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GRAPHENE NANOPLATELETS (GNPS) EXFOLIATION AND DISPERSION IN METAL POWDER USING DIFFERENT SOLVENTS

Zeeshan Baig, Othman Mamat, Mazli Mustapha, Khurram Altaf and Raphael Joshua Mailabari
Departmental of Mechanical Engineering, Universiti Teknologi Petronas, Tronoh, Perak, Malaysia
E-Mail: meteng81@gmail.com

ABSTRACT

Graphene possesses attractive mechanical and physical properties than available nanomaterials and considered as ideal reinforcement in many metals to enhanced mechanical properties. Incorporation and uniform dispersion of graphene in metals is the ultimate challenge due to difference in surface energies of both contents. Graphene usually available as stacks of multisheets and need exfoliation to obtain single or bi layer because reported unique properties are associated with single layer graphene. In current work, colloidal processing of graphene is employed and processed with iron powder. In this contest exfoliation has been achieved by using different solvents and dispersion attained by mechanically stirred with iron powder at fixed rate. The effect of graphene exfoliation in different solvents and dispersion in iron powder is systematically investigated by FESEM, energy-dispersive X-ray spectroscopy, particle size measurement. To study dispersion effect, hardness and density measurements were conducted on vacuum sintered nanocomposite compacts.

Keywords: grapheme, nanocomposites, dispersion, powder processing.

INTRODUCTION

Metal matrix nanocomposites are attracted to many researchers owing to their enhanced mechanical properties, high temperature resistance, improved electrical and physical properties as compared to monolithic metal matrix[1]. Nanofillers such as graphene and CNTs are mostly considered as ideal reinforcement in many metals (Al, Cu, Mg, Ni Fe) due to incredible and admirable properties specifically high mechanical strength, low density and high aspect ratio. As compared to CNTs, Graphene has been widely investigated to reinforced metals now a days and would be the excellent replacement because of 2D morphology, high specific area, less tendency to twist, impede atomic diffusion effectively at high temperatures, good dispersion ability [2].

Graphene is a one atom thick carbon two-dimensional sheets consisting of hexagonal rings of sp^2-hybridized carbon atoms. This unique structure made it ultimate choice to enhance the mechanical properties of the composites and it is being widely used in different matrices like polymers, ceramics and metals for various applications [3]. After successful incorporation of graphene in polymers and exhibited remarkable improvement in mechanical properties build confidence of researchers to incorporate in different metals as well. It has been thought that graphene has the ability to produce same results if it can be used in metals to increase mechanical properties. It is expected that utilizing the remarkable specific strength and modulus nature of graphene, metallic nanocomposite having combination of both high strength and stiffness which couldn't be yet received from conventional metal and alloys can be achievable Though a volume of graphene polymer nanocomposite research papers is available but on the other hand, research of graphene metallic nanocomposite is in very early stages. [4]. There are some challenges faced by the researchers during fabrication of graphene metal nanocomposites are non-uniform dispersion, structure stability, high tendency of graphene sheets to made clusters , absence of wetting ability between graphene and metals due to large surface tension, unwanted interfacial products and formation of weak interface[5]. After extensive of research, investigators came to know that among those issues, dispersion of graphene is the most important and basic step of metallic nanocomposite manufacturing[6]. Excellent dispersion of graphene in metals define the resultant properties of the metallic nanocomposites. Otherwise, agglomeration concentrated at certain points cause lower strength, higher porosity and forms a weak matrix-nanofillers interface[7]. Therefore, there is much need to focus attention having uniform dispersion of graphene in metallic matrix.

A lot of efforts has been consumed for achieving uniform graphene dispersion in metals using different approaches such as solid state processing also known as powder metallurgy route. In order to mix both graphene and metals, high energy mixing is required to reduce the surface energies, therefore, mostly researchers has followed mechanical alloying or high energy ball milling for this purpose[8]. Though improved dispersion of graphene and properties in metals has been reported by researchers but some issues associated with this process are also reported. During ball milling, sever structural damage of graphene has been observed leading to structure loss otherwise high defect concentration produced on graphene surface[9]. These defects are the favorable sites for chemical reactions with metals and resulting in unwanted interfacial product which degrades the final properties of nanocomposites [10].

