respectively. This model can be applied to all the MMCs irrespective of the crystal structure of the matrix. In simplistic terms, \( f_1 = 0.5 V_{rs} \) and \( f_d = k G_M b \sqrt{\rho}/\sigma_M \) where \( V_{rs} \) = volume fraction of reinforcements, \( k = \) constant whose value is 1.25, \( b \) is the burgers vector of the matrix and it can be calculated using \( b = a/(\sqrt{2}) \) for FCC metals (\( a \) is the lattice constant). The lattice constant can be calculated using Vengard’s law [51] for binary alloys, i.e. \( a = y a_{Sn} + (1 - y) a_{Cu} \) where \( y \) is the volume fraction of Sn. \( \rho \) is the enhanced dislocation density and is given by \( \rho = 12 \frac{\Delta \alpha T V_{rs}}{b d_p (1-V_{rs})} \) shear modulus is \( G_M = \frac{E_M}{(1+\nu)} \) and difference in CTE is \( \Delta \alpha = \alpha_{bronzse} - \alpha_{CNT} \). \( E_M \) is the elastic modulus of the matrix and \( \nu \) is the Poisson’s ratio of the matrix.

This was modified by Zheng and Chen [69] to give a relationship to include the effect of Orowan looping in nano-Al\(_2\)O\(_3\) particles reinforced magnesium (HCP) composites using:

\[ \sigma_c = \sigma_m(1 + f_1)(1 + f_d)(1 + f_o) \]  \hspace{1cm} (8)

where, \( f_o \) is the improvement factor associated with Orowan looping. It is given by \( f_o = \frac{0.15 G_M b}{\lambda} \ln \frac{r}{b} \) [71], \( r \) is the interparticle distance given by \( \lambda = d_p \left[ \frac{1}{2 V_{rs}} - 1 \right] (d_p = 2r) \). Since this model is just an extension of Ramakrishnan’s model, it should be applicable for all crystal
systems as well. In order to compare our results with the above mentioned models we assumed the reinforcements to be spherical (Figure 4-9). Following data was used:

\[ r = 20 \text{nm}, \quad a_{cu} = 3.610 \text{ Å}, \quad a_{Sn} = 5.820 \text{ Å}, \quad E_M = 7.0068 \text{ GPa}, \quad \beta = 0.3, \quad \alpha_{\text{br}onze} \approx 10.2 \times 10^{-6} \text{ K}^{-1}, \quad \alpha_{\text{CNT}} \approx 0, \quad T = 1100-25 = 1075 \text{K}. \]

Initially our results match the predictions by Ramkrishnan but later they follow the predictions of Zheng’s model more closely. This suggests that strengthening in our composites is due to the combined effect of load transfer, thermal mismatch and Orowan looping. However it seems that Orowan looping becomes effective only after the volume fraction of the added MWCNTs exceeds a certain minimum number.

![Figure 4-9](image-url):

**Figure 4-9**: Yield Strength of the MWCNT-Bronze composites as a function of MWCNT volume fraction and comparison with a few analytical models and their predictions.
Since we assumed the reinforcements to be spherical, we expected the yield strength predicted by these models to be lower than our experimental results. This is because carbon nanotubes have a high aspect ratio which increases the interaction between the matrix and the reinforcements and causes more strengthening. Our experimental results were close to the predictions of these models because of the presence of process induced defects like porosities, which have a detrimental effect on the yield strength. The yield strength of the composites in absence of porosities was calculated using rule of mixtures;

\[ \sigma_E = V_P \sigma_p + (1 - V_P) \sigma_A \]  \hspace{1cm} (9)

Where, \( \sigma_E \) is the experimental yield strength, \( V_P \) is volume fraction of porosities, \( \sigma_p \) is the yield strength of porosities (=0) and \( \sigma_A \) is the average yield strength of the composite in absence of porosities, i.e. of a fully dense composite. The volume fraction of porosities was evaluated from the relative density of these composites. In Figure 4-9 the hollow squares represent \( \sigma_A \) and it can be seen that the strength of the composite in absence of the porosities is much higher compared to the predictions of the models, although a similar trend is followed.

