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Processing of Graphene/CNT-Metal Powder

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Abstract

In recent days, the demand for powder metallurgy components has increased due to unusual combination of properties. Carbon allotropes such as graphene and CNT are the novel material to enhance the properties of powder metallurgy component. However, processing of such materials is in infancy stage due lack of advance processing technique. This can be addressed through integration of several fabrication techniques to meet the industrial demands. The processing method and its important parameter will define the final property of the component. Such materials have found its applications in various fields like, sports, bio implants, aerospace and automobile sector.

Keywords: graphene, CNT, powder technology, sintering, metal matrix composite (MMC)

1. Introduction

Combinations of two or more physically and chemically distinct materials that results in improved properties compared to individual materials are termed as “composites.” Due to the adequate combination of such distinct materials, the properties of composites can be enhanced due to the presence of various materials. Composite materials bring the additional strength, stiffness apart from reducing the overall density compared to monolithic and non-aggregates allowing considerable reduction in the weight. Additionally, composites possess unidirectional properties (specific tensile strength) and increased fatigue endurance. The reinforcement plays an important role by providing the additional strength, stiffness and tribological properties in the composite. In many cases, the important properties of the reinforcement are strength, hardness and stiffness which are normally higher than the matrix

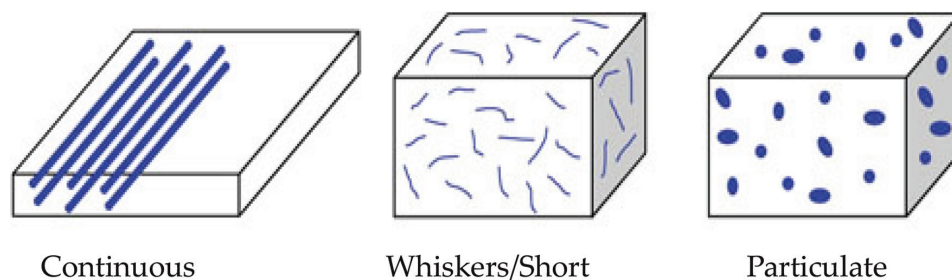


Figure 1. Type of reinforcements used for the composites.

materials. Today, the most man made engineered composites includes mortar; concrete; reinforced plastics; ceramic composites and metal composites. Particulates, whiskers/short fibers are the common type of reinforcements (**Figure 1**) used successfully for the fabrication of composite. Particulates are available in platelets, spherical and various regular or irregular shapes which may be having equal geometry in all directions. The particulate reinforcement was limited to 30–40 vol% in the composite due to its brittleness and fabrication difficulties. Fiber glasses were the first modern composites and are used for sports materials, car bodies, ship and other structural applications. But, due to the advancement in the composite technology, carbon fibers replaced the glass reinforcement in the composite and were used for many expensive sporting equipment and aircrafts structures. Carbon nanotube is being used successfully in these days for making of stronger and lighter composites. Another advantage of any composite material is that their properties are tailorable to certain extent along any direction. Further, these developed composite materials have design—flexibility, close tolerance, high durable, chemical inert and corrosive resistance. Also, the innovation in the fabrication techniques and combination of advanced materials resulted in superior thermal stability, high temperature retention and outstanding electrical properties. Composite materials are used for various applications such as building blocks, structures, bridges, automobile components, race car bodies, aerospace structural materials, space crafts and more.

2. Metal matrix composites (MMCs)

Metal matrix composites (MMCs) comprises lightweight and low-density materials (aluminum, magnesium, copper, etc.) reinforced with fiber or particulate of ceramic (silicon carbide, alumina, graphite, etc.). MMCs gave the opportunity to tailor the desire properties for specific applications. The important properties of metal matrix composites are stiffness, specific strength at elevated operating temperature and high tribological performance. On the other hand, fabrication cost of MMCs found to be higher for high performance application such as space and military and conceding the ductility and toughness. Also, MMCs have wide applications and are used in jet engines, aircrafts, satellite materials, and piston materials, cutting tools and space shuttle (NASA). MMCs with high strength and specific stiffness could be used in high speed machinery tools, robots, ships and rotating shaft where weight is an important criterion. MMCs also exhibit good wear resistance with high specific strength which is favorable for brake and engine components. Further, flexibility in tailorable thermal conductivity

and thermal expansion, MMCs are very good candidate for precision machinery, lasers and electronic packaging. In order to make use of MMCs in all the production areas and commercially attractive, prioritized research and development should be made on highly reliable manufacturing process with lowering the processing costs. Also, advanced processing techniques in powder metallurgy, plasma spraying, liquid metal infiltration, innovative casting methods and innovative combination of advanced reinforcing materials is needed very much. Further, functionalization and coating on the matrix/reinforcement are very much necessary which can prevent the deleterious chemical reaction at higher operating temperature conditions.

3. Powder metallurgy process

Powder metallurgy consists of a sequence of activities where, a feedstock in powder form μm to nm is used for fabricating the components of several shape and structures. **Figure 2** shows the general sequence of operations involved in a typical powder metallurgy production technology to obtain a finished component. Mechanical alloying, milling, electrolytic decomposition and gas atomization are the few metal powder techniques. Metal or alloy powder comes in various shapes and sizes which are dependent on the production method and parameters. Mixing of powders involves the introduction of various metal/alloy powders along with calculated quantity of reinforcement materials. Thus obtained powder mixtures are subjected to consolidation using rigid tool set comprising of die and punches. Thus obtained green compacts are sintered to make the particle bonding, (**Figure 3**) enhance the strength and the integrity which is usually done in protective atmosphere. The powder metallurgy process exists for the past 100 years, over the past years it has become a superior method to produce high-quality realistic industrial components with integration of novel reinforcements during preprocessing stage.

