PROCESSING AND CHARACTERIZATION OF NICKEL-CARBON BASE METAL MATRIX COMPOSITES

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Carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs) are attractive reinforcements for lightweight and high strength metal matrix composites due to their excellent mechanical and physical properties. The present work is an attempt towards investigating the effect of CNT and GNP reinforcements on the mechanical properties of nickel matrix composites. The CNT/Ni (dry milled) nanocomposites exhibiting a tensile yield strength of 350 MPa (about two times that of SPS processed monolithic nickel ~ 160 MPa) and an elongation to failure ~ 30%. In contrast, CNT/Ni (molecular level mixed) exhibited substantially higher tensile yield strength (~ 690 MPa) but limited ductility with an elongation to failure ~ 8%. The Ni-1vol%GNP (dry milled) nanocomposite exhibited the best balance of properties in terms of strength and ductility. The enhancement in the tensile strength (i.e. 370 MPa) and substantial ductility (~40%) of Ni-1vol%GNP nanocomposites was achieved due to the combined effects of grain refinement, homogeneous dispersion of GNPs in the nickel matrix, and well-bonded Ni-GNP interface, which effectively transfers stress across metal-GNP interface during tensile deformation. A second emphasis of this work was on the detailed 3D microstructural characterization of a new class of Ni-Ti-C based metal matrix composites, developed using the laser engineered net shaping (LENS™) process. These composites consist of an in situ formed and homogeneously distributed titanium carbide (TiC) as well as graphite phase reinforcing the nickel matrix. 3D microstructure helps in determining true morphology and spatial distribution of TiC and graphite phase as well as the phase evolution sequence. These Ni-TiC-C composites exhibit excellent tribological properties (low COF), while maintaining a relatively high hardness.
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CHAPTER 1
INTRODUCTION

Metal matrix composites (MMCs) are the new class of advanced materials in which rigid ceramics reinforcements/ceramic fibers/ceramic particulates exhibiting excellent strength as well as elastic modulus are embedded in a ductile metal such as nickel, copper, aluminum, titanium, magnesium, iron, or alloy matrix to overcome the inadequacy of metals and alloys in providing both strength and stiffness to the structure [1-13]. In the metal matrix composites, strength and ductility is provided by metal matrix, and strength and stiffness is provided by reinforcements in the metal matrix [6, 8]. Metal matrix composites possess excellent physical as well as mechanical properties, such as high strength in shear and compression, high service temperature capabilities, high specific modulus, fatigue strength, temperature stability, which make them suitable for structural applications, ground transportation, thermal management devices, and industrial (chemical and transportation), recreational, and infrastructure applications, as well as automotive and aerospace usages [6-8, 12, 14-17]. There is an increase in demand of metal matrix composites for automotive and aerospace applications availability of inexpensive reinforcements and the development of various processing routes [12]. Metal matrix composites are widely used in electronic packaging applications due to their low co-efficient of thermal expansion and higher thermal as well as electrical conductivity [6, 7]. Carbon nano fiber/graphite reinforcements exhibit high thermal conductivity, low co-efficient of thermal expansion, high damping capacity, good self-lubricating property, which imparts significant dimensional stability to metal matrix composites [11, 16-21]. Due to excellent physical and mechanical properties, metal matrix composites are candidates for space applications if subjected to extreme conditions such as vacuum, ionizing, radiation, and plasma [22-24].
Polymer matrix composites are quite well developed and thoroughly studied by materials scientists in many research labs as well as in many industries; in practice they have many shortcomings including, low operating temperature, low mechanical strength, and high degradation rate when exposed to harsh environments such as oxidation, radiation, moisture, and fire [17]. Metals exhibit high mechanical strength, stiffness, and melting temperatures as compared to polymers, which makes metals suitable matrix materials for structural composites, but, still, metal matrix composites experience limited commercial utilization, unlike polymer matrix composites, due to high production cost, poor wettability with reinforcement (of carbon by molten metal), formation of interfacial reaction products, and galvanic corrosion issues of the metals [25-28].

Based on the type of reinforcement introduced into the metal matrix, metal matrix composites are categorized into (1) Continuous fibers reinforced MMCs (2) Discontinuous short fibers reinforced MMCs or whiskers/particulates reinforced MMCs [29]. Continuous fiber reinforced metal matrix composites exhibit higher mechanical strength and stiffness, but complicated processing methods and the high expense of fiber make them un-economical for most of the industrial applications [29]. In contrast, the family of discontinuously reinforced metal matrix composites includes both particulate/whiskers/short fibers, which have attracted considerable attention because of:

(a) Availability of various types of reinforcement at competitive cost [29]

(b) The successful development of manufacturing processes to produce metal matrix composites with reproducible structure and properties [29]

(c) The availability of standard or near-standard metal working methods which can be utilized to fabricate the metal matrix composites [29]
Due to ease of fabrication procedures, lower cost, and near-isotropic properties particulate reinforced metal matrix composites have received increasing attention in many industries [12, 29]. Discontinuously reinforced metal matrix composites, also termed as conventional or ex-situ metal matrix composites, have been fabricated in ways such as mechanical alloying (MA), spray deposition, powder metallurgy, squeeze casting, rheocasting, and compocasting [1-5, 15, 30-35]. During these techniques, ceramic reinforcements were externally added prior to composite fabrication into the matrix material (which may be in molten or powder form). The main disadvantages of these conventional ex situ metal matrix composites involve size limitation of reinforcing phase which is nothing but the starting powder size, interfacial reaction between the reinforcement and matrix, and poor wettability between the reinforcements and the matrix due to surface contamination of reinforcements [12]. The physical and mechanical properties of metal matrix composites are primarily governed by size and volume fraction of reinforcement as well as the nature of the matrix reinforcement interface [12]. The uniform dispersion of fine and thermally stable ceramic particulates in the metal matrix is desirable for achieving optimum mechanical properties of metal matrix composites. This leads to the development of novel in situ metal matrix composites in which precipitates are synthesized in metallic matrix by a chemical reaction between elements or between elements and compounds during the composite fabrication. The in situ metal matrix composites exhibit many advantages over ex-situ metal matrix composites [12, 14, 36]:

(a) In situ formed reinforcements are thermodynamically stable and lead to less degradation at elevated temperatures.
Strong interfacial bonding between the matrix and the reinforcement due to clean matrix-reinforcement interface due to absence of any interfacial reaction between matrix and reinforcement.

Better physical and mechanical properties due to homogeneous dispersion of fine-scale reinforcements into matrix.

In situ formation of reinforcement is the promising fabrication route for processing metal matrix composites in terms of both technical and economical considerations. In situ metal matrix composites have better control over physical and mechanical properties due to their greater control on the size and level of reinforcements, as well as the matrix-reinforcement interface. Mechanical and physical properties of metal matrix composites are mainly governed by properties of the matrix, dispersion of the reinforcement, interfacial bonding between matrix and reinforcement, and finally the processing method. Various processing routes have been developed due to the great potential and widespread applications of these in situ metal matrix composites that involve matrix materials (titanium, nickel, aluminum and copper) and in situ reinforcements (carbides, nitrides, and borides) [12, 23, 25, 28, 36]. While in situ metal matrix composites exhibit excellent physical and mechanical properties, they also have many advantages over conventional metal matrix composites; the fabrication routes and the processing features of in situ metal matrix composites (the in situ precipitate formation mechanisms) are not well understood. These issues need to be addressed to increase the commercial applications of the in situ metal matrix composites. Tjong et al. categorized the processing methods of in situ metal matrix composites, based on the temperature of metallic matrix and reactants during processing [12]. The processing routes based on this terminology can be classified into the following four categories:
(a) Solid-liquid reaction process

(b) Vapor-liquid-solid reaction process

(c) Solid-solid reaction process, and

(d) Liquid-liquid reaction process

Among all these processing routes, solid-liquid reaction process has been widely adopted to create in situ metal matrix composites. In this process, reactants react with each other in situ in the presence of a third liquid metallic phase or reactants react with some component in the melt to form in situ ceramic reinforcement. This is a solvent assisted reaction process, wherein reinforcing particles are generated in the matrix through diffusion of the components. This processing route is further sub-categorized into self-propagating high-temperature synthesis (SHS) [37-41], exothermic dispersion [42-49], reactive hot pressing (RHP) [50, 51], combustion assisted cast (CAC) [52-55], direct reaction synthesis (DRS) [56-60], flux assisted synthesis (FAS) [61], reactive spontaneous infiltration (RSI) [62], directed melt/metal oxidation (DIMOX) [63-66], rapid solidification processing (RSP) [67-69], and reactive squeeze casting (RSC) [70]. Solid-solid reaction process, also sub-categorized into mechanical alloying and reactive hot pressing route. Metal matrix composite exhibits high specific strength as well as high specific modulus because it combines and tailors the best properties of (their two constitutes) metals (ductility and toughness) and (high modulus and strength) reinforcement particles. The strength, ductility, and fracture mode of the composites mainly governed mainly by the size of reinforcing particulates, shape as well as the interface between metal-reinforcements. The tensile strength and ductility of metal matrix composites decreases with increasing particle size. The mechanical properties of metal matrix composites can be further increased by reducing the reinforced particle size leads to the development of novel metal matrix
nanocomposites [8]. In the broad pool of metal matrix composites, the present work mainly focused on Nickel-Carbon nanotube/ graphene nanoplatelet (GNP) and Nickel-Titanium Carbide (TiC) composites mainly due to their high temperature structural applications.
CHAPTER 2
LITERATURE REVIEW

2.1 Metal-Carbon Nanotube (CNT)/Graphene Nanoplatelet (GNP) Nanocomposites

2.1.1 Importance of Metal Matrix-Carbon Nanotube (CNT)/Graphene Nanoplatelet (GNP) Nanocomposites

Carbonaceous nanomaterials including carbon nanotube (CNTs) and graphene carry excellent mechanical and physical properties, such as high mechanical strength, high elastic modulus as well as high electrical and thermal conductivity, which makes them suitable candidates for structural engineering and functional device applications [17]. Due to their large aspect ratio (i.e., length to diameter, or length to thickness ratio), GNP and CNTs are considered to be the most effective reinforcing materials in the metal matrix composites for improving their mechanical as well as physical properties [71]. Metal-CNT composites are widely used for thermal management components in electronic devices due to excellent thermal conductivity of CNTs helping to dissipate the heat [17]. Owing to increase in fuel prices and in order to reduce carbon dioxide emission, there is a need for lightweight structural materials in aerospace and automotive industries and this need leads to the development of novel metal-carbon base composites [29]. Metal-CNT composites possess wide advantages over polymer base composites [17]:

(a) Inherent stability at elevated temperature

(b) High strength and stiffness

(c) Superior electrical and thermal conductivity
However, less attention is given to metal-CNT/GNP nanocomposites due to the many challenges and difficulties involved in their processing [6, 17]:

(a) Agglomeration of CNTs into metal matrix

(b) Poor wettability between CNT and metal matrix due to large difference in surface tension

(c) To retain chemical and structural stability of CNTs.

Recently, large efforts have been spent on achieving homogeneous dispersion of CNTs into metal matrix by using various processing routes [29, 72-76]. This section is brief literature review on metal-CNT/GNP nanocomposites, which includes basic introduction of CNTs and GNP, various processing techniques of metal-CNT/GNP composites, strengthening mechanisms as well as mechanical and physical properties of metal-CNT/GNP composites along with potential applications of metal-CNT/GNP nanocomposites.

2.1.2 Carbon Nanotube (CNT)

Carbon nanotubes, originally discovered by Iijima almost two decades ago have attracted significant interest as reinforcements in various metallic, ceramic, and polymeric matrices due to their unique atomic structure and attractive properties, such as high tensile strength, high elastic modulus, low density, high aspect ratio, and excellent thermal as well as electrical conductivity [71, 73, 77-87]. Carbon nanotubes are mainly classified as single-walled (SWNT), double-walled (DWNT), and multi-walled nanotubes (MWNT) depending on the number of graphene layers wrapped into a seamless cylinder. Typically, the diameter of a single-walled nanotube ranging from 1-2 nm and that of a double-walled and multi-walled nanotube, ranging from 4-20 nm [17]. Single walled nanotubes are further classified into armchair, zigzag, and chiral, based on the
arrangement of hexagons around the circumference [71], shown in Fig. 2.1. Chiral vector is also given by [17],

$$\vec{Ch} = n\vec{a}1 + n\vec{a}2$$

Where, n and m are integers

$$\vec{a}1$$ and $$\vec{a}2$$ are grapheme lattice vector.

The armchair nanotube (n=m) has metallic behavior and the zigzag (m=0) or chiral (m≠n) exhibits semiconducting behavior [17, 71, 88, 89]. The main processing routes for synthesizing carbon nanotubes involve physical vapor deposition (PVD) including electric arc discharge process, laser ablation method, and the chemical vapor deposition (CVD) technique.

Fig. 2.1 Three classes of carbon nanotube structure (a) armchair, (b) zigzag, and (c) chiral [71]
Electric arc discharge process is one of the simplest and cheapest methods for synthesizing CNTs. In this process, electric direct current arc is generated between two graphite electrodes in an inert atmosphere under the application of a large current, which leads to vaporization of carbon atoms into a plasma. The carbon vapor then condenses and deposits on cathode to form carbon nanotubes (CNTs). Quality of CNTs synthesized by this method mainly depends on the processing conditions, such as gap between electrodes, efficient cooling of cathode, reaction chamber pressure, uniformity of plasma arc, and plasma temperature [29].

In the laser ablation process, CNTs are produced by using a high-energy laser beam to generate carbon vapor species from a graphite target followed by condensation of those species. Even though this method is simple, and though the high quality of CNTs obtained due to better control over processing parameters, the high cost of the laser source restricts its practical applications. Pulse laser beam, CO₂, Nd: YAG, and ultraviolet UV (excimer) laser can be used to synthesize the CNTs using laser ablation technique [29]. The diameter and yield of SWNT synthesized by this laser ablation technique mainly depends on processing parameters, such as furnace temperature, chamber pressure, laser properties (e.g., energy, wavelength, pulse duration, and repetition rate), and composition of target material.

Chemical vapor deposition (CVD) is the most promising and famous technique for large-scale production of CNTs, among all the processing routes of synthesizing CNTs [17, 90-92]. In CVD process, CNTs are synthesized by decomposition of hydrogen gases over a metal nanoparticle catalyst (Fe, Co, Cu, Ni, and rare earth nanoparticles) placed in a horizontal or vertical furnace, as shown in Fig. 2.2 at a very high temperature. In vertical furnace, CNTs nucleated and grew on metallic catalyst and collected at the furnace bottom. As shown in Fig. 2.2, in fluidized bed reactor furnace, supported catalysts were suspended by upward gas flow and
provided high space velocity, which was particularly suitable for mass production of CNTs [17]. In the CVD process, nucleation and growth of CNTs depend on processing parameters, such as synthesis temperature, type and size of nanoparticles, type of hydrocarbon gas precursor, and gas flow rate [17, 93].

**Fig. 2.2** Schematic demonstration of CVD method: (a) horizontal furnace, (b) vertical furnace, and (c) fluidized bed reactor [17, 92].

Mechanical properties, mainly Young’s modulus and tensile strength of CNTs, were measured by using both theoretical and experimental approaches. The theoretical measurement of mechanical properties is mainly affected by length and chirality of nanotubes. Theoretical young’s modulus of CNTs ranges from 0.6-5.5 TPa [94-98]. But most of the MD simulations calculated the young’s modulus of CNTs to be around 1 TPa [94-96, 98]. Treacy et al. first carried out in situ measurement of intrinsic thermal vibration of CNT in TEM and determined the average young’s modulus of 1.8 TPa, with a wide range from 0.410 TPa-4.15 TPa [99].
Many other researchers also measured young’s modulus by different experimental techniques such as AFM and TEM, and found the average value of young’s modulus of CNTs to be 1 TPa and tensile strength close to 63 GPa [17, 71, 100-104].

Thermal properties of CNTs are mainly governed by the conduction of phonon. This is affected by several factors such as the length of main free path of phonons, inelastic Umklapp scattering, and number of phonon active modes. Diameter and length of nanotubes as well as the presence of impurities also affect the thermal conductivity of CNTs [17, 105]. CNTs exhibit thermal conductivity of 6600 W/mK calculated by MD simulations [106], whereas experimentally measured thermal conductivity value varies from 1750-5800 W/mK [106-109]. Table 2.1 summarizes the properties of carbonaceous materials.

**Table 2.1** Measured properties of carbon nanotube and graphene [17].

<table>
<thead>
<tr>
<th>Material</th>
<th>Diameter, nm</th>
<th>Tensile Strength, GPa</th>
<th>Tensile Modulus, GPa</th>
<th>Elongation to failure, %</th>
<th>Thermal conductivity, W/mK</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT</td>
<td>1-2</td>
<td>-</td>
<td>1000</td>
<td>-</td>
<td>3500</td>
</tr>
<tr>
<td>MWNT</td>
<td>5-50</td>
<td>150</td>
<td>270-950</td>
<td>12</td>
<td>500-2069</td>
</tr>
<tr>
<td>Graphene</td>
<td>-</td>
<td>130</td>
<td>1002</td>
<td>-</td>
<td>4840-5300</td>
</tr>
</tbody>
</table>

2.1.3 Graphene

Graphene is a two-dimensional (2D) building block of carbon material with a single atomic layer of sp² hybridized carbon atoms densely packed in a honeycomb lattice [17]. The main processing routes for synthesizing graphene include thermal evaporation of silicon carbide [110, 111], chemical vapor deposition (CVD) of hydrocarbon on metal or carbide substrates [112, 113], and wet chemical synthesis of graphene oxides followed by the reduction [114, 115].
These chemical synthesis routes of graphene exhibit many advantages over the mechanical cleavage method; including peeling of graphene from graphite using abrasive tapes [116]. Thermal evaporation of silicon carbide (SiC) substrate involves the synthesis of graphene through sublimation of silicon atoms by graphitization of a single crystal silicon carbide substrate in an ultrahigh vacuum (UHM) chamber at high temperature. But, the high production cost (high cost of single crystal substrate and UHV facility) as well as the poor quality of obtained graphene (fragile and with many atomic scale defects) significantly limits the using of this process [111]. In the chemical vapor deposition (CVD) process, graphene grows epitaxially on metallic substrate (e.g., nickel (Ni), copper (Cu), cobalt (CO), ruthenium (Ru) etc.) or on metal carbides (e.g., tantalum carbide (TaC), titanium carbide (TiC)) by dissolution of hydrocarbons at high temperatures [117, 118]. CVD processed graphene has potential in microelectronic applications due to its large surface area [17]. In wet chemical synthesis, the graphene oxides are followed by the reduction process. The graphite oxide is synthesized due to the reaction between graphite and strong oxidizing agents such as sulfuric acid, potassium chlorate, and potassium permanganate, and then the reduction of graphite oxide can be performed either with hydrazine in the presence of stabilizer or by rapidly heating in an inert atmosphere to obtain chemically converted graphene (CCG) and thermally reduced graphene oxide (TRG) or thermally expanded graphene oxide (TEGO), respectively [17, 119-122]. Graphene nanoplatelets (GNPs) are also widely used as reinforcements in many polymer-matrix composites due to their low cost and ease of operation [123-126]. GNP consists of a stack of graphene layers attached to each other due to weak van der Waals forces. GNPs are mainly synthesized from a graphene intercalation compound (GIC) precursor, which involves the reaction between graphite and electron donors or accepters [127, 128]. Mechanical properties of
graphene measured experimentally and calculated using theoretical simulation approaches. Graphene exhibits 1.02 TPa young’s modulus and 130 GPa tensile strength, measured using Nano indentation of the atomic force microscope (AFM) [129]. Numerical simulation approaches include quantum mechanical, equivalent continuum, and atomistic modeling. Young’s modulus of graphene is approximately 1 TPa, calculated by using equivalent continuum simulation [130], molecular dynamics (MD) [131], interatomic potential model, and the quantum mechanical approach [132]. Baladin et al. reported the thermal conductivity of single layer graphene to be extremely high (i.e., 4840-5300 W/mK) [133, 134]. Due to this high thermal conductivity, graphene can be used as a material for heat dissipation and thermal management in electronic applications.

2.1.4 Processing of Metal-CNT/GNP Nanocomposites

The processing of graphene/carbon nanotube (CNT) reinforced metal matrix composites is rather challenging due to harsh processing conditions (i.e., high temperature and high pressure) [17]. The main challenges involved in the processing of metal matrix-CNT/GNP composites are [6, 17]:

(a) Homogeneous dispersion of carbonaceous reinforcing materials (CNT/GNP) into the metal matrix

(b) Strong interfacial bonding between CNT/GNP and metal matrix

(c) Retention of chemical and structural stability of carbonaceous materials (CNT/GNP)

The main processing techniques currently employed for the fabrication of metal matrix-CNT/GNP nanocomposites include powder metallurgy, melting and solidification,
electrochemical deposition, and thermal spray, as shown in Fig. 2.3. Each of the main processing routes can be further sub-categorized. For example, the powder metallurgy route includes all of mechanical alloying and sintering, mixing/mechanical alloying and hot pressing, spark plasma sintering, and deformation processing of powder compacts.

**Fig. 2.3** List of different processing routes of metal matrix-CNT composites [6].

Melting and solidification as another case in point can be divided into casting, metal infiltration, melt spinning, and laser deposition. As well, Thermal spray includes plasma spraying and HVOF and cold spraying. And, for a final example, finally electrochemical deposition can
be further subdivided into electrodeposition and electroless deposition. New processing routes, which include molecular level mixing and friction stir processing have developed for obtaining uniform dispersion of CNTs/GNPs into metal matrix. Among all the processing routes mentioned above, powder metallurgy is the most widely used processing technique due to its simplicity, flexibility, and near-net shape capability [6, 17].

2.1.4.1 Powder Metallurgy Processing

Powder metallurgy is the most widely used processing technique for the fabrication of metal-CNT/GNP nanocomposites due to its simplicity, flexibility, and near-net shape capability [6, 17]. Nearly the majority of metal (Cu, Al, W-Cu, Mg, Ag, Ni)-CNT composites were prepared using this technique [6]. The basic processing steps involved in this technique are:

(a) Mechanical alloying/grinding/mixing CNTs/GNPs with metal powder followed by
(b) Consolidation by compaction and sintering, cold isostatic pressing, hot isostatic pressing, or spark plasma sintering (SPS).

