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Forming a Metal Matrix Nanocomposite (MMNC) with Fully Dispersed and Deagglomerated Multiwalled Carbon Nanotubes (MWCNTS)

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FORMING A METAL MATRIX NANOCOMPOSITE (MMNC) WITH FULLY DISPERSED AND DEAGGLOMERATED MULTIWALLED CARBON NANOTUBES (MWCNTs).

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ABSTRACT

Carbon Nanotubes (CNTs) with their exceptional properties will facilitate the Metal matrix composites (MMC) to exhibit good mechanical properties, thermal and electrical conductivities, corrosion resistance, etc. The critical factor that holds the development of the Metal matrix Nanocomposites (MMNC) by using CNTs is the tendency of CNTs to form clusters (agglomerations) due to their high Van der Waals attractions. Due to this factor, low density and other properties of the CNTs, there has been a delay in harnessing their ultimate potential.

Existing literature in contemporary times from the works of few researches in Nanocomposites shows the prevalence of using surfactants / dispersing agents for dispersing CNTs in the metal matrix. But the addition of these dispersing agents will form inclusions in the metal thus closing the avenue for developing ballistic electrical conductors and high purity MMNCs. Also the vol% of CNTs is limited to 1% in many cases and further increase reduces the mechanical strength. The reason for decreasing the strength is attributed to the agglomeration of CNTs and their disorderly alignment.

In this work we developed a process where total dispersion and deagglomeration of CNTs up to 5 vol% is achieved without the addition of any surfactants / dispersing agents in the Magnesium Metal matrix. The process developed in this work can be applied to other metals with proper process parameters to develop various MMNCs with exceptional properties relative to the base metal. This process will open doors for the future works for developing high strength, High electrical and thermal conductive Metal Matrix Nanocomposites.

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CHAPTER I

INTRODUCTION

In the world of shrinking energy resources humans are in quest for developing advanced technologies with capabilities of optimal utilization of resources. Iijima's paper in 1991 on Carbon Nanotubes preparation [1] created a flurry of excitement all around world. The exceptional properties of Carbon Nanotubes (CNTs) such as high Young's Modulus (approximately 1TPa) [2], thermal conductivity of 3000 W/(mK) [3], High current carrying capacity ($>10^9 A/cm^2$) [4] attracts researchers around the world to harness the potential applications from their unique properties.

CNTs are chemically inert and sublimate under vacuum at around 3652°C – 3697°C making them thermally stable to mix with most of the liquid metals and embed in metal matrices. Since the discovery of Nanotubes and invention of preparation processes researchers are motivated to develop nanocomposites.

The process of producing Nano Composites consists of continuous mixing of Carbon Nanotubes with desired dispersion technique is critical. Dispersion of CNTs in metal matrix is difficult owing to the tendency of nanotubes to agglomerate due to their high Van der Waals attractions among the CNTs. Other factors such as low density, physical entanglements of nanotubes, waviness are need to be considered.

Few dispersion techniques such as Mechanical stirring, Sonication, Electro Magnetic Induction and other methods individually or in combination of one or more methods are being used for developing nanocomposites. Few instances where scientists are able to develop metal nanocomposites by successful dispersion of Nanotubes in metal matrix, experimental results shows improvement in the results such as strength and thermal conductivity only to an extent of addition of CNTs at 1 vol% but further increase reduces the base metal properties [5-7]. In few instances replication of the process is uncertain. The major reason behind this perplex behavior is attributed to the alignment and agglomeration of CNTs in the metal matrix. The anisotropic orientation of CNTs and low level agglomerations in metal matrix can lead to catastrophic failures in attaining enhanced properties such as Thermal and Electrical conduction, specific strength, Yield Strength, Stiffness, Hardness, corrosion resistance etc. of the nanocomposite.

While researchers are busy developing new methods for dispersion by adding surfactants for better wetting of CNTs, with these methods we might achieve new composite metals with higher strength [6] and thermal conductivities. But to attain high electric conductance it is essential for the base metal to be as pure as possible without adding any surfactants or dispersants. These surfactants or dispersants are impurities to the base metal and will lower the electrical conductivity of the nanocomposite.

1.1 History of Ultra conductive Copper:

The nanocomposite materials program at CSU was started in 2006 in collaboration with and with seed funding from the Space Power Branch at NASA/GRC to develop stronger materials for use in the rotors of flywheels in order to increase the tip speed of rotors and thus to increase the energy stored in flywheels with a mission to

develop efficient processes to breakup nanotube agglomerations and to uniformly disperse the nanotubes in the resin base in order to produce a nanocomposite matrix with superior mechanical properties. Dr. Nayfeh's observation of aligned glass fibers in the direction of the flow of the glass fibrils in polypropylene blends is caused by the large shear forces that are generated during high velocity laminar flow in injection molding. He concluded that fluid dynamic processes are capable of breaking up agglomerations and also orienting nano-scale objects such as nanotubes.

The success from forming strong Nanocomposite E-glass fibers at CSU attracted one of DARPA's program managers to provide seed funding for using similar techniques to develop ultra conductive copper. The possibility of using metallic nanotubes as ballistic conductors was becoming popular in the literature with a large number of publications indicating its feasibility and the potential huge benefits that could be gained from the development of at room temperature, ultra conductive materials.

The Nanocomposite wire formed by uncontrolled injection of Mg-functionalized MWCNT into molten copper via high velocity die casting and subsequent wire drawing operations upon electron microscopy imaging revealed well dispersed and aligned nanotubes in the zones where higher conductivity is recorded. The results are highlighted in US Patent # 8347944.

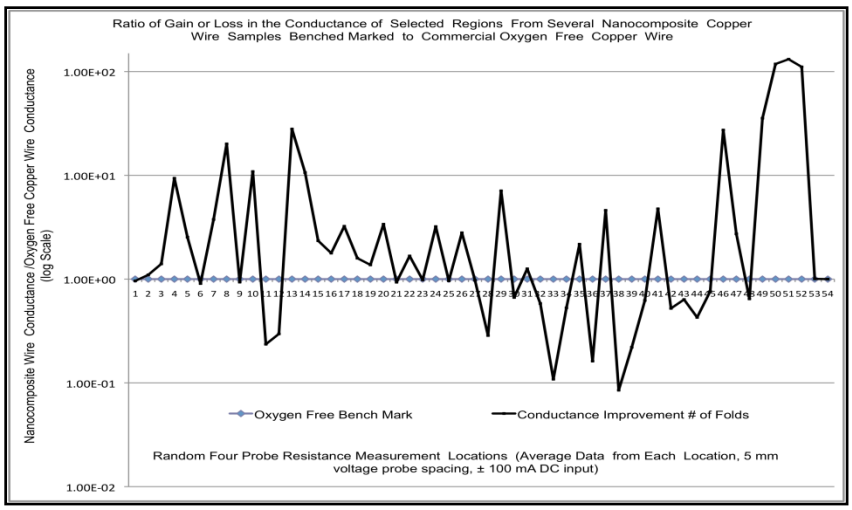

Figure 1: Numerical results from the feasibility study.

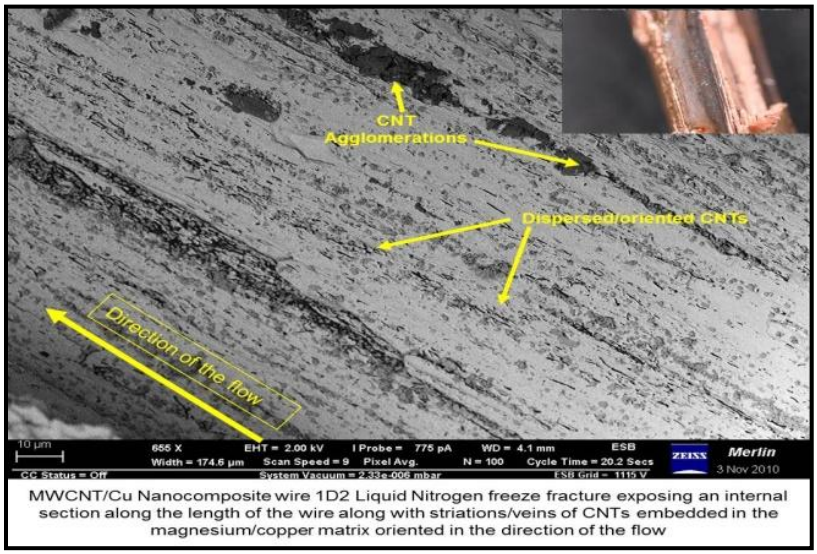

Figure 2: Electron Microscope (FESEM) image of a nanocomposite

In the zones where lower conductivity is recorded it is indicated that the nanotubes are not dispersed and acted as impurities to reduce the electrical conductivity. Figure 1 shows the Numerical results from the feasibility study showing gains reaching 23+ folds (100+ beyond the range of the instruments) and also showing large reductions in the conductivity. Figure 2 shows Electron Microscope image of a Nanocomposite steak showing areas of well dispersed and aligned Nanotubes along with large

agglomerations. In process of improving the process to achieve ultra conductive copper in large scale, this project envisions a precision system for infusing, dispersing and aligning the functionalized nanotubes into a magnesium precursor matrix via mixing and sintering followed by multiple rounds of extrusion at a temperature below the melting temperature of magnesium. Since copper does not wet CNTs, Magnesium was chosen as precursor matrix which has high surface energy with good electrical conductivity as an intermediate material to fabricate ultra conductive copper wire.

1.2 History on Magnesium Melting:

Pressure die casting is the most commonly used casting process and because of the low casting temperature (650–700°C), hot chamber die casting machines can be used. The traditional method of casting a metal is sand casting, which is extensively used for producing commercial metals and alloys. Magnesium on the other hand reacts aggressively with fire bricks, sand moulds, refractory lining and even with quartz.

Magnesium on reaction with silica or silicon oxide at elevated temperatures readily oxides to form Magnesium silicide which can be seen as follows:

- $2Mg + SiO2 \rightarrow MgO + Si$
- $2Mg + Si \rightarrow Mg2Si$
- $2MgO(s) + SiO2\ (g) \rightarrow Mg2SiO4$

This indeed causes inclusions in Magnesium cast billets in sand castings often for magnesium sand castings Olivine sand or Zircon sand are used as facing sand.

Preferably Pressure die casting is used for casting Magnesium and its alloys and because of the low casting temperature (650–700°C), hot chamber die casting machines can be used.

1.3 Background for Thesis:

The Ongoing research at Cleveland State University (CSU) in the development of an ultra conductive copper wire need a solid core of Mg/MWCNT composite with no dissolved gases or porosity in its metal matrix. The major risk to the success of achieving ultra conductive copper is the potential for oxygen contamination during the processing of Mg/MWCNT composite and during the many extrusion rounds. To mitigate the risk of oxygen contamination the process of developing Mg/MWCNT composite is performed in vacuum. Developing an ultra low porosity Mg/MWCNT composite is not a simple task due to the high vapor pressures of Magnesium in vacuum and readily reacting with silica, also Magnesium is prone to contain dissolved gases and inclusions in its as-cast form.

For developing the Mg-CNT composite a novel approach of low vacuum melting of Magnesium and mechanical stirring of the Nanotubes in a Semi solid Metal (SSM) is incorporated. Since Magnesium is a high shrinkage metal proper consideration of contraction allowance is estimated experimentally.

1.4 Thesis past and present work:

This Thesis work explains the experimental procedures followed in developing ultra low porosity Magnesium Nanocomposite (Mg/MWCNT composite). The major obstacle in developing the ultra low porosity composite is the presence of dissolved gases in as cast Mg/MWCNT composite. The high vapor pressure of Magnesium limits the composite to cast under ultra high vacuums and electromagnetic stirring.

Initially Electro Magnetic Induction (EMI) melting is used for better dispersing of MWCNTs in the molten metal of Magnesium. The major advantage of using EMI is eliminating the inclusions in the metal matrix due to usage of alien devices in the test

tube for dispersion of MWCNTs in the molten Magnesium pool. But the formation of Magnesium vapors in the test tube under low pressure limits the experimental procedure. Since magnesium vapors are metallic they conduct electricity and due to this inherit behavior of metals it creates electrical arcing inside the test tube and thus destroys the experimental procedure. To compensate for the high vapor pressures of Magnesium at elevated temperatures Argon is added for suppressing Magnesium vapors. This indeed created gaseous defects in Mg/MWCNT composite, which are expanded dramatically during further operations of quest for Ultra Conductive Copper Wire.

After proving EMI is not a appropriate approach in the pursuit of developing an ultra low porous Mg/MWCNT composite, traditional melting process using conventional heating accompanied by mechanical stirring using 316 stainless steel impeller under low pressure is followed.