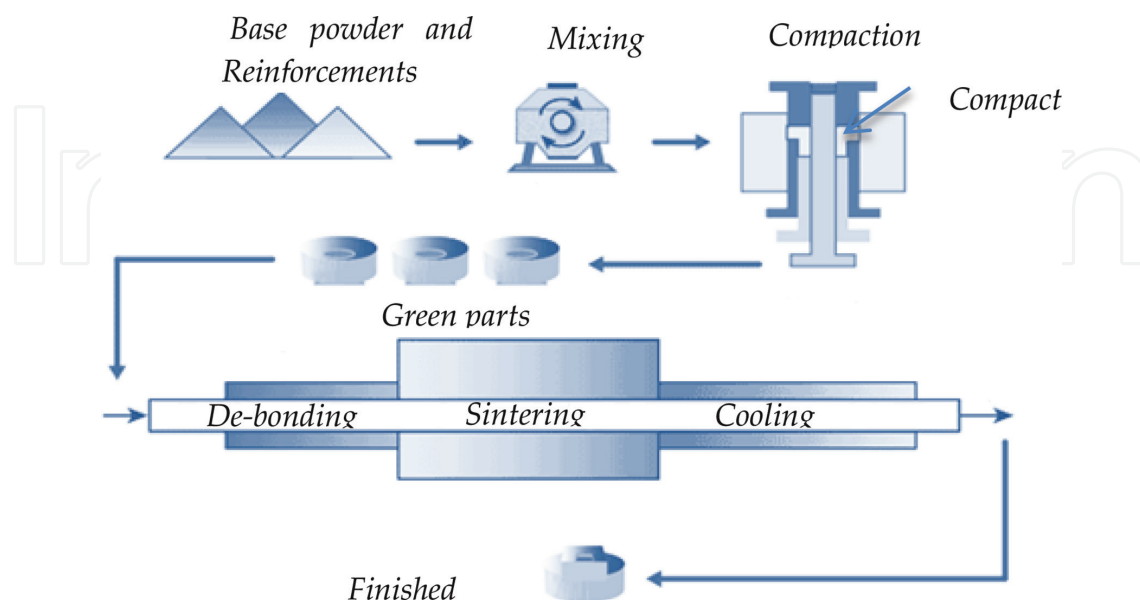


Figure 2. Conventional powder metallurgy process.



Figure 3. Powder to bonded structure during sintering.

With the several advantages of powder technology it become highly sustainable processing method over many conventional metal forming methods in producing complex shape, effective raw material utilization and the high tolerance. In the recent years, powder metallurgy process has been upgraded to consolidate pores or fully dense structures. Out of several new methods like hot isostatic pressing (HIP), metal injection molding (MIM), composites produced using powder forging (PF) and metal additive manufacturing (AM) have gained much popularity. **Figure 4** shows some of the structures produced through powder metallurgy route. Most of the powder metallurgy parts include filtration systems, magnetic assemblies, automobile components and structural parts. Gears, bushes and bearings produced through powder metallurgy process exhibit the more porous but they naturally reduce the noise. Powder metallurgy is also a very feasible technique for producing parts with magnetic properties. Further, magnetism can be enhanced by varying the sintering parameters.

3.1. Advantages of powder metallurgy process

The main advantage of powder metallurgy process is its ability to compress the powder into final size of closed dimensions and there is no need of any other subsequent forming process. Further, the process utilizes the 100% raw materials to get final component there by reducing the production cost compared to other conventional process (5–10% wastage). In the powder metallurgy process metal or alloy will not melt completely. So, there will not be any impurities by oxidation or deoxidizing or impurities from the crucible. Also, the process enables the production of high purity materials where, sintering is carried out in vacuum or gas atmosphere which will remain as the unique atmosphere throughout the process. Powder metallurgy enables the correctness of the material composition/weight/volume ratio and its homogeneity and it is suitable for mass production of same shape components.

3.2. Post processing of powder metallurgy

According to the specific densification requirements, sintered metal or alloy compacts are subjected to post processing treatments which includes impregnation, repressing, heat treatment, surface treatment and extrusion. Impregnation is performed by dipping oil or plastic into molten metal. The specific purpose of this process is to improve the self-lubrication,

