

Studying the Effect of Process Controlling Agent on the Microstructure, Electrical and Thermal Conductivities of Copper /Graphene Composite Prepared by PM

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Abstract

Copper-graphene composite is prepared with 0.25,0.50,0.75,1.00,1.25 and 1.50 wt.% graphene. Powder metallurgy technique is used for the preparation process. In which copper powder is mechanically milled with graphene nanosheets (GNSs) by 10: 1 ball to powder ratio, and 400 rpm for 12 hr milling time. The mixtures are compacted by a uniaxial press under 700 Mpa pressure. The compacted samples are sintered under a controlled atmosphere at 950 °C for 1.5 hrs. A comparison between methanol & hexane as a process control agent is established. The effect of both on the microstructure, electrical and thermal conductivities of the prepared Cu /graphene nanocomposites is studied. All results indicated that hexane samples have a more homogeneous microstructure with low porosity. For the two groups (Hexane and Methanol group samples), the density was decreased gradually by increasing the graphene percentage. The results indicated that both the electrical and thermal conductivities decrease by increasing graphene content. 1wt. % graphene sample has the most homogenous microstructure, while, 0.25 wt. % graphene is the most one for the methanol group samples. Generally, all results indicated that hexane is the better PCA than methanol.

Keywords: Copper composites; Graphene; Mechanical alloying; Process control agent (PCA); Electrical conductivity.

1. Introduction

Copper alloys and composites have been broadly utilized as designing parts because of their great thermal and electrical properties and synthetic steadiness. In most cases, they suffer from poor mechanical properties, particularly under temperature load. For both electronic and mechanical applications Cu amalgams need decent physical and mechanical properties. The upgrade of their mechanical presentation is progressively required. The best system to accomplish unrivalled strength is the presentation of support stages in Cu composites and compounds to create Cu lattice composites [1]. Cu tragically has a high coefficient of thermal expansion (CTE) and low strength. So fabricating Cu composite supported with a low (CTE) material with high strength produces materials appropriate for many applications. Graphene,

has a significant properties as a nanofiller material because of its extraordinary electrical $105 \times 10^4 \text{ cm}^2/\text{Vs}$, thermal ($5 \times 10^3 \text{ W/mK}$), and mechanical (1 TPa Young's modulus and 130 GPa tensile strength) properties. It is a solitary layer of sp^2 -hybridized covalently reinforced carbon particles, masterminded in a two-dimensional, hexagonal cross-section see. Fig.1. Graphene surface can be effectively polished via airborne hydrocarbons, as presented to encompassing air and covering their wettability characteristic.

The innovative difficulties in assembling graphene - built up MMCs are more normal than on account of polymer-lattice composites. This is because of the solid van der Waals forces between fragrant rings of graphene is difficult to scatter consistently into a metal framework as it will agglomerates to decrease its

surface energy during the preparation process. Likewise, the interfacial holding is difficult because of the helpless affinity of graphene to metals. Specifically, copper (Cu) doesn't wet graphene and covalent holding is absurd as no responses happen among Cu and graphene, which simply leaves feeble mechanical grip and van der Waals connections, the frequently wrinkled construction of graphene assumes a significant part in improving the mechanical interlocking between the graphene and Cu, which prompts a superior burden move. A final challenge is that graphene can without much of a stretch become harmed during the brutal creation conditions (i.e. High temperature and high pressing factor) normally utilized to deliver MMCs, debilitating its inborn properties. Accordingly, a critical test in assembling graphene MMCs is their creation, which typically delivered by powder metallurgy courses.