This thesis is focused on the development of SSM of Magnesium and dispersion of MWCNTs in the slurry of metal for mass scale production and industrial use. The success with this work can be used for mass scale manufacturing of Mg/MWCNT composites with slight modifications in the current manufacturing facilities of Magnesium and its alloys.

1.5 Document Organization:

The material in this work is presented in the following order:

Chapter two covers background information on developing Nanocomposites, different approaches during the current research in manufacturing of ultra low porous composites. Chapter three deals with previous work and literature survey on this subject. Chapter four describes the research methodology and phases of work. Chapter five describes the

experimental setup and different equipment used. Chapter six discusses the proposed process flow for making the Nanocomposite, and experimental results with (Scanning Electron Microscope) SEM images. Chapter seven discusses the results of Energy dispersive spectroscopy (EDS). Chapter eight presents the conclusion of this thesis and future recommendations.

CHAPTER II

BACKGROUND

2.1 Carbon Nanotubes:

2.1.1 Hybridization of Carbon:

Carbon materials are found in various crystalline structures in nature, for example, Carbon fibers, fullerenes (Bucky balls), graphite, diamond, CNTs. The reason for exhibiting variety of structural forms is that carbon can shape a variety of orbital hybridization. The sp^n hybridization is fundamental for deciding the dimensionality of carbon based particles as well as carbon based solids. Carbon forms isomers that take 0-dimension to 3-dimensions as shown in Table. In sp^n hybridization, $(n+1)$ σ bonds per carbon particle are formed, which frame a skeleton for the neighborhood structure of the n-dimensional structure. In sp hybridization, two σ bonds form a one-dimensional chain structure, which is known as a carbyne.

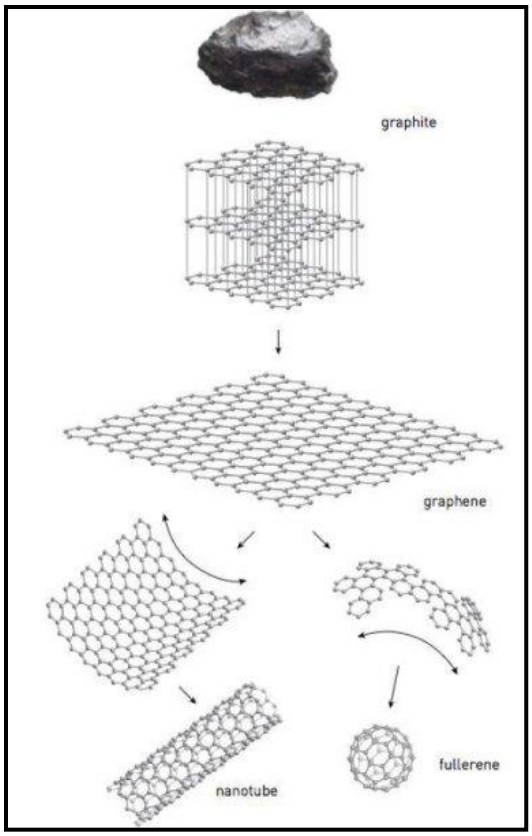

Figure 3: Various forms of Carbon

Credit: © Airi Iliste/The Royal Swedish Academy of Sciences

In sp^2 hybridization, which forms a planer structure in two-dimensional graphite also forms a planar neighborhood structure in the closed polyhedra (zero-dimensional) of the fullerene family and the one-dimensional cylinders called carbon nanotubes (CNTs). Carbon fibers are assumed to be one-dimensional materials similar to CNTs because of their remarkable length to width ratios but due to presence of various graphitic planes they exhibit electronic properties as two-dimensional structures. Amorphous Graphite with layers of Graphite stacked randomly exhibit sp^2 hybridization. Due to these randomly stacked graphitic layers which have poor bonding are prone to slip over each other thus acting as solid lubricant, this behavior leads amorphous graphite to act like a

two dimensional material. In sp^3 hybridization four σ bonds form a tetrahedron, a three dimensional structure similar to diamond. Thus carbon in its amorphous form can produce various structures depending on the arrangement of layers or hybridization.

Table 1: Isomers of Carbon [8]:

Dimension	**0-D**	**1-D**	**2-D**	**3-D**
Isomer	C_{60}, fullerene	Nanotube, carbyne	Graphite fiber	Diamond amorphous
Hybridization	sp^2	sp^2	sp^2	sp^3
Density (g/cc)	1.72	1.-2.0	2.26	3.515
Bond Length (Å)	1.4 (C=C) 1.46 (C-C)	1.44 (C=C)	1.42 (C=C) 1.44 (C=C)	(C-C)
Electronic Properties	Semiconductor E_g = 1.9eV	Metal or Semiconductor	Semimetal	Insulating E_g = 5.47eV

2.1.2 Classification of CNTs:-

CNTs, which are sometimes termed as quasi one dimensional carbon whiskers, are essentially categorized into two types depending on number of layers of graphene sheets wrapped to form cylindrical tubes.

1. Single walled Carbon Nanotubes (SWNT)
2. Multi walled Carbon Nanotubes (MWNT)

Few researchers use Double walled Carbon Nanotubes to describe the properties of interlayer interactions of nanotube systems. They provide an ideal working model for investigation of the physical and chemical properties of MWCNTs.

2.1.2.1 Single Walled Carbon Nanotube:

Single walled carbon nanotubes (SWCNTs) are graphene wrapped into a seamless cylinder. Graphene is one atom thick layer of carbon. It can also be treated as single layer of graphite sheet rolled into a cylinder shape. The way the graphene sheets are rolled results in different chirality/helicity of the nanotubes. A single-wall nanotube is a graphene sheet rolled into a cylindrical structure with diameter of about 0.7 - 10.0 nm, typically most of observed single-wall nanotubes have dimensions of diameters <2 nm. The substantial aspect ratio (length/diameter) of CNTs is 104-105 which enables nanotubes to be considered as one dimensional nanostructure.

Depending on the distortion of curvature of carbon nanotube, CNTs can be classified as Achiral and Chiral. As per the name Achiral (symmorphic) carbon nanotubes are mirror images of their original structures and they were further classified into Armchair and Zigzag depending on the shape of cross section. Chiral (non-symmorphic) carbon nanotubes are not identical to the mirror image of the original structure but exhibit spherical symmetry.

2.1.2.2 Multi Walled Carbon Nanotubes:

Multi walled carbon nanotubes (MWCNTs) are nanotubes that consists of more than one layer of graphene sheet, more formally more than one wall. Depending on the formation of the layers MWCNTs can be classified into two models. One Russian Doll which is like a concentric SWCNTs with different diameters. Second Parchment model which is graphite (Graphene) sheet rolled in around itself. Figure 5 shows TEM images of Multi walled Carbon Nanotubes (MWCNT). Figure6 shows the cross section of

MWCNT, this image was taken by Ultra Conductive Copper research team at CSU in collaboration with Zeiss.

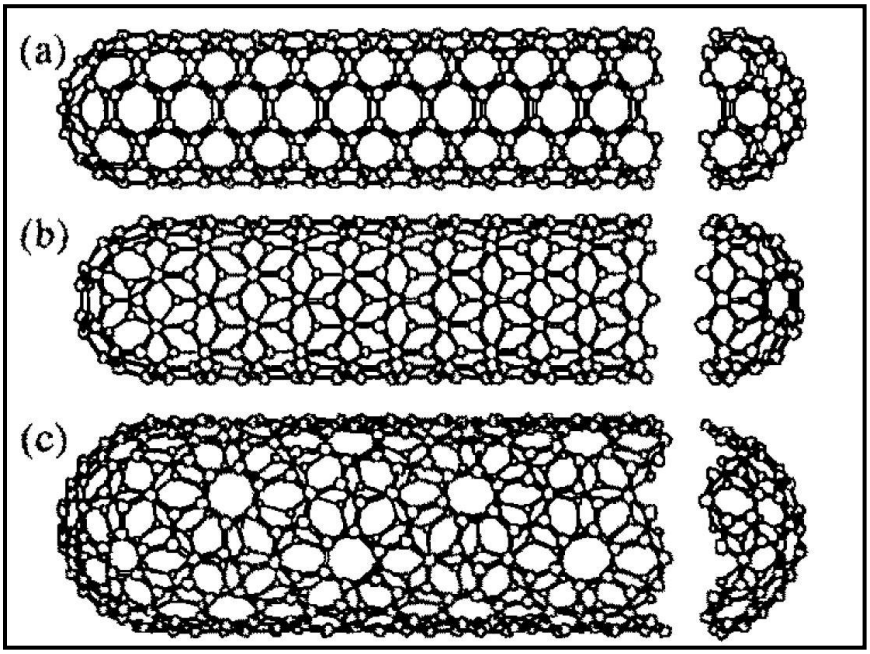

Figure 4: Classification of CNTs. a) arm chair, b) zigzag and c) chiral nanotubes

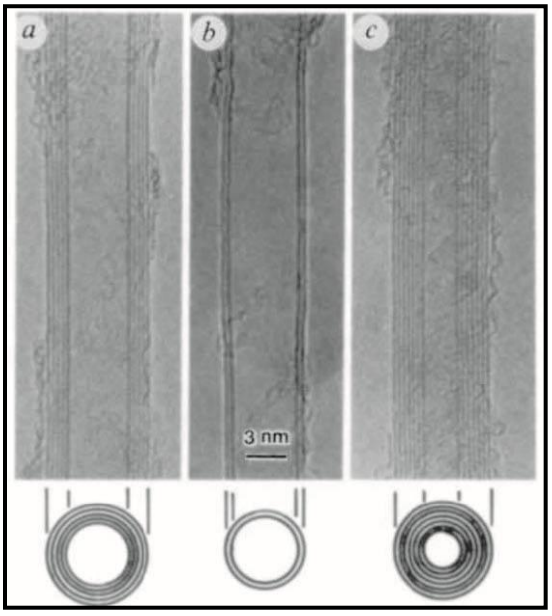

Figure 5: TEM images of CNTs

Fig. a) Tube consisting of five graphitic sheets, diameter 6.7 nm. b) Two-sheet, diameter 5.5 nm. c) Seven-sheet, diameter 6.5 nm, which has the smallest hollow diameter (2.2 nm) [9]

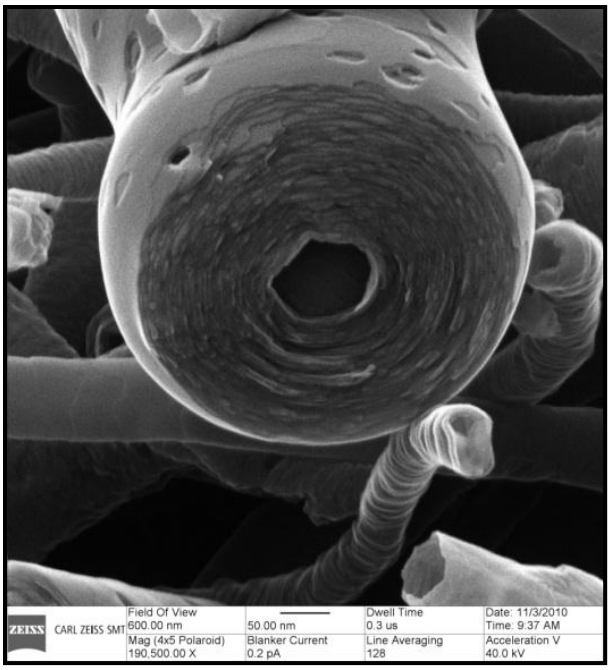

Figure 6: SEM image of MWCNT

2.1.3 Properties of Carbon Nanotubes

2.1.3.1 Mechanical

Carbon Nanotubes are considered to poses high tensile strength and elastic modulus. Studies revealed individual axially loaded CNT shells have strength of about 100GPa with agreement to the quantum models. They also have high strength to weight ratio and Low density. Due to their high aspect ratio and hollow structures CNTs are prone to buckling under compression tests.

2.1.3.2 Chemical

CNTs show enhanced chemical reactivity in comparison with a graphene sheet. CNTs reactivity directly related to pi-orbital mismatch. Thus a distinction must be made between the sidewall and the end caps of the nanotube. Due to this reason, a smaller nanotube diameter results in increased reactivity.

2.1.3.3 Optical

The useful optical absorption, photoluminescence and Raman spectroscopy allow us to characterize the quality of nanotube in terms of their structures, carbon content and defects. Optical activity of chiral nanotubes disappears as nanotube becomes larger. These features determine other properties such as mechanical and electrical.

2.1.3.4 Electrical

Depending upon the chirality or helixity of nanotube, they can be either metallic or semi-conducting. Experimental results show the ballistic and super conductivity of nanotubes. For embedding Nanotubes into metal matrix composites for developing higher conductive composites scientists are using Multi walled carbon nanotubes because of their multi channel electron transmission which leads a ballistic quantum channel. In theory, metallic nanotubes can carry an electric current density of 4×10^9 A/cm2, which is more than 1,000 times greater than those of metals such as copper [10].