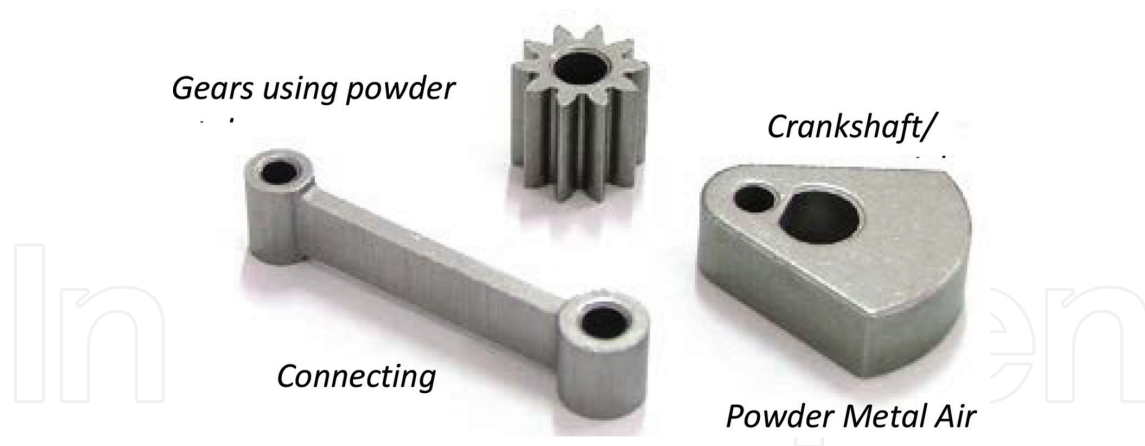


Figure 4. Complex structures produced through powder metallurgy.

wear resistance, strength and rusting proof. Repressing is carried out to improve the various mechanical properties, surface roughness and physical properties. In order to improve the product performance, sintered components are heated to a certain temperature and cooled with controlled temperature. Thermomechanical treatment, chemical treatment and heat hardening are the commonly used methods. Heat treated parts exhibits the well refined grain structure, high strength and high fracture toughness. Surface heat treatment methods such as steam treatment, galvanizing, plating, etc., are performed to make pores free and dense surface. In addition, extrusion, forging, welding and special processing method are used to obtain a desired shape, improved mechanical properties and high tolerance sintered structures of the final requirement to improve the product quality and its performance.

4. Allotropes of carbon

Carbon (C) is a chemical element with atomic number 6 and having [He] 2s²2p² electron configuration [1]. It is the fourth most abundant chemical element on the earth by mass. Diamond, amorphous carbon, graphite, and fullerenes are the well-known allotropes of the carbon. **Figure 5** shows the various crystallographic physical structures of these allotropes. Diamond is well known for its high hardness, which consist of pure sp³ hybridized carbon atoms with the strong covalent bonding among carbon atoms (**Figure 5**). Diamond is frequently used as cutting and polishing tools [2]. Graphite is made up of layers of carbon atoms in a planar structure (**Figure 5b**). The carbon atoms are organized in a hexagonal lattice. Graphite is the softest structure in which the carbon atoms are sp² hybridized and the layers are hold by van der Waals force of attraction. Graphite is mainly used in industrial lubrication purposes. Other allotropic form is the amorphous carbon. It is soot and black carbon which does not have any crystalline structure (**Figure 5**). Amorphous carbon can be used as inks, paints, and industrial rubber filler [3]. Fullerene is the fourth allotrope of carbon at nanoscale. **Figure 5d–f** demonstrates the structures of fullerene family members. It includes the ellipsoidal fullerenes, spherical fullerene (buckyball), cylindrical carbon nanotubes, and planar graphene. In the buckyball (C₆₀) all the carbon atoms are arranged in the three adjacent carbon atoms

with covalent bonding (**Figure 5d**) and these are having promised applications in polymer as filler to increase the mechanical strength. Ellipsoidal fullerenes; C70 (**Figure 5e**), C84, C72 and C76, icosahedral fullerene; C540 is also synthesized in the laboratories [4]. Carbon nanotubes (CNTs) (**Figure 5f**) and the graphene are discussed in the next sections.

4.1. Carbon nanotube (CNT)

In 1991 CNTs were first discovered by a scientist Sumio Iijima (NEC Company, Tsukuba, Japan) [5]. The discover looks like concentric carbon tube called as multi walled carbon nanotube as shown in **Figure 6**. At the later stages another form of CNT called single walled carbon nanotube (SWCNT) was discovered. One dimensional fullerene with tubular structure of carbon atom is called as SWNT which poses a lower aspect ratio compared to SWCNT and also have different mechanical and electrical properties. CNT poses excellent thermal conductivity which is equal to diamond [1]. In the recent years, carbon nanotubes (CNTs) are known to be one of the most efficient nanomaterials making next generation engineering and industrial revolution. Extraordinary properties of CNTs are of high demand mainly in semi-conductors, electronics and aerospace fields, etc. **Figure 6** shows the various types of CNTs which are depending on the number of carbon single atom layers (x). CNTs are referred to as SWCNTs (**Figure 6a**) if $x = 1$ (single layer of carbon atom), DWCNTs (**Figure 6b**) if $x = 2$ (double layer of carbon atom) and MWCNTs (**Figure 6c**) if $x > 2$ (multilayer of carbon atom). The diameter of CNTs is in nanometric scale and the length will be several micrometers to millimeter. CNTs exhibit unique properties such as high tensile strength (up to 100 GPa) and young's modulus (up to 1500 GPa) [6].