In current research work, we have adopted colloidal processing in which graphene nanoplatelets (GNPs) was exfoliated by sonication and not faced severe milling conditions. In this view, we have put efforts to exfoliate GNPs in different solvents to unbundle graphene clusters and make available single or few layer sheets, then

mechanically stirred with iron powders for mixing to achieve dispersion. It has been reported that graphene nanoplatelets can be exfoliated and dispersed in solvents like aqueous (water) or non-aqueous (ethanol, acetone, ethylene glycol, NMP, DMP etc.)[11, 12]. GNPs dispersion is different in these solvents depending upon surface energy and Hansen solubility parameter between them. Surface energy of graphene is estimated as 46.7 mN/m, therefore, solvents which matches this or near to graphene surface energy showed good exfoliation and dispersion [13]. Amongst solvents, non-aqueous, NMP, DMF consist of surface energy close to graphene, hence showed better dispensability. On the other hand, there is a much difference in surface energy between water (72.8 mN/m) and graphene. So water has less capability to disperse graphene. In order to make available graphene disperse in water, functionalization of graphene was normally carried out. This implies the practice of several surfactants via wrapping to provide aid in dispersion. So in this work we have used water with surfactant (SDBS) to get graphene dispersion obtainable. Others solvents are used as such for the said purpose.

This is first time reported that we have processed GNPs in iron (Fe) metal powder. A no of theories and simulations has showed that transition metals like iron (Fe) has great affinity to make strong bond with graphene [14, 15]. Therefore, it is expected that by integrating graphene in iron, mechanical properties will be enhanced. In this paper effect of GNPs exfoliation and dispersion in iron powders along with vacuum sintering to form compacts has been studied. Hardness and density measurement were conducted to evaluate the effect of graphene and processing on iron metal.

EXPERIMENTAL PROCEDURES

Materials

As received raw materials were used in this work. Pure iron (Fe) powder (99.7% purity, average size < 10 μm) was used as the metal matrix purchased from Merck, Germany. Graphene nanoplatelets (GNPs) prepared from wet method were bought from U-Gent technology, Malaysia. Figure-1 shows the SEM images of as-received Fe powder having range of particle size and spherical shape (Figure-1(a)) and GNPs (Figure-1(b)).

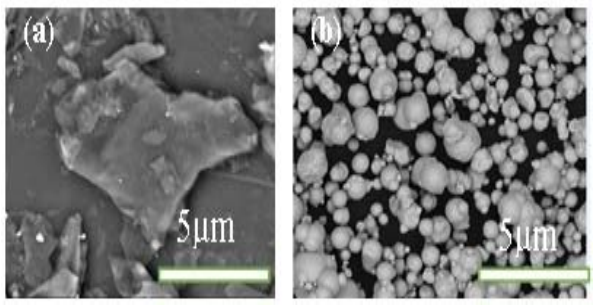

Figure-1. SEM image of (a) pure Iron powder and (b) graphene nanoplatelets (GNPs).

An average thickness of GNPs was 0.68-1.75nm, size equals to 0.1μm-5μm having < 5 sheets contains >99.5 wt. % C (from data sheet) showing stacks of graphene layers. The densities of Fe powder and GNPs were 7.78 g/cm^3 and 2.2 g/cm^3, respectively.

Materials processing

To achieve uniform dispersion, selection of process is a very crucial step. In present work, authors use combination of the ultra-sonication, mechanical stirring and turbula mixing to fabricate 0.1wt%GNPs-iron nanocomposite having homogeneous dispersion. Firstly, 0.05 g of GNPs was added separately into the three solvents (50ml each) namely DI water, Ethanol, and N-Methyl-2-pyrrolidone (NMP) along with suitable surfactant like SDS to stabilize the dispersed graphene sheets. Graphene was then exfoliated in each solvent by ultra-sonication for 1.5 hrs to separate sheets of graphene into single or bi layers by high ultrasonic frequency. Meanwhile, 49.95 g of iron powder was added into the three solvents (50ml each) namely DI water, Ethanol, and NMP and mechanically stirred (IKA RW 20 D S2) at 500rpm for 1 hrs to separate particle agglomerates and homogenization. Subsequent exfoliated graphene of each solvent added drop wise into the iron powder solution of each solvent. Mechanical stirring at 500 rpm was again carried out for 0.5 hrs in order to achieve uniform graphene dispersion and attachment on iron particles. Eventually, three as-blended solutions were dried at on hotplate for solvent evaporation at respective solvent boiling points. After drying, lumps were obtained, in order to breaks theses lumps into uniform composite powder, turbula mixing was carried out. Fe–0.1 wt. % GNP composite powder along with 6 of ZrO_2 balls (diameter: 10 mm) were added in plastic bottle and placed in a TURBULA Mixer for 15 min at a speed of 101 rpm. Subsequently, the GNPs/Fe composite powders were compacted by uniaxial pressure at 300 MPa and were sintered at 1120 °C for 1 h under vacuum (1mtorr) atmosphere to obtain 3mm height and 13 mm dia cylindrical shape samples. For comparison, the pure iron was also prepared by following the same steps.