2.1.3.5 Thermal

Carbon Nanotubes possesses very high thermal conductors and exhibit ballistic thermal conduction. Thermal conductivity of SWNT along its axis is about 3500 $W \cdot m^{-1} \cdot K^{-1}$ [11], which is almost 10times higher than copper (385 $W \cdot m^{-1} \cdot K^{-1}$). Thermal stability of carbon nanotube is estimated to 2800^{o}C in vacuum and 750^{o}C in air.

2.1.3.6 Toxicity

Due to the structural similarity of carbon nanotubes to that of asbestos safety concerns are raised by few organizations. Studies showed CNTs can enter human cells and accumulate in cytoplasm leading to death. Organizations such as United states

National Institute for Occupational Safety and Health (NIOSH), European Union's Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) have taken measures in recommending exposure limits of nanotubes and commercialization of nanotubes.

2.2 Nanocomposites:

A composite is a material made from two or more constituent materials with significantly different physical or chemical properties that, when combined, produces a material with characteristics different from the individual components. The individual components remain separate and distinct within the finished structure. A composite material is also defined as a macroscopic combination of two or more distinct materials, having a recognizable interface between them.

Nanocomposites are composite materials that are formed by incorporating one or more nano sized particles or structures in a metal matrix or an alloy. By definition Nanocomposite is a multiphase solid material where one of the phases has either one, two or three dimensions of less than 100 nanometers (nm), or structures having nano-scale repeat distances between the different phases that make up the material. Table 2 shows the different kinds of Nanomaterials at each Dimension.

Table 2: Nanomaterials with various dimensions [12]

Dimension	**Nanomaterial**
One (1D)	Surface coatings, Engineered surfaces, Thin films

Two (2D)	Carbon nanotubes or CNT, Inorganic nanotubes, Biopolymers, Nanowires
Three (3D)	Quantum dots, Nanoparticles, Fullerenes or carbon 60, Dendrimers, Precipitates, Colloids

Nanoscale reinforcement of a metal matrix in larger amounts will lead to significant changes of its properties on macroscopic levels. Addition of CNTs into a metal matrix dramatically enhances the electrical and thermal properties of the base metal. While not restricting to electrical and thermal properties the inclusion of CNTs often alter optical, dielectric and mechanical properties such as strength, stiffness and corrosion properties etc. In general, the nano reinforcements are dispersed in the metal matrix during processing. The orientation and alignment of nanoparticles, concentration and polydispersity of nanoparticles also have a predominant role in the macroscopic properties of the base metal [13].

2.2.1 History

The existences of nanocomposites are pre historic but the science behind it is being studied vigorously in recent years. Damascus steel which was used to forge weapons during eight century A.D. [14] indeed contains carbon nanotubes [15] encased in cementite nano wires. Mesopotamia potters in ninth century generated glittering effect on the surface of pots [16].

2.2.2 Classification

Nanocomposites can be broadly classified into three types:

1. Ceramic-matrix Nanocomposites

2. Polymer-matrix Nanocomposites

3. Metal-matrix Nanocomposites

2.2.2.1 Ceramic-matrix Nanocomposites

To overcome intrinsic brittleness, lack of containing crack propagation, low fracture toughness [17] without defying their desired properties of high-temperature stability, high corrosion resistance, light weight and electrical insulation, CNTs are used to reinforce the Ceramic composites. In addition to these, depending upon the type of Nanotube embedding in a ceramic matrix will also benefit other properties such as electrical, thermal conductivities, thermal shock resistance, hardness, thermal expansion coefficient.

2.2.2.2 Polymer-matrix Nanocomposites

A polymer or copolymers having nanoparticles or nanofillers in their matrix well dispersed are considered as Polymer Nanocomposites. The higher surface area of the nano-particles, the interaction with the other particles within the mixture is more and this increases the strength, heat resistance, etc. of the composite. Many bio degradable polymer nanocomposites are being developed for bone tissue engineering and their novel properties of high strength, light weight and corrosion resistance are being used for making bone implants.

2.2.2.3 Metal-matrix Nanocomposites

Metal matrix nanocomposites (MMNCs) are still being developed and are considered as next generation composites because of their remarkable properties. By

embedding CNTs into metal matrix the range of applications are almost into every field. The high strength to weight ratio, high electrical conductivity, high thermal stability, increased tensile strength are the expected outcomes. Different traditional and nontraditional manufacturing techniques are being investigated for manufacturing MMNCs, with every method having its own advantages and limitations.

2.3 Methods of Producing Nanocomposites

Metal Matrix Nanocomposites (MMNCs) can be fabricated by variety of processing techniques. Figure7 shows various processing techniques for fabricating MMNCs. As per S. R. Bakshi et al[7] review on processing metal matrix Nanocomposites, powder metallurgy is widely used to process Metal matrix-CNT composites where as liquid metal processing techniques such as melting and solidification is viable method to process low melting point metals such as Mg and bulk metallic glasses.

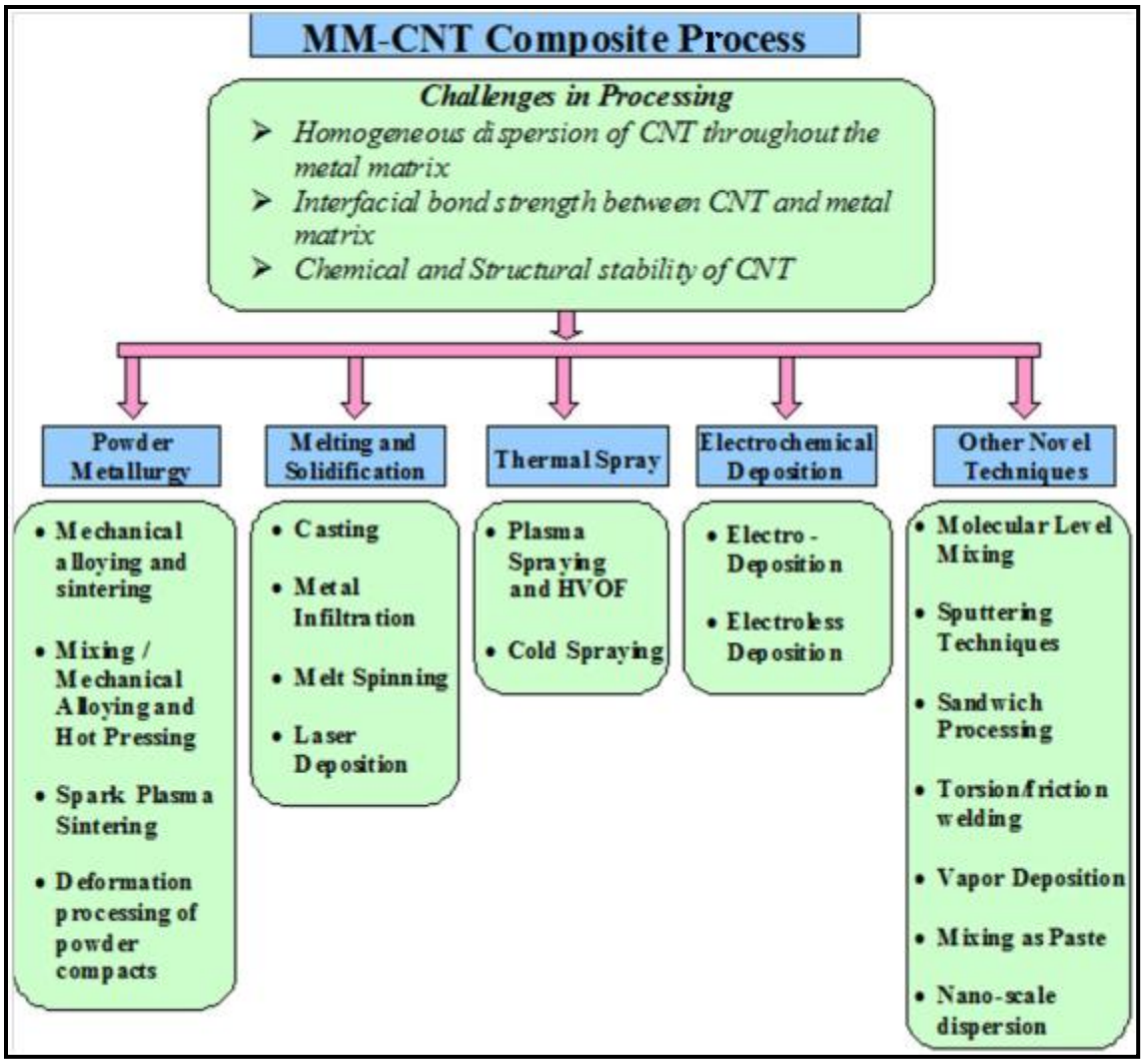

Figure 7: Various processing techniques for fabricating MMNCs. [7]

2.3.1 Stir Casting:

For producing Metal matrix composites Stir Casting is considered as the most economical and productive process. Stir Casting as the name implies melting metal in a crucible by conventional route and dispersing any reinforcing material into this molten metal by mechanical stirring. After mechanical stirring of discontinuous reinforcements in molten metal, it is allowed to solidify. The major advantage of stir casting is in its design, flexibility and simplicity. According to M.K. Surappa [18] classification of various

manufacturing processes, Liquid metallurgy (stir Casting) have high economical and yield aspects compared with other major manufacturing processes for producing Discontinuously Reinforced Metal Matrix Composites (DRMMC).

Table 3: A comparative evaluation of the different techniques used for DRMMC fabrication [18]:

Method	**Range of Shape and Size**	**Metal Yield**	**Range of vol. fraction**	**Damage to reinforcement**	**Cost**
Liquid Metallurgy (stir Casting)	wide range of shapes; larger size; up to 500 kg	very high>90%	up to 0.3	No damage	least expensive
Squeeze casting	limited by preform shape; up to 20 cm height	Low	Up to 0.45	Severe Damage	Moderately Expensive
Powder metallurgy	wide range; restricted size	High	Up to 0.4	Reinforcement Fracture	Expensive
Spray casting	limited shape; large size	Medium	-	-	Expensive
Lanxide technique	limited by preform shape; restricted size	-	0.3 - 0.7	-	Expensive

2.3.2 Stages of Stir Casting

Depending upon the desired outcome in the product, stir casting can be classified in different stages but the most general phases of stir casting are

1. Incorporation of reinforcements into metal matrix
2. Homogenous mixing/dispersing of reinforcements in molten metal matrix
3. Solidification of Metal Matrix Composite.

2.3.2.1 Incorporation of reinforcements into metal matrix

Depending on the criteria and requirements of experimental procedure reinforcements are added before melting or after melting the base metal/alloy. This thesis is focused on developing an ultra low porous composite which requires minimum atmospheric contaminations and gases in the melting crucible (in this case it is a test tube). High vacuum is generated in the test tube containing pre mixed dispersoids and base metal chips, shots and solid billet in predefined weigh fractions.

2.3.2.2 Homogenous mixing/dispersing of reinforcements in molten metal matrix

Once the base metal/alloy is melted in crucible, reinforcements are stirred into molten metal pool with the help of a mechanical stirrer which is made up of corrosion free metal or a non reacting material with the metal pool or the usage of electromagnetic stirring to eliminate any alien particle contamination in metal pool. Molten metal is stirred for significant time to disperse the dispersoids and break any agglomerations within molten pool.

2.3.2.3 Solidification of Metal Matrix Composite

The homogenous MMC slurry is allowed to solidify after dispersing the reinforcement particles in the metal slurry. The rate of cooling is crucial in attaining the desired microstructures. If slower cooling rates are used, due to buoyancy reinforcements will have the tendency to either float to surface of liquid metal or segregate at the bottom. It is essential to have a proper cooling rate and a mechanism to ensure the composite slurry is in a homogenous state.

2.3.3 Impeller

The device that provides required shear force for breaking the agglomerations and dispersing of the particles for homogenous mixing of two or more phases of fluid with the help of an external motor. It is also used to increase or decrease the pressure and flow of a fluid. Depending upon the flow pattern impellers can be classified into two types

1. Axial flow impellers
2. Radial flow impellers

2.3.3.1 Axial flow impellers

Axial flow impellers are used when homogenous fluid is required with bulk motion from bottom of the crucible to top. They are preferred when mixing solid-liquid suspensions as they prevent the solid particles from segregating at the bottom.

2.3.3.2 Radial flow impellers

Radial flow impellers are used when high shear stresses are essential to mix immiscible fluids. They are preferred when high shear rates such as dispersion are required.