The experimental values of elastic modulus are compared with Cox model [65] and Halpin-Tsai model [63] using equation (1) and equation (3) (Page 17, 2.5) in Figure 4-10. The experimental values were in good agreement with the predictions of Halpin-Tsai model for 2 vol % and 4 vol % MWCNT-Bronze composites. However, deviation from these predictions was observed later.

The difference between the values predicted by the Halpin-Tsai model can be due to the presence of porosities in our composites. It is also known that the Halpin-Tsai model gives a good estimate at low volume fractions of MWCNTs [63], however at higher volume fractions they over predict the elastic modulus.
This is because clustering of MWCNTs can take place at higher volume fractions. In LENS™, the rapid solidification of the molten metal pool can prevent agglomeration to some extent but it can occur during mechanical alloying, which is evident from Figure 4-3(b).

### 4.3 Thermal Conductivity

Figure 4-11 shows thermal conductivity of the MWCNT-Bronze composites as a function of MWCNT volume fraction. The 12 vol% MWCNT- Bronze composite showed 26% higher thermal conductivity than pure bronze. It is also observed that the thermal conductivity of these composites increased with temperature. Increase in thermal conductivity is attributed to high thermal conductivity of MWCNTs. The enhancement in thermal conductivity showed a linear trend with increase in volume fraction of MWCNTs in the composite.
The maximum achievable value of thermal conductivity can be found by assuming all the MWCNTs to be aligned in the direction of heat flux and minimum value can be found by assuming all the MWCNTs perpendicular to it.

For the upper bound we can use;

$$K_c = V_{CNT}K_{CNT} + (1 - V_{CNT})K_M$$

and for lower bound;

$$\frac{1}{K_C} = \frac{V_{CNT}}{K_{CNT}} + \frac{(1-V_{CNT})}{K_M}$$ \hspace{1cm} (10)

Where, $K_c = $ thermal conductivity of the composite, $V_{CNT}$ is volume fraction of MWCNTs in the composite, $K_M$ is the thermal conductivity of bronze and $K_{CNT}$ is the thermal conductivity of the carbon nanotubes. For upper bounds this value was assumed to be 3000W/m-K and for lower bound it was 1.5 W/m-K.

According to the rule of mixtures;

$$[K_c = (1 - V_{CNT})K_M + V_{CNT}K_{Eff}^{CNT}]_T$$ \hspace{1cm} (11)

where, $K_{Eff}^{CNT}$ is the effective thermal conductivity of MWCNTs in a randomly oriented state in the composite and $T$ is the temperature at which thermal conductivity is evaluated. It is known that the thermal conductivity of MWCNTs is very high along the tube axis.

By using equation (10) and the equation of trend lines for each temperature, we can find the effective thermal conductivity of randomly oriented MWCNTs in our composites and plot it as a function of temperature (Figure 4-13). The general equation for these trend lines will be;

$$[K_c = mV_{CNT} + K_M]_T$$ \hspace{1cm} (12)
where, $m \ (dK_c/dV_{CNT})$ is the slope of the corresponding trend line.

**Figure 4-11:** Thermal conductivity of MWCNT-Bronze composites at various temperatures plotted against MWCNT-volume fraction

**Figure 4-12:** Experimental values of thermal conductivity fall between upper bound and lower bound values due to random orientation of MWCNTs.
By comparing (10) and (11) and simplifying, we arrive at;

\[ K_{CNT}^{Eff} = m + K_M \]  \hspace{1cm} (13)

The values of \( K_{CNT}^{Eff} \) calculated in this manner can be used to calculate thermal conductivity for different volume fractions using rule of mixtures (equation (10)). Hone et al. [72] and Borca-Tasciuc et al. [73], have previously shown that the thermal conductivity of MWCNTs increases linearly with temperature, which explains the improvement in effective thermal conductivity of randomly oriented MWCNTs with temperature in Figure 4-13. Equation (12) gives a lower bound estimate of \( K_{CNT}^{Eff} \) since it is assumed that all the nanotubes were retained in the samples after processing. It should also be mentioned that at higher MWCNT concentrations the thermal conductivity enhancement might have non-linear dependence on volume fraction of MWCNTs.