CHARACTERIZATION OF POWDER MIXTURES AND SINTERED COMPACTS

Microstructure characterization

The samples for pure Fe, pure graphene, and (Fe + 0.1wt% GNPs) composite powders were analyze to study surface morphology and dispersion of reinforcement particle in the matrix. FESEM (Supra 55 VP, Germany) equipped with an energy dispersive X-ray spectrometer (EDS) was used to examine the graphene dispersion, surface morphology and elemental analysis of the prepared powders. SEM analysis (Phenom- Pro X) equipped with an energy dispersive X-ray spectrometer (EDS) were carried out to investigate the microstructure and grain analysis of the composite sintered samples.

Density and hardness measurement

The hardness measurements were conducted on polished samples using Rockwell hardness tester. At least three measurements were taken for each samples.

Density of the samples were done by measuring the respective dimensions of the samples and calculating by following formulas:

The actual composite density ρ_C can be calculated by:

$$\rho_C = W_A/V_C$$

and the theoretical density calculated by:

$$\rho_{th} = 1/ \{Wf_m/ \rho_m + Wf_g/ \rho_g\}$$

Where, Wf_m and Wf_g are weight fractions of the matrix and the particles respectively; ρ_m and ρ_p the density of the matrix (7.87 g/cm^3 and the graphene (2.1 g/cm^3) respectively.

Particle size analysis

Particle size analyzer (Master Sizer 2000) was used to investigate the cumulative particle size distributions of pure Fe powder and (Fe + 0.1wt% GNPs) powders in different solvents to study turbula mixing effect.

RESULTS AND DISCUSSION

Powder morphologies

Figure-2 presents a comparative morphological exploration for Fe/GNP nanocomposite powders processed in different solvents. All the scans were clearly depicts the extent of effective graphene exfoliation and dispersion with iron powder in respective solvent. As can be seen from Figure-2a, graphene is properly wrapped the iron particles and attached on the surface also see magnified image Figure-2a along with EDX results confirming presence of graphene. As graphene nanoplatelets available as no of sheets attached to each other by cohesive forces so exfoliation in solvent is efficient to breaks and separate them together. It is important to note that agglomerations of the iron particles have not observed but some graphene stacked sheets were present on the particles. This can be attributed to the improper graphene exfoliation of some platelets and tendency to re-agglomerate after the removal of surfactant. On the other hand, Fe/GNP powder mixture in ethanol showing absence of graphene on the surface as shown in Figure-2b and clean surface is observed as seen in magnified image of figure 2b. EDX results evident the presence of graphene on the surface which can be attributed to the thin sheets of graphene on surface which has not detected on this magnification. Also, iron particles are agglomerated and welded together as compared to Fe/GNP water powder which may be due to inefficient removal of solvent and surfactant which binds the particles still after drying and turbula mixing process. Similarly, Figure-2c shows the morphology of the Fe/GNP powder mixture in NMP. As known NMP is a good solvent for graphene exfoliation and stabilizing nature so graphene is exfoliated and attached to the surface of the particles as shown in Figure-2c. It is worth noting that graphene as single or few layers are seen on the surface of the particle as in magnified view of Figure-2c. Fe particles as agglomerates were still stayed but in smaller proportion may be due to improper evacuation of the NMP which still binds them together.

The role of surfactant is also very important to exfoliate and stabilize the graphene sheets in solvents. The purpose of the surfactant is to provide steric or repulsive hindrance to graphene to avoid restacking and stabilize them in solvents. In our experiments, SDS an ionic surfactant has properly performed its role as seen from the all the powder mixture that graphene is nearly available as exfoliated sheets and also assist in attachment on the surface of the particles.