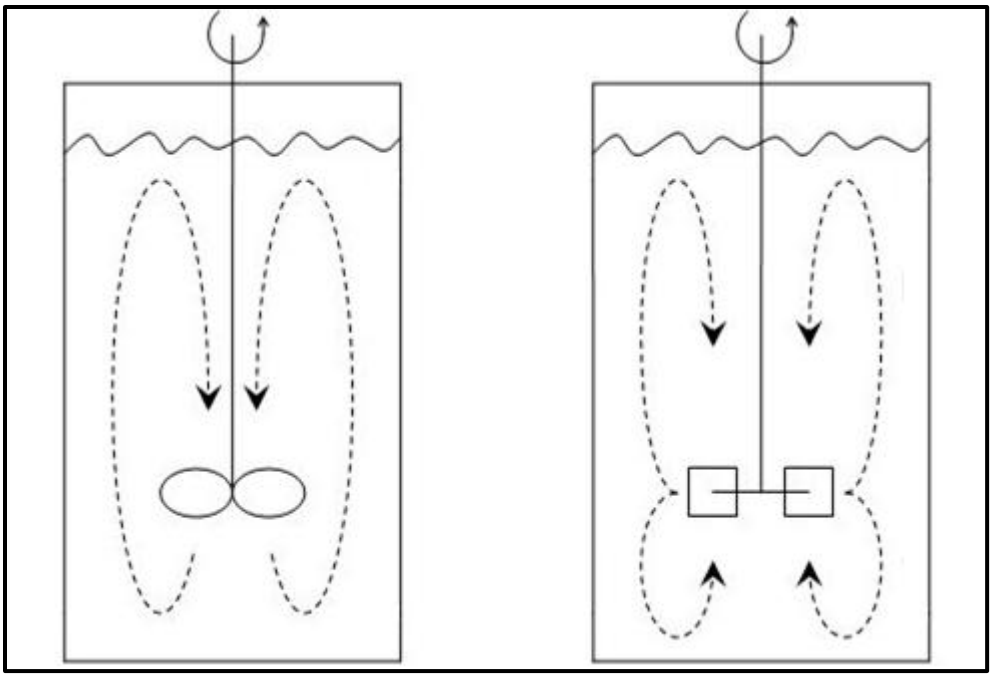

Figure 8: Direction of flow in Impellers

Direction of flow in Axial flow impellers (left) and Radial flow impeller (Right)

CHAPTER III

LITERATURE REVIEW

3.1 Metal Matrix Composites (MMCs):

Metal matrix Composites (MMCs) can be fabricated either by liquid metal processing or by powder particle processing. The reinforced composites generally have enhanced mechanical properties when compared with monolithic or unreinforced base metal or alloy [19]. In MMNCs when isotropic dispersion of reinforced material is achieved, then the composites are expected to be Orowan strengthened [20]. Pure Orowan strengthening effect is explained by Ashby-Orowan Equation by assuming all the precipitates are widely arranged and spherical [21].

$$\Delta\sigma_{Oro} = 0.1836 G_m b \left(\frac{{V_f}^{1/2}}{r}\right) \ln\frac{r}{b}$$

Where $\Delta\sigma_{Oro}$ is increase in yield strength by Orowan strengthening in MPa, $G_m$is the shear modulus of the matrix in MPa, b the Burgers vector, V_f is the Volume fraction of precipitate and r is the average particle radius in m.

Strengthening of Metal Matrix Composites (MMC) is also facilitated by other strengthening mechanisms such as Hall-Petch strengthening due to grain size. The

strengthening effect of MMC due to their grain refinement is expressed by the equation [22]

$$\sigma_y = \sigma_0 + k_1 {d_g}^{-1/2}$$

where $\sigma_y$is the yield stress, $\sigma_0$is the lattice friction stress which includes contribution from solutes and particles, $k_1$is a material dependant constant and $d_g$is the grain diameter.

Kang et al [23] reported increase in hardness and tensile behaviors of Aluminum matrix composites reinforced with nanometric Al2O3particulates. However the strengthening effect leveled off as the concentration of Al2O3 increased over 4% volumetrically, which is attributed to the clustering of Al2O3. He also reported that the major strengthening mechanism of Orowan strengthening is due to the evenly distributed Al2O3 in particles in the metal matrix.

3.2 Nanocomposites:

Goh et al [24] synthesized monolithic and CNT reinforced magnesium materials using disintegrated melt deposition (DMD) process where ingots were hot extruded at 350C with an extrusion ratio of 20.25. They reported that lighter nanocomposites are fabricated by incorporating CNTs into the Monolithic Magnesium metal matrix. They found that the increase in yield, tensile strengths and ductility of the CNT-Mg composite up to a threshold of 1.3wt% CNT. Their results are summarized in the tables 4 & 5. [24]

Table 4: Effect of conc. of CNTs on Macrohardness of CNT-Mg Composite:

Material	CNT (wt%)	Density (g/cc)	Macrohardness (HR15T)
Mg (99.9%)	0.0	1.738±0.010	45±1
Mg-0.3wt% CNT	0.3	1.731±0.005	48±1
Mg-1.3wt% CNT	1.3	1.730±0.009	46±1
Mg-1.6wt% CNT	1.6	1.731±0.003	42±1
Mg-2.0wt% CNT	2.0	1.728±0.001	39±1

Table 5: Effect of Conc. of CNTs on Mechanical properties of CNT-Mg Composite:

Material	0.2% YS (MPa)	UTS (MPa)	Elongation (%)
Mg (99.9%)	126±7	192±5	8.0±1.6
Mg-0.3wt% CNT	128±7	194±9	12.7±2.0
Mg-1.3wt% CNT	140±2	210±4	13.5±2.7
Mg-1.6wt% CNT	121±5	200±3	12.2±1.7
Mg-2.0wt% CNT	122±7	198±8	7.7±1.0

Muhsan et al [6] used Metal Injection Molding technique for fabricating Copper based Nano Composite by dispersing MWCNTs with in the copper matrix by using paraffin wax as a medium to disperse nanotubes in the copper powder to form Cu-MWNTs-Binder feed stock. They reported to follow a multilevel mixing approach of Nanoscale dispersion for preparing feedstock of Cu-MWNTs-Binder followed by Metal Injection Molding process (MIM). In their experimental study they reported to have 11%

increase in the thermal conductivity with addition of 1 vol% of MWNTs to the Copper powder upon further increase in concentration of MWCNTs the thermal conductivity of the composite decreased. The decrease in the conductivity is attributed to the agglomerations of MWNTs in the metal matrix.

The work from Muhsan et al shows the necessity for the development of an approach for dispersing and aligning of reinforcing material in the metal matrix is essential for attaining unique and enhanced properties of Nano Composites.

3.3 Ballistic Conductance of Carbon Nanotubes:

Metallic Carbon Nanotubes (CNTs) are known as ballistic conductors [25]. Researchers are working on developing composite materials that can replicate high conductance of CNTs at Nanoscale to macro scale applications. In 1997 Smalley et al and Tans et al reported the electron transport measurements in nanotube devices many other researchers tried to address questions on fundamental physics and device performance.

Collins and Avouris [26] reported in their experimental analysis that in MWCNTs unlike the outer wall or inner wall contributing to electron conduction, all the shells in a MWCNT are actually contributing for conduction this break through discovery paved path for the future works on developing ultra conductive materials.

Li et al [27] reported in their experimental observations that MWCNTs have the capability to carry higher currents at low bias voltage with perfect ohmic contacts. They reported the behavior of MWCNT is due to quasi-ballistic conductance of inner walls of the CNT. Their experimental results showed higher conductance of MWCNT compared with theoretical value of SWCNT.

In the report submitted by Oak Ridge National Laboratory (ORNL) in 2015 for priority research areas for developing Ultra conductive Copper Conductors[28], fabrication route of Nayfeh et al from ISSL, CSU have been highlighted which shows the importance of developing ultra conductive materials. Nayfeh et al reported in their patent (US Patent#8,347,944) electrical conductivity of 113% IACS by copper nanocomposite produced by die casting. These results encourage researchers in pursuit for developing Nano composites which can exhibit higher conductive behavior.

3.4 Stir Casting:

Ghosh et al [29] reported size of impeller and stirring speeds are among the crucial factors that influence the development of porosity in stir casting. The porosity formed in casting can be related both due to the shrinkage porosity and gas entrapment.

According to Harnby et al [30], study on different designs of impellers that provide shear force and stirring in the molten metal, turbine blade stirrer is popular. Impellers are essential for transferring particles into liquid and to maintain the reinforcements in the state of suspension such that it avoids both segregation of particles on the bottom of mix or float onto the top of mix due to buoyancy.

The formation of vortex in stir casting has both positive and negative implications. Due to pressure difference in inner and outer layers of the melt the particles are pulled into the molten pool of mix thus enabling the reinforcements to stay in the suspension. Also rigorous stirring will cause air bubbles in the mix which will create porosity in the composite. So it is essential to have optimal speed of rotation of stirrer.

CHAPTER IV

RESEARCH METHODOLOGY

The objective of this research is to develop a manufacturing process for producing Metal Matrix Nano Composites (MMNCs) without the addition of surfactants or dispersing agents. The necessity for eliminating such agents is to reduce the percentage of impurities in the metal matrix.

According to the patent on Nano-engineered ultra-conductive nanocomposite copper wire (US Patent No. US 8347944) by Nayfeh and Weiderholt, they propose a novel approach for developing Copper Nano Composite wire. In the process of development, the team at CSU used $MgCl_2$ as an aid for coating Carbon Nanotubes (CNT) with Magnesium by ultrasonically mixing the graphitized CNTs with an $MgCl_2$ Solution and followed by flow-milling for predetermined number of cycles, thus functionalizing MWCNTs with Magnesium.

On further iterations for scaling up of the ballistic conducting zone of Copper Nanocomposite wire a new research methodology is proposed and investigated by the team of Cleveland State University (CSU) lead by Nayfeh for developing ultra conductive copper composites materials.

4.1 Research Methodology

The work in this research is carried out in different phases to explore the feasibility of fabricating Magnesium and Copper based Nanocomposites. To develop a reliable process the mechanism for breaking the agglomerating the Carbon Nanotubes and dispersing them in the metal matrix is critical. In this thesis the process for breaking agglomerations and dispersing Carbon Nanotubes in the magnesium metal matrix are discussed. Different phases in the research are summarized below:

- Phase 1: Investigated layering of MWCNTs in the experimental setup which will lead to low sedimentation on bottom of test tube and low amount of MWCNTs floating on to the surface of molten metal.
- Phase 2: Developing a method for breaking the agglomerations of MWCNTs and dispersing them in the Molten Magnesium pool.
- Phase 3: Consolidation of Magnesium Nanocomposite to reduce the porosity in the sample and densification of the Mg-MWCNT composite.
- Phase 4: Inserting the Mg-MWCNT composite in Copper billets. The copper billet with Magnesium based Nanocomposite is extruded to form rods, which is further drawn into fine wire.

CHAPTER V

EXPERIMENTAL SETUP

5.1 Material Selection

5.1.1 Base Metal:

The base metal used as the matrix for forming Metal Matrix Nanocomposite is High purity Magnesium. Magnesium is a group 2, alkaline earth metals, and the eight most abundant elements in the Earth's crust. After Iron, Oxygen and Silicon, Magnesium is the most common element in the Earth, is a light, silvery-white metal. Magnesium has high strength to weight ratio and have many potential applications in automotive, aerospace and structural industries.

Magnesium in various forms is selected in this study for facilitating in the process of layering in Phase 1 study. Different forms of Magnesium used in this study are briefed below.

i. High Purity Magnesium Granules
ii. High Purity Magnesium Slugs
iii. High Purity Magnesium Billet
iv. High Purity Magnesium Chips

High purity Magnesium Granules, Shots and chips used in this study are purchased from Alfa Aesar and their composition are attached in Appendix. Other parameters of Magnesium raw material can be seen in the tables 6-9.

Table 6: Magnesium Granules Parameters

Commercial Name	Magnesium Granules
Purity	99.8%
Average Particle Size	-12+50 mesh
Supplier	Alfa Aesar
Lot Number	Z22X028
Color	Silvery White

Table 7: Magnesium Slug Parameters

Commercial Name	Magnesium Slug
Purity	99.95%
Average Particle Size	6.35mm dia X 6.35mm width
Supplier	Alfa Aesar
Lot Number	Z05C015
Color	Silvery White

Table 8: Magnesium Billet Parameters

Commercial Name	Magnesium Billet
Purity	99.9%
Diameter	33mm
Length	77mm
Color	Silvery White

Table 9: Magnesium Chips Parameters

Commercial Name	Magnesium Turnings
Purity	99.8%
Average Particle Size	2.3mm wide
Supplier	Alfa Aesar
Lot Number	J03X015, K22Z043
Color	Silvery White

5.1.2 Reinforcing Material:

Metallic Carbon nanotube have higher current carrying capacity and less sensitive to electron mitigation [31][32]. Multi walled Carbon Nanotubes (MWCNTs) are selected as the reinforcing material for this study. MWCNTs are preferred over Single walled Carbon Nanotubes (SWCNTs) because of their ability to conduct electricity with lower resistance and conduction in multiple layers of MWCNTs also have the ability to sustain even after vigorous shear forces during fabrication process unlike SWCNTs and their relatively higher current carrying capacity over SWCNTs.