**Figure 4-13**: Effective thermal conductivity of MWCNT calculated using equation (12) as a function of temperature.

The values of \( K_{CNT}^{Eff} \) calculated in this manner can be used to calculate thermal conductivity for different volume fractions using rule of mixtures (equation (10)). Hone et al. [72] and Borca-Tasciuc et al. [73], have previously shown that the thermal conductivity of MWCNTs increases linearly with temperature, which explains the improvement in effective thermal conductivity of randomly oriented MWCNTs with temperature in Figure 4-13. Equation (12) gives a lower bound estimate of \( K_{CNT}^{Eff} \) since it is assumed that all the nanotubes were retained in the samples after processing. It should also be mentioned that at higher MWCNT concentrations the thermal conductivity enhancement might have non-linear dependence on volume fraction of MWCNTs.
in the composite [74]. However since all of our composites showed a linear dependence so far, it is safe to use equation (12) for lower volume fractions of MWCNTs.

The thermal conductivity of a composite can be evaluated using Maxwell-Garnet effective medium theory as proposed by Nan et al [75,76], which also predicts a linear concentration dependence on reinforcements, from the relation;

\[
\frac{K_c}{K_M} = 1 + \frac{fp}{3} \cdot \frac{K_{CNT}/K_M}{p + \left(\frac{2R_k K_{CNT}}{d K_M}\right)}
\]

(14)

where, \(K_c\) is the effective thermal conductivity of the composite, \(K_r\) is the thermal conductivity of the reinforcement (CNTs in this case), \(R_k\) the thermal resistance of the interface between reinforcement and matrix, \(p = L/d\) (L and d are the length and diameter of the CNTs respectively).

**Figure 4-14:** Comparison of Enhancement in Thermal Conductivity at Room Temperature with Model by Nan et al.
Since effective thermal conductivity is inversely proportional to thermal resistance at the interface, any factor which leads to the increase in thermal resistance will decrease the thermal conductivity of the composite. There are several instances where the addition of CNTs led to a decrease in thermal conductivity [77]. For example Chu et al. reported a decrease in thermal conductivity of CNT/Cu metal matrix composites fabricated by spark plasma sintering when the volume fraction of CNTs was increased beyond 0.05. Thermal resistance can increase due to formation of porosities at the matrix-CNT interface and agglomeration of CNTs. Melting routes reduce the formation of such defects at the CNT-matrix interface [1], however agglomeration is a major concern. LENS processing can solve this problem since molten pool is rapidly solidified, which would prevent the agglomeration of CNTs and formation of CNT clusters. Since molten metals have a very high surface energy compared to the MWCNTs, poor wetting is expected which reduces the thermal conductivity of these composites. Another reason can be damaging of the MWCNTs due to high processing temperatures involved. It should also be mentioned that although this model predicts thermal conductivity of MWCNT reinforced composites for randomly oriented MWCNTs, it does not take into account the degradation of thermal properties due to the presence of porosities. It also doesn’t take into account the saturation in the thermal properties when percolation threshold is reached.

Maxwell-Eucken relation is an empirical expression which can be used to find out the thermal conductivity of metal matrix composites with accuracy. It is given by [78];

\[
K_c = \frac{K_M V_M + K_{CNT} V_{CNT} (3K_M / 2K_M + K_{CNT})}{V_M + V_{CNT} (3K_M / (2K_M + K_{CNT}))}
\] (15)
In this case we found that our experimental data was closer to the prediction of this model when we used $K_{CNT} = K_{CNT}^{Eff}$. Figure 4-15 shows the comparison with Maxwell-Eucken relationship and it can be seen that the thermal conductivity is very close the predictions of Maxwell-Eucken relationship.