In certain cases, post-sintering deformation techniques such as hot extrusion, hot forging, hot rolling, friction stir processing, and equal channel angular (ECAP) processing were applied to increase the densification of composites. Very expensive raw material powder is the main obstacle of powder metallurgy process.

Mechanical alloying is a solid state processing of powder materials at room temperature to synthesize a metal matrix composite with homogeneous dispersion of CNTs into metal matrix. In order to improve the interfacial bonding, CNTs are coated with nickel, through electroless deposition, mixed with copper powder, followed by compaction and sintering of Cu-CNT
composites. Homogeneous dispersion of CNTs was observed in the composites due to this pre-treatment on CNTs [6]. In order to avoid agglomeration of CNTs due to poor van der Waals forces between them, wet mixing was also an effective technique. Wet mixing technique involves dispersion of metal powder and CNTs/GNPs in certain organic solvents (e.g., such as ethanol, acetone). This composite powder mixture was then dried followed by mechanical alloying [17]. Yang et al. achieved homogeneous dispersion of CNTs into Mg metal matrix by using wet mixing [135]. Wang et al. prepared Al-0.3 wt.% GNP composite using wet mixing and found uniform dispersion of GNPs into aluminum matrix [136]. Mg-CNT and Fe₃Al-CNT composites were processed via mechanical alloying and hot pressing and have shown significant improvement in mechanical properties (e.g., hardness, compressive strength, and bend strength) due to homogeneous distribution of CNTs into metal matrix as well as grain refinement. This grain refinement is mainly associated with grain growth inhibition caused by interlocking CNTs [17]. Dispersion of CNTs/GNPs in the starting composite powder plays an important role in their dispersion into metal matrix because subsequent compaction, sintering, and hot pressing do not affect and improve the dispersion of carbonaceous materials [17]. Uniform dispersion of CNTs into metal matrix processed via mechanical alloying mainly depends on types of nanotubes, functionalization of nanotubes, nanotube content, matrix material, and milling time [17]. Mg-CNT nanocomposites fabricated using mechanical alloying followed by sintering and hot pressing showed improvement in mechanical properties [137-146].

Titanium and titanium alloys possess several excellent properties, such as high melting point, low density, high tensile strength, good biocompatibility, and good corrosion resistance which make them suitable for aerospace and automotive applications, chemical processing plants, marine and biomedical engineering sector, but on the other hand, they have low wear
resistance and low mechanical strength at high temperature. To overcome these drawbacks, CNT/GNP reinforced into titanium matrix will be a good option. Kondoh et al. fabricated Ti-CNT composites by SPS and found uniform dispersion of CNTs into titanium matrix [147]. Similar to titanium, copper has excellent electrical and thermal conductivity but has poor mechanical properties. If this issue can be overcome, copper will prove an ideal material for heat sink applications for electronic devices. Its mechanical strength can be improved by reinforcing CNTs and GNPs into the copper matrix. Hong et al. fabricated nanocomposites using ball milling followed by park plasma sintering. The composites exhibited significant improvement in mechanical properties as compared to pure copper [148, 149]. Cu-CNT composites were mainly processed via the powder metallurgy technique [86, 87, 150-153]. The interfacial bonding between Cu-Cr alloy and CNT significantly improved, by the formation of thin Cr$_2$C$_3$ carbide layer at Cu-Cr matrix and CNT interface [154]. The new approach of coating the CNTs with metal powder and sintering to obtain metal-CNT composite showed significant improvement in interfacial bonding strength between metal matrix and CNT [150, 153, 155, 156].

Spark plasma sintering (SPS) is a novel-processing tool to fabricate the metal-CNT/GNP nanocomposites. In SPS process, a local high-temperature state is generated when spark discharges in a gap or at the contact point between the particles of powder help the evaporation and melting on the surface of powder particles to obtain a fully dense nanocomposite. SPS is a high-speed powder sintering technology capable of processing materials and utilizes uniaxial force and ON-OFF direct current (DC) pulse energizing. Consolidation of nanopowders is possible in SPS without excessive grain growth due to the high heating rates and lower sintering times and temperatures involved. The detailed overview of spark plasma sintering (SPS) is given in the subsequent chapter. Kim et al. first reported the fabrication of Cu-CNT composites
processed via SPS, shown uniform dispersion of CNTs with improved density [148, 149]. Hong’s group also fabricated Cu-GNP, Al-Cu-CNT composites processed via SPS, which exhibited significant improvement in their mechanical properties [157-159]. The main reasons in the improvement in the mechanical properties are (a) uniform dispersion of CNTs into metal matrix and (b) strong metal-CNT interfacial bonding.

Cu-CNT and Al-CNT composites fabricated via deformation processing of powder compacts route exhibited improvement in density as well as in dispersion of CNTs into metal matrix. Significant improvements in wear resistance and strength was observed in rolled Cu-CNT composites rather than Cu-CNT processed via extrusion route. Cu-CNT composites processed via equal channel angular processing exhibited uniform dispersion of CNTs into metal matrix with an increasing number of passes [6].

Uniform dispersion of CNTs into metal matrix and interfacial bonding between CNT and metal matrix are the two main issues associated with powder processing of metal-CNT composites. Efficient mixing techniques and shorter sintering time can effectively overcome these issues. Ball milling or mechanical alloying can significantly help to homogenize uniform dispersion of CNTs into metal matrix. But, it is found that the benefits obtained from this ball milling process can be easily lost in the later consolidation stages. Spark plasma sintering looks to be a promising tool and to be widely used for consolidation of metal-CNT/GNP nanocomposites with uniform dispersion of CNTs into metal matrix and with strong interfacial bonding between metal matrix and CNT/GNP.
2.1.4.2 Melting and Solidification Technique

The melting and solidification technique is the most economical, simple, and conventional processing route for fabricating metal-CNT/GNP nanocomposites. But still there are many limitations in their practical applications due to the difficulty in achieving homogeneous dispersion of CNTs/GNPs into metal matrix, poor wetting of carbonaceous materials (CNT/GNP), preferential formation of interfacial products, and the high temperature required for melting [6, 17]. This melting and solidification route is further sub-categorized into casting, metal infiltration, metal spinning, and laser deposition. Due to the requirement of a high temperature for melting, this technique is particularly suitable for composites having low melting point matrices [6].

Magnesium (Mg) exhibits low density, good damping properties, and excellent castability, which make it suitable for structural engineering applications. But it has poor mechanical strength and poor creep and corrosion resistance. This low mechanical strength of Mg can be improved by reinforcing CNTs/GNPs into Mg matrix. There is an increasing demand for and interest in Mg in automotive and aerospace applications due to its lighter weight. Mg-CNT composites fabricated through melting and casting route exhibited significant improvement in mechanical properties [6]. Li et al. [160] synthesized Mg-CNT composites via liquid state ultrasonic processing and solid state stirring; the schematic of the process is shown in Fig. 2.4. The Niobium probe helps to breakdown the clusters of CNTs and brings about homogeneous dispersion of CNTs into metal matrix. A subsequent fabrication treatment, such as friction stir processing will additionally help to obtain homogeneous dispersion of CNTs into metal matrix [17]. Gupta et al. fabricated many Mg base composites via liquid processing routes and observed significant improvement in mechanical properties such as yield strength and ultimate tensile
strength [161-166]. The wetting behavior of molten aluminum on carbon significantly improved after coating CNT or GNP with metal (Cu, Ni, Si) [167, 168]. These coated CNTs then used to fabricate Al-CNT composites showed good improvement in wetting behavior as well as in mechanical properties.

![Diagram](image)

**Fig. 2.4** (a) Melt stirring and (b) pressureless infiltration facilities [17].

The basic steps involved in the metal infiltration process are two: (1) preparation of a porous solid structure with homogeneously dispersed CNTs and (2) infiltration of molten metal into the porous structure followed by solidification in order to obtain a fully densed composite structure [6, 17]. Mg-CNT and Al-CNT composites are widely fabricated through this technique,
exhibiting good improvement in the mechanical properties due to homogeneous dispersion of CNTs into metal matrix.

Our research group has pioneered laser processing for fabricating Ni-CNT and Ni-graphite composites [169-171]. Both the composites were fabricated via mixing of elemental blend nickel powder with CNTs/graphite followed by laser deposition using laser engineering net shaping (LENS™) equipment. A detailed overview of the LENS™ process is explained in later chapters. In Ni-graphite composites, graphite was dissolved in liquid metal and reprecipitated as primary and eutectic graphite. In Ni-CNT composites, MWNT retained their identity, as CNTs are more stable structures than graphite. But there is an increment in the graphitization of CNTs and their defect density.

The main issues in all the above-mentioned liquid processing routes are poor dispersion of CNTs into metal matrix and poor interfacial bonding between CNT and metal matrix. All these melting routes have a high chance of agglomeration of CNTs, mainly due to large density difference between CNT and metal. Therefore, powder metallurgy, being a solid state processing, has the advantage of obtaining the metal-CNT/GNP composites with both better dispersion of CNTs/GNPs into metal matrix as well as stronger metal-CNT interfacial bonding.

2.1.4.3 Thermal Spray Technique

Thermal spray technology has been widely used in aerospace blades, orthopedic prostheses, automotive engines, and electronic devices [172-176]. This technique consists of spraying the molten or semi-molten particles onto a substrate to form a coating or deposit via impact and solidification. A nanocrystalline structure was obtained using thermal spray technique due to high cooling rate $10^8$ k/s [6]. Thermal spray technique was further
subcategorized into flame spraying, plasma spraying, high velocity oxy-fuel (HVOF) spraying, and cold spraying based on the heating source employed during process. The schematic diagrams of plasma spray and high velocity oxy fuel (HVOF) spray are shown in Fig. 2.5 and 2.6, respectively. In plasma spraying technique, heat source is a plasma created by ionization of inert gas between tungsten cathode and copper anode whereas, in HVOF process, heat source is a high-pressure combustion of a fuel-oxygen mixture. The gaseous fuel used will be methane, propane, propylene gas, and the liquid fuel used will be kerosene. From the heat source the composite powder particles will absorb the heat as well as the kinetic energy and projected onto the substrate with very high velocities. (1000m/s: Plasma spraying, 1500m/s: HVOF). Agarwal et al. fabricated metal-CNT composites via plasma spray, HVOF spraying, and cold spraying techniques [6, 172-176].

![Fig. 2.5 Schematic of plasma spray facility [17, 172].](image-url)
Al-Si-CNT composites fabricated using spray forming techniques exhibited uniform dispersion of CNTs into metal matrix. The composites processed via HVOF technique exhibited higher hardness and elastic modulus values as compared to plasma spray technique. Due to very high temperatures present in the thermal spraying technique that leads to structural changes of CNTs [177], these changes can be avoided by employing cold spray technique. In the cold spray technique, powder particles were accelerated to a very high velocity (500-1200 m/s) at a lower temperature. This kinetic energy of particles was then converted to plastic deformation energy when impacted on substrate, and lead to good adhesion and bonding of particles on the substrate [178]. Bakshi et al. fabricated Al-CNT composites using this technique [6, 176]. The composite exhibited uniform distribution of CNTs into Al matrix as well as improved interfacial bonding due to the formation of Al₄C₃ or SiC thin layer at the interface.
2.1.4.4 Electrochemical Route

Electrochemical route is the second most widely used technique for fabricating metal-CNT/GNP composites after the powder metallurgy route. The electrochemical deposition technique is mainly used for fabrication of composite coatings rather than bulk composites. This technique is widely used for coating metal on CNTs, which can be used as nano-sensors, electrodes, inter-connects, and magnetic recorder heads in computer applications. Electrodeposition technique is broadly classified as direct current (DC), pulse current (PC) and pulse reverse current (PRC) electrodeposition based on nature of current supplied during deposition process [179]. Pulse electrodeposition offers many advantages over direct current electrodeposition, such as uniform deposition and high deposition rate. Grain size, microstructure, and chemistry of the coating are mainly governed by electrodeposition parameters such as peak current density, frequency, and duty cycle as well as electrodeposition conditions such as bath composition, temperature, pH, and electroplating time [17]. Electrodeposition technique is widely used to fabricate Ni-CNT and Cu-CNT composite coatings [6, 17]. CNT content in the coating increases with increasing CNT content in electroplating bath [6]. The electroplating bath used for nickel coating is termed as “Watts Bath”, which mainly contains the solution of nickel sulfate, nickel chloride, and boric acid. Ni-CNT composite coating exhibited improved microhardness as well as wear resistance compared to pure nickel coatings mainly due to homogeneously dispersed CNTs into nickel matrix [180]. In Co-deposition of metal-CNT coatings, homogeneous dispersion of CNTs in the bath and good suspension plays an important role in obtaining uniform distribution of CNTs into composite coatings [6]. Surfactant addition also helps in functionalizing CNTs and achieving uniform dispersion of CNTs into composite coatings [180-182].
Electroless deposition is a chemical technique in which coatings are deposited onto a surface by decomposition of metal by catalytic action, without application of any current [6]. This technique has been widely used to fabricate Ni-P composite coatings. Ni-P composite coatings exhibit excellent properties, such as corrosion and wear resistance, uniformity of coating thickness on complex shapes and have therefore found many industrial applications. CNTs are used as reinforcement in Ni-P coatings to improve their wear resistance further, due to CNTs self-lubricating behavior [183-188].

Both electrodeposition and electroless deposition techniques are mainly suitable for fabrication of thin composite coatings, not of bulk composites. There are two main challenges that to be overcome if to obtain better composite coatings: (1) uniform dispersion and (2) suspension of CNTs in the electroplating bath/ electrolyte. PC and PRC electrodeposition techniques have the following advantages and disadvantages over DC electrodeposition technique [179]:

**Advantages:**

- Limiting current density significantly increases by replenishing metal ions in the diffusion layer only during off time.
- Flexibility in pulse parameters reduces the process limitations.
- Fine-grained deposit with lower porosity and reduced stress.
- Improved adhesion of deposit creates uniform thickness.
- Higher rate of deposition improvements in physical and mechanical properties.

**Disadvantages:**

- Pulse generators are more expensive than DC unit.
• This technique needs proper advance planning with a series of procedures ready, in order to attain better results.

2.1.4.5 Molecular Level Mixing Process

Hong et al. group has pioneered molecular level mixing technique for synthesis of metal (Cu, Ni, Al-Cu)- CNT/GNP composite powders. The process of fabricating metal/CNT composite powders using molecular level mixing consists of four steps. First, CNTs produced by thermal chemical vapor deposition (CVD) process are dispersed in ethanol to make a stable suspension by functionalizing the CNT surfaces. The electrostatic repulsive force between the CNTs overcomes the Vander Waals force to obtain stable suspension within solvent due to functionalization of CNTs. Second, a salt containing Ni ions is dissolved in the CNT suspension. Additional ultrasonication helps the dispersion of Ni ions among the suspended CNTs and promotes a reaction between the Ni ions and functional groups on CNT surfaces. The third step is to dry the mixture by heating to remove the solvent and ligands, and leads to Ni ions on the CNTs getting oxidized to form powders. The fourth and final step is the calcination and reduction process to obtain chemically stable CNT/Ni composite powder. Reducing agents directly used in the bath to avoid final step of reduction of metal-CNT composite powder [6]

Steps involved in the processing of molecular level mixed Ni-CNT composite powder is schematically shown in Fig. 2.7. The fabrication of CNT/Ni (MLM) composite powders begins with purification and functionalization of CNTs using HF and acid solution mixture of H₂SO₄ and HNO₃. CNT/Ni precursors were prepared through a chemical reduction process, using hydrazine hydrate as reducing agent, sodium hydroxide as oxidation agent, and ethylene glycol
as solvent. Finally, CNT/Ni composite powders are obtained by reduction process in H₂ and CO mixed atmosphere for 2 hours at 400° C.

**Fig. 2.7** Schematic diagram showing experimental steps for molecular level mixing process of CNT/Ni powders [189].

The fabrication of CNT/Ni (MLM) composite powders begins with purification and functionalization of CNTs using HF and acid solution mixture of H₂SO₄ and HNO₃. CNT/Ni precursors were prepared through a chemical reduction process, using hydrazine hydrate as reducing agent, sodium hydroxide as oxidation agent, and ethylene glycol as solvent. Finally, CNT/Ni composite powders are obtained by reduction process in H₂ and CO mixed atmosphere for 2 hours at 400° C [189].
Hong et al. fabricated Cu-CNT composites using molecular level mixed composite powder followed by spark plasma sintering, which exhibited about 3 times increment in yield strength as compared to pure copper, mainly due to uniform dispersion of CNTs into metal matrix [190]. CNTs exhibited the most effective strengthening efficiencies among all other reinforcements. Similarly Al-Cu-CNT composites fabricated using molecular level mixing, followed by SPS process, exhibited significant improvement in yield strength as compared to Al-Cu alloy with 30% enhancement in the elastic modulus of the composite [159].

Hwang et al. processed Ni-CNT composites via molecular level mixing of Ni-CNT composite powder followed by SPS exhibited significant improvement in yield strength (about 3.7 times) as compared to pure nickel [189]. This significant improvement in mechanical properties is mainly attributed due to homogeneous dispersion of CNTs into nickel matrix, as well as to a very sharp and clean Ni-CNT interface without any interfacial reaction that leads to a strong Ni-CNT interfacial bonding.

Recently, Hong’s group fabricated Cu-GNP composites via molecular level mixing of Cu-GNP composite powder followed by spark plasma sintering, which exhibited almost 2 times improvement in yield strength as compared to pure copper due to homogeneous dispersion of GNP into copper matrix as well as strong Cu-GNP interfacial bonding [157]. Reported elastic modulus and the yield strength values for Cu-2.5 vol% GNP composite values are 131 GPa and 284 MPa, respectively. This significant improvement in Cu-GNP composite leads to GNP as a potential candidate for the reinforcement of metal matrix nanocomposites.
2.1.4.6 Other Techniques

Metal-CNT/GNP composites also fabricated via sputtering techniques, sandwich processing, torsion/ friction welding, and vapor deposition process. Huang et al. deposited several metal coatings on CNTs using sputtering technique and found Ti, Mo, and Zr metals to have a strong interfacial bonding with CNT, but in contrast Ag, Au, and Cu were found to have a very weak bonding with CNTs [6]. Al-CNT composites fabricated using this technique exhibited \( \text{Al}_4\text{C}_3 \) formation at the interface, which leads to significant improvement in mechanical properties of composites. In sandwich processing, metal matrix-CNT composites were synthesized by putting them in layers of either CNT or GNP alternatively with a layer of metal followed by consolidation of the sandwich composite using high pressure. Cu-CNT composites fabricated via this sandwich technique exhibited significant improvement in young’s modulus of the composites. Recently, Kim et al fabricated Ni/Cu-graphene nanolayered composite via a sandwich technique exhibited significant enhancement in strength (1.5 GPa- Cu/graphene, 4.0 GPa- Ni/graphene) of composites due to effectiveness of graphene in blocking dislocation movement across the metal-graphene interface [191]. Metal-CNT composites also fabricated via torsion/ friction welding process. Al-CNT composites fabricated using torsional force of 2.5 GPa and 1 rpm rotation speed exhibited good improvement in a grain refinement obtained by constraining dislocation movement towards the grain boundary, due to the presence of CNTs [6]. Mg-CNT composites fabricated using frictional force with various travel speeds. Uniform dispersion of CNTs into Mg matrix was obtained for a low travel speed of the tool due to increase in mixing time [6].

Hwang et al. deposited nickel coating on vertically aligned CNTs via the physical vapor deposition (PVD) technique [192]. A 3D atom probe tomography coupled with high-resolution
transmission electron microscopy and with the help of density functional theory (DFT) calculations, observed the formation of Ni$_3$C at the nickel-CNT interface. The CNTs not only act as template for the nickel nanocystal but provides a source of carbon. This is the only report found in the literature, which clearly showed the Ni$_3$C formation at the nickel-CNT interface using both experimental and theoretical approaches. Si-CNT composite fabricated via the chemical vapor deposition (CVD) technique has a potential application as lithium-ion battery anode [6].

From all of the above discussion on processing of metal-CNT composites, two main challenges are known to exist in their processing: achieving (1) homogeneous dispersion and (2) good reinforcement of CNTs into metal matrix. Electrodeposition is very simple and attractive technique in terms of achieving uniform dispersion of CNTs into composite coatings, but the only limitation is, this technique is best suited for the deposition of composite coatings, rather than for bulk composites. Liquid processing routes are a good option for low melting alloy matrix, but one very difficult for achieving homogeneous dispersion of CNTs into metal matrix due to large density difference between metal and CNT/GNP. Thermal spray techniques serve as good processes for obtaining metal-CNT composites as they offer many advantages such as rapid solidification as well as rapid prototyping over liquid processing routes. Powder metallurgy is the best, most widely used, and most feasible technique for fabricating metal-CNT/GNP composites, but still it needs some modifications in order to achieve homogeneous dispersion of CNTs into metal matrix. Molecular level mixing of metal-CNT/GNP composite powder followed by spark plasma sintering is an good option to overcome the issue of uniform dispersion of CNTs, but the lengthy synthesis time to obtain MLM mixed composite powder is an obstacle for large scale production.
2.1.5 Strengthening Mechanisms in CNT/GNP Reinforced Composites

The main objectives of addition of CNTs/GNPs into metal matrix are to enhance the tensile strength as well as elastic modulus of the metal matrix composite. The processing routes play an important role in achieving effective metal-CNT/GNP interfacial stress transfer during the mechanical test which is mainly governed by stiffening and strengthening effects of the CNTs/GNPs [17]. Load transfer efficiency of CNTs depends on the aspect ratio, uniform dispersion of CNTs/GNPs into metal matrix, and the formation of interfacial product [193]. Hall-petch effect due to (1) grain refinement, (2) orowan looping, and (3) dislocation generation due to thermal mismatch between CNT/GNP and metal matrix, also contribute to the strengthening effect of metal-CNT/GNP nanocomposites [6, 17]. For the development of advanced composites for structural applications, basic understanding of the strengthening mechanisms in CNT/GNP reinforced composites is essential. Several micromechanical models, such as cox model, combined voigt-reuss model, halpin-tsai equations, modified eshelby model, dispersion based model, and shear lag model have been developed to determine mechanical properties of CNT/GNP reinforced metal-matrix composites [6, 17]. Micromechanical models calculate the mechanical properties based on properties and geometries of individual materials in the composites.

