MICROSTRUCTURE AND MICROHARDNESS OF COPPER COATED MULTIWALLED CARBON NANOTUBE-GRAPHENE REINFORCED ALUMINIUM 6061 ALLOY NANOCOMPOSITES

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ABSTRACT

Multiwalled Carbon Nanotubes (MWCNTs) and graphene reinforced with Aluminium 6061 alloy was synthesized by using powder metallurgy route. MWCNTs were copper (Cu) coated by electroless deposition to increase interfacial bonding between matrix and reinforcement. Aluminium 6061 alloy (Al6061) powder was reinforced with 2 wt.% of coated and uncoated MWCNTs with varying Graphene of 0.5 wt.%, & 1 wt.%. High energy ball milling was used to mix the powders followed by compaction and sintering. The samples were characterized using FESEM-EDS and X-ray diffraction technique. Microhardness of the nanocomposites samples was determined. It was found that the hybrid nanocomposites showed accentuated properties than the base alloy.

KEYWORDS: Multiwalled Carbon Nanotubes, Graphene, Aluminium 6061 Alloy, Coatings & Microstructure

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1. INTRODUCTION

Recently interest in aluminium composites has been increasing, due to its broad applications in advanced material engineering technology. Aluminium alloys exhibit extraordinary performance in industrial applications with good workability, corrosion resistance, low density and good strength [1]. Many industries are developing Metal Matrix Composites (MMCs) with nanomaterials are finding increased use in fields such as, aerospace, automobile industry and other structural applications [2-3]. Iijima developed Carbon nanotubes (CNTs) in 1991 [4] and graphene as 2-dimensional single layer graphene lattice assembled from sp²-hybridized carbon atoms [5].

The outstanding properties of carbon nanotubes and graphene promise for future reinforcing materials [6-7]. These two materials with good applications were served by many researches because of their unique and good properties which make them perfect fit for many engineering applications [8]. H. R. Ram et.al. studied nanomechanical behavior of copper and nickel coated MWCNTs/aluminium alloy 6061 for varying volume fraction, the results showed with uniform dispersion of MWCNTs, it indicated an increase in Young's modulus and nanohardness of the composites for copper coated MWCNTs [9]. Adnan Maqbool et.al. had conducted an experiment on CNTs coated aluminium composites to improve the bonding between the alloys and matrix. Scanning Electron Microscopy (SEM) images had showed homogenous in nature and also there was an increase in yield strength, micro hardness by increasing 1.0 wt.% of uncoated and copper coated composites [10]. M. Jagannatham et.al. studied on CNTs copper coated by electroless deposition with varying time of deposition on the

tubes. The results showed that 45min deposition time has optimum deposition time for uniform deposition on CNTs. The Aluminium (Al) powder and CNTs were ball milled, nanocomposites were fabricated by spark plasma sintering. Microstructure images showed the homogeneous allocation of MWCNTs in matrix. However, the mechanical properties of Al-MWCNTs coated samples were superior compared to Al composites [11]. Al composites have a homogeneous diffusion with exceptional difficulties for the innovative approach to implement the nano particles with encapsulating Silicon carbide (SiC) using graphene sheets during ball milling [12]. Mina Bastwros et.al. investigated to improve the mechanical properties by adding graphene and ball milled of graphene to Al6061matrix at different time periods. During the bending performance the fracture surface of the specimen were analyzed, results revealed maximum improvement in the flexural strength compared to Al6061matrix [13].

Most of the studies on coated CNTs and graphene reinforced MMCs have focused on improving mechanical and tribological properties, but it is difficult to generalize to matrices with a different composition or particle size. However, due to the wettability of the matrix, the CNTs reinforced metal matrix has not been bonded and referred as weak interface between the materials [14-18]. In this research work, MWCNT (2 wt.%) were coated with copper by electroless method with a two step sensitization-activation method and graphene with varying composition (0.5 wt.% and 1 wt.%) was used with Al6061alloy powder to prepare nano composites through powder metallurgy. The work then constituted to evaluate the microhardness and assess the microstructural characterization of the nanocomposites.