Figure 4-15: Comparison of experimental values of thermal conductivity with Maxwell Eucken relationship
Chapter 5
MWCNT-Al-12Si Coatings

In this chapter various properties of LENS™ processed CNT-Al-12Si composite coatings are discussed. The CNT-Bronze composites showed an improvement in tribological properties and thermal conductivity. We were not able to find any MWCNTs in the micrographs; however the improvement in thermal conductivity indicated that the MWCNTs were able to survive post-processing.

5.1 Microstructure and Hardness

Figure 5-1 shows the SEM micrographs of the top surfaces of the LENS™ fabricated Al-Si and MWCNT-Al-Si composite coatings. No MWCNTs are seen in the Figure 5-1 (b), which is the SEM image of the MWCNT-Al-Si coating. This makes it unclear whether the MWCNTs were retained in the composite coatings or not. The micrographs mainly show -Al (dark gray phase) and Si (light gray phase). During processing “balling” effect was observed in the MWCNT-Al-Si composites. In LENS™, laser beam scans the composite surface line by line, causing melting along a row of powder particles, thereby forming a track of molten region of cylindrical shape. “Balling” occurs when this cylinder breaks up into a row of spheres so as to reduce the surface area, leading to the formation of the agglomerates. Balling led to formation of porosities in composite coating as seen in Figure 5-2. Figure 5-3 shows the optical micrographs of the coating-substrate interface for both Al-Si coated Al-2024 and MWCNT-Al-Si coated Al-2024. The interface in the LENS™ deposited coatings is not sharp and is a region in which coating and substrate phase are intermixed and form a supersaturated solid solution.
Figure 5-1: SEM micrographs of polished surfaces of (a) Al-Si coating (b) MWCNT-Al-Si composite coating

Figure 5-2: Optical micrographs of surfaces of (a) Al-Si coating (b) MWCNT-Al-Si composite coating

Figure 5-3: Optical Micrographs of coating-substrate interface for (a) Al-Si/Al (b) MWCNT-Al-Si/Al
However, MWCNT-Al-Si composite coatings showed more porosity owing to “balling” effect.

Figure 5.4 shows a plot of Vicker’s Hardness vs the distance from the coating-substrate interface

In the present case, the solidifying molten pool consists of a mixture of coating materials and Al-2024 creating an intermixed/diffuse interface region rather than a sharp interface during plasma spraying or roll bonding to create such composites. The absence of sharp interface between the coating the substrate would potentially reduce the thermal contact resistance at the interface and improves heat transfer capability between the two materials. The image of the interface for both types of composite coatings shows presence of some porosity in the interface region.

for Al-Si coated Al-2024 and MWCNT-Al-Si coated Al-2024. It can be seen that the hardness decreases as we move from the substrate to the interface before reaching a minimum value and then increases again from interface to the coating.
The hardness of the substrate is higher than the coating. In case of MWCNT-Al-Si composite coating the hardness of the interface is higher compared to the Al-Si coating. Apart from the change in hardness across the substrate, hardness of the top surface of the coatings was measured and found out to be 111.3±4.1 HV and 121±7 HV for Al-Si coating and MWCNT-Al-Si coating, respectively.

The Al-2024 substrate used here was processed by solution heat treatment and natural age hardening (T4-heat treated). This means that the Al-2024 substrate was solutionized, i.e, heated just above its solvus temperature (~500°C), rapidly quenched and then aged at room temperature for several days (5-10 days). Heating above solidus temperature is avoided since that would have a negative effect on the hardness and mechanical strength. In LENS™ process, since the substrate was melted and solidified a reduction in its hardness was expected due to which the hardness from the substrate to the interface decreased. Both type of coatings had a higher hardness compared to the interface. In case of MWCNT-Al-Si coated Al, the hardness of the interface is higher possibly due to the presence of MWCNTs at the interface. Similarly the hardness of the top surface is higher in MWCNT-Al-Si coating due to the reinforcing effect of MWCNTs.