2.1.5.1 The Cox Shear-Lag Model

This model assumes the short fibers are reinforced in the matrix with strong interface and are in tension along the fiber direction [17]. The applied stress is transferred from matrix to the fiber through interfacial shear stress ($\tau$). Tensile stress is maximum at fiber center and zero at the ends of fiber. Elastic modulus of composite is given by equation1:
\[ E_c = \eta E_f + E_m (1 - V_f) \]  

(1)

Where, \( E_f \) = fiber modulus

\( E_m \) = matrix modulus

\( V_f \) = fiber volume fraction parameter is given by:

\[ \eta = \text{parameter is given by equation 2:} \]

\[ \eta = [1 - \frac{\tanh(\beta a)}{\beta a}] \]  

(2)

Where, \( a = l/d \) (aspect ratio of fiber with length and diameter) and

\[ \beta = \sqrt{\frac{2E_m}{E_f(1+n_m)\ln(1/V_f)}} \]  

(3)

Where, \( n_m \) = poisson’s ration of the matrix.

The maximum stress transfer to the fiber is mainly depends on critical length \( (l_c) \) such that,

\[ \text{Maximum stress in the fiber} = \text{ultimate fracture strength of fiber} \ (\sigma_{fu}) \]

Fiber critical length is related with ultimate fracture strength of fiber considering shear stress at the interface is constant and is given by equation 4:

\[ \frac{l_c}{d} = \frac{\sigma_{fu}}{2\tau} \]  

(4)

Where, fracture strength of the composite is given by equation 5 and 6:

\[ \sigma_c = \tau \left( \frac{1}{d} \right) + \sigma_m \left( 1 - V_f \right) \quad \text{for} \ l < l_c \]  

(5)

\[ \sigma_c = \sigma_{fu} V_f \left( 1 - \frac{l_c}{2l} \right) + \sigma_m \left( 1 - V_f \right) \quad \text{for} \ l > l_c \]  

(6)
where, $\sigma_m$ = tensile strength of matrix.

For $l < l_c$: Fiber can reach its maximum strengthening efficiency

For $l > l_c$: Maximum stress in the fiber may never reach $\sigma_{fu}$. Fiber will not experience fracture and composite eventually fails by the matrix tensile failure.

The strength of the composite considering critical fiber length is given by equation 7:

$$\sigma_c = \sigma_f V_f \left(\frac{l}{l_c}\right) + \sigma_m \left(1 - V_f\right) \text{ for } l < l_c$$  \hfill (7)

2.1.5.2 Shear-Lag Model

The strength of composite taking effect of fiber orientation into account is given by equation 8 [17]:

$$\sigma_c = \frac{V_f \sigma_m a_{eff}}{2} + \sigma_m$$  \hfill (8)

Where, $a_{eff}$ = effective aspect ratio of fiber obtaining through the modification of the aspect ratio ($a$) with an orientation angle $\theta$ respect to the loading axis i.e.

$$a_{eff} = a \cos^2 \theta + \left(\frac{3\pi - 4}{3\pi}\right)(1 + \frac{1}{a}) \sin^2 \theta$$  \hfill (9)

Kim et al. observed two step yielding behavior in Cu-CNT composites fabricated via ball milling followed by spark plasma sintering process [194]. This two-step yielding behavior is mainly due to difference in yield strength values of copper and CNT. Tensile behavior of Cu-CNT composite was analyzed using shear-lag model, which derived from load-transfer theory between copper (matrix) and CNT (reinforcement) in the composites. $\sigma_{y,1}$ and $\sigma_{y,2}$ are the
primary and secondary yield strength associated with the matrix and composite respectively. The matrix yield strength is given by equation 10:

$$\sigma_{y,1} = \frac{\nu_f \sigma_m}{2} S_{eff} + \sigma_m$$

(10)

where,

$$S_{eff} = S \cos^2 \theta + \left(\frac{3\pi - 4}{3\pi}\right)(1 + \frac{1}{S}) \sin^2 \theta$$

(11)

Where, $S_{eff}$ = effective aspect ratio of misaligned fiber

$\theta$ = misorientation angle between longitudinal axis of fibrous CNT/Cu composite region and loading axis of tensile test.

The probability density function of misorientation angle of fibrous CNT/Cu composites is introduced to obtain an average effective aspect ratio of CNT/Cu composite region, which is given by equation 12:

$$S_{eff,a} = \int_0^{\pi/2} S_{eff}(\theta)F(\theta)(2\pi \sin \theta)d\theta$$

(12)

Where, $S_{eff}$ = average effective aspect ratio

$F$ = probability density function of misorientation angle of fibrous CNT/Cu composite region.

The composite (secondary) yield strength is given simply by using rule of mixture in equation 13:

$$\sigma_{y,2} = \sigma_{y,1}(1 - V_f) + \sigma_f V_f$$

(13)

Where, $V_f$ = volume fraction of fiber
\[ \sigma_f = \text{yield strength of fiber} \]

### 2.1.5.3 Halpin Tsai Micromechanical Model

This model gives the elastic modulus of randomly oriented fiber reinforced composites [17]. Longitudinal modulus \( E_{CL} \) and transverse modulus \( E_{CT} \) of randomly oriented fiber reinforced composite is given by equation 14 and 15:

\[
\frac{E_{CL}}{E_m} = \frac{1+\xi \eta_L V_f}{1-\eta_L V_f} \quad (14)
\]

\[
\frac{E_{CT}}{E_m} = \frac{1+2 \eta_T V_f}{1-\eta_T V_f} \quad (15)
\]

Where, \( E_m = \text{elastic modulus of matrix} \)

\( V_f = \text{volume fraction of fiber} \)

\[
\eta_L = \frac{(E_f/E_m) - 1}{(E_f/E_m) + \xi} \quad (16)
\]

\[
\eta_T = \frac{(E_f/E_m) - 1}{(E_f/E_m) + 2} \quad (17)
\]

Where, \( E_f = \text{elastic modulus of fiber} \)

\( \xi = 2(l/d) \text{ for fiber and } (2l/3t) \text{ for sheet like fiber, where } t = \text{thickness} \)

Elastic modulus of randomly oriented fiber reinforced composite is given by equation 18:

\[
E_{\text{random}} = \frac{3}{8} E_{CL} + \frac{5}{8} E_{CT} \quad (18)
\]
2.1.5.4 Combined Voigt-Reuss model

Elastic modulus of randomly oriented fiber reinforced composite is given by equation19 [6]:

\[ E_{\text{Random}} = \frac{3}{8} E_{CL} + \frac{5}{8} E_{CT} \]  

(19)

Where, \( E_{CL} = V_f E_f + (1 - V_f) E_m \)  

(20)

\[ E_{CT} = \frac{E_f E_m}{E_f (1 - V_f) + E_m V_f} \]  

(21)

\( E_{CL} \) = Longitudinal modulus (along the direction of fiber)

\( E_{CT} \) = Transverse modulus (along the direction normal to fiber)

2.1.5.5 Dispersion Based Model

All the above-mentioned micromechanical models calculate the mechanical properties of metal matrix-CNT composites assuming uniform dispersion of CNTs into metal matrix. But this cannot be valid for every metal-CNT composite. As many of the metal-CNT composites processed via powder metallurgy route exhibited CNT clusters rather than uniformly distributed individual CNTs. Viloria and Miravete have developed mathematical model considering clustering phenomenon of CNTs into metal matrix composite and calculated values were much more accurate as compared to Cox model, also were closely matched with that of experimentally obtained values [195]. Bulk modulus of the composite is given by equation 22:

\[ k_{dsc} = k_m + \frac{(k_{\text{cluster}}-k_m)C_c}{1 + \frac{k_{\text{cluster}}-k_m}{k_m + 4\mu_m/3}} \]  

(22)
\[ \mu_{dsc} = \left[ 1 - \frac{15(1-\nu_m)(1-\frac{\mu_{cluster}}{\mu_m})C_c}{7-5\mu_m+2(4-5\mu_m)\frac{\mu_{cluster}}{\mu_m}} \right] \]  

(23)

where, \( k \) and \( \mu \) stands for bulk modulus and rigidity modulus

\( C_c \) refers to volume fraction of clusters which is related to overall CNT fraction

\[ V_f = C_f C_c \]

where, \( C_f = \) CNT concentration in of a cluster.

All of the above-mentioned micromechanical models are taken CNTs with large aspect ratios and high mechanical stiffness as short fiber reinforcements are taken into account. Also, both CNTs and matrix are considered to be a continuum. The predicted mechanical properties of the composites using these micromechanical models sometimes are misleading, as microstructure and dispersion of CNTs are not taken into account. The load transfer efficiency of CNTs is mainly by nanotube morphology including diameter and chirality as well as the CNTs dispersion into matrix. Therefore, in order to predict accurate mechanical properties of metal-CNT composites, there is a need to consider the structure of CNTs in the design of micromechanical model.

2.1.5.6 Metallurgical Factors

The CNT/GNP addition helps for achieving grain refinement of metal matrix. The yield strength of metals is given by using the Hall-Petch relationship [17]:

\[ \sigma_m = \sigma_o + bd^{-1/2} \]

(24)

Where, \( d = \) grain size

\[ \sigma_o = \) friction stress}
\[ b = \text{Hall-Petch slope} \]

The dislocations generated due to the mismatch of elastic modulus and co-efficient of thermal expansion between matrix and reinforcement (CNT/GNP) also contribute to the strengthening of the composites. The strengthening of composite is given by equation 25:

\[ \Delta \sigma_y = \alpha G b \rho^{-1/2} \]  

(25)

Where, \( \alpha = \text{constant} \)

\( G = \text{shear modulus} \)

\( b = \text{burger vector of dislocations} \)

\( \rho = \text{density of dislocations} \)

CNT reinforcement in the composites restricts the dislocation motion during mechanical testing and leads to dislocation bowing and subsequent formation of dislocation loops around CNT, i.e., an Orowan looping mechanism. Orowan stress is given by equation 26:

\[ \tau_y = \frac{0.84 M G b}{(L_m - s)} \]  

(26)

Where, \( \tau_y = \text{Shear yield stress} \)

\( M = \text{Taylor factor (~3)} \)

\( b = \text{burger vector} \)

\( s = \text{size of particle} \)

\( L_m = \text{mean-interparticle distance.} \)
2.1.6 Mechanical Properties

The mechanical properties of metal matrix-CNT/GNP composites are mainly governed by uniform dispersion of CNTs into metal matrix, interfacial reaction, and interfacial bonding between metal and CNT. Therefore, processing routes play an important role in achieving good mechanical properties of metal-CNT composites. This section is focuses on mechanical properties of CNT/GNP reinforced metal matrix (Al, Mg, Cu, and Ni) composites.

Al-GNP composites fabricated via powder metallurgy followed by sintering process exhibited improvement in hardness and compressive strength of the composites with increasing GNP content [196]. Wang et al synthesized Al-graphene composites using wet mixing followed by sintering and extrusion [136]. The composite exhibited significant improvement in tensile strength mainly due to efficient stress transfer across the matrix-graphene interface and strong interfacial bonding. Kwon et al. also fabricated Al-CNT composites via wet chemical mixing followed by spark plasma sintering [197]. There is a significant improvement in tensile strength due to homogeneous dispersion of CNTs into aluminum matrix. Al-CNT composites processed via simple ball milling followed by sintering exhibited about 25% increment in yield strength and elastic modulus of composites due to the addition of 2 vol% CNT as compared to pure aluminum [146]. Proper selection of ball milling times factors largely in the improvement in mechanical properties of Al-CNT composites. It was observed that yield strength and elastic modulus of composite increases with milling time, mainly due to grain refinement and strain hardening effect. Elastic modulus and yield strength of composites also increases with increasing CNT content due to a strengthening and toughening behavior of CNTs [198]. Matrix grain refinement significantly contributed to (1) the enhancement of yield strength of composites and (2) to the compromised work hardening capacity. All of the above-mentioned studies showed
load transfer and grain refining mechanisms significantly contribute to the improvement in the strength of the composites. Wet mixing process was found very beneficial in achieving homogeneous dispersion of CNTs into metal matrix [199]. This homogeneous dispersion of CNTs is very important in the improvement in strength and stiffness of aluminum-CNT composites. Various researchers fabricated Al-CNT composites via simple powder metallurgy followed by sintering and/or hot deformation [6, 17, 139, 146, 197, 199, 200]. Al-10vol% CNT exhibited about 100% improvement in tensile strength. There is a 350% increase in yield strength of Al-1.6vol% CNT composites processed via nano scale dispersion method due to homogeneous dispersion of CNTs into aluminum matrix. So, homogeneous dispersion of CNTs and strong metal-CNT/GNP interfacial bonding mainly governed the mechanical properties of metal-CNT/GNP composites [6].

Bakshi et al. studied various Al-CNT nanocomposites fabricated by a powder metallurgy process and compared the experimentally determined mechanical property values with the theoretically calculated values using several micromechanical models as shown in Fig. 2.8 [201]. The values for $E_m = 69 \text{ GPa}$, $E_f = 1 \text{ TPa}$, poisson’s ratio $\nu_m = 0.33$ and $\nu_f = 0.3$, were used for the theoretical calculation. For MWNT up to 2 vol%, experimentally determined values were accurately matched with the calculated voigt micromechanical model values. For MWNT content between 2-5vol%, the experimentally determined values matched with the theoretically calculated Halpin-Tsai and combined voigt-reuss model values. The Cox model gave a poor prediction of mechanical property values as compared to experimentally measured values. Normalized tensile strength and yield strength versus MWNT content in MWNT/Al composites are shown in Fig. 2.9. Homogeneous dispersion of CNTs is very essential to improve the tensile
strength of composites. At higher CNT content, mathematical models gave poor predictions, as they were not taking into account the clustering phenomenon of CNTs.

**Fig. 2.8** Variation of normalized elastic modulus with MWNT content of MWNT/Al composites and Al samples prepared by identical processing route [201].

**Fig. 2.9** Variation of normalized strength (UTS or fracture strength, yield strength) with MWNT content of MWNT/Al composites and Al samples prepared by identical processing route[201].
Fig. 2.10 (a) Yield strength vs volume content for ATCNT/Al–Cu and PCNT/Al–Cu composites
and (b) elastic modulus vs volume content for ATCNT/Al–Cu and PCNT/Al–Cu composites. Predicted elastic moduli from generalized shear-lag model with different effective aspect ratios are shown in dash lines[159].

Hong et al. fabricated Al-Cu/CNT composites via molecular level mixing followed by a spark plasma sintering process [159]. Two types of CNTs (acid functionalized nanotube:
ATCNT and PVA coated CNT: PCNT) were used to compare the effect of aspect ratio of CNT on the mechanical properties of metal-CNT composites. Variation in yield strength of composites with respect to CNT content is shown in Fig. 2.10, which is very linear due to homogeneous dispersion of CNTs, there is effective load transfer across the matrix-CNT interface. Experimental values of elastic modulus accurately matched with the theoretically calculated values via the shear-lag model by taking the aspect ratio of CNT as 10 and 30, respectively. In addition to CNT effect, precipitation-hardening effect in the improvement in yield strength of composite is also clearly shown in Fig. 2.10.

Mg-CNT/GNP composites are fabricated by both the liquid processing route as well as the conventional powder metallurgy route. Liu et al. fabricated Mg-CNT composites via mechanical stirring, and high intensity ultrasonic processing exhibited good enhancement in yield strength, tensile strength, and ductility due to the presence of CNTs to bridge the propagating cracks effectively during mechanical tensile testing[202]. Zeng et al. processed Mg alloy-CNT composites via liquid processing routes and found there was reduction in the mechanical properties as CNT content increases above the critical value due to agglomeration of CNTs [203]. Gupta et al. fabricated Mg-CNT composites via DMD and extrusion process and found such similar results as yield strength, tensile strength, and ductility increases till 1.3 wt% CNT content and there is a reduction in those properties as CNT content increases up to 1.6-2 wt% [165, 204]. CNTs help to improve ductility of Mg-based composites by activating prismatic and cross-slip dislocations in matrix during extrusion. Mg-CNT composites processed via liquid processing routes, such as melting and casting, and powder metallurgy routes exhibited significant improvement in the mechanical properties. Sun et al. synthesized Mg-CNT composites via CVD method exhibited uniform dispersion of CNTs into matrix as well as
improvement in tensile strength of composites [205]. Mg-3 wt% CNT exhibited lower tensile strength as compared to Mg-2.4 wt% CNT due to agglomeration of CNTs; there was no effective load transfer across the metal/CNT interface.

Ti-MWNT composites fabricated via surfactant addition followed by spark plasma sintering and hot extrusion techniques exhibited significant improvement in yield strength and tensile strength of composites due to grain refinement and strengthening contributed by MWNT and TiC particles [147].

Hong et al. fabricated Cu-GNP composites via molecular level mixing followed by spark plasma sintering technique [157]. Cu-2.5 vol% GNP exhibited about 80% increment in yield strength and about 30% increment in elastic modulus as compared to pure copper due to the combined effect of homogeneous dispersion of GNPs into copper matrix as well as strong interfacial bonding between Cu and GNP. Similar groups also fabricated Cu-CNT nanocomposites via molecular level mixing followed by spark plasma sintering technique [190]. Cu-5vol% CNT composites exhibited 2.4 times higher yield strength as compared to pure copper, and Cu-10vol% CNT composites exhibited about 3 times higher yield strength that of pure copper. This significant improvement in yield strength is mainly attributed to strong interfacial bonding between copper and CNT as well as due to grain refinement of copper matrix. The predicted yield strength values by generalized shear-lag model matches accurately with experimentally measured mechanical property values for the aspect ratio 40 and 50. Cu-CNT composites fabricated via simple conventional powder metallurgy techniques exhibited improvement in mechanical properties of composites [6, 17].

Hong et al. processed Ni-CNT composites via molecular level mixing followed by spark plasma sintering route. Ni-6vol% CNT composite exhibited elastic modulus of 210 GPa and
tensile strength of 710 MPa, which were higher than that of pure nickel (elastic modulus: 189 GPa, yield strength: 189 MPa) [189]. This significant improvement in Ni-CNT composites is mainly attributed to uniform dispersion of CNTs into metal matrix and high load transfer efficiency due to a strong and clean Ni-CNT interface without the presence of any interfacial product. Electrodeposited Ni-CNT composites exhibited significant improvement in microhardness due to uniform dispersion of CNTs [6, 17, 179, 180].

2.1.7 Tribological Properties

Generally, ceramic materials are used as reinforcement to improve strengthening of metal matrix composites due to their high hardness. These ceramic reinforced composites exhibited excellent wear resistance, but also have very high coefficient of friction. Carbonaceous materials, such as CNTs and GNP's exhibit high mechanical strength and stiffness as well as self-lubricating behavior, which make them potential candidates to overcome the issue of high-coefficient of friction related with ceramic reinforced composites. CNT/GNP reinforced metal matrix composites exhibit excellent tribological properties, such as high wear resistance and lower coefficient of friction [170, 206, 207].

Zhou et al. fabricated Al-Mg/CNT composites via pressureless infiltration techniques that showed high mechanical strength, stiffness, and hardness as well as weight that loss of composites decreases with increasing CNT content due to the self-lubricating behavior of CNT [207]. Al-CNT composites processed via ball milling and hot rolling technique exhibited very low co-efficient of friction (0.06) as compared to pure aluminum (0.35) [206]. Al-Si-CNT composites synthesized using plasma spray technique showed the reduction in coefficient of friction as compared to Al-12Si alloy [6].
Copper-graphite composites exhibiting good electrical and thermal conductivities and excellent wear resistance are widely used for brushes in industrial motors and generators as an electrical sliding contact [208-212]. Cu-5-20vol% GNP composites processed via powder mixing followed by compaction and sintering showed significant enhancement in the reduction in wear rate and coefficient of friction as compared to Cu-graphite composites [209]. Dong et al. found that Cu-CNT composites exhibited a lower co-efficient of friction and wear rate than that of Cu-carbon fiber composites [213]. Hong et al. fabricated Cu-CNT composites via molecular level mixing followed by spark plasma sintering exhibited reduction in wear rate about 3 orders of magnitude as compared to composites fabricated by conventional sintering process [214].

Banerjee et al. fabricated Ni-CNT composites using a laser engineering net shaping (LENS™) process [169, 170]. Ni-CNT composites exhibited lower co-efficient of friction than pure nickel. CNT bundles were uniformly distributed into nickel matrix. The self-lubricating behavior of CNT leads to formation of graphitic film during sliding significantly lowers the coefficient of friction of Ni-CNT composites. Electrodeposited Ni-CNT composite coatings exhibited better tribological properties, such as low coefficient of friction and less wear rate, due to uniformly distributed CNTs into nickel matrix and the self-lubricating behavior of CNTs. [180, 215-217] Ni-CNT composite coatings deposited via electroless deposition, also showed significant reduction in their coefficients of friction and wear rate [218, 219].

The improvement in tribological properties such as wear resistance and low coefficient of friction is mainly due to the self-lubricating behavior of CNTs. As CNTs avoid the direct contact between matrix and wear pin, they behave as a spacer.
2.1.8 Corrosion Properties

Electrodeposited Ni-CNT composite coatings have been widely studied to determine the corrosion properties of the composites [6]; some scattered corrosion studies have focused on Zn-CNT, Al-CNT, and Al-GNP composites. The formation of a protective passive layer on the surface of metal matrix governed the corrosion resistance of metal matrix composites [17]. Al-GNP nanocomposites fabricated via powder metallurgy route exhibited improvement in corrosion resistance as compared to pure aluminum, which makes the graphene an ideal reinforcing material for inhibition corrosion of metals. Prasai et al. fabricated Ni/Cu-GNP composites by depositing a graphene layer on copper via CVD technique followed by transferring it mechanically onto nickel substrate [220]. Cu-Gr composites exhibited lower corrosion current density and more noble corrosion potential ($E_{corr}$) as compared to pure copper, with significant reduction in corrosion rate as shown in Fig. 2.11. Fig. 2.11 (c) also shows that Ni-Gr corrodes very slowly as compared to pure nickel. Kirkland et al. processed Cu-GNP and Ni-GNP composites via CVD process, which exhibited improvement in corrosion performance due to the addition of GNPs into metal matrix [221]. Zn-CNT composites exhibited twice service life as compared to pure Zn coatings [6]. Addition of CNTs/ GNPs improve the corrosion resistance of composite coatings mainly due to that

(a) CNTs can fill pores in the electrodeposited coatings, leaving almost no place for initiation of localized corrosion.