2. MATERIAL AND EXPERIMENTATION

2.1 Materials and Methods

Al6061alloy powder was procured from DMRL, Hyderabad, 300 mesh of particle size and density of 2.7 g/cm³. Chemical composition of matrix material is shown in Table 1. MWCNTs from cheap tubes USA and graphene having thickness 8-10nm, density 2.2 g/cm³ (United nanotech innovations Pvt.Ltd.) were used in the present study. The Table 2 shows the typical properties of MWCNTs as received. Morphology of MWCNTs and graphene, shown in Figure 1(a), (b) and (c). Al6061 alloy XRD plot is shown in Figure 1(d).

Table 1: Chemical Composition of Al6061 Alloy

Elements	Si	Cu	Fe	Mn	Mg	Zn	Pb	Ti	Al
Wt(%)	0.62	0.23	0.22	0.03	0.84	0.22	0.10	0.01	BAL

Table 2: Properties of MWCNTs

Properties	Diameter	Length	Density
Values	20-30 nm	20-40 μ m	2.1g/ cm ³

2.2 Electroless Copper Coating to MWCNTs

The MWCNTs was initially purified to remove impurities present [11]. After purification, MWCNTs were subjected to copper coating by electroless deposition. In order to achieve uniform copper coating thickness on MWCNTs, the following pre-requisite steps were followed; oxidization, sensitization, activation and decoration of copper. Purified MWCNTs were oxidized with H₂SO₄ (98%) and HNO₃ (70%) at 140⁰ C for 8h and tubes were washed with millipore water and dried at 120⁰C. The oxidized MWCNTs were subjected to sensitization and followed by activation using stannous chloride (SnCl₂)/Hydrochloric acid (HCl), later the tubes were activated by Palladium chloride (PdCl₂)/HCl solution by magnetic steering for 40min. The activated MWCNTs were subjected to electroless copper coating for 30 min in an electroless

copper bath at a pH value 12 ± 0.6 for uniform deposition of copper. The copper bath composition of the chemicals used for study is shown in Table 3. The morphology of coated MWCNTs and EDS are shown in Figure 2(a), (b) and (c).

Table 3: Chemical Composition of Copper Bath [15]

S. No	Chemical composition	Quantity(g/l)
1	Copper sulfate-5H ₂ O	40
2	EDTA Disodium salt	48
3	HCHO(add after 10 min)	25
4	Na ₂ SO ₄ -10 H ₂ O	35
5	HCOONa	15
6	Polyethyleneglycol	6.6
7	PH (adjust with NaOH)	12-13
8	Temperature(°C)	80

2.3 Preparation of Nanocomposites

In this study, Al6061alloy powder-2wt.% MWCNTs (coated and un-coated) and 0.5 wt.%, 1.0 wt.% graphene were mixed by ball milling to disperse MWCNTs/Graphene in Al6061matrix. The milling time is maintained for 2h with 200rpm speed to all the samples, ethanol as process control agents in small amounts was added with ball to powder ratio of 10:1 [9,13]. Powder metallurgy technique was used to prepare the nanocomposites, the samples were compacted in harden steel die-punch. Before compacting the powder, samples were pre heated and compacted with compaction load of 90-110kN for all the samples to compacts of 20mm diameter and 30mm length were prepared. The green compacted samples were subjected to sintering at 580°C with a dwell time of 60min for all the samples in conventional furnace with nitrogen atmosphere.

2.4 Microhardness and Micro Characterization of Nanocomposite

Different methods were used to characterize the Al6061 alloy and nanocomposites. The procured materials were characterized by using SEM-EDS and XRD techniques. Ball milled powder samples of Al6061-coated and uncoated MWCNTs/graphene composites were characterized by FESEM-EDS. Archimedes principle and rule of mixture were used to determine the theoretical density, actual density of the composites. To determine the hardness of the nanocomposites, the surface of the specimen were polished using emery paper to remove the dust and to make the surface smooth, it is subjected to alumina and disc diamond polisher. Then specimens were placed in the buehler micro hardness tester by applying the load of 25gf for 15sec dwell time. Meanwhile the hardness of the average of four indentations at different location was taken in to consideration.