MWCNTs used in this study are purchased from Applied Materials and are graphitized by processing them at 3000°C. The Parameters of MWCNTs are shown in Table10.

Table 10: MWCNTs parameters

Commercial Name	Graphitized Multiwalled Carbon Nanotubes
Average Length	10-15 μm
Average Diameter	150 nm
Supplier	Applied Science
Color	Dark Grey

5.2 Experimental Apparatus

5.2.1 Heating Unit:

The heating unit is custom designed for the study by collaboration between Manufacturing Advocacy and Growth Network (MAGNET) and the Industrial Space systems Laboratory (ISSL) from Cleveland State University. WATLOW heating source is used for the Heating unit. Stirring unit is embedded within the system designed by Magnet in collaboration with ISSL. The motor for rotating stirrer is used from Caframo Universal Model BDC3030. To reduce weight on the linear actuator flex shaft is used for driving impeller. The figure shows the existing setup for casting Mg/MWCNT composite. Figure 9 shows the Heating unit currently in use for casting Mg/MWCNT composite at CSU.

Figure 9: Heating unit at CSU

5.2.2 Vacuum Pump:

High vacuum turbo pumping system Agilent TPS-mini is used for generating vacuum in the test tube. Agilent T-plus software is used to control and communicate to pump through computer. Input voltage of 90V to 240V AC and frequency of 50/60 HZ. Rotational speed of pump is 81000rpm. Figure shows the existing agilent TPS-mini vacuum pump. Table shows the capabilities of TPS-mini vacuum pump.

Figure 10: Agilent TPS-Mini

		KF40	ISO63	CFF 4 ½"
Pumping speed (l/s)	N_2	38	52	52
(with inlet screen)	He	30	50	50
	H_2	24	35	35
Base pressure*		2×10^{-7} mbar	2×10^{-7} mbar	5×10^{-8} mbar
Bakeout temperature		80 °C at inlet	80 °C at inlet	120 °C at inlet
Shipping weight kg (lbs.)		7.9 kg (17.4 lbs)	7.5 kg (16.4 lbs)	8.8 kg (19.4 lbs)
Pumpdown time (1 liter volume)	60 sec. to 17 mbar; 114 sec. to 1×10^{-4} mbar; 140 sec. to 5×10^{-5} mbar			
Turbo pump rotational speed	81,000 rpm			
Start-up time	122 sec.			
Operating position	Vertical, Horizontal, Upside down position			
Operating ambient temperature	5 °C to 35 °C / 32 °F to 122 °F			
Input voltage and frequency	90V to 240V AC; 50 Hz / 60 Hz			
Maximum input power	220 VA			
Serial communications	RS-232 cable, 9-pin D-type male, 9-pin D-type female, T-Plus Navigator Software			
* *According to standard DIN 28 428.*				

Figure 11: Parameters of Agilent TPS-Mini

5.2.3 Pressure Gauge:

Various pressure gauges at different locations are used to ensure no vacuum leaks in the set up. Pressure gauge FRG-700/702 Pirani Inverted Magnetron Gauge from Agilent Technologies with measuring range of 5x10-9 to 1000mbar (3.8 x 10-9 to 760 Torr) and accuracy of ± 30 % of reading with repeatability of ± 5 % of reading is used to measure pressure at the mouth of pump.

Figure 12: Agilent / Varian 531 Thermocouple Gauge

Figure 13: Pirani Inverted Magnetron Gauge

Agilent / Varian 531 Thermocouple Gauge model number F0472301 with measuring range of 1mTorr to 760 Torr and 15% accuracy is used to measure pressure in test tube at lower vacuum levels. Varian 531 thermocouple gauge is used to measure the pressure in the test tube. Since the pressure readings are not accurate in Argon atmosphere, the gauges need to be calibrated for Argon environments to get actual readings. Pirani gauges are calibrated for Argon environments, datasheet is attached in

appendix. To get actual readings varian 531 gauge is calibrated with respect to Pirani gauge for experimental purpose and the results are plotted and can be seen in figure14.

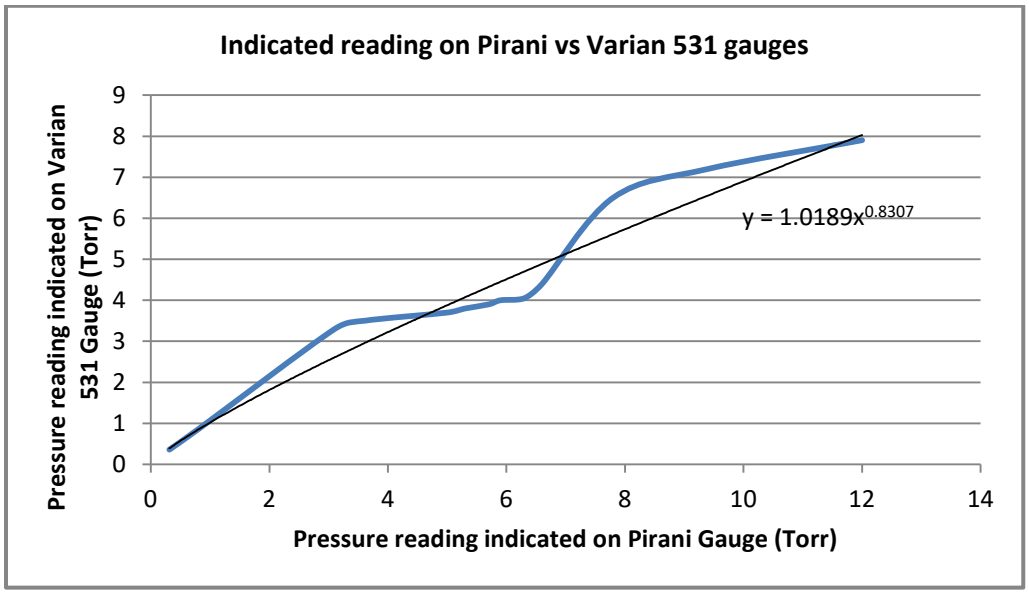

Figure 14: Graph showing Calibration of Varian 531 with Pirani Gauge

5.2.4 Quartz tubes:

Melting of metal is carried out in quartz test tubes which are purchased from Across International and MTI Corporation. Specifications of quartz tube are mentioned in table. Figure15 shows the quartz tubes used for casting Mg/MWCNT composite. Dimensional parameters and Maximum operating temperatures of the quartz tube can be seen in table 11.

Table 11: Parameters of Quartz tube:

Suppliers	Across International, MTI Corporation
Diameter of tube	44mm (1.73”)
Thickness of tube	3mm
Length of Tube	300mm
Maximum operating Temperature	1200°C

Figure 15: Test tube for casting Mg-MWCNT Composite

5.2.5 Vacuum Furnace:

Vacuum furnace is used for consolidation of as cast billet from phase 2, the as cast billet is pressed in the vacuum furnace custom built for ISSL by The Furnace Source is used. Edwards High vacuum E2M80 Oil-Sealed Rotary Vane Vacuum Pump is used for generating vacuum in the furnace. Figure16 shows the vacuum hot press used for consolidation of Mg/MWCNT composite to densify.

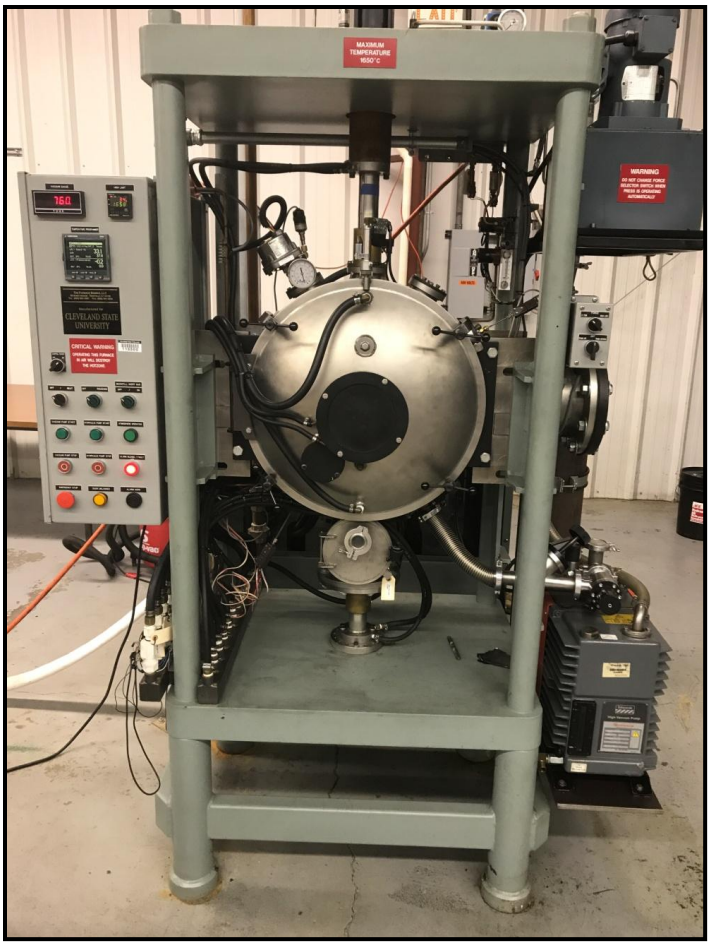

Figure 16: Vacuum Hot Pressing unit

5.2.6 Scanning Electron Microscope:

Billets after hot pressing and initial drawing operations are examined to verify the dispersion and presence of nanotubes by using scanning electron microscope (SEM). Oxford Instruments Inca X-ray spectroscopy (EDS) system is used for validating the distribution and presence of chemical elements in the metal matrix.

5.2.7 X-ray Imaging:

The as cast Mg/MWCNT billets and NanoComposite billet after vacuum hot pressing are imaged using X-ray techniques. The X-ray imaging is performed at G&S Titanium, Wooster, Ohio.

CHAPTER VI

RESULTS AND DISCUSSION

Different methods are investigated to get better engulfment of MWCNTs within magnesium metal matrix. Owing to low surface energy and density of carbon nanotubes it is difficult to disperse them in a metal matrix without the addition surfactants/ dispersants.

Initially Electromagnetic induction heating is employed for melting Magnesium billet under 10psi but due to high vapor pressure of Magnesium, the metal is sublimated on the low temperature end of test tube walls. Figure17 shows partially sublimated Magnesium billet processed via Electromagnetic Induction under low pressure regimes. Instead of melting and forming molten metal pool due to high vapor pressure Magnesium started to sublimate on the cold end of the test tube. To eliminate sublimation of Magnesium partial atmosphere of Argon is introduced in the test tube by purging Argon gas and holding pressure at 11psi. This process helped to melt Magnesium and disperse MWCNTs in the metal pool without contaminating the nanocomposite by introducing alien material for stirring.

Figure 17: Magnesium billet processed using Electromagnetic Induction

Further on later stages of processing the Mg/MWCNT composite it was discovered that the gas entrapped in the nanocomposite lead to catastrophic exploding of extruded rod during extrusion process and breaking of the rod during wire drawing operation.

Figure 18: Exploded Cu-Mg/MWCNT composite rod.

Figure18 shows the exploded Cu-Mg/MWCNT composite during extrusion process from the initial experiments using Electromagnetic Induction Melting process. To minimize the entrapped gas, conventional method of heating is opted in the later stages of producing Mg/MWCNT composite. Conventional heating enable uniform heating of feed stock and melting the material in test tube. During heating process once the metal is at sublimating temperature magnesium vapors increases the pressure in the test tube due to Magnesium sublimation and coating test tube walls by thin layer of Magnesium. At this part Argon gas at low pressure is purged to suppress the Magnesium vapors thus enabling feed stock to melt rather than sublimate.

6.1 PHASE I - Layering mechanism:

Layering nanotubes is a critical step in melting the feed stock. Improper layering can cause either nanotubes to float onto the surface of metal pool or sediment on bottom. Even if nanotubes are in contact with test tube walls is it difficult to break them apart. Since the experimental setup is designed to work under vacuum conditions, Nanotubes are placed in test tube along with the other charge material for melting.

Initially magnesium chips are placed in test tube and then pre-defined amount of nanotubes are loaded over these chips and Magnesium billet is placed over them but this method failed due to most of the Nanotubes sediment on the bottom of the test tube.