The quality of produced CNTs highly relies on the method of synthesis. Arc discharge method, laser ablation and chemical vapor deposition technique (CVD) are the three main methods to manufacture CNTs. However CVD method got the immense attraction due better quality, high purity and better control during the synthesis [7]. CNTs which are produced through this methods is very much ideal to use for composite due to high purity during production. All other methods will induce the some percentage of impurities such as graphite, fullerenes and other various catalysts during production. Thus synthesized individual CNTs will have agglomerated, interwoven and entwined. So, dispersion of such CNTs becomes a crucial challenge while processing CNTs—metal matrix composite. Moreover, due to van der Waals force of attraction of carbon surfaces also will increases the much difficulty in CNTs dispersion [8]. An independent separated CNT is the main objective of the dispersion where it can orient in one dimension or as two dimensional (as a flat sheet) or like a three dimensions (as a bulk solid). Dispersion of CNTs was carried out through chemical or mechanical processing. Dispersion through mechanical means was done by ultrasonic liquid processor (ULP); whereas, chemical dispersion is carried out through functionalizing the surface energy of CNT. Advantage of functionalization will help in adhesion characteristics to the matrix, which imparts the reduction in agglomerations. Ultrasonication method usually results in improvement of the uniform and homogeneous dispersion of the CNTs by shortening the size of CNT. Also, the disadvantage of this technique involves the risk of tube wall damage or breakage, removal of outer one layer in MWCNTs and shortens [9]. A study showed that, ~ 70 – $\sim 90\%$ purification take place during ultrasonication of CNTs [15]. Ball milling is the other option for the CNTs dispersion, to modify the aspect ratio, to obtain CNTs nanoparticles and for

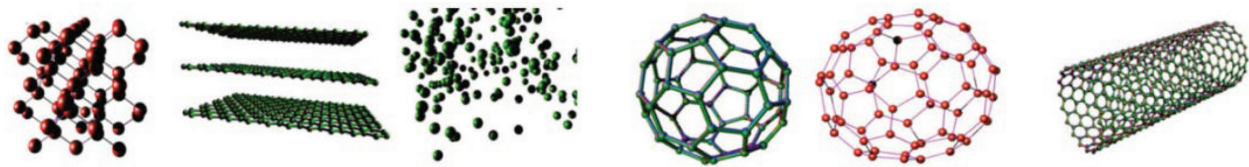


Figure 5. Allotropes of carbon (a) diamond (b) graphite (c) amorphous carbon (d) spherical fullerene, C60 (e) ellipsoidal fullerene, C70. (f) SWCNT.

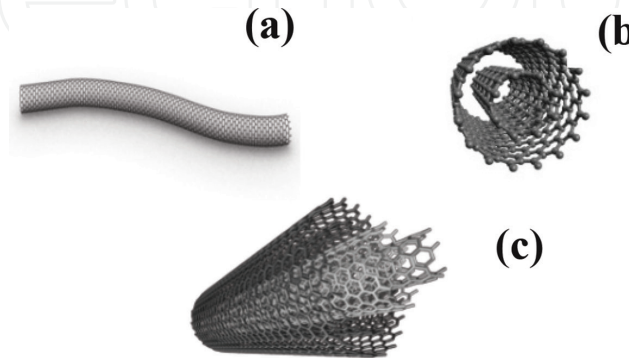


Figure 6. Different types of CNTs based on their number of carbon single atom cylinders: (a) single wall CNT (SWNT); (b) double wall CNT (DWCNT); and (c) multi wall CNT (MWCNT).

functionalizing. Various chemical-mechanical reactions are initiated during ball milling of CNTs. During ball milling CNTs are subjected to severe mechanical strain and may break the structure depending on the milling ratio.

4.2. Graphene

Graphene is a two dimensional sp^2 hybridized, one-atom-thick planar sheet of carbon atoms form a honeycomb crystal lattice (**Figure 7**). The graphene sheet exists in hexagonal structure in which each atom possesses three bands (σ bonds) which are together with its adjacent neighbor [10]. The term graphene was derived as combination graphite with the suffix “-ene” which describes the single layer of carbon [11].

Graphene is the basic structural element for all the allotropes of carbon and it is reflected as the mother of all graphitic forms group. Graphene can be wrapped and structured into buckyball (0D), rolled into carbon nanotube (1D), and can be stacked into graphite (3D) as shown in the **Figure 8**. Distance between the two adjacent graphene sheets is approximately 0.3 nm and these are held together with the weak van der Waals forces [12]. Graphite has been studied extensively for decades but experiments on graphene are on infancy stage. This might be due to difficulty in dispersion or isolation of single layer of graphene.

4.3. Carbon nanotube: metal matrix composite

Due to the astonishing properties, CNTs received the attention of the researchers in utilizing it for developing composites. The research took place in polymer, ceramic and metal-based composite. But, major research was carried out on polymer composites due low stress

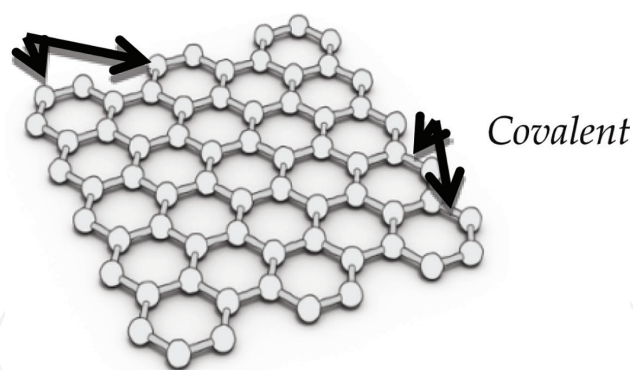


Figure 7. Molecular model (single sheet) of a graphene.