3. RESULTS AND DISCUSSIONS

3.1 Morphology of Matrix and Reinforcing Materials

The MWCNTs as received was synthesized by chemical vapor deposition and it contains different forms carbon, to remove excess carbon content and other impurities from the tubes, the procured MWCNTs was purified [15]. Figure 1 (a) & (b) shows TEM and SEM images of purified MWCNTs. It shows the bundle form of MWCNTs with less impurities. SEM image of graphene is shown in Figure 1(c) which reveals that graphene morphology having the layers are stacked upon each other and curve free. Figure 1(d) show plot of XRD Al6061 alloy reveals the three peaks of aluminium and no other constituent peaks present.

Figure 1: (a) TEM Micrograph of MWCNTs (b) SEM Image of MWCNTs (c) SEM Image of Graphene (d)XRD Plot of AL6061 Alloy.

3.2 MWCNTs of Copper Coated Characterization

Figure 2: (a) FESEM of Coated MWCNTs (b) Copper Coated MWCNTs Morpology (c) EDS of Copper Coated MWCNTs.

The detailed process for the electroless copper coating on MWCNTs includes oxidation, sensitization, activation and deposition as explained by Ang et. al. [15]. The quantity of deposition increases with increasing deposition time. It shows that time of 45 min for deposition was maintained to get uniform deposition on the surface of MWCNTs.[11]. Figure 2(a) show microstructure image of coated MWCNTs and Figure 2(b) & (c) morphology and EDS of coated MWCNTs. The EDS of MWCNTs copper coated shows the presence of copper in Figure 2(c).

3.3 Characterization of Ball Milled al6061 Alloy and MWCNTs/Graphene Nanocomposite Powders

Figure 3(a) shows the FESEM image of 2 wt.% copper coated MWCNTs mixed with Al6061 alloy, Figure 3(b) shows 2 wt.% uncoated MWCNTs and 1 wt.% graphene mixed with Al6061 alloy, Figure 3(c) shows 2 wt.% Cu-coated MWCNTs with 1 wt.% graphene mixed with Al6061 alloy. It is observed from the FESEM image that 2 wt.% Cu-coated MWCNTs are uniformly distributed in the Al6061 matrix. However in Al6061-2 wt.% uncoated MWCNTs and 1 wt.% graphene, it led to agglomeration but Al6061-2 wt.% Cu- coated MWCNTs and 1 wt.% graphene reveals uniform distribution and the morphology of coated MWCNTs were not damaged after ball milling for 2h. Figure (d) and (e) clearly indicates that copper is present in the powder samples.

Figure 3: (a) FESEM of 2 wt.% MWCNTs Coated of Copper Mixed with al6061 Alloy (b) 2 wt.% Uncoated MWNCTs with 1 wt.% Graphene Mixed with Al6061 Alloy (c) 2 wt.% cu-coated MWNCTs with 1 wt.% Graphene Mixed with Al6061 Alloy (d) and (e) FESEM and EDS Analysis of Ball Milled Al6061-Coated MWCNTs and Graphene Powder Sample.

3.4 Density of Nanocomposites

To ensure high density and less porosity of the samples, a cold compaction with sintering was adopted. The prepared Al6061alloy with nanocomposites of theoretical and actual density values is shown in Table 4. It reveals that the density of the theoretical values decreases with an increase in MWCNTs with graphene due to low density of MWCNTs (2.1g/cm^3) and Graphene (2.2g/cm^3) when compared with density of Al6061alloy (2.7g/cm^3). The prepared samples were subjected to hot pressing and after sintering at 580°C to achieve the full dense effect and to reduce the porosity of the nanocomposites.

$$\text{Density (pc)} = (\rho\text{M})\text{Al6061} + (\rho\text{v})\text{MWCNTs} + (\rho\text{v})\text{Graphene} \text{ -----} \quad (1)$$

Where, ρ and v are the density and volume fractions of Al6061alloy, MWCNTs and graphene.