Figure 19: Improper layered MWCNTs in Test tube

Figure 20: Defective Mg/MWCNT composite due to improper layering of MWCNTs

Figure 19 shows the improper layering method that resulted in MWCNTs adhering to the walls of the test tube due to poor handling. Figure 20 shows the defective Mg/MWCNT composite due to Nanotubes adhering to the face of the test tube and are not dispersed during the stirring operation. During process it was observed that the Nanotubes that stick to the walls do not disperse and continue to stay on the surface of test tube even after completion of the experimental run. After continuous improvement in layering process an optimized layering method was developed. The layering of the nanotubes is designed in such a way to ensure minimum contact with the walls of the test tube and loaded at relatively different heights with careful attention. This approach showed positive results with low amount of nanotube the sediment on bottom of the test tube sticking to walls. This process of layering gave flexibility for the replication of casting Mg/MWCNT composite.

6.2 PHASE II – Dispersing MWCNTs:

The scope of this thesis is the development of a process for dispersing MWCNTs within a pure metal matrix Magnesium without the addition of surfactants or dispersants.

Once the metal is layered, the loaded test tube is fitted to vacuum sealed heating system. After achieving low vacuum, the temperature of the system is raised to 250ºC and held for 24 hours to allow nanotubes to degas.

The heating process is designed in a step by step process rather than continuous heating for facilitating uniform heating of the raw materials. Once the magnesium in test tube is melted, stainless steel stirrer is used to break the agglomerations of nanotubes and disperse them in the molten metal pool. Figure 21 shows defective Mg/MWCNT composite due to improper stirring resulted in non embedded Nanotubes. The molten

metal is stirred vigorously at different speed for a minute at each speed. The stirrer is moved pneumatically in the test tube to disperse the Nanotubes at different heights. The process of stirring is carried for five minutes. Holding Magnesium in molten form for longer periods will cause the Nanotubes to float onto the surface of the metal due to the buoyancy effect. Figure 22 shows the desired as-cast Mg/MWCNT composite with no visual casting defects. Once the Nano Composite is produced it was sent to G&S Titanium Inc. for X-Ray imaging of the billets. Figure 23 shows the X-Ray images of the as-cast Mg/MWCNT composite. Voids due to shrinkage during solidification and gaseous can be observed on the top of the composites.

Figure 21: Defective Mg/MWCNT composite due to improper stirring

Figure 22: As-cast Mg/MWCNT Billet.

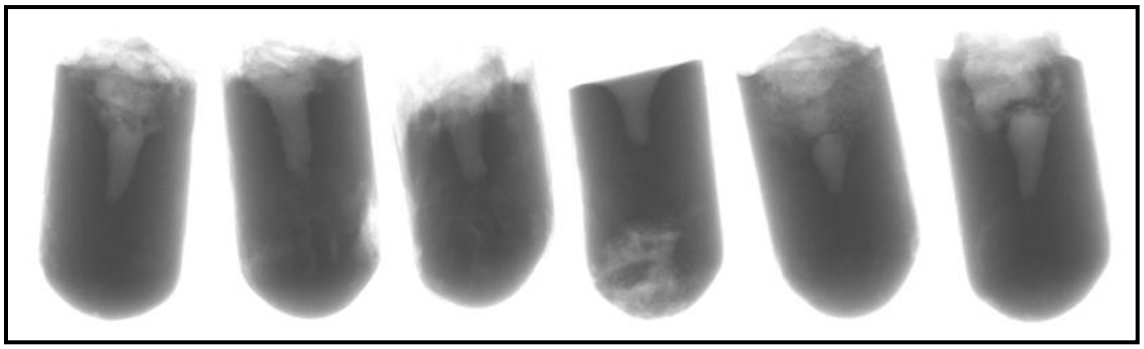

Figure 23: X-ray images of as-cast Mg/MWCNT composite

6.3 PHASE III – Consolidation of Mg-MWCNT composite:

The as cast Mg-MWCNT composite consists of v-neck on the top of billet. The piping is attributed to solidification of composite from the walls and the generation of vortex during stirring operation in Phase II. The as-cast Mg/MWCNT composite is prone

to contain micro shrinkage and micro porosity due to gas entrapment. Figure 24 shows casting related defects such as shrinkage and blow holes in as-cast Mg/MWCNT.

The as-cast billet from Phase II is cleaned to remove the silicide layer and oxide regions by turning operation. Figure 25 shows the cleaned Mg/MWCNT billet that will be further processed. The Cleaned billet from Phase II is loaded in Graphite die for hot pressing in Vacuum hot press. Heating and cooling cycle of vacuum furnace is programmed in eight steps to ensure uniform heating of the Mg-MWCNT composite. Figure 26 shows the X-ray images of hot pressed Mg/MWCNT composites.

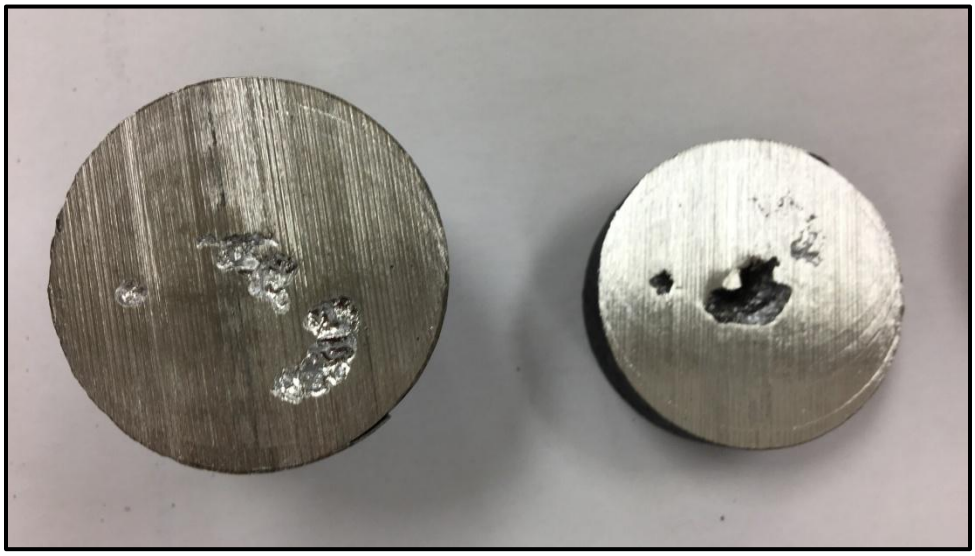

Figure 24: Casting defects in as-cast Mg/MWCNT composite.

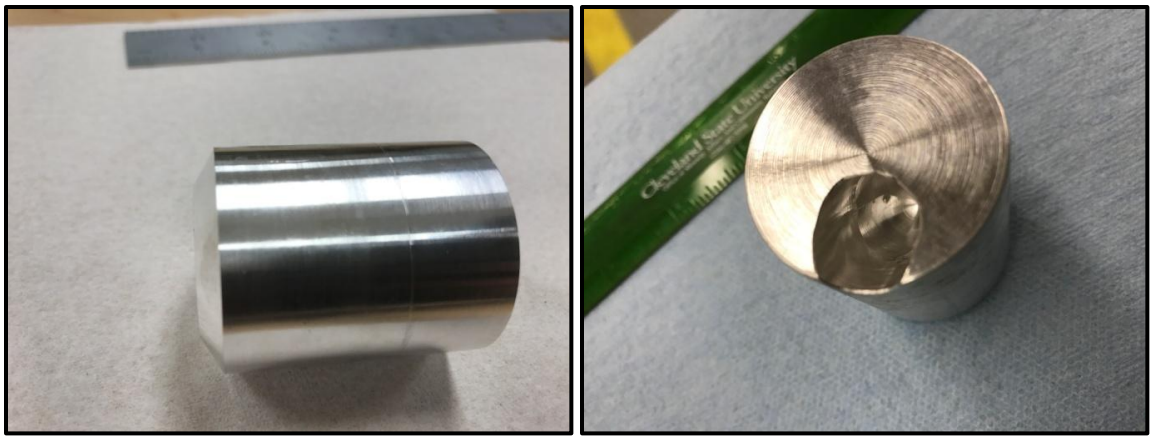

Figure 25: Cleaned Mg/MWCNT composite before vacuum hot pressing

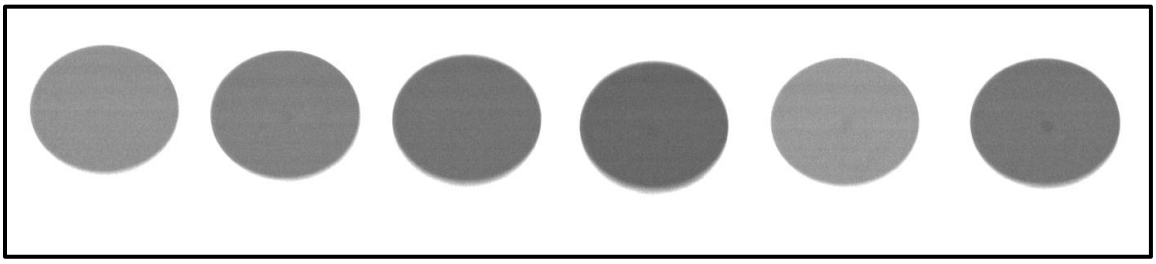

Figure 26: X-ray images of Mg/MWCNT composite after vacuum hot pressing

6.4 Phase IV – Embedding Mg-MWCNT composite in Copper billet and Extrusion:

The nanocomposite obtained from the vacuum hot press is machined to the desired dimensions of 1.25 inch in diameter and one inch in height. This machined composite is later embedded into a copper billet of 3inch diameter and 2.5 inch height. Figure 27 shows the copper billet embedded with Mg/MWCNT composite. The Mg/MWCNT composite acts as the core for the copper billet, which is further extruded to form a rod of 0.625inch diameter. Extrusion is performed at the Air Force Research Laboratory (AFRL) at Wright-Patterson Air Force base, Ohio. The process parameters for extrusion are listed in the table 12.

Table 12: Process parameters of Extrusion at AFRL:

Extrusion Die Temperature	500 F
Ram Speed	15 rpm
Extrusion Nose Diameter	0.55 inch
Extrusion Ratio	22.34

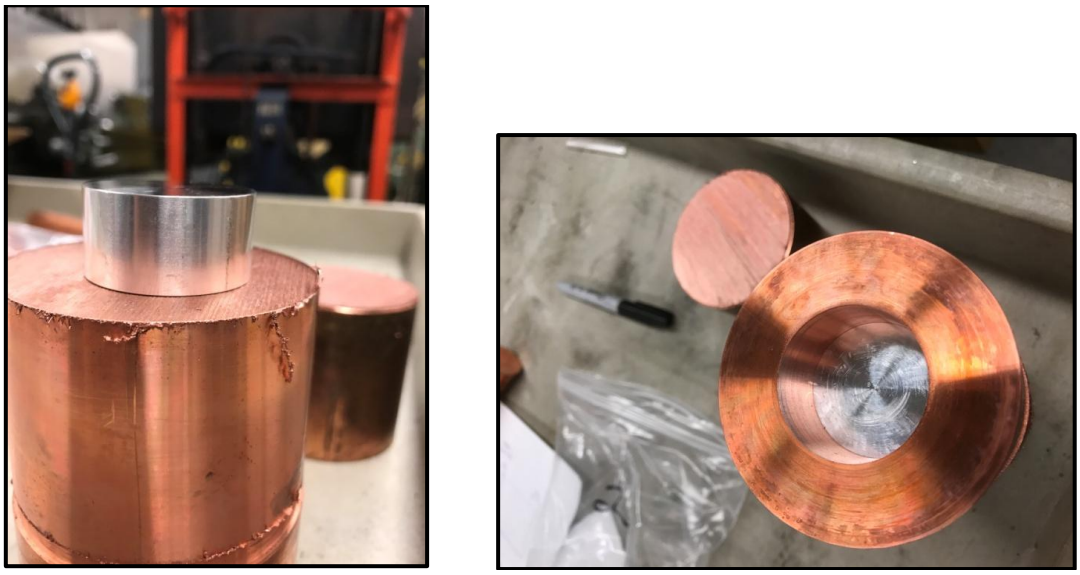

Figure 27: Mg/MWCNT composite embedded in Copper Billet

6.5 SEM Results:

The composite rod Cu-Mg/MWCNT is further drawn to 1/8th inch wire. To validate the process of dispersing the nanotubes within the wire, parts of wire at different stages of drawing process along with the Magnesium nano composite after vacuum hot consolidation process studied under SEM to verify the presence of nanotubes in the magnesium metal matrix.