(b) Passive layer formed on coating surface due to chemical inertness of the CNTs, which help to improve corrosion resistance of metal-CNT composite coatings.
Fig. 2.11 (a) Tafel plots of Cu and Gr/Cu samples in a sodium sulfate solution; inset: Raman spectrum of the Gr/Cu sample after the polarization measurement displays small defect-related D-peaks, (b) corrosion rates of Cu and Gr/Cu samples extracted from Tafel plots; three measurements were made for each Cu and Gr/Cu, and (c) corrosion rates of Ni and samples where graphene was transferred onto Ni substrate [17, 220].
2.1.9 Thermal Properties

Graphene and CNTs exhibited excellent thermal conductivity and very low co-efficient of thermal expansion, which make them candidates to serve as heat sinks for advanced electronic systems. Metal matrix-CNT composites may therefore be suitable for thermal management applications. CNT and GNP addition into metal matrix can significantly improve the thermal properties of metal-CNT composites, such as enhancing thermal conductivity and reducing the co-efficient of thermal expansion. There was a significant improvement in thermal conductivity of electrodeposited Ni-graphene composite coatings as compared to pure nickel [222]. Similarly, jagannadham electroplated Cu-GNP composite coatings on copper substrate, exhibited higher thermal conductivity (440 W/mk) than that of electrodeposited pure copper (380 W/mk) [223]. Tong et al. fabricated Al-SWNT composites via wet powder mixing followed by hot pressing, which exhibited significant reduction in co-efficient of thermal expansion as compared to pure aluminum, and those values decreased with increasing CNT content [224]. Similarly, Deng et al. also reported a significant reduction in the co-efficient of thermal expansion due to addiction of CNTs. There is a decrease in the co-efficient of thermal expansion of Mg from $28.57 \times 10^{-6}$ to $25.90 \times 10^{-6} \circ C^{-1}$ observed, due to the addition of 0.3 wt% MWNT [225]. Copper exhibited a lower co-efficient of thermal expansion than aluminum and magnesium and can be ideal for thermal management applications in microelectronic devices by reinforcing CNTs into copper matrix. The co-efficient of the thermal expansion value of copper was significantly reduced due to the addition of 5-10 vol% CNTs, which is shown in Fig. 2.12 [148]. Uniform distribution of CNTs and strong interfacial bonding between CNT and matrix governed the thermal properties of metal matrix-CNT composites, and which mainly depends on CNT content and processing route of composites.
Fig. 2.12 Variation of (a) thermal conductivity and (b) coefficient of thermal expansion with temperature for MWNT/Cu nanocomposites prepared by molecular-level mixing and spark plasma sintering [148].

2.1.10 Electrical Properties

CNTs exhibit excellent electrical properties, such as large current density from $10^7$ to $10^9$ A/cm$^2$, and room temperature resistivity is in the order of $10^{-6}$-$10^{-4}$ $\Omega$cm [17]. Therefore, CNTs are widely used as reinforcement into metal matrix to improve their electrical properties. Electrical resistivity of electrodeposited Cu-GNP composite coatings reduced by 10-20% with the addition of 8-11% TRG [226]. Al-CNT composites fabricated via hand grinding followed by hot pressing exhibited reduction in electrical resistivity [227]. But, electrical resistivity increases with increasing CNT content. Yang et al. reported no difference in electrical resistivity between electrodeposited Cu-SWNT composite and pure copper coatings [228]. Al-CNT composites processed via powder metallurgy exhibited increments in the thermal resistivity [6].
2.1.11 Potential Applications

Carbon nanotube reinforced metal matrix composites so far exhibited no commercial application, but there is a lot of research going on over the globe for just that, their potential commercial applications. Table 2.2 gives a broad overview on potential applications of CNT reinforced metal matrix composites.

Table 2.2 Potential applications of CNT-reinforced metal matrix composites in various industries [6].

<table>
<thead>
<tr>
<th>Industry</th>
<th>Application</th>
<th>Property desired</th>
</tr>
</thead>
<tbody>
<tr>
<td>Automobile industry</td>
<td>Break shoes, cylinder liners, piston rings, gears</td>
<td>High strength, wear resistance, good thermal conductivity, low density</td>
</tr>
<tr>
<td>Aerospace industry</td>
<td>Aircraft brakes, landing gears</td>
<td>Good wear resistance, good thermal conductivity, low density, high strength</td>
</tr>
<tr>
<td>Space applications</td>
<td>High gain antenna boom, structural radiators</td>
<td>Low density, high strength, low coefficient of thermal expansion, good electrical conductivity</td>
</tr>
<tr>
<td>Sports industry</td>
<td>Light weight bicycles, tennis and badminton rackets</td>
<td>High strength, high elastic modulus</td>
</tr>
<tr>
<td>Electronic packaging</td>
<td>Heat sinks for thermal management, solders</td>
<td>High thermal conductivity, low coefficient of thermal expansion, increased strength</td>
</tr>
<tr>
<td>MEMS and sensors</td>
<td>Micro-beams, micro-gears</td>
<td>High elastic modulus, high surface area</td>
</tr>
<tr>
<td>Battery and energy storage</td>
<td>Anodes and anode coatings, hydrogen storage materials</td>
<td>Large surface area, high current density, reduced response times, increased H2 adsorption–desorption rate</td>
</tr>
</tbody>
</table>

Both CNTs and GNP s exhibited excellent strength, stiffness, wear and corrosion resistance, high thermal and electrical conductivity, which make them candidates for reinforcement in metal matrix. Metal matrix-CNT/GNP composites can be used in structural
applications, as a load bearing member, tribological coatings, functional applications, thermal management device in electronic packaging, hydrogen storage, catalyst, structural materials for microelectromechanical systems in the form of microbeams and microgears), ideal heat sink materials for microelectronic devices, and electrode materials for fuel cells. Al-carbon fiber composites are widely used in aerospace, automotive, and transportation industries, as conductive heat sinks for electronic devices, and also as a high gain antenna boom in space applications [17]. Still there are many difficulties in the processing of metal-CNT/GNP composites, already discussed in the “processing technique” section. The physical and mechanical properties of metal-CNT/GNP composites depend on many factors, such as the properties of matrix, interfacial bonding, dispersion of CNTs/GNPs, and processing techniques. Metal-CNT/GNP interface plays an important role in obtaining effective load transfer from metal matrix to CNTs during mechanical deformation. Therefore, a very strong interfacial bonding confirms the significant improvement in mechanical and physical properties, by ensuring effective load transfer across the metal-CNT interface. Many researchers are developing new processing techniques to obtain meat-CNT composites with uniform dispersion of CNTs into metal matrix as well as clean and strong interface having a very strong metal-CNT interfacial bonding leads to very effective and strong metal-CNT composites for future structural and functional applications.

2.2 Nickel-Titanium Carbide Composites

Nickel and nickel base superalloys are widely used in automotive and aerospace applications (aircraft jet engines, land base turbines, and petrochemical plants) due to their excellent properties such as high resistance to corrosion and fatigue as well as low thermal
expansion [14]. Titanium carbide (TiC) has a very high hardness (2859-3200 HV), high melting point (3420 K), low density (4.93 g/cm²), and high mechanical strength, but it is very brittle and cannot be used as a monolithic ceramic [229-242]. Therefore, TiC reinforced nickel matrix composites are considered as a good candidate for high temperature refractory, abrasive, and structural applications. Also, among all the metals, nickel has low wetting angle with titanium carbide, which leads to significant improvement in interfacial bonding of TiC reinforced nickel matrix composites [243]. Ni-TiC composites exhibited combination of metallic properties (ductility and toughness) as well as ceramic properties (high strength and modulus) that lead to enhancement in shear and compression strength, which make them a suitable candidate for high temperature structural applications [231]. TiC reinforced nickel matrix composites exhibiting excellent physical and mechanical properties and can be used as potential replacements for WC-Co based hard metals [236]. TiC can be used as a field emission electron source in high-resolution scanning electron microscope and other electron microprobe instruments [229, 230, 244]. Nickel (metal)-Titanium Carbide composites were fabricated by various processing routes including combustion synthesis, medium frequency induction melting-casting technology, spark plasma sintering (SPS), electrodeposition, high temperature synthesis technique, laser engineering net shaping (LENS™), combustion synthesis combined with quasi isostatic pressing (QIP), direct laser fabrication (DLF), self-propagating high temperature synthesis combined with pseudo heat isostatic pressing, laser cladding, laser melting furnace, and laminated object manufacturing. Zong et al. fabricated in situ TiC reinforced nickel matrix composites using medium frequency induction melting-casting technology [232]. The Ni-20vol%TiC composites exhibited high hardness (450 HV), moderate yield strength (σ=385 MPa), high ultimate tensile strength (σf= 591 MPa), and excellent flexural strength (1362 MPa). The composite
microstructure exhibited cuboidal primary TiC and needle-like eutectic TiC precipitates uniformly distributed within nickel matrix. The improvement in the mechanical properties of Ni-TiC composites is mainly associated with a sharp and clean Ni-TiC interface that leads to good interfacial bonding. Electrodeposited Ni-TiC composites exhibited significant improvement in microhardness and wear resistance, but have poor oxidation resistance as compared to electrodeposited pure nickel [245]. Strzeciwick et al. obtained TiC crystals via high temperature synthesis using nickel as high temperature solvent. Ternary phase diagram of Ni-TiC exhibited 2 ternary eutectics in a nickel rich corner as shown in Fig. 2.13 [229]. Ni-TiC composites exhibited primary as well as eutectic TiC precipitates. Ni-TiC composites displayed incoherent interfaces, which lead to formation of dislocations.

![Fig. 2.13 Modified Ni-rich corner of the Ni-Ti-C ternary system [229].](image)

Han et al. fabricated TiC-xNi composites via combustion synthesis reaction combined with quasi isostatic pressing (QIP) technique. TiC-20wt%Ni composites exhibited full density, excellent hardness, as well as transverse rupture strength [233]. Nickel acts as a diluent and
binder of TiC grains in Ni-TiC composites. The size of TiC precipitates decreases with increasing nickel content in composites. Liquid phase nickel not only helps in densification but also in microstructural evolution of materials.

Fig. 2.14 HRTEM image showing interface between Ni matrix and TiC (a), higher magnification image showing semi-coherent interface, and (c) FFT spectra [14].
Sundeep et al. laser deposited in situ TiC reinforced nickel matrix composites via LENS™ process [14]. Ni-TiC composite microstructure exhibited cuboidal primary TiC precipitates and needle-like eutectic TiC precipitates uniformly distributed within nickel matrix. Fig. 2.14 shows HRTEM image of Ni-TiC interface. Ni-TiC exhibited semi-coherent interface with misfit dislocations separating coherent region of two phases. Ni-TiC composites exhibited significant improvements in microhardness as well as in wear resistance, which make them potential candidates for structural and surface engineering applications. Yuxin et al. processed Ni-TiC metal matrix composites via direct laser fabrication technique with varying volume fraction of TiC [234]. Size of TiC precipitates increases with increasing TiC content. Similarly, microhardness and wear resistance of Ni-TiC composites increases with increasing TiC content. Ni-60vol%TiC composites exhibited high microhardness (1897.6 HV) and lower weight loss as compared to other Ni-TiC composites. Xinghong et al. fabricated TiC-xNi cermets via combustion synthesis combined with pseudo heat isostatic pressing [246]. Combustion temperature as well as TiC precipitate decreased due to nickel addition, as grain growth is an exponential function of combustion temperature. Liquid nickel helps for densification as well as in microstructure evolution of the cermets. TiC-20wt%Ni composites exhibited high relative density and rupture strength as compared to other TiC-Ni cermets. Douglus et al. fabricated functionally graded NiTi-TiCx composites via combustion synthesis process [242]. The good interfacial bonding was obtained within each layer of functionally graded material (FGM). The TiC precipitate sizes as well as hardness decreased with increasing NiTi content in FGM. The reduction in TiC grain size was associated with a decrease in Ostwald ripening. Chen et al. synthesized titanium carbide reinforced nickel aluminide composites using laser-melting furnace [247]. There was an increase in TiC and NiAl phase volume fraction with increasing titanium
and carbon content in the elemental powder blend, which lead to increase in microhardness of TiC-nickel aluminide composites. The precipitated TiCs exhibited faceted morphology due to their lateral growth during rapid solidification. Yumin et al. synthesized TiC/Ni functionally graded materials via laminated object manufacturing (rapid prototyping) and combustion synthesis technique [248]. High strength (950 MPa) and high density (5.2 g/cm³) was obtained in TiC-20wt%Ni composites. Weiping et al. laser deposited functionally graded TiC/Ti composites by LENS™ process [249]. The microhardness of the composites increased with increasing TiC content in the composites. Sen et al. fabricated TiC reinforced nickel matrix composite coatings on carbon steel substrate via laser cladding technique [250]. TiC exhibited globular, cluster, and flower-like morphology at different sections in the coatings. The microhardness of Ni-TiC composite coating increased with increasing wt% of TiC. Ni-20wt% TiC exhibited maximum microhardness of 920 HV as compared to Ni-10wt%TiC and Ni-15wt%TiC composites. Chengyun et al fabricated TiC reinforced gray cast iron composites using precursors/ mixture of Ni-Ti-C powder by laser cladding [251]. TiC precipitates exhibited three different types of morphologies, namely, dendritic, flower-like, and large blocky type. The microhardness and wear resistance of TiC reinforced grey cast iron significantly improved due to in situ TiC formation in the coating.

2.3 Critical Issues Discovered

Not much work has been done on the processing of nickel matrix composites with very little information available. There are many issues in the processing of nickel-CNT/GNP nanocomposites, which mainly are to obtain homogeneous dispersion of CNTs into metal matrix, to retain structural and chemical stability of CNTs during processing, and to avoid interfacial
reaction to promote strong metal-CNT interfacial bonding. Many processing routes fail to achieve these qualities except for a few techniques. Molecular mixing of nickel-CNT nanocomposite powder followed by SPS proved a significant improvement in the mechanical properties due to homogeneous dispersion of CNTs into metal matrix; the metal-CNT interface being sharp and clean, leads to strong interfacial bonding that effectively transfers stress during mechanical deformation. But large-scale production of molecular level mixed metal-CNT composite powder is difficult, time consuming, and very expensive. There is a need to discover a simple, fast, and cost effective processing route, which can reasonably improve the mechanical properties of nickel-CNT nanocomposites. Also, there has not been any research on the optimization of SPS processing parameters to investigate their effects on the mechanical properties of pure nickel. To investigate the influence of processing parameters on density as well as on grain size is very important, as these parameters govern the mechanical properties of pure nickel. Also, it will help in determining accurately the reinforcement effect on the mechanical properties of metal-CNT/GNP nanocomposites. Graphene is cheap and also easy to handle as compared to CNTs, but got ignored by the scientific community. Due to its excellent physical and mechanical properties, graphene can be a potential candidate as reinforcement in the metal matrix. Ni-Ti-C is a relatively new composite system and still many things need to be discovered. Most of the work has been completed till identifying the primary and eutectic phases using 2D characterization tools such as SEM and TEM. Three-dimensional morphology of the TiC precipitates still is unknown to the scientific community. For complex compositions, it is very difficult to determine the sequence of phase evolution only on the basis of 2D characterization. Therefore, 3D characterization of Ni-Ti-C composites is essential to study the exact phase evolution sequence during their solidification.
3.1 Spark Plasma Sintering (SPS)

3.1.1 Introduction

Spark plasma sintering (SPS) is a novel tool for processing of metal matrix composites at lower temperatures and shorter processing times. A schematic diagram of spark plasma sintering machine is shown in Fig. 3.1. SPS is a relatively new powder metallurgy process, which involves simultaneous application of uniaxial pressure and pulsed direct current [252].

![Schematic of spark plasma sintering system](image)

**Fig. 3.1** Schematic of spark plasma sintering system [8].

The unique mechanisms involving joule heating at the particle contacts and for localized spark discharges in the gaps or at contact point between powder particles cause localized surface...
heating and solid state sintering of nanopowders without significant grain growth. In the SPS process, a local high temperature state is generated when sparks discharge in a gap or at the contact point between the particles of powder, causing evaporation and melting on the surface of powder particles, and “necks” are formed around the area of contact between particles, thus helping in the formation of fully dense nanocomposites [253-269]. The basic mechanism of neck formation during SPS process is shown in Fig. 3.2. This initiation of the spark discharge in the gap between particles is assisted by fine impurities and gases on and between the surfaces of the particles.

![Fig. 3.2 Basic mechanism of neck formation by spark plasma [268].](image)

SPS is a high-speed powder consolidation (sintering) technology capable of processing conductive and non-conductive materials, and it utilizes uniaxial force and on-off DC pulse energizing. This high frequency transfers and disperses the joule heat phenomenon throughout the specimen, resulting in a rapid and thorough heat distribution, ensuring high homogeneity and
consistent precipitate densities. Consolidation of nanopowders is possible in SPS without excessive grain growth due to the high heating rates and lower sintering times and temperatures involved. SPS is effective for any powder material applications, but interest is especially high for nano-crystalline structures, because of high surface area per volume. “Net” or “Near-net” shapes are also possible with SPS directly from powder to finished product, having symmetrical and simple geometry in one step. However, for complex shapes, further machining may be required.

SPS exhibited high thermal efficiency due to direct heating of graphite die and stacked powder material by large spark pulse current. Homogeneous as well as high quality sintered compacts can be easily consolidated by SPS due to uniform heating, surface purification, and activation made possible by dispersing the spark points. SPS has many advantages over conventional sintering techniques including ease of operation, high reproducibility, accurate control of sintering energy, as well as high sintering speed, safety, and reliability [264, 269].

3.1.2 Mechanisms of SPS Process

In recent years, SPS process has attracted significant attention due to its significant advantages over conventional sintering processes to obtain bulk compacts in lower sintering temperature and shorter sintering time without excessive grain growth. But still SPS effect, i.e., effect of pulsed high current on generation of spark plasma and usually beneficial properties in consolidated materials still unclear. Tokita proposed following four basic ideas on the mechanisms of SPS processing [264, 269], which involves the ON-OFF DC pulse energizing method generates: (1) Spark plasma

(2) Spark impact pressure

(3) Joule heating
(4) An electric field diffusion effect

Due to micro and macro level transfer of materials getting promoted in SPS process, powder particle surfaces are easily activated and purified, which leads to consolidation of high-quality sinter compacts in shorter sintering time and at lower temperatures as compared to conventional sintering process [264, 269]. Fig. 3.3 how DC ON OFF pulse current flows through powder particle inside the SPS die.

![Fig. 3.3 DC pulse current flow through the particles](image)

SPS process applies pulse voltage and high current, in addition to joule heating generated by the power supply (I²R) to the powder particles [269]. High temperature field is generated by spark plasma, when sparking occurs and impurities, adsorption gases, and oxide films on powder particles are removed by spark impact pressure. Electro-magnetic field enhances high-speed migration of ions through a diffusion mechanism, which leads to enhancement of sinterability and densification rate of materials. Even though there are many controversies involved in the mechanisms of SPS process, mainly on the presence or the absence of plasma during SPS
process, Dustin et al. investigated the existence of plasma via in situ atomic emission spectroscopy, direct visual observations, and ultrafast in situ voltage measurements, and concluded that there was no plasma present during SPS process [262]. Still, it is very difficult to conclude anything regarding this mechanism only with this report. The effectiveness of SPS process to obtain high quality compacts in shorter time with novel microstructure remains unchallenged [262].

3.1.3 Effect of SPS Processing Parameters on Densification

SPS user defined processing parameters, such as heating, maximum temperature, cooling rate, load application rate, maximum load hold, and load removal rate, play an important role in the microstructure and densification of sintered compacts. In this section, effects of temperature, heating rate, and pressure on the densification of SPS processed material are briefly discussed.

3.1.3.1 Temperature

Powder densification during SPS processing mainly depends on temperature. In the SPS process, resistance joule heat is the main heat source. Density of the material increases with increases in SPS processing temperature. Garay obtained density-temperature relationship through linear curve fit, which is given in equation 27 [267]:

$$\rho = s \left( \frac{T}{T_m} \right) + b$$  \hspace{1cm} (27)

where, $\rho$ = relative density

$s$ = slope/ temperature sensitivity

$b$ = intercept of density axis
Temperature sensitivity value of the carbide and oxides lies between 1.5 and 3, whereas metal has a very low temperature sensitivity value (i.e., \(0.5 \leq s \leq 1\)). Due to large temperature sensitivity value, ceramics are more affected by SPS processing temperature than metals. Metals have low temperature sensitivity value due to other mechanisms (i.e. plastic deformation, electromigration, etc.) and are operative in their densification.

3.1.3.2 Heating Rate:

Many researchers have investigated the effect of heating rate in the densification of SPS sintered compacts. Still there is an uncertainty in their conclusions. In SPS process, high heating rate is used to prevent grain growth and enhance densification of materials. Some researchers found that, there is positive effect of high heating rate on improving the density of compact, but there are some other researchers who have investigated that no effect or even negative effect of high heating rate acts on densification of materials. These differences in observations mainly occurred due to inaccuracy in SPS temperature measurements, as most of the temperatures were measured using a pyrometer on the surface of a graphite die. Therefore, accurate temperature measurement is necessary to resolve the effect of heating rate on densification of materials [254].

3.1.3.3 Pressure

Higher densification of powder is achieved when powders are sintered under a pressure for same temperature. Pressure has a dual role in sintering mechanisms (i.e., mechanical and intrinsic role). Mechanically pressure helps in re-arrangement of particles and destruction of agglomeration of nano-powder particles. Intrinsic effect of the pressure can be calculated from the driving force for sintering [254] and can be given by equation 28:
\[
\frac{d\rho}{(1-\rho)dt} = B(g \frac{\gamma}{x} + P)
\]  

(28)

where, \( \rho \) = fractional density

\( B \) = term includes diffusion co-efficient and temperature

\( G \) = geometrical constant

\( \gamma \) = surface energy

\( x \) = parameter represents particle size

\( t \) = time

\( P \) = applied pressure

The first term on the right hand side of the equation (i.e. \( g \frac{\gamma}{x} \)) represents intrinsic driving force for sintering and the second term (\( P \)) represents intrinsic contribution to the driving force by the applied pressure [254]. According to the above equation, significance of pressure on sintering depends on particle size. Relative contribution of pressure is small for particle sizes, but it increases as particle size increases.