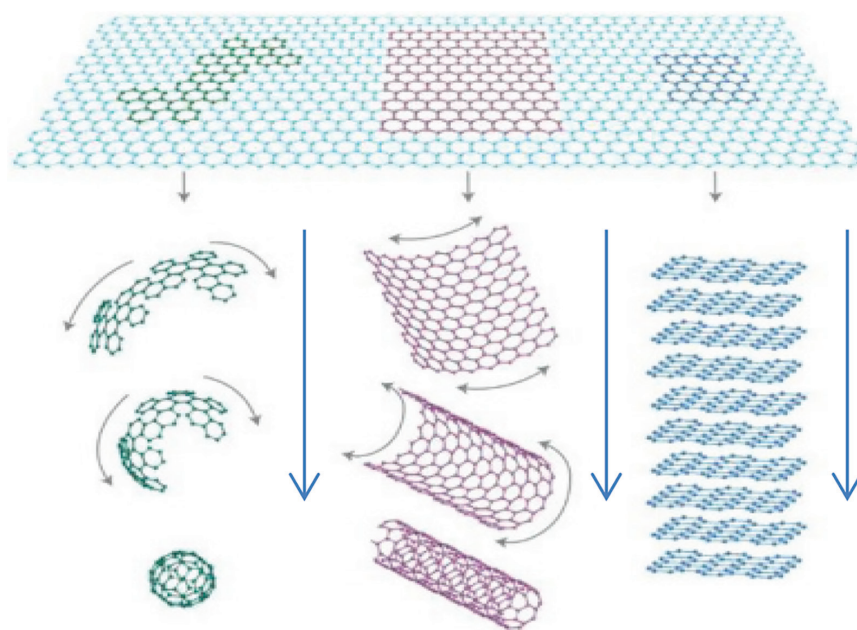


Figure 8. Graphene is a building material (2D) for other carbon-based dimensionalities [36] such as buckyball 0D (left), rolled into nanotubes 1D (middle) or stacked into graphite 3D (right).

and low temperature operating conditions compared to ceramic or metal matrix composites. Metal matrix composite processing requires high pressure, high temperature and the process should be carried out in a controlled atmosphere. CNT reinforced metal matrix composites exhibited enormous improvement in the strength and stiffness. But, there are still several challenges in development of CNT-metal matrix composites to make use of its complete properties. The primary challenge is obtaining a uniform and homogeneous dispersion. CNT always tends to agglomerate cluster formation due to large surface area and tubular structure. Also, it exhibits a non-wetting property with the molten metal which leads to agglomeration. Other challenge of CNT is retaining its structure along with the chemical stability when processed at high temperature and stressed condition. But CNTs are capable of producing a stronger material to the human mankind for many applications have been reported in terms of mechanical and functional material.

Uniform distribution of carbon nanotube in the metal matrix is the main criteria for the successful processing and it includes minimal damage to CNTs physical structure. The retention of its structure is subjected to operating temperature and the applied stress. At elevated temperature, CNT is subjected to react with the molten metal/alloy and leads to carbide formation. Formation of carbides within the matrix material may have some advantages but it is not favorable when concentrating for particular application. Alignment of the CNT during processing will constitute the overall property of the developed composite. It is also possible to achieve unidirectional properties depending upon the sequence and method of processing. Currently, CNTs with various combinations of matrix such as aluminum (Al), nickel (Ni), copper (Cu), magnesium (Mg), titanium (Ti), silicon (Si), cobalt (Co), and zinc (Zn), etc., are successfully developed. Among metals, aluminum with CNTs combination constitutes a major literature followed by copper and magnesium [13].

4.4. Processing methods of CNT-metal matrix composite

Casting process has been used to fabricate Mg-CNT composites. CNT was coated by Ni electroless deposition method for better wetting with the Mg before adding to the Mg, which was melted at 700°C followed by pouring of CNTs to the melt by stirring and cast into ingots. Thus produced Mg-CNTs composites exhibited 150% improvement in the tensile strength and 30% improvement in the ductility for only addition of 0.67 wt% CNT. Also, mechanical properties are deteriorated at higher concentrations of CNTs due to agglomeration [14].

Powder metallurgy technique has been widely used for synthesis of aluminum and copper-CNTs composites majorly. It is also been used to fabricate Ni, Mg, Ti, Au, Sn and its alloys with CNT reinforcement. The powder metallurgy technique becomes very flexible to fabricate CNTs composite because its quality of dispersion and its mainly depends on the matrix particle size. Liquid media can be used for the processing of matrix and the CNT where it prevents the oxidation and controls the heat generation during processing. The consolidation of these powder precursors was carried out through various methods. Cu-CNT composite processed through ball milling followed by isostatic pressing and sintering at 800°C for 2 h are found to be least porosity (2.4%). Ball milling process shown to be effective process in producing an Al-CNT composites [15, 16] and also this process is used for process Si-CNT composite powders for Li-ion batteries [17]. Silver-CNT composites were blended and compacted at 320 MPa and sintered at 700°C. Thus developed composites exhibited uniform distribution of CNTs without agglomeration of CNT at 8 wt% in the matrix.