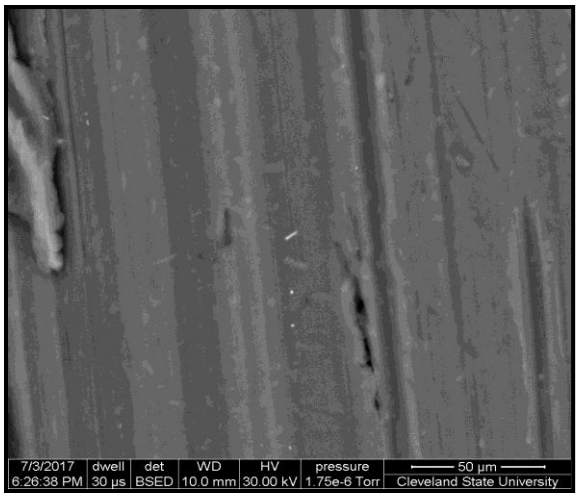

Figure 28: Dispersed MWCNTs in Magnesium Matrix

Figure 28 shows the presence of the MWCNTs in the magnesium metal matrix and well dispersed. Although there is probability of finding agglomerations they will be broken on subsequent drawing operations. To get the specimen ready for imaging in SEM they are milled, during this process copper on the outer surface smeared onto the surface of the magnesium. Figure 29 shows the smeared copper on the cross section.

Cleaning the sample with the ethanol or water corrodes the Magnesium matrix. Figure 31 shows the effect of washing on the specimen. In future work a better route of cleaning the specimens will be studied. Polishing the specimen will also damage the nanotubes on the surface by tearing them and smearing the carbon on the surface. This approach is avoided knowing difficulties faced during washing in prior research work by Dr. Nayfeh and team at CSU. Figure 30 shows the Nanotubes embedded in the Magnesium metal matrix. Robust ways to determine the nanotubes dispersion levels and quantifying will be studied in future work.

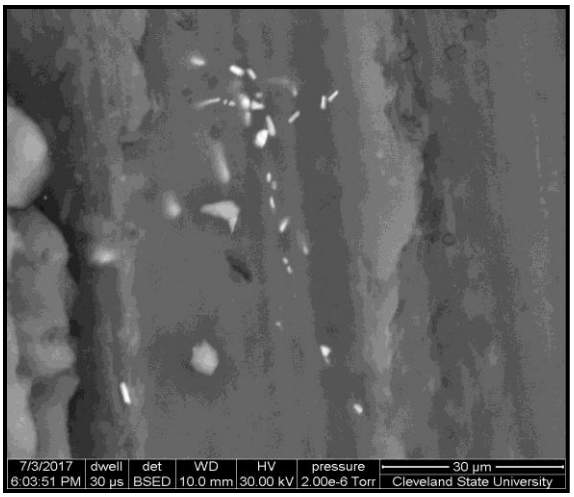

Figure 29: Debris of nanotubes and copper examined with SEM.

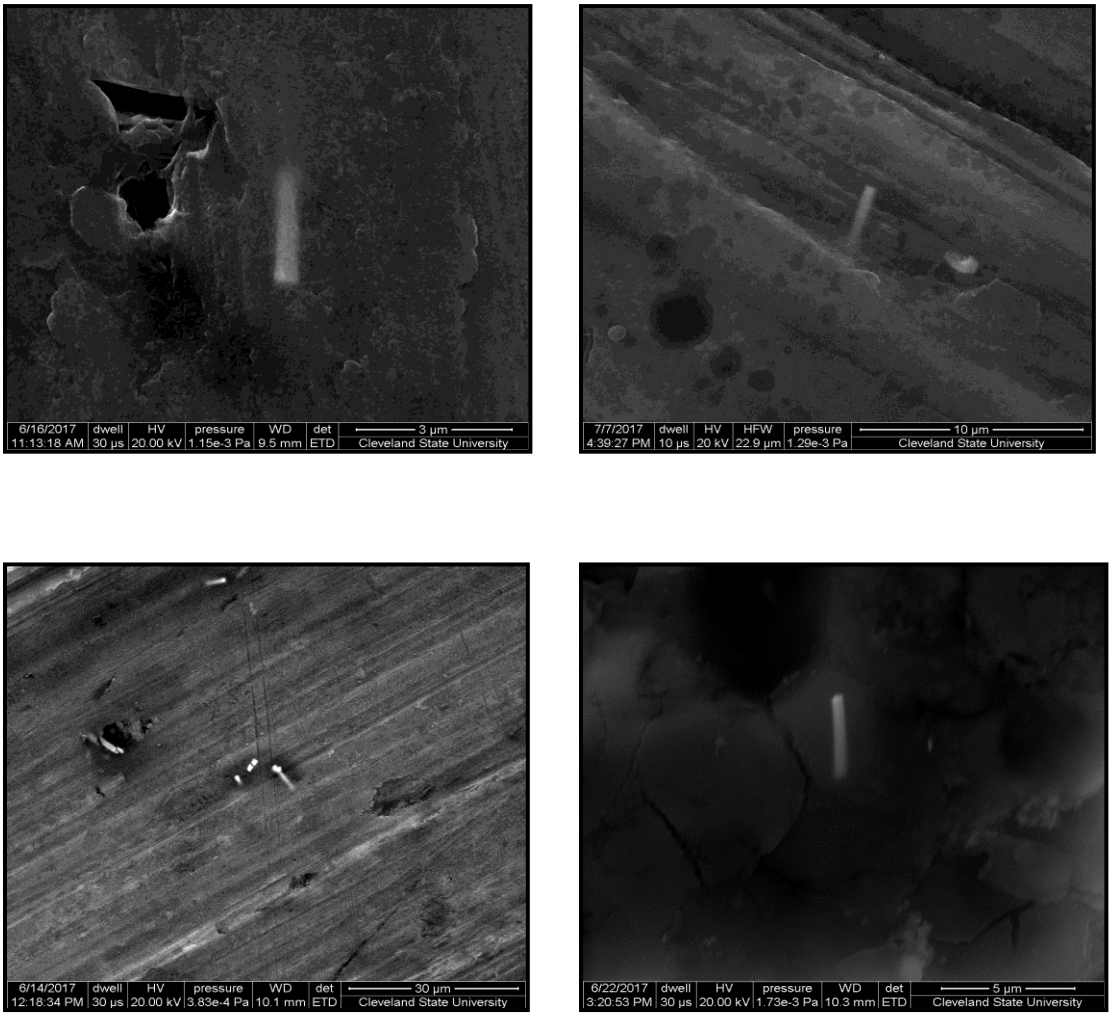

Figure 30: Embedded MWCNTs in Magnesium matrix

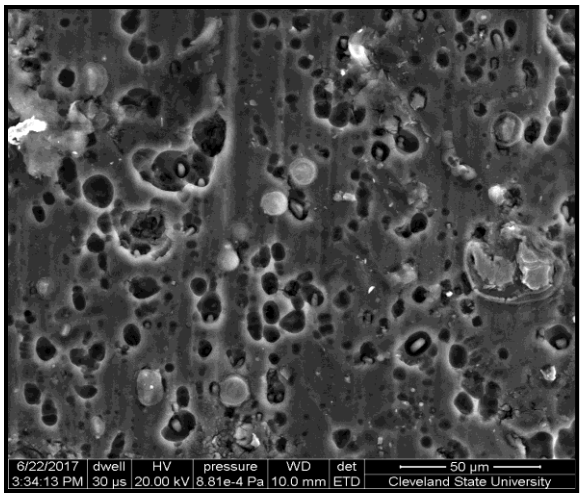

Figure 31: Damaged test specimen due to washing with ethanol

CHAPTER VII

ENERGY DISPERSIVE SPECTROSCOPY

To validate the presence and concentration of the Nanotubes in the wire and to quantify them the test specimens that consists of 5 vol% were examined to find the carbon content using Energy Dispersive Spectroscopy.

From the EDS analysis study it can be shown that the carbon content is uniform within the cross section of wire but to quantify the amount of carbon Nanotubes is not possible. It is because of the EDS inaccuracy in identifying hydrocarbons and quantifying carbon.

The results of the EDS for wires of different diameter at varying depths are listed in table 13. Each wire of different diameter with each step of 1 mil height was analyzed for validating the presence of CNTs.

Table 13: Concentration of elements in Cu-Mg/MWCNT rods of different diameters at different depth:

D1 (1/5th of Inch)						
Step		**C**	**O**	**Mg**	**Si**	**Cu**
I	**Weight %**	**10.68**	**2.72**	**84.67**	**1.17**	**0.77**
	Atomic %	19.35	3.69	75.79	0.9	0.26
II	**Weight %**	**10.89**	**3.82**	**83.48**	**1.19**	**0.62**
	Atomic %	19.58	5.16	74.14	0.92	0.21
III	**Weight %**	**9**	**3.46**	**85.49**	**1.33**	**0.72**
	Atomic %	16.5	4.76	77.45	1.04	0.25
IV	**Weight %**	**10.33**	**5.2**	**82.42**	**1.41**	**0.64**
	Atomic %	18.55	7.01	73.13	1.09	0.22
V	**Weight %**	**10.01**	**3.65**	**84.59**	**1.18**	**0.57**
	Atomic %	18.15	4.97	75.77	0.92	0.19
D2 (1/6th of Inch)						
Step		**C**	**O**	**Mg**	**Si**	**Cu**
I	**Weight %**	**13.4**	**5.69**	**77.51**	**1.74**	**1.65**
	Atomic %	23.51	7.49	67.15	1.3	0.55
II	**Weight %**	**15.54**	**4.15**	**79.32**	**0.55**	**0.44**
	Atomic %	26.71	5.36	67.37	0.41	0.14
III	**Weight %**	**16.2**	**3.3**	**78.65**	**1.13**	**0.72**
	Atomic %	27.85	4.26	66.82	0.83	0.24
IV	**Weight %**	**16.45**	**5.19**	**74.79**	**2.56**	**1.01**

	Atomic %	28.08	6.66	63.07	1.87	0.33
V	**Weight %**	**14.07**	**5.77**	**75.84**	**1.11**	**3.21**
	Atomic %	24.7	7.6	65.8	0.83	1.07
D3 (1/8th of Inch)						
Step		**C**	**O**	**Mg**	**Si**	**Cu**
I	**Weight %**	**18.54**	**5.19**	**74.72**	**0.94**	**0.91**
	Atomic %	31.02	6.52	61.5	0.67	0.29
II	**Weight %**	**23**	**4.42**	**71.02**	**0.98**	**0.58**
	Atomic %	37.14	5.36	56.65	0.68	0.18
III	**Weight %**	**21.01**	**4.51**	**72.71**	**1.04**	**0.73**
	Atomic %	34.5	5.56	58.99	0.73	0.23
IV	**Weight %**	**21.27**	**4.47**	**72.37**	**1.14**	**0.76**
	Atomic %	34.86	5.5	58.61	0.8	0.24
	Atomic %	16.71	5.07	76.89	0.15	1.18
	Atomic %	17.18	3.1	78.43	0.11	1.18

Presence of copper is attributed to the smeared copper during milling operation to prepare specimens for SEM analysis. Figure 32 shows the Cu-Mg/MWCNT composite rod used for SEM and EDS analysis. The specimen is milled in steps to facilitate observing concentration of Nanotubes at different level of depths. Highlighted region in the figure 33 shows the area of interest for EDS analysis. Figure 34 shows the plot of the variation of carbon content with respect to the change in area of the site of interest for

EDS. It can be seen as the area of interest for EDS increases the carbon content decreases. These results are needed to be studied in further works.