Cu/graphene composites have some difficulties in the manufacturing process, such as the homogeneous scattering of graphene in the grid, the arrangement of a solid interfacial holding and the maintenance of the underlying soundness of graphene. Powder metallurgy is an adaptable interaction for assembling composites with graphene because of its straight forwardness, flexibility, and close shape capacity [1]. The measure fundamentally includes blending graphene with crude metallic powders to set up the composite powders followed by their combination into a mass shape. This last advance contains the compaction of the composite cycle and additionally densification cycles, for example, sintering, squeezing, and additionally rolling [2]. The crude metallic powders utilized will in general be unadulterated Cu powders or Cu compounds comprising of atomized Cu blended with alloying powders [3]. Mechanical blending can deliver composites with great microstructures and homogeneous dispersion of graphene in the Cu grid. The composite powders can be set up by basic blending strategies including mechanical or attractive sonication and vortex technique. High-energy ball processing (BM) or mechanical alloying (MA) have been likewise employed.[4] Mechanical alloying is the strong state preparing of powder materials which is frequently used to create combinations and composites that are difficult to get from regular dissolving and projecting techniques [1-3]. The processing energy can be controlled by fluctuating the ball to powder proportion, the processing time speed, also the processing environment. A process control agent (PCA), like stearic acid or ethanol, is added to forestall extreme staying and agglomerations of Cu powders during the manufacturing processing [4]. Natural solvents (for example ethanol) should be dissipated to get dry

composite powders before compaction and consolidation [5].

A couple of methods to clean the graphene surface is thermal toughening, UV-O₃ openness, dissolvable, and cleaning. Thermal toughening has the advantage utilized to eliminate poly-methyl. Thermal tempering at 550 °C eliminates air-borne hydrocarbons from the graphene surface. The utilization of UV/O₃ brings about a similar impact of eliminating the hydrocarbons from the graphene, diminishing the water contact point. This procedure can't be utilized for a long time since UV radiation may be harmful for the graphene surface causing abandons that can likewise bring down the contact point of the graphene with the metal matrix. In some methodology, single-layer graphene was sur-adjusted with initiated carbon and thermal tempering at 210 °C. This work aims at studying the effect of methanol or hexane as a PCA on the microstructure & physical properties of Cu-graphene nano composites for electrical & electronic applications.

2. Experimental work

In this work, powder metallurgy method was used for manufacturing of Cu-Graphene (GNSs) nanocomposites. Copper and graphene microstructure is shown in Fig.1(a, b) in which, Cu with 75 µm and 99.90 % purity supplied from (International Co. for Scientific & Medical) is reinforced with 0.25, 0.50,0.75, 1.00,1.25 and 1.50 wt. % graphene nanosheets that has 50 nm particle size and 99.95 purity supplied from (Fiber Max Composites company, Greece). High energy ball mill is used in mixing Cu with nano graphene by 400 rpm mixer/mill with a ball-to-powder ratio of 10:1 & 12 hr milling time

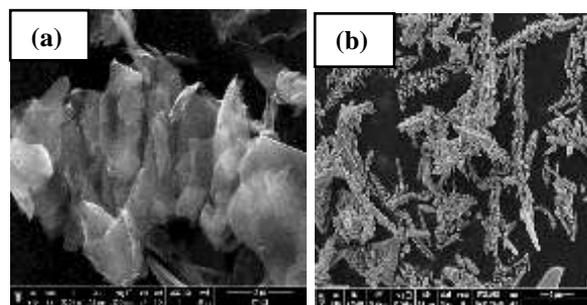


Fig. 1 SEM images of: (a) Graphene (b),Copper.

The mechanical alloying technique is processed using two types of process controlling agent (PCA) which are hexane & methanol. So, 10 % from each one is added separately to the milled mixture to study their effects on the microstructure of the produced Cu-graphene nanocomposites. Also, paraffin wax as a

lubricant material is added by 0.5wt % during the compaction process to decrease the friction with the die. The mixing process was established using a stainless-steel vessel then, the mixed powders were dried in an oven for one hour at about 100 °C to melt the paraffine wax and to let it mix well with Cu-GNSs mixture. Then, the mixture was compressed in a cylinder die has 8 mm diameter and 12 mm height made from Cr-Mo alloy steel (DINW302). The hydraulic uni-axial pressing was done under compaction pressure of 700 MPa. The sintering process was achieved in a vacuum furnace at 950 °C for 1.5 hr by a heating rate of 3 °C/min up to 250°C where the temperature was holded for 15 min. in a dewaxing step. Then the heating rate was increased to 950 °C by 4°C /min. and holding for 90 min then the furnace was cooled. For microstructure examination, the specimens were grinding with 220, 400, 600, 800, 1000, 1200, 2000, and 3000 grit SiC paper and polished with 6-micron diamond paste. Microstructure was studied using a digital camera type cannon PC1049 fitted with ZIESS lenses, also by field emission scanning electron microscope (FESEM; QUANTA-FEG250). The actual density of the prepared samples was estimated according to Archimedes rule, using water as a floating liquid. The sintered specimens were weighed in air and in distilled water and the actual density ($\rho_{act.}$) were determined according to the following equation (1): -