Use of pressure to the dies containing a matrix and reinforcement precursor during sintering results in dense compact. This operation was done in inert atmosphere as well as vacuum conditions for metal matrix-CNT composites. Al-CNTs composites were fabricated through hot pressing found to be agglomeration of CNT. Also, the process leads to formation of carbide compounds. Further, precursors are also processed through ultrasonic dispersion of CNT in alcoholic media and isostatic pressing leads no chemical reaction between the SWCNT and aluminum. Cu-CNT was hot pressed after ball milling the powder at 1100°C in graphite die successfully. Mg-CNT [16] and Ti-CNT [17] combinations are also prepared through hot pressing in vacuum conditions which results in CNT agglomeration [18].

Spark plasma sintering (SPS) or electric field assisted sintering (EFAS) was found to be different from hot pressing and the heat was generated by pulsed DC current which is passed to powder kept in die. Great improvement in the compressive strength of Cu-10 vol% CNTs composite was observed for SPS processed compacts [19]. Improvement in hardness and sliding wear resistance were observed for the various metal matrix-CNT composites. SPS processed Al-1 wt% CNTs compacts are exhibited slight improvement in the hardness, flexural and improvement in the wear resistance. Compared to other conventional process SPS process became a promising method to obtain high density metal matrix-CNT composites. Other advantage was small sintering time which ensures the minimal reaction of the CNT with matrix component during consolidation [20].

Density of the metal matrix-CNTs compacts can be increased by deformation process and the method was suitable for aluminum- and copper-based composites. Hot extrusion is the commonly used deformation technique for metal matrix-CNTs composite. Equal channel angular extrusion (ECAE) and cold rolling are the other deformation techniques to process the composites. Aluminum and CNTs powders are processed through ultra-sonication in ethanol followed by drying, compaction and extrusion at 500°C with an extrusion ratio 25:1 [21]. In the other case, aluminum-CNT mixtures were ultra-sonicated and ball milled followed by sintering (580°C) and extrusion at 560°C successfully [30]. During deformation, CNT clusters are broken and are aligned in the direction of shear stress. Efforts have been made to process Mg-CNT and Mg-SiC-CNT composites through hot extrusion and 36% improvement in the yield strength was observed [22, 23]. Au-Sn-Cu solders with 1 wt% SWCNTs produced through hot extrusion shown 18% increase in the tensile strength [24].

Disintegrated melt deposition (DMD) was used to improve the CNT dispersion. This was carried out to fabricate Mg-CNT composite [25] where, the molten Mg-2 wt% CNT at 750°C is made to pass through an orifice and was disintegrated by two argon jets. Thus disintegrated molten melt is deposited in the metallic mold and thus obtained ingot is extruded at 350°C to get the Mg-CNT rods. Improvement in strength and ductility was observed for such fabricated materials. Also, increase in the content of CNTs affected the fatigue performance by reducing the number of cycle due to presence of voids and the matrix-CNT interface [26].

Melt filtration method was the commonly used technique to develop the Metal matrix composite. This method enables the high chances of homogeneous distribution of CNTs in the metal matrix. The key factor in this method includes proper filling up of pores and that constitute the final dense of the product. Mg-CNT was prepared in this manner and found to be enhanced in the shear modulus [27]. Aluminum-CNT mixtures were ball milled (7 h at 300 rpm) and compacted to make preform. Thus prepared preform was infiltrated spontaneously by LY12 Aluminum alloy at 800°C in nitrogen atmosphere and core shell type microstructure developed in the preform. Such a type of an infiltrated composite with 20 vol% of CNT showed a decrease in wear rate and the coefficient of friction. The decrease in the coefficient of friction was seen up to 15 vol% of CNT [27]. Melt infiltration is quite economical method to fabricate composite with CNT combination and properties are completely rely on degree of homogeneity of the CNT in the matrix. Further, due to partial melting of the matrix in connection with the CNTs lead to inevitable reactions and that can be prevented through surface coatings methods.

Thermal spray was used in many mass production industries. In this process the material to be subjected to spraying is fed into the heating source in the form of wire or powder and it get melted. Thus melted molten metal was accelerated by carrier inert gas and impinged on the substrate. Splats are formed on the substrate in the form of layer by layer and accumulation of these splats became a coating. Such a method was used to synthesis of ceramic-CNT [28, 29] and metal-CNT [30, 31] composite. Once the CNTs were uniformly distributed within the single splats, then the complete composite structure which was built layer over layer will also have CNTs homogeneous distribution. Thus, the near net shaped metal-CNT composite structures can be produced for the real time applications such as aerospace and heavy machinery surfaces with reasonable corrosion and wear resistance.

Plasma spraying forming (PSF) was carried out for Al-Si alloys reinforced with CNTs [30]. Blending was carried out through ball milling process and the mixed powders are plasma sprayed. The spraying process was done through cryogenically cooling environment on AA 6061 aluminum mandrel. Further, the current proved the retaining the CNT structure at higher temperature and there no carbide formation. Also, it was inferred that the sintering did not produced any perceptible damage to the CNT structure. Thus produced composite exhibited 78% increase in the elastic modulus for the 10 wt% of CNTs [32].

High Velocity Oxy-Fuel Spraying (HVOF) was found to be other novel thermal spray method which uses the heat source from the combustion of fuels in oxygen. Al-10 wt% composite produced through this method exhibited 49% improvement in the elastic modulus and 17% improvement in the microhardness which was more compared to same composite produced through PSF [30]. HVOF process has the capability to produce metal matrix-CNTs composite with high homogeneous dispersion, which enhances the mechanical properties.