Figure 32: Specimen used for EDS analysis

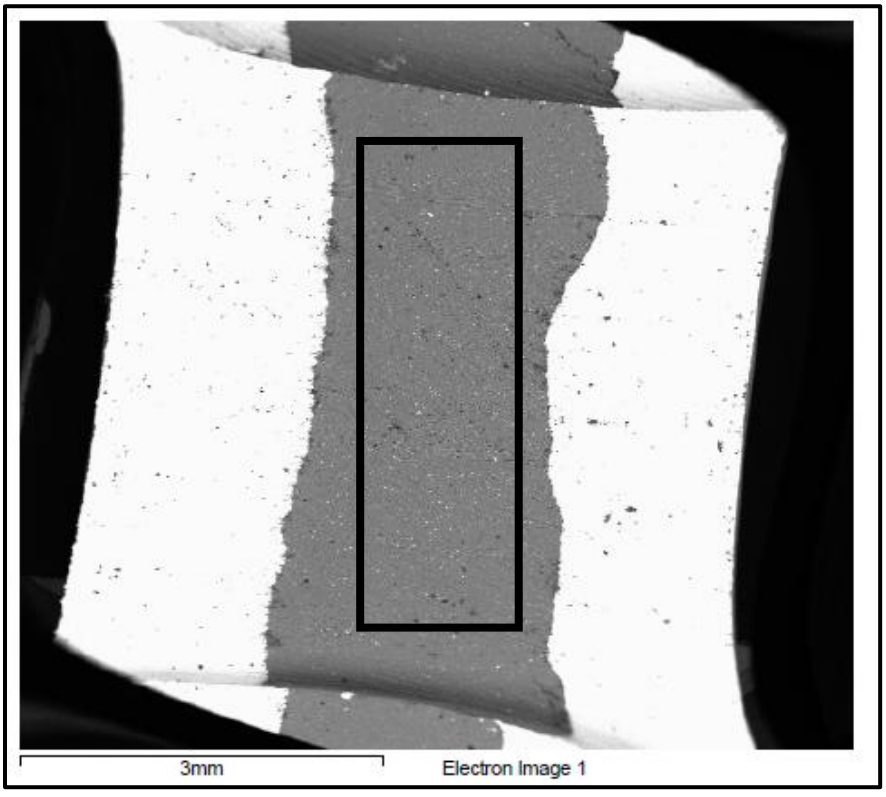

Figure 33: Area of interest during EDS analysis

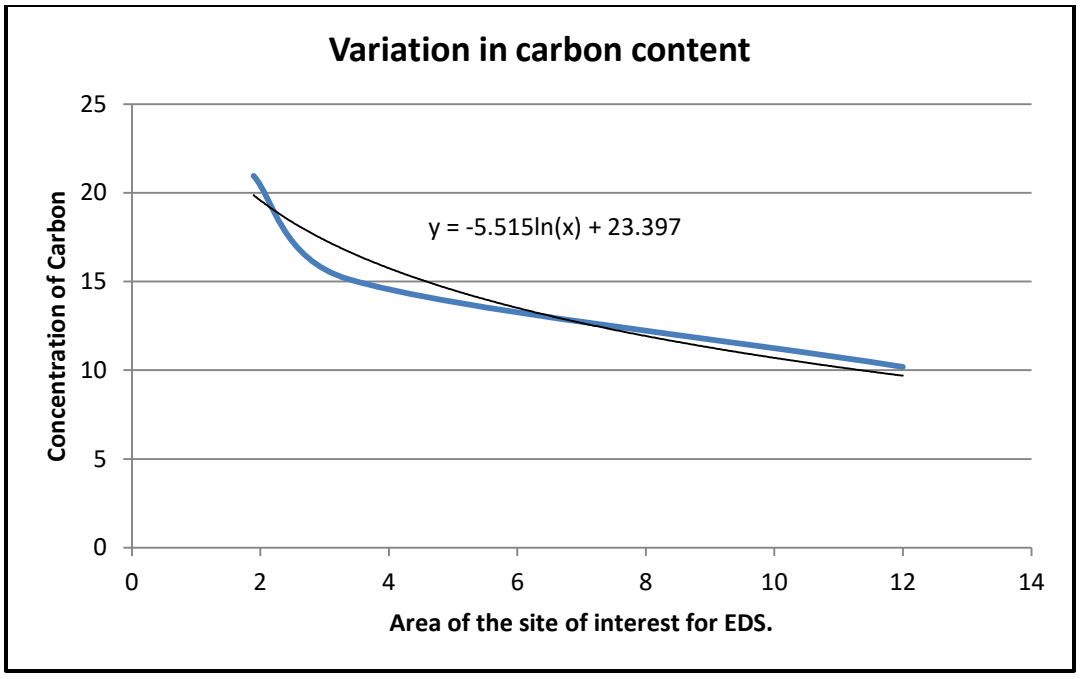

Figure 34: Graph showing variation in conc. of Carbon with respect to Area of SOI for EDS

CHAPTER VIII

CONCLUSION

The objective of this work is to develop a process for fabricating the Mg-MWCNT composite material by breaking the agglomerations of nanotubes and dispersing them within the magnesium metal matrix. Throughout the work various processing techniques were investigated and resulted in a process map. By the current processing technique replication of the process can be achieved.

8.1 Summary of the results:

- Different layering techniques are investigated and came up with the method of using different kinds of material and layer-wise addition of nanotubes.
- Using mechanical stirring showed promising results by breaking the agglomerations and dispersing them in molten metal pool.
- EDS and SEM analysis supports the objective of dispersing nanotubes.
- This process can be implemented in mass production within current production sites with few additions to the existing process route.

8.2 Future work:

- Need to develop a robust method to determine the dispersion and quantify nanotubes in the metal matrix.
- Wire needs to be drawn further fine into micron levels to ensure all agglomerations are broken.
- Fine wires are to be sintered and observe their mechanical and electrical properties.
- Use the current approach to develop more nanocomposites with Aluminum, Lead and other elements.

REFERENCES

[1] Iijima, S: Helical microtubules of graphitic carbon. Nature 354, 56–58 (1991)

[2] M. M. J. Treacy, T. W. Ebbesen and J. M. Gibson: Nature, 1996, 381, 678–680.

[3] P. Kim, L. Shi, A. Majumdar and P. L. McEuen, "Thermal Transport Measurements of Individual Multiwalled Nanotubes," Physical Review Letters, Vol. 87, No. 21, 2001, Article ID: 215502. doi:10.1103/PhysRevLett.87.215502

[4] B. Q. Wei, R. Vajtai, P. M. Ajayan, Reliability and current carrying capacity of carbonnanotubes. Appl.Phys.Lett. 79, 1172 (2001).10.1063/1.1396632doi:10.1063/1.1396632

[5] Daoush WM, Lim BK, Mo CB, Nam DH, Hong SH. Electrical and mechanical properties of carbon nanotube reinforced copper nanocomposites fabricated by electroless deposition process. Materials Science and Engineering: A. 2009;513:247–253.

[6] Ali Samer Muhsan, Faiz Ahmad, Norani M. Mohamed, Puteri Sri Melor Megat Yusoff, and Muhammad Rafi Raza, "Uniform Dispersion of Multiwalled Carbon Nanotubes in Copper Matrix Nanocomposites Using Metal Injection Molding Technique," International Journal of Manufacturing Engineering, vol. 2013, Article ID 386141, 9 pages, 2013. doi:10.1155/2013/386141

[7] S.R. Bakshi, D. Lahiri, A. AgarwalCarbon nanotube reinforced metal matrix Composites-a review Int Mater Rev, 55 (2010), pp. 41-64

[8] R. Saito, G. Dresselhaus, and M. Dresselhaus, Physical Properties of Carbon Nanotubes.London: Imperial College Press, 1998.

[9] S. Iijima, 1991 Helical Microtubules of Graphitic Carbon. Nature, 354(6348), 56 EOF58 EOF

[10] Hong, Seunghun; Myung, S (2007). "Nanotube Electronics: A flexible approach to mobility". Nature Nanotechnology.

[11] Pop, Eric; Mann, David; Wang, Qian; Goodson, Kenneth; Dai, Hongjie (22 December 2005). "Thermal conductance of an individual single-wall carbon nanotube above room temperature". Nano Letters

[12] http://nanogloss.com/nanotechnology/an-overview-on-nanotechnology-materials/#ixzz4bi9UblzH

[13] Tian, Zhiting; Hu, Han; Sun, Ying (2013). "A molecular dynamics study of effective thermal conductivity in nanocomposites". Int. J. Heat Mass Transfer. 61: 577– 582. doi:10.1016/j.ijheatmasstransfer.2013.02.023

[14] Legendary Swords' Sharpness, Strength From Nanotubes, Study Says. National Geographic (2010-10-28). Retrieved on 2011-11-13.

[15] Materials: Carbon nanotubes in an ancient Damascus sabre

[16] Reiss, Gunter; Hutten, Andreas (2010). "Magnetic Nanoparticles". In Sattler, Klaus D. Handbook of Nanophysics: Nanoparticles and Quantum Dots. CRC Press. pp. 2– 1. ISBN 9781420075458.

[17] Review: Structural Ceramic Nanocomposites by Martin Sternitzke

[18] Microstructure Evolution during Solidification of DRMMCs (Discontinuously Reinforced Metal Matrix Composites): State of Art by M.K.S

[19] Hajo Dieringa, Properties of magnesium alloys reinforced with nanoparticles and carbon nanotubes: a review

[20] D.L. Ellis, B.A. Lerch, Increased Mechanical Properties through the Addition of Zr to GRCop- 84, NASA Technical Reports, 2012.

[21] Scripta Materialia 51 (2004) 801-806 Niels Hansen, Hall-Petch relation and boundary strengthening

[22] Hall, E. The deformation and ageing of mild steel: III discussion of results. Proc. Phys. Soc. Sect. B 1951, 64,

[23] Y. C. Kang, S. L. Chan, Mater. Chem. Phys. 2004, 85, 438..

[24] Goh CS, Wei J, Lee LC, Gupta M (2006) Mater Sci Eng A423:153[R1]J Mat. Sci (2011) 46:289-306

[25] A. P. Garrido and A. Urbina, Carbon 40, 1227 (2002)

[26] P.G. Collins, M.S. Arnold, P. Avouris, Engineering carbon nanotubes and nanotube circuits using electrical breakdown, Science 292 (2001) 706e709

[27] H. J. Li, W. G. Lu, J. J. Li, X. D. Bai, C. Z. Gu, "Multichannel ballistic transport in multiwall carbon nanotubes", Phys. Rev. Lett., vol. 95, no. 8, pp. 86601, Aug. 2005

[28] D. F. Lee, M. Burwell, and H. Stillman, “Priority Research Areas to Accelerate the 59 Development of Practical Ultra-conductive Copper Conductors,” 2015.

[29] P.K. Ghosh, S. Ray, Indian J. Technol., 26 (1988), p. 83

[30] N. Harnby, M.F. Edward, A.W. Nienow, Mixing in Process Industries, Butterworths, London, 1985

[31] H. Dai, E. W. Wong, and C. M. Lieber, Science 272, 523 (1996).

[32] S. Frank, P. Poncharal, Z. L. Wang, and W. A. deHeer, Science 280, 1744 (1998).

APPENDIX

Product Specification of Magnesium Granules:

Product Specification

Alfa Aesar

00870 Magnesium granules, -12+50 mesh, 99.8% (metals basis)

Product Number:	00870
CAS number:	7439-95-4
MDL number:	MFCD00085308

Product Specification

Total Metal Impurities:	0.2% max.

Date of Print:	July 23, 2017
Version:	1

Product Specifications are subject to amendment and may change over time.

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Product Specification of Magnesium Turnings:

Alfa Aesar

Certificate of analysis

Product No:	10235
Product:	Magnesium turnings, 99.8% (metals basis)
Lot No.:	K22Z043

Typical Analysis

Total of all impurities	0.20 % max
Cu	0.02 % max
Pb	0.01 % max
Mn	0.10 % max
Ni	0.001 % max
Na	0.006 % max
Sn	0.01 %
Other impurities	0.05 % max, each
Mg	99.80 % min

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ThermoFisher SCIENTIFIC

Product Specification of Magnesium Slugs:

Alfa Aesar

Certificate of analysis

Product No.: 43298

Product: Magnesium slug, 6.35mm (0.25in) dia x 6.35mm (0.25in) length, 99.95% (metals basis)

Lot No.: Z05C015

Mg 99.98 %

Ag	< 0.01	Al	21	As	0.07	Au	< 0.1
B	< 0.01	Ba	0.11	Be	< 0.005	Bi	0.07
Br	< 0.05	Ca	0.41	Cd	< 0.05	Ce	0.09
Cl	3.2	Co	< 0.005	Cr	0.78	Cs	< 0.01
Cu	0.64	Dy	< 0.005	Er	< 0.005	Eu	< 0.005
F	< 0.05	Fe	10	Ga	0.24	Gd	< 0.005
Ge	< 0.05	Hf	< 0.01	Hg	< 0.05	Ho	< 0.005
I	< 0.01	In	< 0.05	Ir	< 0.01	K	< 0.05
La	0.03	Li	0.01	Lu	< 0.005	Mn	28
Mo	< 0.05	Na	1.4	Nb	0.07	Nd	0.03
Ni	1.1	Os	< 0.005	P	3.9	Pb	20
Pd	< 0.5	Pr	< 0.005	Pt	< 0.05	Rb	< 0.01
Re	< 0.01	Rh	< 0.01	Ru	< 0.01	S	8.4
Sb	< 0.05	Sc	< 0.001	Se	< 0.05	Si	25
Sm	< 0.005	Sn	< 0.05	Sr	< 0.01	Ta	≤ 27
Tb	< 0.005	Te	< 0.01	Th	< 0.005	Ti	< 0.01
Tl	< 0.01	Tm	< 0.005	U	< 0.001	V	< 0.05
W	< 0.01	Y	< 0.01	Yb	< 0.005	Zn	47
Zr	0.1						

Values given in ppm unless otherwise noted
All elements determined by GDMS

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