$$\rho_{act.} = \frac{W_a}{W_a - W_w} \dots\dots\dots \text{Eq. (1)}$$

Where W_a and W_w are the weight of the sample in air and water, respectively. The theoretical density ($\rho_{th.}$) for the investigated composite was determined according to the following equation (2):-

$$\rho_{th.} = (V_M * \rho_M) + (V_R * \rho_R) \dots\dots\dots \text{Eq. (2)}$$

Theoretical Density Where V_M and R_M are the volume fraction and density of the matrix while V_R and ρ_R are those for the reinforcement sample. [7-8]

$$\text{Relative Density} = \rho_{act.} / \rho_{th.} \dots\dots\dots \text{Eq. (3)}$$

The electrical conductivity, resistivity and IACS % were estimated for the sintered samples. The test was established using (Material Tester for Metal, PCE-COM20). Then thermal conductivity is calculated using Wiedemann and Franz equation, which is a relation between electrical and thermal conductivity [7]. Wiedmann-Franz relation as shown in the following equation (4):-

$$K / \sigma = LT \dots\dots\dots (4)$$

Where , K is the thermal conductivity in W/ m.k , σ is the electrical conductivity s/m , L is Lorenz constant which equals $2.44 * 10^{-8} \text{ w.}\Omega/\text{k}^2$ value and T is the absolute temperature in oK.

3. Results and discussion

Two groups of samples are prepared; one of them is the Cu-Graphene nanosheets (GNSs) composite with hexane as a PCA and the other with methanol. This section illustrates and discusses the microstructure, electrical and thermal conductivities of the sintered composites.

3.1 Microstructure Examination

Fig. 2 shows the microstructure of Cu-Graphene nanosheets (GNSs) composites, (a, b, c and d) represent the prepared samples by methanol as a process controlling agent, while (e, f, g and h) are those for the hexane ones. Generally, by comparing the two groups, one can notice that samples prepared using hexane have a good microstructure, good homogeneity between Graphene nanosheets (GNSs) and Cu matrix. Etch microstructure area divided to three regions watch are white grey, grey and black areas. The white grey area represents the Cu matrix, the grey area represents the Graphene nanosheets (GNSs) and the black ones are belonging to the pores.

Generally, GNSs did not wet copper as the surface energy between them is high, so no good dispersion of the GNSs in the copper matrix takes place [13]. Addition of PCA and good milling parameters (milling time, ball to powder ratio and number of rotations rpm) are controllable to adjust the composite preparation. It is clear that in case of hexane samples, no pores are observed and Graphene nanosheets (GNSs) are good distributed all over the Cu matrix with very small agglomerations. While the methanol group samples have some porosity. This may be attributed to the hexane nature in which hexane is a long chain organic solvent, has six carbon atoms with no oxygen, so it is an inert organic solvent with low evaporation temperature.

Hexane dissolves all the organic contaminants on the graphene nanosheets surface, which facilitate the dispersion of it in the Cu matrix with a relative wettability, and no agglomerations are observed. While methanol contains oxygen in its structure, which can react with any contaminations on the graphene surface, so the graphene surface may be not cleaned totally by methane, consequently some aggregations takes place. Another observation from the microstructure is the 1 wt. % Cu-graphene sample for the hexane group has the most homogeneous microstructure and lowest pore percent, while 0.25 wt.% graphene sample for the methanol group is the best one.