Spark plasma sintering equipment, model SPS 10-3 manufactured by Thermal Technology LLC, was used to fabricate Nickel and GNP/CNT-Nickel nanocomposites. The SPS system consists of punch electrodes, uniaxial press, water-cooled vacuum chamber, DC pulse generator, and temperature and pressure measuring units. This SPS machine has a capability of generating a temperature of 2500°C in less than 5 minutes due to 3000 Amperes and 5 volts DC pulse generator. It is capable of achieving a very high heating rate (i.e., 600°C/min). High cooling rate inside the SPS furnace chamber can be obtained by purging nitrogen or argon gas. All the experiments were performed under a controlled argon atmosphere to avoid any contamination. Graphite punches and dies were used for fabrication of samples. Maximum pressure that can be attained using graphite toolings are 100 MPa. “K” type thermocouple, which
is placed inside the bottom punch, was used to accurately measure the temperature during SPS sintering experiments. SPS sintering is carried out in four main stages. The first stage is to create vacuum by removing unwanted gases. The pressure is applied in second stage followed by resistance heating in the third stage and finally, cooling is the fourth stage.

3.2 Laser Engineering Net Shaping (LENS™)

The LENS™ process, in recent years, has had a strong impact on the rapid prototyping, small-scale fabrication and repair of complex parts in industry [270-275]. Originally, the LENS™ process was developed at Sandia National Laboratories and subsequently commercialized by Optomec Design Company [273, 275, 276]. LENS™ process is an advanced version of rapid prototyping technology, which enables direct fabrication of metallic parts directly from the computer aided design (CAD) solid model. LENS™ is a solid freeform fabrication process where fully dense compacts are obtained from 3D CAD solid model via laser processing of fine metal powders. Complex shapes, high strength near net shape metallic components were fabricated via LENS™ process that leads to time and machining cost saving [249]. Varieties of metals, alloys, and composites have been successfully fabricated by LENS™ process [14, 169-171, 249, 270-282]. That LENS™ process exhibits a very rapid cooling rate during fabrication improves the microstructure and mechanical properties of the metals due their finer grain size. An Optomec LENS™ 750 system was used to fabricate Ni-Ti-C composites. LENS™ system consists of mainly four parts: laser system (Nd:YAG laser), powder delivery system, the controlled environment glove box, and motion controlled system. The Nd:YAG laser has a 0.5-1 mm diameter circular beam at the focal zone with the Gaussian intensity distribution and maximum output power of 750 W [249]. Due to presence of multiple hoppers, LENS™
offers much flexibility in the processing of different alloys as well as functionally graded materials. LENS™ process uses focused laser beam for melting metallic powders and 3D CAD files for designing the solid 3D object prior to fabrication.

**Fig. 3.4** Schematic of the LENS™ system[14].

LENS™ process begins with CAD file of a three-dimensional component, which is sliced into series of layers electronically. The information about each of these layers is transmitted to the manufacturing assembly. Entire laser deposition was carried out in controlled environment (argon gas) glove box to avoid any contamination. The stainless steel substrate was used as base material for LENS™ deposition. Powder feedstock was delivered through an inert gas flowing through multi-nozzle assembly into molten pool produced by focused high power laser (Nd: YAG laser emitting near infrared radiation at a wavelength of 1064 nm), the schematic of which
is shown in Fig. 3.4. The nozzles are designed in such a way so that powder feedstock converges at the same point into a focused laser beam. In order to accurately deposit these layers of required width and thickness, the substrate moves relative to laser beam on a computer-controlled stage [273, 275, 276]. After deposition of each layer, entire nozzle assembly as well as laser focal point is moved vertically along z-axis by distance equal to the thickness of each layer to obtain homogeneity during laser deposition. Each successive layer is deposited in a different scan direction than that of the previous layer to obtain homogeneity [170]. During LENS™ deposition of Ni-Ti-C composites, scan speed of laser was maintained about 10 inches/min and the hatch width used for deposition was 0.018 inch with layer thickness of 0.01 inch. Each successive layer was deposited by 60° rotation to that of the previous layer to ensure uniformity. The oxygen content in the glove box was maintained below 10 ppm to avoid any contamination. Powder flow rate and argon volumetric flow rate was maintained at about 2.57 g/min and 3 liter/min, respectively.
CHAPTER 4

OPTIMIZATION OF SPARK PLASMA SINTERING (SPS) PROCESSING PARAMETERS FOR PURE NICKEL

4.1 Abstract

This chapter is a brief investigation on the effect of SPS processing parameters on mechanical properties (i.e., tensile yield strength and ductility) of pure nickel. The bulk polycrystalline nickel was fabricated from high purity micron-size powder via spark plasma sintering for three different pressures (i.e., 50, 65, and 80 MPa) and for three different temperatures (i.e., 700, 850, and 1000° C). Optimization of the processing parameters yielded bulk pure nickel samples exhibiting an average grain size from 5-45 μm, tensile yield strength from 130 to 278 MPa, and ductility from 40 to 60%. Temperature plays an important role in SPS processing of pure nickel, to control grain growth and apparently the mechanical properties of SPS processed pure nickel.

4.2 Introduction

Nickel and nickel base alloys have been widely used in automotive and aerospace applications due to their high specific strength, high corrosion and fatigue resistance, and toughness [14, 169-171]. The powder metallurgy technique can be advantageously used to produce nickel base structural parts, as there is much more flexibility in the powder metallurgy processing parameters (i.e., pressure, temperature, holding time, etc.). The processing parameters significantly govern the resulting microstructure, which has a decisive influence on the mechanical properties (i.e., tensile yield strength and ductility). Powder metallurgy is the most widely used processing technique for the fabrication of metals/ alloys due to its simplicity,
flexibility, and near net shape capability. Powder metallurgy technique involves such methods such as hot isostatic pressing (HIP), cold isostatic pressing, compaction and sintering, spark plasma sintering, and shock consolidation [283-293]. Among all the above-mentioned techniques, spark plasma sintering is one of the most novel techniques for fabrication of metals, alloys, and metal/alloy composites in a shorter sintering time and of finer grain size.

Spark plasma sintering has many advantages over conventional powder metallurgy methods, including ease of operation, high reproducibility, accurate control of sintering energy, as well as high sintering speed, safety, and reliability [264, 269]. In SPS process, a local high-temperature state is generated when spark discharges in a gap or at the contact point between the particles of powder cause the evaporation and melting on the surface of the powder particles to help obtain fully dense nanocomposites [256, 257, 264, 265, 268, 269]. Consolidation of nanopowders is possible in SPS without excessive grain growth due to the high heating rates and lower sintering times and temperatures involved. In the SPS process, temperature is the main governing parameter for controlling microstructural features, such as grain size, grain boundary misorientation distribution, and coincidence site lattice, such as the Σ3 grain boundaries. These microstructural features are responsible for controlling the mechanical properties of metals, such as high angle grain boundaries (including twin boundaries) and multi grain size distributions are responsible for high ductility, whereas high dislocation density and refined grain structure are responsible for high strength [283-285, 294, 295]. Therefore the processing parameters are important in optimizing ductility and strength of metals. This investigation mainly focuses on the effect of SPS processing parameters (i.e., pressure and temperature) on the microstructure and mechanical properties of pure nickel.
4.3 Experimental Details

The starting material was a high purity (99.99%) nickel powder supplied by Alfa Aesar, size ranging from 1 to 5 μm. The pure nickel powders were precompacted in a graphite mold under a pressure of 5 MPa. The precompacted powders were sintered by SPS system at a temperature of (700, 850, and 1000°C), for 5 minutes under a controlled argon atmosphere under a pressure of (50, 65, and 80 MPa). In total, 9 pure nickel samples were sintered for 3 different pressures as well as three different temperatures. The heating rate was maintained at 100°C/min. The obtained samples were disc-shaped and had dimensions of about 20 mm in diameter and 2 mm in thickness. Sintered pure nickel samples were characterized in FEI-Quanta Nova-SEM. Grain sizes were measured using ImageJ software, and an average of 50 grains were reported in this paper. To assess tensile properties of the composites, mini-tensile testing was carried out on a custom-built mini-tensile tester. The tensile samples were prepared using Electric discharge machining (EDM). The gauge length, width, and thickness of the gage section of the samples were 5.0 mm, 1.0 mm, and 1.35 mm, respectively. Each sample was ground and polished (in the order of 600, 800, 1200 grit size silicon carbide (SiC) papers) and final polishing was accomplished with 0.04 μm colloidal silica before tensile testing. The test was carried out at room temperature at a crosshead speed of 0.02 mm/min.

4.4 Results and Discussion

4.4.1 SEM Microscopy Analysis

Back-scattered SEM images of the SPS sintered pure nickel at 50 MPa for 700, 850 and 1000°C temperatures are shown in Fig. 4.1 (a-c), which clearly shows that the average grain size increases with the SPS processing temperature for same pressure (i.e., 50 MPa). The results are
summarized in Table 4.1. Pure nickel processed at 50 MPa and 700° C, exhibited much less porosity. As temperature increases from 700° C to 1000° C, average grain size increases that leads to increase in relative density by decreasing porosity even further. Both pure nickel samples processed at 850° C and 1000° C, exhibited close to 100% density. From the grain size measurement, it is clear that SPS processing temperature has a strong effect on grain growth, which is associated with diffusion mechanisms.

4.4.2 Tensile Properties Investigation

The tensile yield strength and elongation properties of SPS processed pure nickel are listed in Table 4.2. The corresponding engineering stress-strain curves for pure nickel processed at 50 MPa for 700, 850 and 1000°C temperatures are shown in Fig. 4.2 All the pure nickel samples exhibit ductile behavior. Even more striking is that the tensile yield strength of the pure nickel decreases with the increase in processing temperatures, but elongation to failure increases with such an increase in processing temperatures. Reduction in tensile yield strength with enhancing ductility is mainly associated with significant grain growth observed for high temperatures. This phenomenon can be more precisely explained by correlating with Hall-Petch equation [296-301]:

\[ \sigma_y = \sigma_o + k \cdot d^{-1/2} \]

Where, \( \sigma_o \) and \( k \) are constants.

The tensile yield strength increases as average grain size decreases. During tensile deformation, dislocation pileup takes place at the deforming grain boundary, which produces stress concentration to activate slip in the neighboring non-deforming grains. High stress concentration is developed in the neighboring grain for larger grain size and, therefore, applied
stress required to activate slip/flow in the grain is relatively low which leads to a lower tensile yield strength.

Fig. 4.1 Backscatter SEM images of SPS sintered pure nickel at 50 MPa for (a) 700°C, (b) 850°C, and (c) 1000°C temperatures.
Table 4.1 Grain size measurements of SPS sintered pure nickel.

<table>
<thead>
<tr>
<th>SPS processing parameters and grain sizes (μm)</th>
<th>700°C</th>
<th>850°C</th>
<th>1000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 MPa</td>
<td>5</td>
<td>27.8</td>
<td>47.8</td>
</tr>
<tr>
<td>65 MPa</td>
<td>5.4</td>
<td>25.8</td>
<td>42.5</td>
</tr>
<tr>
<td>80 MPa</td>
<td>5.7</td>
<td>26.7</td>
<td>44.7</td>
</tr>
</tbody>
</table>

Fig. 4.2 Stress-strain curves of SPS processed pure nickel at 50 MPa for 700, 850, and 1000°C temperatures, obtained from tensile test.
Fig. 4.3 Backscatter SEM images of SPS sintered pure nickel at 65 MPa for (a) 700°C, (b) 850°C, and (c) 1000°C and at 80 MPa for (d) 700°C, (e) 850°C, and (f) 1000°C temperatures.
Similarly a high tensile yield strength phenomenon in finer grain size metals can be explained. Grain sizes play an important role in governing the tensile yield strength of pure nickel. All pure nickel samples exhibited significant ductility due to the presence of a large fraction of twin boundaries as frequency of $\Sigma 3$ boundaries increases with temperature [287]. Pure nickel sample processed at 50 MPa and 1000°C exhibiting high ductility/strain hardening due to presence of twins and large grains which effectively block and store dislocations.

**Fig. 4.4** Stress-strain curves of SPS processed pure nickel at 65 MPa for 700, 850, and 1000°C temperatures, obtained from tensile test.
Fig. 4.5 Stress-strain curves of SPS processed pure nickel at 80 MPa for 700, 850, and 1000°C temperatures, obtained from tensile test.

Fig. 4.6 Stress-strain curves of SPS processed pure nickel at 700°C for 50, 65, and 80 MPa pressures, obtained from tensile test.
Fig. 4.7 Stress-strain curves of SPS processed pure nickel at 850°C for 50, 65, and 80 MPa pressures, obtained from tensile test.

Fig. 4.8 Stress-strain curves of SPS processed pure nickel at 1000°C for 50, 65, and 80 MPa pressures, obtained from tensile test.
Similar kinds of observations were found for pure nickel samples processed at 700, 800, and 1000°C for 65 MPa and 80 MPa. Corresponding backscattered SEM images are shown in Fig. 4.3 and tensile stress-strain plots are shown in Fig. 4.4 and 4.5, respectively. Fig. 4.6-4.8 show tensile stress-strain plots for pure nickel processed at 700, 850, and 1000°C for different pressures (50, 65, and 80 MPa) by keeping temperature constant for the three different pressures, respectively. It is clearly observed that there is not much difference in yield strength as well as in ductility of pure nickel processed at the same temperature but for different pressures.
4.4.3 Modified Hall-Petch Equation

In spark plasma sintering, temperature is the main governing parameter to control microstructure and mechanical properties of pure nickel, rather than the pressure. Table 4.1 and 4.2 show grain size and yield strength values of SPS processed pure nickel for 9 different processing conditions. Fig. 4.9 shows plot of yield strength versus the reciprocal of the square root of the grain size by considering 4 extreme SPS processing conditions (i.e., 50 MPa- at 700 and 1000°C and 80 MPa- at700 and at 1000°C). These 4 points in the graph were fitted linearly to obtain an equation. The equation obtained from the linear line was compared with Hall-Petch equation to obtain constants $\sigma_o$ and k. So, a modified Hall-Petch equation for SPS processed pure nickel is given by:

$$\sigma_y = 77.7 + 434.5 \ast d^{-1/2}$$

Where, $\sigma_o = 77.7$ and $k = 434.5$ (obtained from graph)

This modified Hall-Petch equation can be used to determine the grain size strengthening effect in SPS processed CNT/Ni and GNP/Ni nanocomposites.

**Table 4.2** Yield strength and elongation properties of SPS sintered pure nickel.

<table>
<thead>
<tr>
<th>SPS processing parameters and yield strength and ductility</th>
<th>700°C</th>
<th>850°C</th>
<th>1000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 MPa</td>
<td>278 MPa/43%</td>
<td>154 MPa/59%</td>
<td>134 MPa/67%</td>
</tr>
<tr>
<td>65 MPa</td>
<td>265 MPa/49%</td>
<td>158 MPa/56%</td>
<td>130 MPa/65%</td>
</tr>
<tr>
<td>80 MPa</td>
<td>253 MPa/43%</td>
<td>166 MPa/43%</td>
<td>150 MPa/43%</td>
</tr>
</tbody>
</table>
4.5 Summary and Conclusions

SPS processed pure nickel exhibited significant grain growth as processing temperature increased. The tensile yield strength of pure nickel increases as average grain size decreases, following similar trend of Hall-Petch rule. In SPS sintering processing temperature is the main governing parameter for optimizing microstructure and mechanical properties of pure nickel. The modified Hall-Petch equation obtained for SPS sintered pure nickel is given by:

\[ \sigma_y = 77.7 + 434.5 \times d^{-1/2} \]
CHAPTER 5
STRENGTH VERSUS DUCTILITY IN CARBON NANOTUBE REINFORCED NICKEL MATRIX NANOCOMPOSITES

5.1 Abstract

Two types CNT/Ni nanocomposites were processed, both involving spark plasma sintering (SPS). The first type involved simple mechanical dry milling (DM) of nickel and CNT powders, followed by sintering using SPS, resulting in nanocomposites exhibiting a tensile yield strength of 350 MPa (about two times of SPS processed monolithic nickel ~ 160 MPa) and an elongation to failure ~ 30%. In contrast, the nanocomposites processed by SPS sintering of powders prepared by molecular-level mixing (MLM) exhibited substantially higher tensile yield strength (~ 690 MPa) but limited ductility with an elongation to failure ~ 8%. While the former type of processing involving dry-milling is expected to be lower in cost as well as easy to scale-up, the latter processing technique involving molecular-level mixing leads to a more homogeneous distribution of nanotubes leading to extraordinary strength levels.

5.2 Introduction

Carbon nanotubes, originally discovered by Iijima [71, 77-79, 177] almost two decades ago have attracted significant interest as reinforcements in various metallic, ceramic, and polymeric matrices due to their unique atomic structure and excellent properties, such as high tensile strength, elastic modulus, low density, high aspect ratio, excellent thermal as well as electrical conductivity [73, 80-87]. CNT/metal nanocomposites have potentially attractive properties, such as high tensile strength, stiffness, excellent wear and corrosion resistance which make them potential candidates for structural applications including in aerospace and
transportation in general [146, 149, 170, 171, 194, 302, 303]. Most of the investigations focus on CNT/polymer composites because of compatibility and flexibility of CNTs in the polymer matrix aiding the fabrication process [81, 145, 304]. CNT/polymer nanocomposites typically exhibit high interfacial strength between the CNT and the polymer matrix due to the molecular level interaction [305].

CNT/metal nanocomposites have attracted less attention due to their inferior mechanical properties because of the inhomogeneous dispersion of CNTs in the metal matrix, the poor quality of metal-CNT interfaces and the low relative density of CNT/metal nanocomposites. Few researchers have reported improvement in mechanical and tribological properties of CNT/metal nanocomposites fabricated by conventional powder metallurgy techniques. Cha et al. [305] have reported a unique method of fabricating CNT/metal nanocomposites by molecular level mixing process followed by spark plasma sintering (SPS) resulting in a uniform dispersion of CNTs in the metal matrix [305]. CNT/metal nanocomposites sintered from nanocomposite powders prepared by molecular level mixing exhibit significant improvement in mechanical properties mainly due to the homogeneous distribution of CNTs within the metal matrix and the strong interfacial bonding between CNTs and the metal matrix [189].

The process for fabricating CNT/Ni composite powders using molecular level mixing consists of four steps [148, 189, 305-307]. CNTs produced by thermal chemical vapor deposition (CVD) are dispersed in ethanol to make a stable suspension by functionalizing the CNT surfaces. The electrostatic repulsive force between the CNTs overcomes the van der Waals’ force to obtain a stable suspension within the solvent due to functionalization of CNTs. Second, a salt contains Ni ions is dissolved in the CNT suspension. Additional ultrasonication helps the dispersion of Ni ions among the suspended CNTs and promotes reaction between the Ni ions and functional
groups on CNT surfaces. The third step is to dry the mixture by heating to remove the solvent and ligands; leads to Ni ions on the CNTs are get oxidized to form powders. The fourth and final step is the calcination and reduction process to obtain chemically stable CNT/Ni composite powder.

In SPS process, local high-temperature state is generated when spark discharges in a gap or at the contact point between the particles of powder causes the evaporation and melting on the surface of powder particles helps to obtain fully dense nanocomposite [253, 259]. Consolidation of nanopowders is possible in SPS without excessive grain growth due to the high heating rates and lower sintering times and temperatures involved [253, 259, 260, 265]. This section mainly focuses on a comparison of CNT/Ni nanocomposites prepared via two routes. The first of these involves dry milling of nickel and CNT powders, followed by SPS sintering of the dry mixed powders. The second approach involves SPS sintering of powders processed via the novel, recently proposed, molecular-level process. The microstructure and mechanical properties of both types of nanocomposites have been compared and contrasted.

5.3 Experimental Details

Multiwalled CNTs fabricated by chemical vapor deposition (CVD) with an average dia. of about 10 nm and average length of few μm were obtained from Hanhwa Nanotech Co. Ltd., South Korea. For CNT/Ni nanocomposite (ball milled), CNT/Ni nanocomposite powder synthesized by mixing nickel powder and CNTs through high energy ball milling process for 24 hrs. with 400 rpm. The volume fraction of CNTs in both the composite powder was ~ 5%. The CNT/Ni composite powders were precompacted in a graphite mold under a pressure of 5 MPa. The precompacted powders were sintered by SPS system at a temperature of 1073 K for 5 min.
under controlled argon atmosphere under a pressure of 80 MPa. The heating rate was maintained at 100° C/ min.

The fabrication of CNT/Ni (MLM) composite powders begins with purification and functionalization of CNTs using HF and acid solution mixture of H₂SO₄ and HNO₃ [189]. CNT/Ni precursors were prepared through chemical reduction process, using hydrazine hydrate as reducing agent, sodium hydroxide as oxidation agent and ethylene glycol as solvent. Finally CNT/Ni composite powders are obtained by reduction process in H₂ and CO mixed atmosphere for 2 hrs., at 400° C [189]. CNT/Ni nanocomposites were characterized in FEI-Quanta Nova-SEM. X-ray diffraction analysis of nanocomposites was performed using (1.54 Cu Kα) line of Rigaku Ultima III X-Ray diffractometer. Conventional and high-resolution transmission electron microscopy (TEM) analysis was carried out using a FEI TECHNAI F20 Field emission gun (FEG) TEM operating at 200 keV. TEM foils were prepared via jet polishing techniques and then ion milled using Gatan Duo Mill using 4 keV for the further milling. To assess tensile properties of the composites mini-tensile testing was carried out on a custom-built mini-tensile tester. The tensile samples were prepared using Electric discharge machining (EDM). The gauge length, width, and thickness of the gage section of the samples were 5.0 mm, 1.0 mm, and 1.35 mm, respectively. Each sample was ground and polished (in the order of 600, 800, 1200 grit size silicon carbide (SiC) papers and final polishing on 0.04 μm colloidal silica before tensile testing. The test was carried out at room temperature at a crosshead speed of 0.02 mm/min.
5.4 Results and Discussion

5.4.1 SEM Microscopy Analysis

Back-scattered SEM images of the SPS sintered pure nickel and CNT/Ni nanocomposites (DM and MLM) are shown in Fig. 5.1. Pure nickel (Fig. 5.1(a) and (b)) exhibits a uniform grain structure without any porosity with an average grain size ~ 45 µm. The full and rapid densification of powder compacts without any substantial grain growth is one of the major advantages of SPS processing that is a result of sintering by joule heating and the spark plasma generated by the pulsed high electric current passing through the compact. CNT/Ni (DM) nanocomposite shows a substantially refined grain structure (Fig. 5.1(c)), as compared with the pure Ni, even though both samples were prepared with the same initial size of Ni powder. Within the Ni matrix, there appears to be a uniformly distributed second phase or possibly porosity, as shown in Fig. 1(c). However, a higher magnification SEM image, shown in Fig. 1(d), confirms that the regions exhibiting a darker contrast are actually CNT bundles of 1-2 µm in size, rather than porosity. Therefore, based on the comparison of microstructures of the SPS processed pure Ni and CNT/Ni composite (DM), it is apparent that addition of CNTs into the nickel matrix helps in grain refinement by possibly inhibiting grain growth and providing nucleation site for new grains during recrystallization. Fig. 1(e) and (f) show SEM images from the CNT/Ni (MLM) nanocomposites, that also exhibits a uniform grain structure. Previous investigations of such CNT/Ni nanocomposites processed via molecular level mixing and SPS, have clearly shown that there is a uniform distribution of individual CNTs within the nickel matrix [189].
Fig. 5.1 Backscatter SEM images of (a) and (b) pure nickel, (c) and (d) CNT/Ni dry milling, (e) and (f) CNT/Ni molecular level mixing.
5.4.2 XRD Phase Analysis

The XRD patterns for the SPS processed pure nickel and CNT/Ni nanocomposites are shown in Fig. 5.2. The XRD pattern for pure nickel shows peaks corresponding to the (111), (200), and (220) crystallographic planes of nickel. Both the dry-milled as well as molecular level mixed CNT/Ni nanocomposites show an additional (0002) carbon peak. Presence of carbon peak in both the CNT/Ni nanocomposites confirms the presence of carbon nanotubes.