### 5.2 Wear Properties

The wear test results of the unreinforced Al-Si coating and 8vol% MWCNT-Al-Si composites are shown in the Figure 5-5. It can be seen that the presence of MWCNTs in the Al-Si matrix significantly reduced the volumetric wear rate. In general the volumetric wear rate of a material is expected to increase first and stabilize after a certain distance is travelled by the rotating pin in contact with the surface [79]. However, in our case the wear rate for a total path distance of 3000 m is greater than the wear rate for a total path distance of 1000m. This means that the wear rate
was still increasing and had not reached steady state yet. The limitations imposed by the thickness of the coatings did not allow us to determine the steady state wear rate. Figure 5-6

**Figure 5-5:** Volumetric wear rate of Al-Si and MWCNT-Al-Si composite coatings

**Figure 5-6:** Coefficient of Friction of random samples of Al-Si and MWCNT-Al-Si composite coatings was still increasing and had not reached steady state yet. The limitations imposed by the thickness of the coatings did not allow us to determine the steady state wear rate. Figure 5-6
shows the coefficient of friction of a random sample of both compositions tested over a total path distance of 3000m. From the Figure 5-6 it is clear that the presence of MWCNTs in the Al-Si matrix reduced its coefficient of friction.

The coefficient of friction for unreinforced Al-Si coatings seems to increase in the beginning. This is because of the presence of surface porosities which increase the surface roughness, hence increasing the coefficient of friction. A similar spike can be seen for the 8-vol% -MWCNT-Al-Si coating as well. The coefficient of friction for the Al-Si coating and MWCNT-Al-Si after a travel of 1000m was 0.35 and 0.21 respectively. The coefficient of friction did not show appreciable change afterwards and after 3000m of travel the values were 0.39 for Al-Si coating and 0.22 for MWCNT-Al-Si coating. The average coefficient of friction was 0.19 for MWCNT-Al-Si coating which was lower than that for Al-Si coating (0.36). It has been reported in the literature that the presence of MWCNTs near or on the surface of the MWCNT- reinforced MMCs reduces the direct contact between the matrix and the steel ball [50]. Due to the self lubrication of MWCNTs, these tubes shaped reinforcements are able to roll or slide between the bodies in contact. The increase in hardness of the coating surfaces due to the addition of MWCNTs is an additional factor which contributes to the increase in wear resistance.

The SEM micrographs of the wear tracks on Al-Si and MWCNT-Al-Si coatings are shown in the Figure 5-7 and Figure 5-8 respectively. Figure 5-7 (a) and (b), shows the wear debris accumulated on the wear track. In Figure 5-7 (c), the presence of cracks perpendicular to the grooves suggests that there is some adhesive wear as well. The presence of grooves on all the wear tracks shows that wear was due to two body abrasion, while the deformed surfaces in Figure 5-7 (c) and Figure 5-8 (d) shows that there was wear due to three body abrasion as well. Wear due to third body abrasion could have been caused by the microdebris produced by
adhesion wear or large debris from fatigue cracking. Figure 5-8 (a), (b) and (c), show the fatigue cracking in MWCNT-Al-Si composite coating. These cracks grow up and are separated from the surface and therefore become wear debris.