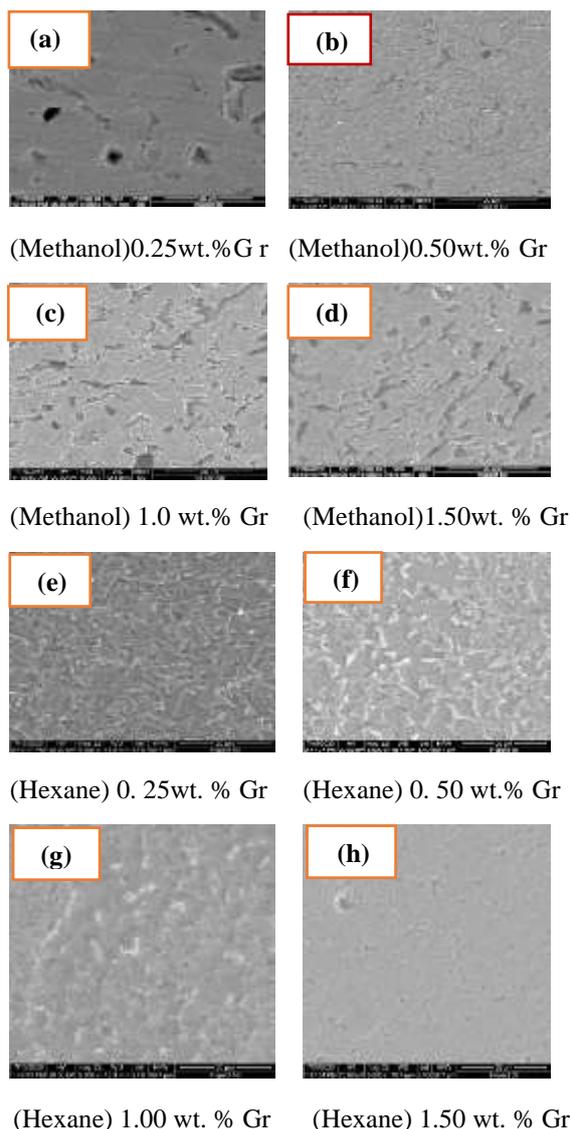


Fig. 2 SEM of sintered Cu-GNSs composite (a, b, c and d) methanol group (e, f ,g and h) hexane group.

Fig. 3 (a, b) shows the EDX of Cu 1 wt. % graphene nanosheets (GNSs) sample with methanol and hexane respectively. It is clear that the samples have a good homogenous dispersion with low Gr agglomerations due to the good milling process between Cu and Graphene nanosheets (GNSs) , also using hexane as a PCA in as shown in Fig. 3 b, while, the reverse for (a) that used methanol (PCA).

Table 1 & Fig. 4 show the effect of Graphene nanosheets (GNSs) on the relative density of Cu-NSs composites prepared with methanol and hexane as a PCA. The Figure shows two phenomena the first is the decreasing density value by increasing the graphene percent for both groups. This is may be attributed to the

lower density value of graphene (2.2 g/cm³) than that of Cu (8.96 g/cm³).

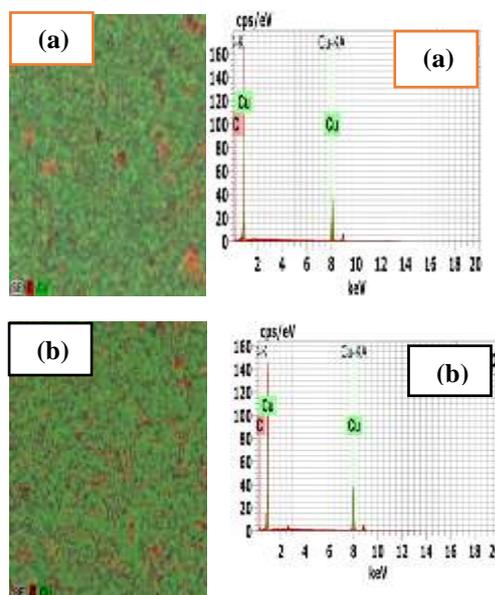


Fig. 3 EDX of sintered (a) Cu /1 wt. % GNSs (M),(b) Cu/1wt. % GNSs (H).

Table 1. Relative density measured value.