![XRD pattern](image)

**Fig. 5.2** XRD pattern obtained from Pure nickel, CNT/Ni dry milled, and CNT/Ni molecular level mixed nanocomposites.

In all three cases, the maximum intensity peak is the Ni(111) peak. The Ni(111)/Ni(002) intensity ratio for SPS processed pure Ni is 2.17, while that for dry-milled and SPS processed is 2.45, and finally for molecular level mixed and SPS processed is 2.25. Comparing these three values with the standard ratio expected for randomly oriented Ni grains in the International
Center for Diffraction Data (ICDD) files obtained from Joint Committee of Powder Diffraction Standards (JCPDS) of 2.38, it is apparent that there is no significant change in texture resulting from the introduction of CNT’s in the nickel matrix. This is in contrast to previous publications on electro-deposited CNT/Ni nanocomposites where a clear increase in the Ni(002) peak intensity has been reported, indicating a change in texture due to the addition of CNTs [180].

5.4.3 Tensile Properties Investigation

The yield strength and elongation (tensile) properties of SPS processed pure nickel and both types of CNT/Ni nanocomposites are also listed in Table 5.1. The corresponding engineering stress-strain curves for these materials are shown in Fig. 5.3. The tensile yield strength of CNT/Ni (DM) nanocomposite is 350 MPa, which is about 2 times higher than that of pure nickel (160 MPa). Even more striking is that the tensile yield strength of the CNT/Ni (MLM) nanocomposite is 690 MPa, about 4 times that of pure Ni and 2 times that of CNT/Ni (DM) nanocomposite. However, comparing the ductility of all three types of nanocomposites, while pure Ni exhibits about 50% elongation to failure, the elongation values for the CNT/Ni (DM) and CNT/Ni (MLM) are 30% and 8% respectively.

Comparing the stress-strain behavior (Fig. 5.3), it appears that while the CNT/Ni (DM) nanocomposite exhibits a modulus similar to that of SPS processed pure Ni, the CNT/Ni (MLM) nanocomposite exhibits a substantial higher modulus. Since the details of the deformation behavior of the CNT/Ni MLM nanocomposite have been discussed in a recent paper [180], these are not being repeated in the present paper. However, it is important to note the contrasting aspects of deformation between the two types of CNT/Ni nanocomposites being compared in the present study. While the CNT/Ni (DM) nanocomposite exhibits a classical strain-hardening
behavior all the way from yield to failure, similar to pure Ni, the CNT/Ni (MLM) nanocomposite exhibits the sharper yield point accompanied by a drop in stress and subsequently strain-hardening to a limited degree before failure.

![Stress-strain curves](image)

**Fig. 5.3** Stress-strain curves of CNT/Ni (DM and MLM) composites and pure Ni obtained from tensile test.

5.4.4 Surface Fractography Analysis

Figs. 5.4(a), (b), and (d) are secondary electron SEM micrographs showing the fracture surfaces of the pure Ni, CNT/Ni (dry-milled) and CNT/Ni (molecular level mixed) respectively. From these images it is evident that while pure Ni and CNT/Ni (DM) exhibit similar fracture surfaces, the CNT/Ni (MLM) nanocomposite exhibits a somewhat different fracture surface. The CNT/Ni
(DM) nanocomposite fracture surface (Fig. 5.4(b)) exhibits typical cup and cone type failure characteristics, showing dimples of the order of few microns in size. This is indicative of a very ductile deformation behavior in agreement with the greater than 30% elongation observed for this nanocomposite.

Fig. 5.4 SEM micrograph showing the fracture surfaces of the (a) pure Ni, (b) CNT/Ni DM, and (d) CNT/Ni MLM composites after tensile test, (c) EDS C map corresponding to the fracture surface of CNT/Ni DM composite, (e) SEM micrograph showing the presence of CNTs in the fracture surfaces of the CNT/Ni MLM composite and circles representing presence of CNTs.
An EDS carbon map, corresponding to the fracture surface shown in Fig. 5.4(b), is shown in Fig. 5.4(c). Based on this map the location of the CNT bundles on the fracture surface can be determined and a few examples of these bundles have been marked with dotted circles in both Figs. 5.4(b) and (c). Contrastingly, the CNT/Ni (MLM) nanocomposite fracture surface (Fig. 5.4(d)), exhibits much smaller dimples of the order of sub-micron to at most a micron. Additionally, regions containing CNTs have been marked with circles in the higher magnification image of the fracture surface shown in Fig. 5.4(e). This is indicative of some strain localization and eventual failure at a lower level of strain. This is agreement with the observed lower ductility of the CNT/Ni (MLM) nanocomposite as compared to the CNT/Ni (DM) nanocomposite. However, from the perspective of strength, the CNT/Ni (MLM) exhibits a yield strength that is almost the twice that of the CNT/Ni (DM) nanocomposite. The enormous strengthening in case of CNT/Ni (MLM) nanocomposites arises mainly due to the homogeneous distribution of individual CNTs within the nickel matrix [24]. The strong interfacial bonding between the CNTs and the Ni matrix is effective to improve mechanical properties of CNT/metal nanocomposites. Despite the fact that the CNTs are in the form of sub-micron bundles in case of the CNT/Ni (DM) nanocomposite, a significant improvement in yield strength is observed and can be attributed in part due to grain size refinement. The experimental observations indicate that the uniform dispersion of CNT bundles is helping in grain refinement as well as possibly in load transfer between the metal matrix and the nanotube bundles. Therefore, comparing and contrasting the mechanical properties of these nanocomposites, it is evident that while the CNT/Ni (MLM) composite exhibits the highest tensile yield strength, the CNT/Ni (DM) composite exhibits a higher tensile ductility. Table 5.1 also, shows the predicted yield strength based on grain size effect and experimentally measured yield strength of CNT/Ni
nanocomposites. In last chapter, modified Hall-Petch equation determined based on grain size and is given by: \( \sigma_y = \sigma_o + k \cdot d^{-1/2} \). The values of \( \sigma_o \) and \( k \) are obtained from the optimization study executed for pure nickel for different SPS processing parameters (for different grain sizes of pure nickel) using linear fit for yield strength versus \( d^{-1/2} \) plot. Both, CNT/Ni (MLM) and CNT/Ni (DM) nanocomposites exhibited significant improvement in tensile yield strength mainly due to the couple effect of grain refinement as well as CNT reinforcement into nickel matrix, which effectively transfers stress during tensile deformation. In CNT/Ni (DM) nanocomposites, the enhancement in the yield strength due to CNT reinforcement is about 100 MPa, whereas in CNT/Ni (MLM) nanocomposites, yield strength improved about 450 MPa due to uniform dispersion of CNTs into nickel matrix.

**Table 5.1:** Grain size, predicted yield strength, experimentally measured yield strength, and elongation properties of pure nickel and CNT/Ni nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grain Size (( \mu m ))</th>
<th>Predicted Yield Strength (MPa)</th>
<th>Expt. Yield Strength (MPa)</th>
<th>Ductility (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Nickel</td>
<td>25.5</td>
<td>164</td>
<td>160±5</td>
<td>50</td>
</tr>
<tr>
<td>CNT/Ni (DM)</td>
<td>6</td>
<td>255</td>
<td>350±4</td>
<td>30</td>
</tr>
<tr>
<td>CNT/Ni (MLM)</td>
<td>7.4</td>
<td>237</td>
<td>690±10</td>
<td>8</td>
</tr>
</tbody>
</table>

Additionally, it is worthwhile to compare the deformation behavior of CNT/Ni MLM processed nanocomposites with ultra-fine grained (UFG) nickel samples. Very high tensile yield
strengths ~ 990MPa, have been reported in the literature for UFG nickel samples, processed via equal channel angular pressing (ECAP) plus cold-rolling [284]. These samples had grain sizes ~ 0.33 µm and exhibited an elongation to failure ~ 7%. SEM images of the fracture surface of these UFG nickel samples appear to exhibit a typical ductile failure with relatively large dimple sizes (larger than the grain size) [284]. Comparing the reported images of the fracture surface in case of UFG nickel with the fracture surface for the CNT/Ni MLM nanocomposite in the present study (Fig. 4(d)), the dimple sizes appear to quite similar and in both cases exhibit extended edges. However, the grain size in case of the CNT/Ni MLM nanocomposite is substantially larger ~ 15-25 µm, almost two orders of magnitude larger than that of the UFG nickel sample. Consequently, it can be concluded that the homogeneous distribution of CNT’s in case of the MLM nanocomposite is primarily responsible for its very high yield strength (~ 690 MPa).

5.4.5 High Resolution TEM (HRTEM) Analysis

Fig. 5.5(a) shows a bright-field TEM image of the CNT/Ni (DM) nanocomposite showing a CNT bundle embedded in the Ni matrix, that is consistent with the results obtained from SEM observations. A high-resolution TEM image from the same nanocomposite is shown in Fig. 5.5(b). This high-resolution image shows a sharp interface between a nanotube and the nickel matrix with no significant evidence of interfacial mixing across the two phases. A selected area diffraction (SAD) pattern of the [011] zone axis of pure nickel is included as an inset in Fig. 5.5(b). A low magnification bright-field TEM image of the CNT/Ni (MLM) nanocomposite is shown in Fig. 5.5(c). This image clearly shows that the CNTs are homogeneously distributed within the nickel matrix. Fig. 5.5(d) shows a high-resolution TEM image of an individual CNT embedded in the nickel matrix.
Fig. 5.5 (a) Bright-field TEM image showing CNT bundle in Ni matrix of the CNT/Ni (DM) nanocomposite and (b) HRTEM image on the CNT/NI interface along with SAD pattern of pure Ni in inset of CNT/NI DM composite, (c) Bright-field TEM images of highlighted CNT region and (d) embedded CNTs in the Ni matrix of CNT/NI MLM composite.

In this case too, the CNT/Ni interface is very sharp without any evident intermixing between the nanotube and the nickel. Unlike, CNT/Ni (ball milled) nanocomposites, in the
molecular level mixed nanocomposite, individual CNTs are homogeneously dispersed within the nickel matrix, thus providing a large number of very strong nickel-CNT interfaces that leads to improvement in mechanical properties such as high yield strength and microhardness. Ni$_3$C phase observed at nickel-CNT interface in the previously studied CNT/Ni (MLM) nanocomposites [189, 192] and also, nickel was used as catalyst for growing CNTs [91, 308], which leads to significant improvement in the nickel-CNT interfacial bonding. The distribution of individual CNTs was found to be more homogeneous in case of the CNT/Ni (MLM) nanocomposite as compared to the CNT/Ni (DM) nanocomposite that largely exhibited a distribution of small bundles of CNTs. Nevertheless, these CNT bundles in case of the CNT/Ni (DM) nanocomposite resulted in a high degree of grain refinement in the nickel matrix. While the CNT/Ni (MLM) nanocomposite exhibits the best nanotube distribution as well as the highest strength level, the processing of the CNT/Ni molecular-level powders is a relatively slow process and the scalability of such a process can be challenging. In contrast, while the CNT/Ni (DM) nanocomposite does not exhibit the ideally desired distribution of nanotubes and consequently exhibits a lower strength level, the processing steps involved are relatively simple and in principle can be scaled up.

5.5 Summary and Conclusions

Two types of CNT/Ni nanocomposites have been prepared by spark plasma sintering (SPS) process, one using ball milled nickel and CNT precursors, referred to as CNT/Ni (DM) and the second one using molecular level mixed CNT/Ni composite powders as a precursor, referred to as CNT/Ni (MLM). While both types of nanocomposites exhibited substantial enhancement in microhardness and tensile yield strength as compared to SPS processed pure Ni,
the CNT/Ni (DM) nanocomposite exhibited much higher ductility while the CNT/Ni (MLM) nanocomposite exhibited much higher tensile yield strength. The improvement in mechanical properties of the CNT/Ni (DM) nanocomposite mainly results from grain refinement of the nickel matrix resulting from the homogeneous distribution of small bundles of CNTs. The microhardness and yield strength of CNT/Ni (MLM) nanocomposite was significantly higher as compared to both CNT/Ni (ball milled) as well as pure nickel. The high strength of CNT/Ni (MLM) nanocomposite is mainly achieved due to the homogeneous distribution of individual CNTs in the nickel matrix and high interfacial strength due to a well-bonded Ni/CNT interface.
CHAPTER 6
SPARK PLASMA SINTERING OF NICKEL-GRAPHENE NANOPlatelet (GNP) NANOCOMPOSITES

6.1 Abstract

GNP/Ni nanocomposites with different volume fraction of GNPs fabricated via powder metallurgy method followed by spark plasma sintering. All GNP/Ni nanocomposites were fabricated by simple mechanical dry milling (DM) of nickel and GNP nanocomposite powders, followed by spark plasma sintering. Ni-1GNP (1vol.% GNP) nanocomposite exhibited a tensile yield strength of 370 MPa (about 2.5 times of SPS processed monolithic nickel ~ 160 MPa) and an elongation to failure ~ 40%. Both Ni-2.5GNP (2.5 vol.% GNP) and Ni-5GNP (5 vol.% GNP) nanocomposites exhibiting good improvement in tensile yield strength due to grain refinement, but there was a significant reduction in ductility/elongation to failure ~ 10% mainly due to agglomeration of GNPs into nickel matrix. The enhancement in the tensile strength and ductility of NI-1GNP nanocomposites achieved due to grain refinement, homogeneous dispersion of GNPs into nickel matrix, and strong metal-GNP interfacial bonding helps effectively transfer load across metal-GNP interface during tensile deformation.

6.2 Introduction

Graphene is a two dimensional (2D) building block of carbon material with a single atomic layer of sp² hybridized carbon atoms densely packed in a honeycomb lattice [17, 309, 310]. In recent years, graphene has attracted considerable attention due to its excellent mechanical and physical properties, such as high young’s modulus (1 TPA), high tensile strength (130 GPa), excellent thermal conductivity (5000 W/mK) wm⁻¹k⁻¹), high electron mobility...
(200,000 $\text{cm}^2\text{s}^{-1}$), large surface area (=2600 $\text{m}^2\text{s}^{-1}$), and very low density (2.2 $\text{gcm}^{-2}$), which make it a suitable candidate for various applications in the fields of solar energy conversion, supercapacitors, field effect transistors, lithium secondary batteries, metallization lines in devices, high speed devices associated with high mobility of carriers, spintronics, and sensors [136, 160, 196, 220, 309, 311-317]. One of the best possible ways to employ such extraordinary properties would be the incorporation of graphene in a composite material.

Graphene nanoplatelets (GNPs) are easier to handle and disperse in all kinds of matrices, as compared to CNTs, have potential to replace CNT reinforcements in most polymer/metal matrix composites [136]. Graphene nanoplatelets (GNPs) are widely used as reinforcements in many polymer-matrix composites due to their cost and ease of operation compared to CNTs. Polymer/graphene nanocomposites exhibited significant improvement in mechanical and electrical properties [310, 318-322]. However, very little work on metal/graphene nanocomposites has been reported, with even less discussing the controversial effect of graphene reinforcement on mechanical properties of composites. The main challenges associated with the processing and development of metal/graphene composites for practical applications are (a) to attain homogeneous dispersion of graphene into metal matrix due to large density differences between metal and GNPs, (b) to form a strong metal-graphene interfacial bonding which effectively transfers the load across the interface during mechanical deformation, and (c) to retain chemical as well as structural integrity of graphene (due to high pressure and high temperature processing conditions of composites) [17].

Recently, metal matrix composites have been widely used in automotive, aerospace, and electronic applications due to their high strength and lighter weight as compared to conventional metals, or alloys [136]. Nickel and nickel base superalloys have been widely used in automotive
and aerospace applications due to their high specific strength, high corrosion as well as fatigue resistance, and toughness [14, 169, 170]. Therefore, graphene reinforced nickel matrix composites would be an ideal material for high temperature structural and surface engineering applications due to their excellent tensile and tribological properties. The powder metallurgy technique is extensively used to fabricate metal/carbonaceous material composites due to its low cost and great versatility. This technique involves mixing of reinforced particles with metallic powders, followed by consolidation and sintering. The mechanical and tribological properties of metal matrix composites fabricated via a powder metallurgy route mainly depends on size, morphology, volume fraction, and overall distribution of reinforced particles [136].

Bartolucci et al. fabricated aluminum-graphene nanocomposites via milling, hot isostatic pressing, and hot extrusion, which exhibited reduction in hardness as well as tensile strength of the composites due to formation of Al₄C₃ (aluminum carbide) which lowers the interfacial bonding and load transfer across the interface [312]. On the other hand, Latief et al fabricated Al-GNP composites via powder metallurgy route exhibited improved mechanical properties and corrosion resistance [196]. Kuang et al. electrodeposited nickel-graphene composite coatings that have shown about 15% improvement in thermal conductivity and about 4 times enhancement in hardness over that of pure nickel [309].

To the best of our knowledge, our results is the first report of showing significant improvement in tensile properties/ mechanical properties of nickel/graphene nanocomposites fabricated via the powder metallurgy route followed by the spark plasma sintering (SPS) process. Spark plasma sintering (SPS) is a novel tool for processing of metal matrix composites at lower temperatures and shorter processing times. In the SPS process, a local high temperature state is generated when sparks discharge in a gap or at the contact point between the particles of powder
causing evaporation and melting on the surface of powder particles, thus helping in the formation of fully dense nanocomposites [264, 269]. This initiation of the spark discharge in the gap between particles is assisted by fine impurities and gases on and between the surfaces of the particles. SPS is a high-speed powder consolidation (sintering) technology capable of processing conductive and non-conductive materials, and it utilizes uniaxial force and on-off DC pulse energizing. This high frequency transfers and disperses the joule heat phenomenon throughout the specimen, resulting in a rapid and thorough heat distribution, ensuring high homogeneity and consistent precipitate densities. Consolidation of nanopowders is possible in SPS without excessive grain growth due to the high heating rates and lower sintering times and temperatures involved [253-257, 264, 265, 268, 269]. SPS is effective for any powder material applications, but interest is especially high for nano-crystalline structures, because of high surface area per volume. “Net” or “Near-net” shapes are also possible with SPS directly from powder to finished product, having symmetrical and simple geometry in one step. However, for complex shapes, further machining may be required. This report mainly focuses on the effect of graphene nanoplatelet volume fraction on microstructure and mechanical properties of graphene/nickel nanocomposites. The microstructure and mechanical properties of these nanocomposites have been compared and contrasted.

6.3 Experimental Details

Graphene nanoplatelets fabricated by chemical vapor deposition (CVD) with an average thickness of approximately 6-8 nm and average length of few μm were obtained from XG Science, South Korea. GNP/Ni nanocomposite powders were synthesized by mixing nickel powder and GNPs through high-energy ball milling process for 24 hrs. with 400 rpm. The volume fraction of GNPs in Ni-GNP composite powder was ~ 1%, 2.5%, and 5%. The GNP/Ni
composite powders were precompacted in a graphite mold under a pressure of 5 MPa. The precompacted powders were sintered by SPS system at a temperature of 1073 K for 5 min under a controlled argon atmosphere under a pressure of 80 MPa. The heating rate was maintained at 100° C/min. GNP/Ni nanocomposites were characterized in FEI-Quanta Nova-SEM. The instrument was also equipped with an electron backscatter detector (EBSD), where investigations of grain sizes and texture of grains/maps were conducted. Analysis of these runs was performed using the TSL OIM™ software. X-ray diffraction analysis of nanocomposites was performed using (1.54 Cu Kα) line of Rigaku Ultima III X-Ray diffractometer. Conventional and high-resolution transmission electron microscopy (TEM) analysis was carried out using a FEI TECHNAI F20 Field emission gun (FEG) TEM operating at 200 keV. TEM foils were prepared via jet polishing techniques and then ion milled using Gatan Duo Mill, using 4 keV for the further milling. To assess tensile properties of the composites, mini-tensile testing was carried out on a custom-built mini-tensile tester. The tensile samples were prepared using Electric discharge machining (EDM). The gauge length, width, and thickness of the gage section of the samples were 5.0 mm, 1.0 mm, and 1.35 mm, respectively. Each sample was ground and polished (in the order of 600, 800, 1200 grit size silicon carbide (SiC) papers) and final polishing was accomplished with 0.04 μm colloidal silica before tensile testing. The test was carried out at room temperature at a crosshead speed of 0.02 mm/min.