Cold spraying method accelerates the powder particle to high velocity and made to impact on the substrate which leads to formation of splats. Al-CNT composite coating was prepared from the blended pure aluminum powders from this method and composite observed to be a dense microstructure [31]. But, CNTs were shortened due to high impact shearing between the particles. Also, necking formation followed by cup and cone type of fracture observed for mild carbon steel and CNT composites [33].

Electrochemical route can be used to synthesis MWCNT composites as well thin films by material deposition. Most of the composites are processed through co-deposition of CNTs and metal-ions [34]. Uniform distribution and homogeneous distribution of CNTs can be achieved in this technique [35]. This method also has flexibility to fabricate CNTs-based one-dimensional (1D) composites [36]. Thus developed composite has an application for nanosensors and precursor for larger MWCNT composite structures. The processing parameters govern the nature of the structures and also different in both electroless deposition and electrochemical deposition technique. Current density and type of power source (AC or DC) plays an important role in case of electrodeposition which was directly proportional to deposition of CNTs. On the other hand pH value and bath temperature are the important key factors in case of thermochemical process which determines the coating composition and morphology of the developed composite. Thus, electroless deposition and electrodeposition have become an effective method to produce thin metal matrix composite and coating techniques. Ni, Cu, Zn and Cr along with CNT combination composite coatings and thin films system were studied so far.

Sputtering method was used to deposit the metal over CNTs. This method was suitable for fabricating the one dimensional (1D) nanostructured composite. Further, sputtering technique enables the alignment of CNTs in the developed composite. Deposition of aluminum on CNTs was carried out by the magnetron sputtering and subjected to various annealing treatment [37]. Sputtering method carried out for Au on SWCNT shows the self-organization and evenly spaced cluster [37]. Sandwich method involves the dispersing of CNTs between many thin metallic or alloy layers followed by cold weld with the application of pressure. This method was successfully used to fabricate Cu-SWCNT composites and good dispersion along with proper bonding was observed [38]. Aluminum-CNT composite also processed by spray deposition which was carried out by spraying CNT on aluminum foil and rolling. Nearly, 59% improvement in the elastic modulus for the Al-2 vol% was observed for such a developed composite.

In the friction stirring process, frictional force was used to weld the metal and the MWCNT composite. This method was used to process the Mg-CNT and Al-CNT composite successfully. The decrease in the grain size was observed due to incorporation of carbon nanotube through this process. Processing of Al-5 wt% SWCNT through this method resulted in the reduction of grain size up to be 80% [39].

4.5. Graphene-metal matrix composite

The explanation of graphene covers all forms of graphitic material from 100 nm < thick platelets down to single layer graphene [40]. However, the obtainability of single-or few-layer graphene that has caused the interest. In fact, it is possible to distinguish between flakes of graphene with different numbers of atomic layers in a transmission optical microscope due to its nature of significant optically energetic [41]. The work to determine the number of layers to be used for the reinforcement was formed and found that monolayer has the higher stress transfer than the bilayer graphene [42] and the flakes are sufficiently large (>30 micro meter) and aspect ratio should be high for the effective reinforcement of both bilayer [43] and monolayer graphene in the composite [44]. There has already been considerable effort put into the development routes of preparing high-quality graphene in large quantities for the research purposes along with the view to possible applications where it is suitable [45]. There are number of motives to develop graphene-metal composites. The strengthening mechanism of graphene reinforcement was thought to be related to the excellent mechanical and the unique structured characteristics of graphene, and good bonding interfaces between graphene and matrix. There are many challenges involved to get graphene dispersed metal matrix composite with the existing conventional metallurgical process or methods due to huge density difference between graphene nanoflakes (GNFs) and metal matrix, more interfacial contact area than carbon nanotubes and also reaction at matrix reinforcement interface [46] because the metals are much reactive. The work relating to this field is still remaining in their infancy. But the increase of publications in this category signifies that growing an interest toward graphene-based metal composites. Research on development of metal-graphene composites is still in its infancy stage as compared to polymer-graphene and ceramic-graphene composites. The metal matrix composites incorporated with the secondary phase graphene includes aluminum, magnesium, nickel, platinum [47], gold [48], cobalt [49], palladium [50], and silicon [51]. Further, these composites found to be application in supercapacitors [52], energy devices (batteries) [52], electrocatalysts and biosensors [53].

4.6. Processing methods of graphene-metal matrix composite

Powder metallurgy route was the commonly used technique for processing of graphene-based Cu, Al, Mg, etc., and alloys composites. It consists of processing of graphene with the metal or alloy powder followed by compaction and sintering. Usually dispersion and compaction is done through various methods. This step will have a great influence on final densification and properties of the developed composite. The common problem associated with the graphene includes agglomeration and it requires high energy to overtake the surface energy of the graphene to make it single flake. Further, high energy was utilized to break the graphene interlayer van der Waals force to obtain an individual sheet of graphene. In many cases graphene has been processed through ball milling and ultrasonication in order to disperse it into the matrix material. During the preparation of graphene-metal matrix composite, dimethylformamide (DMF), isopropanol, N-methyl pyrrolidone (NMP), deionized water and acetone was utilized as liquid media for ball milling.