Sample GNSs %	Hexane group %	Methanol group %
Cu pure	92.39	90.88
Cu +0.25	89.96	85.53
Cu +0.50	88.35	81.23
Cu +0.75	87.88	78.21
Cu +1.00	86.35	76.32
Cu +1.25	84.69	75.83
Cu +1.50	83.20	72.19

The second phenomena are the increasing density value of hexane group samples than those of methanol ones. This is due to the hexane nature in which it facilitates the separation of graphene nanosheets layers from each other, consequently, good dispersion of it in the Cu matrix without aggregations takes place [8].

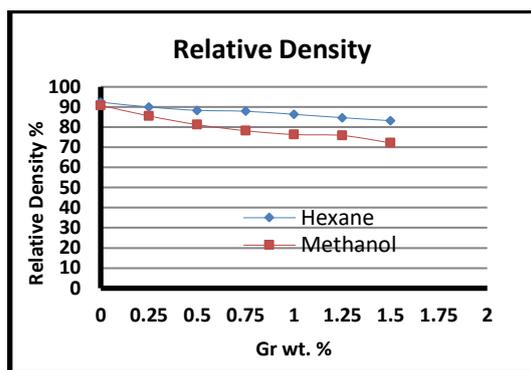


Fig. 4 Relative Density versus graphene wt. % for Cu-GNSs (hexane), Cu-GNSs (methanol) composites.

3.2 Electrical Conductivity

Tables 2, 3 & Fig. 5. show the effect of graphene percent on the electrical conductivity value of Cu-GNSs composites. There are two phenomena; the first is the decreasing of conductivity values by increasing the graphene percent. Although graphene is a conductive material, yet the conductivity of Cu/Graphene nanosheets (GNSs) composites decreases by increasing graphene percent. This may be due to the non-wettability problem between the metallic copper and the graphene nanosheets that has a ceramic nature. In which high surface energy between them has occurred, so. Some agglomerations take place and pores have formed that cause the decrease in the electrical conductivity values as the pores restrict the electron's motion that responsible for the conductance [7]. The second phenomenon is the increase in the conductivity values of the hexane group samples than those of the methanol ones. This may be attributed to the nature of hexane which is a nonpolar solvent that has the ability for dissolving any organic contaminations on the graphene surface and prevent cold welding between particles during the milling process. While methanol is a polar solvent that has a co bond that can be cleavage during the milling process and release oxygen that may react with the milled particles. Also, it cannot dissolve the contaminations on the GNSs surface completely, so some aggregations take place leading to the pore formation. The formed pores have zero conductivity so, the total conductance is decreased [12].

The Cu/graphene electrical conductivity is usually expressed in % IACS which is used to estimate the electrical conductivity for metals and alloys relative to the standard annealed copper metal whose conductivity is 58 MS/m at 20 °C.[9] Owing to the excellent electrical conductivity of graphene, it has been used as a filler for the enhancement of the electrical

conductivity of Cu. As a matter of fact, an improvement as high as 20–30% was recorded for electrodeposited particulate composite films [10]. So, from the literature, one can conclude that the enhancement of the electrical conductivity in Cu/graphene composites is sometimes quite modest or even negative compared with the unreinforced alloys, the improvement enhancements depending on the graphene percent, and the processing route conditions

Table 2. Electrical conductivity for Methanol group.

Sample GNSs % Methanol Group	Ms/m	Ω m ² /m	IACS
Cu pure	42.5	0.02350	73.4
Cu +0.25	31.0	0.03222	53.5
Cu +0.50	23.79	0.04204	41.0
Cu +0.75	21.01	0.04758	36.2
Cu +1.00	20.73	0.04824	35.70
Cu +1.25	15.86	0.06303	27.35
Cu +1.50	10.25	0.09757	17.67

Table 3. Electrical conductivity for Hexane group.