![Figure 5-8](image)

**Figure 5-7:** SEM micrographs of wear tracks on Al-Si coatings

The presence of microdebris from adhesion wear is seen in Figure 5-7 (c) and Figure 5-8 (a). Two-body abrasion is generally more than three-body abrasion [80]. From the SEM images, it appears that abrasive wear is the main wear mechanism involved in the wear of these coatings.
5.3 Thermal conductivity

The thermal conductivity for Al-Si coated Al-2024 showed small improvement over Al-2024 at the room temperature. Its thermal conductivity was 2.1% higher than the thermal conductivity of uncoated Al-2024. The thermal conductivity of Al-2024 was found out to be equal to 127±3.1 W/m-k which is very close to the literature value of 121 W/m-k [81]. The thermal conductivity of Al-Si test block at room temperature was experimentally determined as 138.27±1.8 W/m-K. Thus the slight enhancement in thermal conductivity can be attributed to the higher thermal conductivity of the coating.

Figure 5-8: SEM micrographs of wear tracks on MWCNT-Al-Si composite coating
With temperature, the thermal conductivity of the uncoated Al-2024 improved however there was negligible improvement in the thermal conductivity of the Al-Si coated Al-2024 substrate. This can be again attributed the fact that the thermal conductivity of the Al-Si test block did not show much improvement in thermal conductivity with temperature. For the Al-2024 substrate coated with MWCNT reinforced Al-Si composite, the improvement in thermal conductivity was drastic. When compared to Al-Si coated Al-2024 and uncoated Al-2024, the thermal conductivity of the MWCNT-Al-Si coating improved by 31% and 33% respectively. Figure 5-9 shows a plot of thermal conductivities of the samples.

![Graph](image)

**Figure 5-9:** The thermal conductivity of MWCNT-Al-Si/Al and Al-Si/Al as a function of temperature

The thermal resistance at the coating-substrate interface was found out and was equal to $\sim 4.7 \times 10^{-7}$ m$^2$/KW at room temperature for Al-Si coatings. The thermal contact resistance was very low
due to the absence of a sharp interface between coatings and the substrate as seen in the microstructure of the cross-section in Figure 5-3. The thermal contact resistance at the MWCNT-Al-Si coating and Al-2024 substrate could not be determined since we were not able to make free standing MWCNT-Al-Si bulk structure. However, the thermal resistance at this interface should be lower due to the presence of MWCNTs at the interface, which is reflected by the improvement in thermal conductivity. Since the thermal conductivity was calculated using the equation (5) which relates thermal conductivity (k) with thermal diffusivity (\( \alpha \)), specific heat capacity (\( C_p \)) and density (\( \rho \)), it is obvious that any improvement in thermal conductivity will be because of improvement in one of these factors or their combination. It was observed that due to addition of MWCNTs the thermal diffusivity of the Al-Si coated samples showed negligible improvement, whereas the density decreased.

![Figure 5-10: Specific heat of MWCNT-Al-Si coating/Al and Al-Si coating/Al as a function of temperature](image)

However, the specific heat capacity increased after the addition of MWCNTs. Figure 5-10 shows a plot of \( C_p \) values for Al-Si coated Al-2024; MWCNT-Al-Si coated Al-2024 and Al-2024 alloy samples as measured by the Nanoflash® instrument.
It can be seen that there is a little improvement in $C_p$ values for Al-Si coated Al-2024 samples over the $C_p$ values for Al-2024 samples, whereas a significant improvement in specific heat capacity is observed for MWCNT-Al-Si coated Al-2024 samples.
Metal matrix composites (MMCs) with carbon nanotubes (MWCNTs) as reinforcements have been developed. It has been shown that LENS™ can be used to fabricate MWCNT reinforced metal matrix composites and improve their properties.

- Addition of MWCNTs to bronze by the LENS™ had a positive impact on its properties. The Young’s modulus and yield strength increased by 82.2% and 25 % respectively for 12vol% MWCNT-Bronze composite. Addition of MWCNTs also resulted in improved hardness in the MWCNT-Bronze composites.

- Thermal conductivity increased linearly with the increase in the MWCNT content in MWCNT-Bronze composites. The thermal conductivity of bronze improved by 26% for 12 vol% addition of MWCNTs.