To determine the actual density, Archimedes principle was used for Al6061alloy and nanocomposites. As the MWCNTs wt% and graphene increases, a slight increase in actual density of nanocomposites is found. Table.4 shows that the actual density of nano composite is found to be greater when contrasted with the density for the alloy. Al6061-2 wt.% MWCNTs (coated)-0.5 wt.% graphene composite had the least density of 2.4 g/cm^3 amongst all the other composites processed.

Table 4: Density of Nanocomposites

Sample No.	Particulars	Theoretical Density (g/cm^3)	Actual Density (g/cm^3)
S-1	Al6061 alloy	2.74	2.32
S-2	Al6061-2 wt.% MWCNTs (un-coated)	2.699	2.48
S-3	Al6061-2 wt.% MWCNTs (coated)	2.699	2.53
S-4	Al6061-0.5 wt.% graphene	2.698	2.46
S-5	Al6061-1 wt.% graphene	2.695	2.57
S-6	Al6061-2 wt.% MWCNTs (un-coated)-0.5 wt.% graphene	2.685	2.52
S-7	Al6061-2 wt.% MWCNTs (coated)-0.5 wt.% graphene	2.685	2.47
S-8	Al6061-2 wt.% MWCNTs (un-coated)- 1 wt.% graphene	2.683	2.49
S-9	Al6061-2 wt.% MWCNTs (coated)-1 wt.% graphene	2.683	2.49

3.5 Microstructure of Aluminium 6061 Alloy and Nanocomposites

Al6061alloy appeared to have less particles because of hot pressing and the MWCNTs are observed as clear and homogenous in the base material as shown in Figure 4 (a)-(d). Microstructure analysis shows that the gap between the matrix and reinforcements is minimum and it confirms a better bonding.

Figure 4: FESEM Image of Composites (a) Al6061-2 wt.% (uncoated) MWCNTs-0.5wt.% Graphene (b) Al6061-2 wt.% (coated) MWCNTs-0.5 wt% Graphene (c) Al6061-2 wt.% (uncoated) MWCNTs-1wt.% Graphene (d) Al6061-2 wt.% (coated) MWCNTs-1 wt.% Grapheme.

3.6 Microhardness of Aluminium 6061 Alloy and Nanocomposites

Figure 5 illustrates variation of microhardness of nanocomposite with coated and un-coated MWCNTs and with various wt. % of graphene. It is observed that developed nanocomposite of microhardness with 2 wt.% cu-coated carbon nanotube is 67 HV whereas matrix alloy Al6061alloy is 43 HV and 2 wt.% uncoated MWCNTS is 57 HV. Like wise, nano hybrid composite with 2 wt.% coated with 0.5 wt.% graphene is having high hardness compared to uncoated MWCNTs. The hardness of 2 wt.% uncoated MWCNTs with 1 wt.% graphene exhibits 71HV. 2 wt.% coated MWCNTs with 1 wt.% graphene has a hardness of 74HV; considerable increases in hardness is due to increase in reinforcements. Due to increase in graphene, there is a good improvement in hardness of the nanocomposites. If MWCNTs content is 2 wt.% and 1 wt.% graphene, microhardness ranges from 71 HV to 74 HV, due to agglomeration of MWCNTs and graphene inside Al6061 matrix and instead of reinforment, agglomerates acts as pores.

Figure 5: Variation of Micro Hardness with 2 wt.% of MWCNTs (Coated and Uncoated) and varying Percentage of Grapheme.

4. CONCLUSIONS

Multiwalled Carbon Nanotubes are coated with copper successfully by using electroless deposition method. The uncoated and coated MWCNTs/graphene reinforced Al6061 alloy nano composites were prepared by powder metallurgy technique. Microstructural analysis revealed that coated MWCNTs are uniformly distributed in Al6061 matrix. However, Al6061-coated MWCNT-Graphene nano composites were homogeneously distributed with matrix material compared to uncoated ones. The actual density of nanocomposites slightly decreases with increasing content of MWCNTs and graphene. The copper-coated MWCNTs/Al6061alloy nano composites showed improved hardness than base alloy but the copper-coated and uncoated MWCNTs/graphene/Al6061alloy shows significant improvement in hardness when contrasted with base alloy and other composites are prepared.

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