Sample GNSs % Hexane Group	Ms/m	Ω m ² /m	IACS
Cu pure	42.5	0.02350	73.4
Cu +0.25	36.7	0.02721	63.4
Cu +0.50	25.68	0.03893	44.3
Cu +0.75	25.23	0.03963	43.5
Cu +1.00	24.91	0.04014	43.0
Cu +1.25	23.39	0.04276	40.3
Cu +1.50	16.94	0.05902	29.21

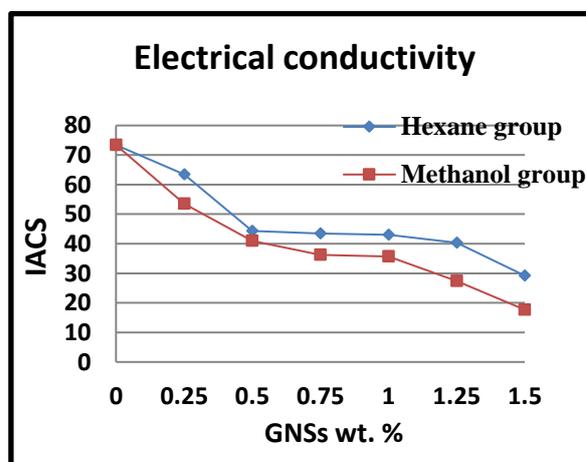


Fig. 5 Electrical conductivity for Cu-GNSs (Hexane & Methanol).

3.3 Thermal conductivity

Tables 4,5 Fig. 6. shows the relationship between the graphene percent and the thermal conductivity of the prepared samples. It is clear that the thermal conductivity decreases gradually by increasing the graphene percent. This is may be attributed to the pores formed during the sintering process due to the agglomerations that take place as a result of the increase of surface energy between Cu and graphene.

Table 4. Thermal conductivity of Methanol group.

Sample GNSs % Methanol Group	(K) W/m.k
Cu pure	305.086
Cu +0.25	222.539
Cu +0.50	170.777
Cu +0.75	150.820
Cu +1.00	148.810
Cu +1.25	113.851
Cu +1.50	73.580

Table 5. Thermal conductivity Hexane group

Sample GNSs % Hexane Group	(K) W/m.k
Cu pure	305.086
Cu +0.25	263.450
Cu +0.50	184.344
Cu +0.75	181.114
Cu +1.00	178.816
Cu +1.25	167.905
Cu +1.50	121.603

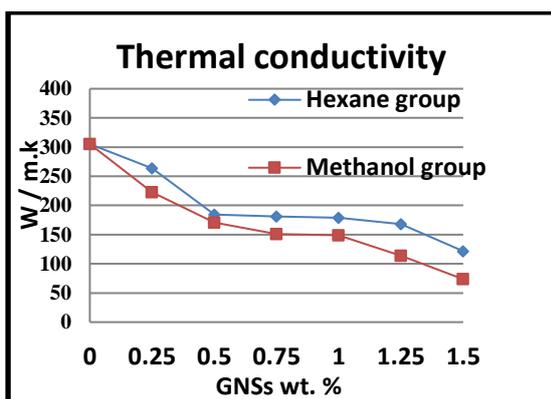


Fig. 6 Thermal conductivity for Cu-GNSs (Hexane & Methanol).

The increase in the aggregation of graphene and the formation of pores that have zero conductivity is the main reason for this phenomenon. Also, the hexane

group has a higher thermal conductivity value than those of the methanol ones. This is also due to the nature of hexane which causes the separation of graphene layers in a good manner and facilitates the motion of the heat in the matrix by conduction and convection due to the low pores. While for methanol group samples, some pores are formed that retards the heat transformation in the formed composites.[11] Although both the electrical & thermal conductivities are decreased by graphene additions, yet is it is still in the working area of Cu composite applications.

4. Conclusions

From the obtained results, one can conclude the followings:

1. Cu- graphene nanosheets can be prepared by the powder metallurgy (PM) technique.
2. Hexane is most suitable as a Process Control agent (PCA) than methanol.
3. Hexane group samples have a good microstructure than the methanol samples.
4. The density values of the hexane group are higher than those of the methanol ones.
5. Both the electrical and thermal conductivities are decreased gradually by increasing Graphene nanosheets (GNSs) percent, but they are still in the working area of Cu composites.
6. To improve the microstructure, electrical and thermal conductivities of Cu-GNSs composites the non-wettability problem must be solved and hexane is preferably used as a PCA.

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