- Effective thermal conductivity of MWCNTs in a randomly oriented state was evaluated and it was found that the effective thermal conductivity of MWCNTs increased with temperature and it was independent of volume fraction of MWCNTs added to the composite. The major drawback of using LENS™ to process MWCNT-Bronze composites was incomplete densification of parts, which was also revealed by the microstructure. The presence of porosities in the microstructure was due to spreading of the melt pool during deposition. This limited the amount of MWCNTs that could be added to bronze matrix.
• Addition of MWCNT to Al-12Si improved its wear resistance and led to a reduction in the coefficient of friction. Due to the addition of MWCNTs to Al-Si, its volumetric wear rate dropped by more than 90%. The coefficient of friction decreased by almost 45%. This means that the MWCNTs can be added to metal matrices to improve their tribological properties.

• Coating Al-2024 substrate with Al-Si led to a small improvement in its thermal conductivity. However, coating the substrate with the MWCNT-Al-Si composite caused significant improvement in the thermal conductivity. This indicates higher thermal conductivity of the MWCNT-Al-Si composite coatings. The high thermal conductivity of the MWCNT-Al-Si is attributed to the improvement in specific heat caused by the addition of MWCNTs.

• Thermal resistance of the interface between the coating and substrate was very low due to the absence of a sharp interface between the coatings and the substrate.

• Further experiments need to be performed to get a conclusive evidence of the presence of MWCNTs in the composite coating. Another drawback was the presence of porosities at the interface as well as on the coating surface.

**Future Work:**

The properties of MWCNT reinforced MMCs largely depends on the strength of the interfacial bond between MWCNTs and metal matrix. This interfacial bond strength in turn depends on the wetting of the MWCNTs by molten metal. The metal matrices which were used in this study, i.e. Tin-bronze and Al-12Si, have a surface tension of 999mN/m [82] and 840mN/m [83] at their respective melting points. This is much higher than the surface tension of MWCNTs (100-200mN/m [65]). A necessary condition for wetting to occur is;
\[ \gamma_{sv} \gg (\gamma_{sl} + \gamma_{lv}) \]  

Where, \( \gamma_{sv} \) is the surface tension of the solid-vapor interface (MWCNT-gas), \( \gamma_{sl} \) is the surface tension at the solid-liquid interface (MWCNT-Metal) and \( \gamma_{lv} \) is the surface tension at liquid-vapor interface (Metal-gas).

Since the difference in the surface tension of the molten metals and MWCNTs is large, this condition cannot be satisfied. This can result in lower interfacial bond strength and lead to formation of porosities at the MWCNT-Matrix interface. Poor wetting will result in reduced interfacial load transfer from the matrix to reinforcements and an increase in the interfacial thermal resistance.

In order to improve the wettability, MWCNTs coated with Ni [30,31], can be used as starting materials instead of pristine MWCNTs. Both Ni and Co have a higher melting point that Bronze and Al-12Si and hence should remain on the MWCNT surface throughout the processing stage. Another approach would be to acid treat the MWCNTs to roughen their surface [67]. Although this might not have any impact on the surface tension of the MWCNTs, it can still help in improving the interfacial bonding between the matrix and the reinforcements.

Since mechanical alloying was used to disperse MWCNTs in the metal matrix, the nanotubes added to the metal powders got damaged (aspect ratio decreased). Also, loss of nanotubes to the milling media and container was unavoidable. In order to preserve nanotubes in their pristine form, a novel mixing technique like molecular level mixing or nanoscale dispersion can be used.

Although the improvement in thermal conductivity of both MWCNT-Bronze and MWCNT-Al-12Si indicates that MWCNTs were retained after processing, an extensive microstructural examination and raman spectroscopy [5] are required to determine the amount of MWCNTs
retained without getting damaged. Also, TEM should be performed on MWCNT-Bronze composites to verify the conclusions that were drawn out after comparing the enhancement in their yield strength with Zheng’s model and Ramakrishnan’s model.
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