Wet chemistry method utilizes the ultrasonication for mixing of matrix and graphene flakes in a liquid media. Sound waves generated during Ultrasonication are used to induce cavitation followed by agitating the particles in liquid media. Tip and bath sonicator are the commonly used ultrasonication devices for processing the graphene-metal powder mixtures. Ultrasonication processes will not use an impact or shear force on graphene sheets unlike ball milling and there is no particle size reduction during processing. Further, wet chemistry method completely eliminates the contamination issues during processing, except from the liquid media. Also, wet chemistry and the ball milling can be combined to process the metal and graphene precursors [54].

Mechanical alloying method was the most commonly used technique for fabrication of the metal-/alloy-based composite. The commonly used metals to fabricate the composite incorporating with the graphene includes: copper (Cu), aluminum (Al) and magnesium (Mg), etc. During alloying, the milling process was carried out to refine the metal or alloy powder in the milling media. Further, the milling process produces the repeated cold welding, re-welding and fracture of the metallic powders. Thus, it leads to simultaneous strengthening during milling by grain refining and work hardening. Microstructure of the composite can be controlled by modification of milling process parameters such as time, milling ratio and media. ZrO_2 [55] are the commonly used balls for mechanical alloying of Al-graphene powder in a milling jar. The quantity of graphene added for the metal powder is typically <12 wt% so far. Further, milling process was carried out usually in argon (Ar) atmosphere to control the oxidation. Methanol, cryomilling and petroleum ether are the commonly involved process control agents during milling. Also, increasing in the milling time will degrade the properties of graphene leading to formation of defects in the developed composites. Additionally, hardness and strength of the graphene-MMCs fabricated via ball-milling followed by compaction and sintering are improved due to improved interfacial reaction, bonding and grain refinement.

Hot extrusion follows a hot working process; it requires a large quantity of powder and preparatory process (ball milling, compaction and sintering) to make a billet to extrude. For aluminum-graphene composites, the prepared billets are heated to >500°C which may lead to carbide formation at the metal graphene interfaces which reduces the strength of the composite. Most of the research has been carried out using spherical shaped aluminum powder

(1–22 μm). But, it is observed that nanoflake size matrix possesses a great compatibility with the graphene and significant improvement in the properties was observed. Graphene synthesized through chemically, thermally exfoliated and Hummer's method are used to fabricate the composite through hot extrusion. Some of the studies used slurry blending technique in which the ethanol or acetone is used as the medium. Thus processed metal matrix and graphene mixtures are consolidated through hydraulic pressing or hot isostatic pressing (HIP) and sintered at $<600^\circ\text{C}$ in argon (Ar) atmosphere followed by extrusion [56].

The metal (Al, Mg)/graphene composite produced through hot extrusion possess densities close to theoretical densities. Further, nanofiller graphene and the metallic grains are aligned along the direction of extrusion. Most of the graphene-MMCs, synthesized through hot extrusion, exhibit an improvement in strength, fracture toughness and hardness. Al-graphene composites extruded at a temperature less than 500°C possess a drastic improvement in the properties and it was found that they are defect free. Also, optimized graphene content for the aluminum matrix induce the extreme strength and larger grain refinement in the developed composite. Further, optimized graphene content in the matrix prevents the agglomeration which helps in preventing the carbide formation sites [57].

Hot rolling involves a combination of ball milling (high energy) and rolling which was used to fabricate the graphene-metal matrix composite effectively. The metal particle size range of 20–200 μm with 97–99.7% purity was considered in the studies. Thus processed powder mixtures were compacted in a thin copper (Cu) tube and subjected to rolling. Usually high speed differential rolling (HSDR) or equal speed rolling (ESR) is used and HSDR exhibited a larger amount of deformation. Solid state friction stirring procedure same as friction stir welding. The process uses a non-consumable rotating tool which was held mechanically by the rotating head and stirs the material. The main challenge in case of graphene/metal matrix system was the huge aspect ratio and small thickness will lead to agglomeration during the surface processing. In addition, a novel combination of liquid state solid stirring followed by friction stir processing to fabricate graphene/metal composite. Lot of agglomeration was found in the current method [58].

Graphene oxide reduction to graphene during chemical mixing was used to form a composite. This method was applied to develop many composite including palladium, platinum, cobalt, gold, etc. In the chemical mixing method solution media was used to disperse GO and metal particles during the synthesis [59]. During the process metal nanoparticles absorbed on the GO flakes and subjected to catalytic reduction reaction of GO with the solution and form a metal-graphene composite. This method enables the metal particle to sit over the reduced graphene nanoflakes and prevents the agglomeration and restacking. Chemical mixing of graphene with metal uses a metallic salts and graphene as a starting material. During the process, metallic salts are reduced in to the solvent and deposited on the graphene sheets to form a composite. The process prevents the agglomeration of the graphene flakes by developing a non-sized metallic particle between each graphene layers.

5. Conclusion

Most of the researchers have discussed the positive aspects of graphene reinforced composites, the extensive property of graphene and its huge potential for industrial applications. Due

to the 2D structure and high specific surface area (SSA) of the graphene, it has several typical and intrinsic merits over the other reinforcements to incorporate in matrix for developing the composite structure. Graphene with very low content addition to the matrix showed a breakthrough improvement and evolved as effective reinforcement for the material over high content particulate and CNT-based reinforcement composite system.

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