6.4 Results and Discussion

6.4.1 SEM Microscopy Analysis

Back-scattered SEM images of the SPS sintered pure nickel and GNP/Ni nanocomposites are shown in Fig. 6.1. Pure nickel (Fig. 6.1(a)) exhibits a uniform grain structure without any
Fig. 6.1 Backscatter SEM images of (a) pure nickel, (b) Ni-1GNP, (c) Ni-2.5GNP, and (d) Ni-5GNP nanocomposites, (e) SEM micrograph of Ni-2.5GNP nanocomposite and (f) corresponding EDS C map and circles are corresponding to GNP clusters.

porosity with an average grain size ~ 12 µm. The full and rapid densification of powder compacts without any substantial grain growth is one of the major advantages of SPS processing.
that is a result of sintering by joule heating and the spark plasma generated by the pulsed high
electric current passing through the compact. Ni-1GNP nanocomposite shows a substantially
refined grain structure (Fig. 6.1(b)), as compared with the pure Ni, even though both samples
were prepared with the same initial size of Ni powder. GNPs are uniformly distributed along the
grain boundaries of nickel without any clustering. The initial ball milling followed by spark
plasma sintering helps to obtain a refined grain structure due to homogeneous distribution of
GNPs within the nickel matrix. The addition of GNPs into the nickel matrix assists in grain
refinement by possibly inhibiting grain growth and providing nucleation sites for new grains
during recrystallization. Similar results were observed in Ni/CNT (DM) nanocomposites sintered
using SPS. Fig. 6.1(c) and (d) show SEM images of the Ni-2.5GNP and Ni-5GNP
nanocomposites that also exhibit a refined grain structure, but clustering of GNPs also is
observed with increasing volume fraction of GNPs in the composites. An EDS carbon map,
corresponding to Ni-2.5GNP, is shown in Fig. 6.1(e) and (f). Based on this map, the locations of
GNP clusters have been marked with dotted circles in both Fig. 6.1(e) and (f) which are exactly
matched. From these observations, it is clear that as volume fraction of GNPs increases in the
composites, more refined grain structure obtained with significant clustering of GNPs, which
support the grain-inhibiting phenomenon of GNPs within nickel matrix. Also, cross-sectional
view of these composites didn’t show any changes in shape of GNP clusters.

6.4.2 Grain Size and Texture Analysis

The Pseudo colored OIM™ map and texture map of pure nickel, Ni-1GNP, and Ni-
2.5GNP nanocomposites are shown in Fig. 6.2, Fig. 6.3, and Fig. 6.4, respectively. Both pure
nickel and Ni-1GNP nanocomposites exhibit random crystal structure, without any significant
change in texture. This is the main advantage of SPS sintered metal and composites having a refined grain structure obtained without any texturing effect. Also, there is no significant change in texture resulting from the addition of GNPs in nickel matrix.

Fig. 6.2 (a) Pseudo-colored OIM™ maps (b) texture map corresponding to SPS processed pure nickel.
Fig. 6.3 (a) Pseudo-colored OIM™ maps (b) texture map corresponding to SPS processed Ni-1GNP nanocomposite.
Fig. 6.4 (a) Pseudo-colored OIM™ maps (b) texture map corresponding to SPS processed Ni-2.5GNP nanocomposite.
6.4.3 XRD Phase Analysis

The XRD patterns for the SPS processed pure nickel and GNP/Ni nanocomposites are shown in Fig. 6.5. The XRD pattern for pure nickel shows peaks corresponding to the (111), (200), and (220) crystallographic planes of nickel. The addition of GNPs leads to the presence of a new peak which is referred to (0002) carbon peak corresponding to $2\theta=26.5$.

![XRD pattern obtained from pure nickel, Ni-1GNP, Ni-2.5GNP, and Ni-5GNP nanocomposites.](image)

**Fig. 6.5** XRD pattern obtained from pure nickel, Ni-1GNP, Ni-2.5GNP, and Ni-5GNP nanocomposites.

Presence of carbon peak in both the GNP/Ni nanocomposites confirms the presence of GNPs, without any other interfacial product/ carbide formation. The different volume fraction of GNPs could be recognized from the fluctuation intensity of GNP peaks/ (0002) carbon peaks, which increases with increasing volume fraction of GNPs. In all three cases, the maximum intensity peak is the Ni(111) peak. The Ni(111)/Ni(002) intensity ratio for SPS processed pure
Ni is 2.35; while that for Ni-1GNP, 2.43; for Ni-2.5GNP, 2.21; and finally for Ni-5GNP, 2.25. Comparing these three values with the standard ratio expected for randomly oriented Ni grains of 2.38 in the International Center for Diffraction Data (ICDD) files obtained from Joint Committee of Powder Diffraction Standards (JCPDS). No significant change in texture results from the introduction of GNPs in the nickel matrix. These XRD results supported the EBSD analysis (i.e., random crystal structure).

6.4.4 Tensile Properties Investigation

The yield strength and elongation (tensile) properties of SPS processed pure nickel and GNP/Ni nanocomposites are listed in Table 6.1. The corresponding engineering stress-strain curves for these materials are shown in Fig 6.6. The tensile yield strength of Ni-1GNP nanocomposite is 370- MPa, which is about 2.3 times higher than that of pure nickel (160 MPa). Also, Ni-1GNP nanocomposite exhibits about 40% elongation to failure/ ductility, which is well comparable with that of pure nickel (i.e., 50% elongation to failure). With increasing volume fraction of GNPs for Ni-2.5GNP nanocomposite exhibits tensile yield strength of 390 MPa, which is about 2.4 times higher than that of pure nickel with a compromise in ductility / elongation to failure (i.e. about 10%). Therefore, for an increasing volume fraction of GNPs from 1 to 2.5-vol%, there is little increment in tensile yield strength of composites with significant reduction in ductility (i.e., from 40% to 10%), mainly due to that the agglomeration of GNPs in the composite fails to transfer load/ stress effectively during tensile deformation. Even more striking is that, the tensile yield strength of Ni-5GNP nanocomposite is 350 MPa, which is lower than that of Ni-1GNP and Ni-2.5GNP nanocomposites due to GNP clustering.
Many researchers have reported similar observations of the deterioration in mechanical properties of metal/CNT composites due to agglomeration of CNTs failing to transfer load/stress effectively during mechanical deformation. Table 6.2 shows the predicted yield strength based on grain size effect and experimentally measured yield strength of all GNP/Ni nanocomposites. The values of $\sigma_0$ and $k$ are obtained from the optimization study executed for pure nickel for different SPS processing parameters (for different grain sizes of pure nickel) using linear fit for yield strength versus $d^{-1/2}$ plot. Ni-1GNP and Ni-2.5GNP nanocomposites exhibited significant improvement in tensile yield strength mainly due to the couple effect of grain refinement as well
as GNP reinforcement into nickel matrix which effectively transfers stress during tensile deformation. Ni-1GNP nanocomposite exhibits reasonable ductility due to uniform distribution of GNPs into nickel matrix without significant clustering of GNPs, which is observed in Ni-2.5GNP and Ni-5GNP nanocomposites.

Table 6.1 Microhardness, yield strength and elongation properties of pure nickel and GNP/Ni nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hardness (HV)</th>
<th>Yield Strength (MPa)</th>
<th>Ductility/Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Nickel</td>
<td>77.52±5</td>
<td>160±5</td>
<td>50</td>
</tr>
<tr>
<td>Ni-1GNP</td>
<td>165±10</td>
<td>370±3</td>
<td>43</td>
</tr>
<tr>
<td>Ni-2.5GNP</td>
<td>170±4</td>
<td>390±3.5</td>
<td>10</td>
</tr>
<tr>
<td>Ni-5GNP</td>
<td>150±3</td>
<td>350±6</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 6.2 Grain size, predicted yield strength and experimentally measured yield strength of GNP/Ni nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grain Size (μm)</th>
<th>Predicted Yield Strength (MPa)</th>
<th>Expt. Yield Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-1GNP</td>
<td>4</td>
<td>295</td>
<td>370±3</td>
</tr>
<tr>
<td>Ni-2.5GNP</td>
<td>3</td>
<td>328</td>
<td>390±3.5</td>
</tr>
<tr>
<td>Ni-5GNP</td>
<td>2</td>
<td>385</td>
<td>350±6</td>
</tr>
</tbody>
</table>
The strong interfacial bonding between GNPs and nickel matrix is effective in improving mechanical properties of GNP/metal nanocomposites. Despite the fact that GNPs are in the form of bundles, in the case of Ni-2.5GNP nanocomposite, a significant improvement in the yield strength is observed, which can be attributed in part due to grain size refinement. Ni-1GNP nanocomposite exhibits a classical strain-hardening behavior, all the way from yield to failure, as similar to pure nickel. The improvement in the yield strength observed in Ni-5GNP nanocomposite is mainly due to the grain refinement effect.

6.4.5 Surface Fractography Analysis

Fig. 6.7 SEM micrograph showing the fracture surfaces of the (a) pure Ni, (b) Ni-1GNP, (c) Ni-2.5GNP, and Ni-5GNP nanocomposites after tensile test; arrows are showing GNP clusters.
Fig. 6.7 (a-d) are secondary electron SEM micrographs showing the fracture surfaces of the pure nickel, Ni-1GNP, Ni-2.5GNP, and Ni-5GNP nanocomposites, respectively. From these images, it is evident that while pure nickel (Fig. 6.7(a)) and Ni-1GNP (Fig. 6.7(b)) nanocomposite offer similar fracture surfaces, the Ni-2.5GNP (Fig. 6.7(c)) and Ni-5GNP (Fig. 6.7(d)) nanocomposites yield a somewhat different fracture surface. The Ni-1GNP nanocomposite fracture surface (Fig. 6.7(b)) exhibits, typical cup and cone type failure characteristics, show dimples of the order of few microns in sizes. This is an indicative of a very ductile deformation behavior in agreement with the greater than 40% elongation observed for these nanocomposites fractured surfaces. Contrastingly, Ni-2.5GNP and Ni-5GNP nanocomposites exhibit much smaller dimples as well GNP clusters marked in arrow in both the composites. This is indicative of some strain localization and eventual failure at a much lower level of strain. The significant improvement in yield strength with reasonable ductility obtained in Ni-1GNP nanocomposite due to grain refinement, homogeneous distribution of GNPs into metal matrix, and strong Ni-GNP interfacial bonding leads to effectively transferring load across metal/GNP during tensile deformation.

6.4.6 High Resolution TEM (HRTEM) Analysis

Homogeneous distribution of individual GNPs in the Ni-1 Vol. % GNP composite is visible in Fig. 6.8(a), where most of the GNPs are found at the boundary of nickel grains (Fig. 6.8(a)). HRTEM micrographs clearly show a relatively sharp interface, which exhibits a well attachment between GNPs and nickel grains (Fig. 6.8(c) and 6.8(d)) and can promote the load transfer capability of the composite and lead into a higher strength and ductility. Fig. 6.9 presents the result of TEM investigation on the structure of the Ni-2.5 Vol. % GNP composite.
Fig. 6.8 (a) and (b) Bright-field TEM image showing GNPs along the boundary of nickel grains, (c) and (d) HRTEM image on the GNP/Ni interface of Ni-1GNP composite.

The low magnification bright field TEM micrograph in Fig. 6.9(a) shows nano-crystals of nickel (nc-Ni) with an average diameter of 50nm that were surrounded by GNPs of 50 nm wide and 300nm long. Z-contrast imaging by using STEM-HAADF imaging in Fig. 6.9(b) further confirms the presence of nanocrystals and micro-crystals of nickel (~1-2µm) in structure in addition to the GNPs that appear as the dark bundles.
Fig. 6.9 (a) and (b) TEM micrographs showing distribution of GNPs and nanocrystalline Ni (nc-Ni) in the composite, (c) and (d) HRTEM image showing the entangled configuration of GNPs in the matrix, (e) HRTEM image of the interface between a GNP and a nc-Ni clearly showing a large difference between the interlunar spacing of Ni and graphite of Ni-2.5GNP composite.
Higher magnification micrographs in Figs. 6.9(b) and (c) clearly indicate the structure of GNPs and their interface with nickel grains. The high resolution TEM analysis of the interface in Fig. 6.9(e) revealed the well bonded and sharp interface between GNPs and nickel grains that the atomic columns are clearly visible on either side of the interface.

6.5 Summary and Conclusions

GNP/Nickel nanocomposites have been prepared by spark plasma sintering (SPS) process using ball-milled nickel with varying volume fraction of GNP (1, 2.5, and 5vol%) precursors. The Ni-1GNP nanocomposite exhibited higher ductility while Ni-2.5 GNP exhibited much higher yield strength. The improvement in mechanical properties of the Ni-1GNP nanocomposites was mainly obtained from grain refinement of nickel matrix resulting from homogeneous distribution of GNPs in the nickel matrix and strong interfacial bonding which effectively transferred load across metal/GNP interface. The high strength of Ni-2.5GNP nanocomposite is mainly achieved from grain refinement of nickel matrix due to homogeneous distribution of GNP clusters, which significantly lower its ductility (i.e. 10%) as GNP clusters causes strain localization and eventually failure at a lower level of strain. The improvement in mechanical properties of Ni-1GNP and Ni-2.5GNP nanocomposites is a combined effect of grain refinement as well as GNP reinforcement. In contrast, Ni-5GNP nanocomposite exhibited about a two times higher tensile yield strength than that of pure nickel mainly due to grain refinement occurring because of GNP reinforcement. Due to a large agglomeration of GNPs in Ni-5GNP composites, GNPs are not effectively transfer loads from the metal matrix to GNPs, which leads to reduction in yield strength as compared to Ni-1GNP as well as to Ni-2.5GNP nanocomposites.
CHAPTER 7

3D MICROSTRUCTURAL CHARACTERIZATION OF Ni-Ti-C COMPOSITES

7.1 Abstract

A new class of Ni-Ti-C based metal matrix composites has been developed using the laser engineered net shaping (LENS™) process. These composites consist of an in situ formed and homogeneously distributed titanium carbide (TiC) phase reinforcing the nickel matrix. Additionally, by tailoring the Ti/C ratio in these composites, an additional graphitic phase can also be engineered into the microstructure. The microstructure of these composites has been characterized in detail in three dimensions, via serial-sectioning in a dual-beam focused ion beam instrument followed by appropriate 3D reconstructions, to determine the true morphology and spatial distribution of the TiC and graphite phases as well as the phase evolution sequence. These three-phase Ni-TiC-C composites exhibit excellent tribological properties, in terms of extremely low coefficient of friction while maintaining a relatively high hardness, and these will be discussed in the presentation.

7.2 Introduction

Metal matrix composites (MMCs) exhibit greater strength in shear and compression by combining the metallic properties (ductility and toughness) with ceramic characteristics (high strength and modulus) [6-8, 17]. MMCs exhibit attractive physical and mechanical properties, such as high specific modulus, fatigue strength, thermal stability, and wear resistance that make them suitable for automotive and aerospace industries and other structural applications [6-8, 14, 17]. MMCs are also used in electronic applications due to their low co-efficient of thermal expansion and higher thermal conductivity [6, 16, 87, 323]. The properties of MMCs are mainly
governed by two key factors: size and volume fraction of reinforcements as well as nature of matrix reinforcement interface [8, 14]. In situ MMCs exhibit thermodynamic stability, good interfacial bonding, and uniform fine particle distribution in the metal matrix, which leads to better mechanical properties, compared to conventional ex situ MMCs [8, 324]. Nickel and nickel base superalloys are widely used in automotive and aerospace applications (aircraft jet engines, land base turbines, and chemical-petrochemical plants) due to their excellent properties such as high resistance to corrosion as well as fatigue and low thermal expansion [8]. Titanium carbide (TiC) has a very high hardness (2859-3200 HV), high melting point (3420 K), low density (4.93 g/cm²), and high mechanical strength, but it is very brittle and cannot be used as a monolithic ceramic [14, 229-231, 233, 234, 236]. Therefore, TiC reinforced nickel matrix composites are considered as a good candidate for high temperature refractory, abrasive, and structural applications [14, 229-231, 233, 234, 236]. Using laser engineered net shaping (LENS™), novel monolithic composites based on Ni-Ti-C have been developed (U.S. patent Application No. 13/769,787) that combine properties such as solid lubrication (e.g. graphite), high hardness (e.g. TiC), and high fracture toughness (e.g. nickel), for structural as well as surface engineering applications. These multifunctional, monolithic composites are needed in industrial applications, such as drilling components (wear band, stabilizer, drill collar, etc.), tunnel boring, and land base turbines.

Three dimensional (3D) microstructural characterization is very important to reveal many microstructural parameters, such as the number of features per unit volume, true size, shape, and morphology of microstructural features, and the connectivity between features, that is not revealed by simple two dimensional (2D) microstructural characterization [325-327]. Tomographic techniques based on the 3D atom probe and transmission electron microscopy
(TEM), focus ion beam (FIB) serial sectioning, synchrotron-based x-ray diffraction and tomography, and sequential mechanical polishing or micromilling are techniques particularly suited for characterizing the local structure, chemistry, and/or crystallography of materials in 3D, from the atomic scale all way up to the millimeter size volumes [325]. Serial sectioning is one of the most common and powerful methodologies used to obtain 3D microstructural data. The dual-beam FIB has become a very powerful tool for such serial sectioning and 3D microstructural reconstruction of metals with multiple phases exhibiting complex morphologies and crystallographic orientations [325, 327-332]. Typically in FIB serial sectioning, to characterize particular microstructural features of interest, the general rule of thumb is that there should be a minimum of 10-20 sections per feature to accurately represent its shape and size [325]. The present paper mainly focuses on 3D microstructural characterization of novel laser deposited Ni-Ti-C composites. The salient features of the present study are to investigate the 3D morphology, size scale and distribution of TiC and graphitic precipitates in a nickel matrix and the implications on the sequence of phase evolution during solidification.

7.3 Experimental Details

7.3.1 Laser Engineered Net Shaping (LENS™) Processing

The titanium carbide (TiC) reinforced nickel based composites used for 3D microstructural characterization were deposited using the laser engineered net shaping (LENS™) process from a feedstock consisting of a blend of elemental nickel, titanium and nickel-coated graphite powders. The processing details for these composites have been described in detail in previous papers [14] but a short summary is included here for completion. The powders used for depositing the Ni-Ti-C composites consisted of commercially pure near spherical Ni (40-150
mm), pure Ti (40-150 mm) and Ni coated graphite powders, which were premixed in a twin roller mixer with the nominal compositions 80Ni-10Ti-10C and 77Ni-3Ti-20C (refer to Ni-10Ti-10C and Ni-3Ti-20C for brevity). These composites were laser deposited in a cylindrical geometry of diameter 10 mm and height 10 mm. The LENS™ deposited in situ Ni-Ti-C composites were characterized by scanning electron microscopy (SEM) in FEI-Quanta Nova-SEM. X-ray diffraction analysis of deposits was performed using (1.54 Cu Kα) line of Rigaku Ultima III X-ray Diffractometer. The micro-hardness was measured using a standard Vickers micro-hardness tester using 300g load. Sliding friction and wear testing was conducted with a Falex (Implant Sciences) ISC-200 pin-on-disk (POD) system at room temperature. The samples were openly exposed in lab air (~40% RH) during the tests. Tests were performed under a 1 N normal load with a 1.6 mm radius Si₃N₄ ball, which correspond to an initial maximum Hertzian contact stress (Pₘₐₓ) of ~1.2 GPa. The sliding speed was fixed at 50 mm/sec. The TEM analysis were performed on FEI Tecnai F20-emission gun (FEG) TEM, operating voltage of 200 keV. The ratio of tangential to normal load is the friction coefficient. Area fraction calculation of TiC and graphite reinforcements was done using ImageJ software, and an average of 50 SEM images were reported in this paper. The details of FIB serial sectioning and 3D reconstruction are explained in the next section.

7.3.2 Dual Beam FIB-SEM Serial Sectioning Methodology

This section will briefly describe the DB FIB SEM serial sectioning methodology employed to study the 3D microstructure characterization of Ni-Ti-C composites. A dual beam workstation (FEI Nova nanoSEM) equipped with FIB column employing a Gallium (Ga) liquid metal ion source, combined with a high-resolution field emission scanning electron microscope
(FEG SEM) was used. Prior to the 3D serial sectioning, the stage was tilted to maintain the 52° angle between the FIB and SEM column as shown in Fig. 7.1(a), so that the sample surface was oriented perpendicular to the ion beam during cross sectioning. A layer of platinum (Pt) was deposited on the top of region of interest, which serves not only as protection but also helps in minimizing curtaining effects and provides a sharp cutting edge during serial sectioning [325, 330, 333]. In addition to this, Pt deposited layer is used as fiducial marking during 3D reconstruction for alignment of obtained 2D SEM images. The sample has been FIB micro machined into cantilevered beam configuration as shown in Fig. 7.1(b) prior to the serial sectioning experiment. This sample geometry has 2 main advantages: first to minimize the redeposition of milled material onto the surface of interest, and second is to eliminate the possibility of shielding the detectors [325]. The serial sectioning procedure has been automated for FIB nova Nano SEM using FEI’s auto slice and view software.

Automation software is essential for this serial sectioning experiment as it ensures consistent serial-section removal rate, and this also eliminates the need for human supervision and interaction, so that the experiment can run for long period of time and contain potentially large number of serial sections [325].

7.3.3 Three Dimensional (3D) Reconstruction

The 2D image stack collected during the serial sectioning procedure was reconstructed into a 3D object using the software package termed MIPAR™ (Materials Image Processing and Automated Reconstruction) based on a MATLAB platform, developed at The Ohio State University, and the commercially available AvizoFire 6.3 software. The entire 3D reconstruction procedure consists of (a) alignment of the stack, (b) cropping of a region of interest, (c) noise
filtering/thresholding, (d) segmentation, and (e) visualization. The first 4 steps were performed using MIPAR™ and AvizoFire 6.3 was used for 3D visualization. In MIPAR™, an FFT filter was applied to minimize curtaining effects (artifacts) obtained from FIB serial sectioning. Thresholding of TiC and graphite phases was done by applying a Gaussian blur subtraction along with the global range thresholding filter prior to segmentation of individual features. Finally, this entire post-processed 2D image stack was exported to AvizoFire 6.3 format for 3D visualization of TiC and graphite reinforcements.

**Fig. 7.1** (a) Schematic of the sample geometry relative to the FIB and SEM columns for serial-sectioning, (b) representative cantilever beam sample geometry used for serial-sectioning.
7.4 Results and Discussion

7.4.1 XRD Phase Analysis

Fig. 7.2 (a) shows the x-ray diffraction (XRD) pattern for the as-deposited Ni-Ti-C composites of nominal compositions Ni-10Ti-10C and Ni-3Ti-20C. In case of Ni-10Ti-10C (lower pattern in Fig. 7.2(a)), the primary diffraction peaks can be consistently indexed based on the face centered cubic (FCC) Ni phase and the $\delta$-TiC phase exhibiting the rocksalt (NaCl type) structure. In case of Ni-3Ti-20C (top pattern in Fig. 7.2(a)), a peak at $2\theta \approx 26^\circ$, corresponding to the $\{0002\}$ planes of graphitic carbon is clearly visible in addition to the FCC Ni and $\delta$-TiC peaks. The absence of peaks corresponding to any Ni-Ti intermetallic phases is also evident in these diffraction patterns indicating that there is no reaction between nickel and titanium, rather titanium and carbon react within a molten nickel pool to form TiC precipitates.

7.4.2 SEM Microscopy Analysis

Backscattered SEM images from the Ni-10Ti-10C composite are shown in Figs. 7.2 (b & c), clearly exhibiting the presence of TiC precipitates with two different morphologies and size-scales. The coarser and faceted carbides are likely to be the primary TiC precipitates while the finer scale needle-like carbides are likely to be eutectic TiC precipitates, homogeneously distributed within the nickel matrix. Backscattered SEM images of the Ni-3Ti-20C composite are shown in Figs. 7.2 (d & e). These images clearly show the presence of TiC precipitates (grey) along with a substantial volume fraction of a phase exhibiting a black contrast, presumably corresponding to the graphitic phase revealed in the x-ray diffraction pattern. Ni-10Ti-10C exhibits approximately 17% (area fraction) of TiC whereas Ni-3Ti-20C exhibits approximately 8% graphite and 4% TiC. These 2D SEM images shown in Figs. 7.2(b-e) give an idea of the
overall microstructure of these composites and typically would be representative of microstructural analysis done in the past on such materials. However, the focus of the present study is a more detailed 3D analysis of the microstructure via serial-sectioning in dual-beam FIB and subsequent reconstruction of the 3D volume, as discussed below.

Fig. 7.2 (a) XRD pattern obtained from the LENS deposited Ni-Ti-C composites, (b) & (c) backscatter SEM images of LENS deposited Ni-10Ti-10C composites, (d) & (e) backscatter SEM images of LENS deposited Ni-3Ti-20C composites.
7.4.3 Three Dimensional (3D) Microstructural Analysis

The reconstructed 3D volume corresponding to the Ni-10Ti-10C composite is shown in Fig. 7.3(a). A cropped version of the entire 3D volume is shown in Fig. 7.3(b) for better visualization purposes. In the cropped view, the primary TiC precipitates have been colored in green, while the eutectic TiC are represented in purple color. While the appearance of this 3D microstructure is rather complex it clearly highlights the following salient aspects of this microstructure:

a. The primary TiC precipitates exhibit a cuboidal morphology.

b. The eutectic TiC precipitates appear to exhibit a plate-like morphology in most cases unlike the needle-like morphology revealed by 2D SEM observations. Some needle-like eutectic TiC precipitates are also visible in the 3D reconstruction.

c. Nearly all the eutectic TiC precipitates are connected to the primary TiC as well as other neighboring eutectic TiC precipitates.

d. The eutectic TiC precipitates form a 3D network with the larger primary TiC precipitates located at the nodes of this network.

The connectivity between the carbide precipitates is impossible to discern based on the 2D SEM images in Figs. 7.2, without the aid of 3D reconstruction. The eutectic TiC precipitates that are connected to the primary TiC, possibly nucleated from the primary precipitate during solidification. Fig. 7.4(a) shows the 3D reconstruction of the Ni-3Ti-20C composite. The major challenge in 3D reconstruction of these Ni-3Ti-20C composites compared to the Ni-10Ti-10C composites is the presence of 2 different precipitates phases i.e. TiC and graphite. During post processing of 2D SEM images, both the phases (TiC and graphite) were
thresholded differently and then exported to reconstruct the 3D volume. The TiC precipitates are yellow in color while

Fig. 7.3 (a) 3D reconstruction of Ni-10Ti-10C composites obtained from the 2D SEM image stack, (b) cropped version of 3D reconstructed volume of Ni-10Ti-10C showing primary and eutectic TiCs.
Fig. 7.4 (a) 3D reconstruction of Ni-3Ti-20C composites obtained from the 2D SEM image stack, (b) cropped version of 3D reconstructed volume of Ni-3Ti-20C showing primary and eutectic TiC engulfed by graphite bundle.
the graphite bundles are pink colored. The carbide precipitates (yellow) are clearly connected to each other and form a complex network in 3D. This connectivity between the carbide precipitates is nearly impossible to visualize based on the 2D SEM images shown in Fig. 7.2. The distinction between the cuboidal primary TiC precipitates and the plate or needle-shaped eutectic TiC precipitates is more difficult in case of this composite since the primary precipitates are smaller in size as clearly shown in the higher magnification view of a cropped section of the 3D reconstruction in Fig. 7.4(b). Furthermore, most of the cuboidal primary TiC precipitates are engulfed by graphite bundles (pink) as shown in both Figs. 7.4(a and b). Referring to the 2D SEM images shown in Figs. 7.2(d and e), there is a gap between the TiC precipitates and the graphite bundles, and it is very difficult to comment on their interconnectivity and association based on these images. The 3D reconstructions shown in Fig. 7.4 conclusively reveal the true nature of the connection between the carbide precipitates and the graphitic bundles in this microstructure. Referring to Figs. 7.4(a and b), the eutectic TiC precipitates in case of the Ni-3Ti-20C composite exhibit both plate-like and needle-like morphologies.

The 3D reconstructions aid in developing a better understanding of the sequence of phase evolution during solidification for both types of composites (Ni-10Ti-10C and Ni-3Ti-20C) as well as the shape, size, and connectivity between the different phases involved. Within the liquid melt pool consisting of Ni+Ti+C, the primary TiC forms appears to be the first solid phase to form during solidification for both types of composites, and at lower temperatures, the eutectic TiC as well as graphitic phases are formed (only for Ni-3Ti-20C). For both types of composites, the cuboidal primary TiC precipitates appear to act as the heterogeneous nucleation sites for the eutectic product. Thus, in case of the Ni-10Ti-10C composite, the primary TiC cuboids act as the nodes from which the eutectic TiC precipitates (plate-like and needle-like)
nucleate resulting in the formation of the complex 3D interconnected network of carbide precipitates. In case of the Ni-3Ti-20C composite, smaller cuboidal primary TiC precipitates form in the liquid and these act as heterogeneous nucleation sites for both the eutectic TiC precipitates as well as graphite bundle that form presumably at lower temperatures and engulf the primary TiC precipitates. While these insights into the solidification sequence could not have been revealed without the 3D reconstructions, it should be noted that more detailed investigations are warranted in order to develop a robust understanding of the microstructural evolution process. The volume fractions of the different phases have also been calculated using the 3D reconstructions. The results indicate that Ni-10Ti-10C exhibits approximately 17% of TiC whereas Ni-3Ti-20C exhibits approximately 7% graphite and 5% TiC which is in very good agreement with the values computed from the 2D area fractions. Based on these phase fractions, it is possible to recalculate the nominal compositions of the two types of composites as Ni-17Ti-17C and Ni-5Ti-12C. These corrected composition values will be employed in the subsequent section discussing the sequence of phase evolution in these composites.

7.4.4 Modeling the Sequence of Phase Evolution

Modeling the sequence of phase evolution in the Ni-17Ti-17C and Ni-5Ti-12C composites has been carried out using a simple phase diagram analysis of the Ni-Ti-C ternary phase diagram. Isothermal sections of the Ni-rich corner of the Ni-Ti-C phase diagram, at four different temperatures, computed using commercially available solution thermodynamic models (PANDAT™ from CompuTherm), are shown in Figs. 7.5 (a-d). The points corresponding to the Ni-17Ti-17C (marked by a circle) and Ni-5Ti-12C (marked by a square) compositions have also been indicated on each of the isothermal ternary sections. A pseudo-binary section of the same
Fig. 7.5 Isothermal sections of Ni-rich corner of the Ni-Ti-C ternary phase diagram at (a) 2725°C, (b) 2500°C, (c) 1800°C, and (d) 1500°C temperatures, and (e) pseudo-binary section of the same ternary system between TiC and Ni [229].
ternary system between TiC and Ni has been plotted in Fig. 7.5(e) [229]. At a very high temperature of 2725°C, both compositions lie in the single liquid phase region. Reducing the temperature to 2500°C results in the Ni-17Ti-17C composition lying within the liquid + primary TiC two-phase field indicating that primary TiC precipitates will nucleate and grow in this composite. Subsequent continuous cooling on to lower temperatures increases the volume fraction of the primary TiC precipitates, depleting the liquid of both Ti and C, and eventually at a temperature of ~ 1280°C, the remaining liquid in the system undergoes a pseudo-binary eutectic solidification to form eutectic Ni + eutectic TiC as shown in Fig. 7.5(e). Contrastingly, the Ni-5Ti-12C composition exhibits a different sequence of phase evolution, starting with a single liquid phase at high temperatures (>2500°C). Continuous cooling of this composition initially results in the primary solidification of TiC at temperatures ~ 1800°C (Fig. 7.5(c)) and at even lower temperatures ~ 1500°C, this composition enters a liquid + TiC + C three phase field (Fig. 7.5(d)) indicating the formation of a second solidification product, C (graphite), in the liquid. Eventually at an even lower temperature ~ 1280°C, the remaining liquid undergoes eutectic solidification to form eutectic Ni + eutectic TiC.

While the sequence of phase evolution can be predicted based on the isothermal sections of the ternary Ni-Ti-C phase diagrams, the resultant microstructure is difficult to visualize without the 3D reconstructions. Thus, these reconstructions aid in developing a better understanding of the shape, size, distribution, and connectivity between the different phases evolving during the solidification of both types of composites (Ni-17Ti-17C and Ni-5Ti-12C). Within the liquid melt pool consisting of Ni+Ti+C, the primary TiC appears to be the first solid phase to form during solidification for both types of composites. These primary carbide precipitates exhibit a cuboidal morphology because of NaCl type crystal structure of TiC,
presumably dictated by surface energy criteria. Continuous cooling results in growth of these cuboidal primary TiC precipitates within the retained Ni-Ti-C liquid, depleting it of Ti and C. In case of the Ni-17Ti-17C composition, the retained liquid eventually undergoes eutectic solidification into Ni + eutectic TiC. The cuboidal primary TiC precipitates act as heterogeneous nucleation sites for the eutectic carbide precipitates, resulting in the formation of a network of eutectic carbide precipitates linked at their nodes by the primary carbide precipitates, as clearly revealed by the 3D reconstructions shown in Fig. 7.3. The regions in between this network form the pure Ni grains. In contrast, while the Ni-5Ti-12C composition also starts its solidification sequence by forming cuboidal primary TiC precipitates, the remaining liquid does not directly undergo eutectic solidification, but rather forms a second solidification phase within the liquid, a graphitic carbon phase. This graphitic carbon phase forms directly in the liquid Ni-Ti-C and nucleates and grows preferentially at the primary TiC precipitates, eventually encompassing the entire carbide precipitate. Eventually, at even lower temperatures, the retained liquid undergoes eutectic solidification to form Ni + eutectic TiC precipitates. The eutectic carbides also appear to heterogeneously nucleate and grow from the cuboidal primary carbide precipitates and form an interconnected three dimensional network linked by the cuboidal primary carbides at the nodes.

7.4.5 Microhardness and Wear Properties

Comparing the microhardness values for the two different composites, the Ni-10Ti-10C composite exhibited a substantially higher hardness of 370 VHN as compared to 165 VHN for the LENSTM deposited pure Ni and 290 VHN & 240 VHN for LENS deposited Ni-7Ti-20C & Ni-3Ti-20C respectively. These microhardness values have been listed in Table 7.1 and clearly show a trend of decreasing hardness as a function of increasing C/Ti ratio in the composite. The
high volume fraction of titanium carbides (both primary and eutectic), in case of the Ni-10Ti-10C composite resulted in the higher microhardness value. Preliminary results of POD tribometry studies carried out on the LENS deposited Ni-10Ti-10C, Ni-3Ti-20C, Ni-7Ti-20C composites and pure Ni samples are shown in Fig. 7.6.

Table 7.1 The microhardness values for the different Ni-Ti-C composites investigated in the present study in comparison with pure Ni.

<table>
<thead>
<tr>
<th>Composite Sample</th>
<th>Hardness(HV)</th>
</tr>
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<tbody>
<tr>
<td>Pure Ni</td>
<td>165 ± 6</td>
</tr>
<tr>
<td>Ni-3Ti-20C</td>
<td>240 ± 6</td>
</tr>
<tr>
<td>Ni-7Ti-20C</td>
<td>290 ± 7</td>
</tr>
<tr>
<td>Ni-10Ti-10C</td>
<td>370 ± 10</td>
</tr>
</tbody>
</table>

From Fig. 7.6, it is clear that the graphite and TiC phases in the composite were beneficial in reducing the friction coefficient with respect to the pure Ni sample. While the presence of TiC reduces the coefficient of friction, as observed in case of the Ni-10Ti-10C composite, the presence of the lubricious graphitic phase can play a more dominant role in reducing the friction for these composites. This is evident from the friction curves for the Ni-7Ti-20C and Ni-3Ti-20C composites. The friction coefficient in case of Ni-7Ti-20C is marginally lower as compared to Ni-10Ti10C due to the presence of the graphitic phase in the former. However, the most promising composite appears to be the Ni-3Ti-20C composite, which exhibits a drastic reduction in friction coefficient (~0.2) as compared to any of the other composites, mainly due to the presence of a substantial fraction of the graphitic phase as well as TiC.
precipitates. Thus, these Ni-Ti-C composites, especially the Ni-3Ti-20C composite, appear to be promising materials for surface engineering applications requiring high hardness with improved solid lubrication.

![Fig. 7.6](image)

**Fig. 7.6** Steady state friction coefficient as a function of sliding distance up to 140 m for LENS deposited pure nickel, Ni-10Ti-10C, Ni-7Ti-20C, and Ni-3Ti-20C composites.
7.4.6 High Resolution TEM (HRTEM) Analysis

Bright-field transmission electron microscopy (TEM) images of Ni-10Ti-10C composites are shown in Fig. 7.7. This shows overall microstructure with primary and eutectic titanium carbide precipitates. Fig. 7.7(a) shows primary titanium carbide exhibiting cuboidal faceted morphology, whereas eutectic titanium carbide exhibiting needle like structure as shown in Fig. 7.7(b). Bright-field TEM images and high-resolution TiC/graphite interface images of Ni-3Ti-20C composites are shown in Fig. 7.8. Fig. 7.8 (a) and (b) clearly shows the graphite phase along with TiC precipitates. Primary TiC exhibiting cuboidal faceted morphology, similar to that of Ni-10Ti-10C composites. Fig. 7.8(d) shows very clean interface between TiC and graphite.

Fig. 7.7 Bright-field TEM image showing the (a) primary TiC phase and (b) eutectic TiC phase.
Fig. 7.8 Bright-field TEM image showing the (a) graphite phase, (b) combine TiC and graphite phases, (c) primary TiC phase, and (d) high resolution TEM image showing interface between TiC and graphite.
7.5 Summary and Conclusions

Novel in situ Ni-Ti-C composites have been deposited using the laser engineered net shaping (LENS™) process. While the Ni-10Ti-10C composite exhibits a large volume fraction of primary cuboidal TiC precipitates as well as eutectic carbide precipitates, both the Ni-7Ti-20C and Ni-3Ti-20C composites exhibit an additional graphitic phase. 3D microstructural characterization of these composites reveals the following salient features of the these composites:

1. The Ni-10Ti-10C composite consists of a complex interconnected network of carbide precipitates with primary cuboidal TiC precipitates at the nodes of the 3D network, connecting plate-like (needle-like in some cases) eutectic TiC precipitates. The primary carbides appear to act as the heterogeneous nucleation sites for the eutectic carbides.

2. The Ni-3Ti-20C composite also consists of an interconnected network of primary carbide precipitates at nodes with eutectic carbides connecting them, but the smaller scale cuboidal primary carbide precipitates in this case are engulfed by graphitic bundles, a second primary solidification product.

Such 3D characterization leads to a better understanding of the sequence of phase evolution during solidification in these novel composites. Tribological and mechanical property measurements reveal that the steady-state friction coefficients for these Ni-Ti-C composites are significantly lower than that of pure Ni, while their microhardness is substantially higher, making them promising candidates for surface engineering applications that require both solid lubrication and high mechanical hardness. Out of all the Ni-Ti-C composites investigated the Ni-3Ti-20C composite appears to exhibit the best balance of properties with the lowest coefficient of friction as compared to pure Ni, Ni-10Ti-10C, and Ni-7Ti-20C, and a microhardness that is
greater than pure nickel, though being somewhat lower than Ni-10Ti-10C or Ni-7Ti-20C composites.
CHAPTER 8
SUMMARY AND FUTURE WORK

The optimization of SPS processing parameters is important in governing the mechanical properties of pure nickel. Detailed investigation was executed to optimize the processing parameters for pure nickel to tailor its mechanical properties. In SPS process, temperature is the main governing parameter to control grain size, which in turn governs the mechanical properties. The tensile yield strength of SPS processed pure nickel increased as average grain size decreased, following similar trend of Hall-Petch rule. The modified Hall-Petch equation obtained for SPS sintered pure nickel is given by:

\[ \sigma_y = 77.7 + 434.5 \times d^{-1/2} \]

After optimizing the SPS processing parameters and establishing the modified Hall-Petch equation, CNT/Ni and GNP/Ni nanocomposites were fabricated to study the effect of reinforcements on the mechanical properties of these nanocomposites. Two types of CNT/Ni nanocomposites have been prepared by spark plasma sintering (SPS) process, one using ball milled nickel and CNT precursors, referred to as CNT/Ni (DM) and the second one using molecular level mixed CNT/Ni composite powders as a precursor, referred to as CNT/Ni (MLM). While both types of nanocomposites exhibited substantial enhancement in microhardness and tensile yield strength as compared to SPS processed pure Ni, the CNT/Ni (DM) nanocomposite exhibited much higher ductility while the CNT/Ni (MLM) nanocomposite exhibited much higher tensile yield strength. By using the modified Hall-Petch equation, the effect of CNT reinforcement on mechanical properties was studied, but still a detailed investigation remains necessary to conclude any possible strengthening mechanisms of these composites. The improvement in mechanical properties of the CNT/Ni (DM) nanocomposite
mainly results from grain refinement of the nickel matrix resulting from the homogeneous distribution of small bundles of CNTs. The high strength of CNT/Ni (MLM) nanocomposite is mainly achieved due to the homogeneous distribution of individual CNTs in the nickel matrix and high interfacial strength due to a well-bonded Ni/CNT interface.

To study the effect of reinforcement content on their mechanical properties, GNP/Nickel nanocomposites have been prepared by spark plasma sintering (SPS) process using ball-milled nickel with varying volume fraction of GNP (1, 2.5, and 5vol%) precursors. All the GNP/Ni nanocomposites exhibited substantial enhancement in microhardness and tensile yield strength as compared to SPS processed pure nickel. The Ni-1GNP nanocomposite exhibited higher ductility while Ni-2.5 GNP exhibited much higher yield strength. The improvement in mechanical properties of the Ni-1GNP nanocomposites was mainly obtained from grain refinement of nickel matrix resulting from homogeneous distribution of GNPs in the nickel matrix and strong interfacial bonding, which effectively transferred load across the metal/GNP interface. The high strength of Ni-2.5GNP nanocomposite is mainly achieved from grain refinement of nickel matrix due to homogeneous distribution of GNP clusters, which significantly lower its ductility (i.e. 10%) as GNP clusters causes strain localization and eventually failure at a lower level of strain. The improvement in mechanical properties of Ni-1GNP and Ni-2.5GNP nanocomposites is a combined effect of grain refinement as well as GNP reinforcement. In contrast, Ni-5GNP nanocomposite exhibited about a two times higher tensile yield strength than that of pure nickel mainly due to grain refinement occurring because of GNP reinforcement. Due to a large agglomeration of GNPs in Ni-5GNP composites, GNPs are not effectively transferring loads from the metal matrix to GNPs, which leads to reduction in yield strength as compared to Ni-1GNP as well as to Ni-2.5GNP nanocomposites.
Three dimensional (3D) microstructural characterization of Ni-Ti-C composites consisting of TiC and graphite phases reinforcing a nickel matrix has been carried out by FIB-based serial sectioning followed by reconstruction of the 3D volume using MIPAR™ & AvizoFire software. The 3D reconstruction of the Ni-10Ti-10C composite reveals a complex interconnected network of carbide precipitates with primary cuboidal TiC precipitates at the nodes of the 3D network, connecting plate-like (needle-like in some cases) eutectic TiC precipitates. The primary carbides appear to act as the heterogeneous nucleation sites for the eutectic carbides. The 3D reconstruction of the Ni-3Ti-20C composite also reveals an interconnected network of carbide precipitates but the smaller scale cuboidal primary carbide precipitates in this case are engulfed by graphitic bundles. Such 3D characterization also leads to a better understanding of the sequence of phase evolution during solidification. Tribological and mechanical property measurements reveal that the steady-state friction coefficients for these Ni-Ti-C composites are significantly lower than that of pure Ni, while their microhardness is substantially higher, making them promising candidates for surface engineering applications that require both solid lubrication and high mechanical hardness.

However, more detailed investigation needs to be conducted to understand the possible strengthening mechanisms in Ni-CNT/GNP nanocomposites. Theoretical modeling can also help to understand strengthening mechanisms of these composites, correlating with obtained experimental results. The effect of varying CNT volume fractions on the mechanical properties of composites will be an exciting task. The effect of CNT and GNP reinforcement on the mechanical properties of SPS processed low solvus, high refractory (LSHR) powder metallurgy advanced disc alloy is also an interesting area. Some of the beginning experiments showed quite promising results, but detailed investigation will be important. Even though 3D microstructural
characterization of Ni-Ti-C composites provided important insights into the sequence of phase evolution during solidification, still this 3D characterization is a qualitative analysis. But what needs to be performed now is a quantitative analysis of 3D characterization for different compositions of Ni-Ti-C composites to understand the detailed phase evolution sequence of these composites.
APPENDIX

PUBLICATIONS


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