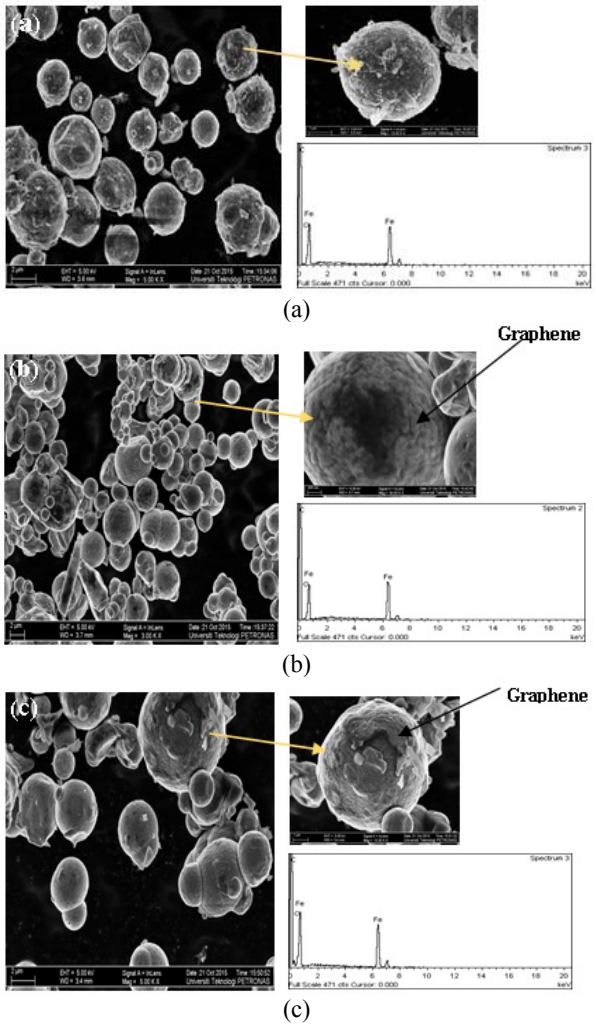

Figure-2. FESEM micrographs of GNPs-Fe powder mixtures processed in (a) DI Water, (b) Ethanol & (c) NMP.

Particle size measurement

The objective of this work is to study the graphene dispersion in Fe powder via mechanical agitation and

turbula mixing. It is important to note any change produce in particle sizes after successive processing steps as particles may turn flatten and welded due to plastic deformation brought by the balls impact in collision during mixing. The size of the particles has pronounced effect during sintering and dictates the final properties of composites.

Cumulative particle size distribution of the mixed powder is normally denoted by X50 which denotes representative particle size of the samples. The line graph Figure-3 shows cumulative particle size of the pure iron and nanocomposite mixture of different solvents obtained after processing. It can be clearly seen that cumulative particle size distribution of Fe/GNP processed in water and Ethanol does not change significantly as compared to raw powder particle of Fe. This behavior of particles shown that particles were not agglomerated and retained the raw shape. This can also be proved by respective SEM images in the Figure-2, presenting particle round shape. This may be attributed to the proper removal of water and ethanol along with effective ball mixing during turbula action. The other reason may be due to the surfactant used which may also cause steric action and repel particles to come near to each other. On the other hand, a significant change in median particle size population of Fe/GNP powder in NMP has been observed. The reason of such increase in particle size is due to the particles agglomerations formation during processing. As, NMP has high boiling points as compared to water and Ethanol, so it may not completely removed or ball mixing has not effectively breaks these agglomeration during mixing step.

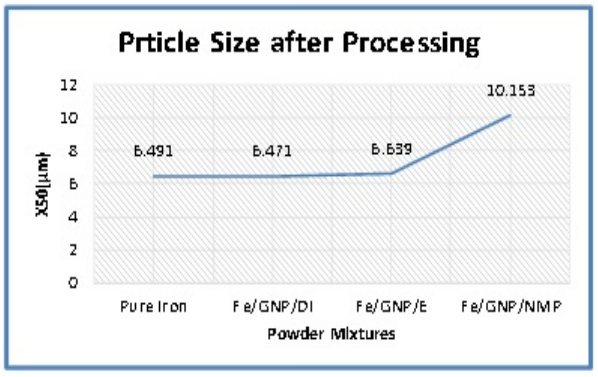

Figure-3. Changes in median diameter (X50) of the GNPs-Fe powder with different solvents.

Density and hardness analysis

Table-1 shows the relative densities of the Fe/GNPs nanocomposites in different solvents. It can be clearly seen that all the samples have not achieved full density which may be attributed to following reasons such as low compacting pressure, presence of graphene agglomerates, possible iron oxidation hindered the full densification. Though overall densities are on low regime but provides certain information related to the effect of graphene addition to the iron. On the other hand, effect of solvents in dispersing graphene on densities is clearly visible in relative density that graphene which is dispersed in DI water has shown maximum density as compared to ethanol and NMP which is also in accordance with the SEM images. It can also be due to the reason that surfactant has usefully exfoliate graphene sheets and help to attached them on iron particles. It can be concluded that surfactant assisted graphene functionalization performs better in water as compared to other solvents used.

Table-1. Relative densities of Fe/GNP nanocomposite with different solvents.

Sample Name	Theoretical Density g/cm^3	Sintered Density g/cm^3	Relative Density g/cm^3
Pure Iron	7.87	7.00	88.94%
Fe + GNP (DI)	7.85	7.40	94.26%
Fe + GNP (Ethanol)	7.85	7.28	92.7%
Fe + GNP (NMP)	7.85	6.51	82.93%

Figure-4 representing the harness values measured by Vickers tester achieved for Fe/GNPs nanocomposites in respective solvents. A considerable increase in hardness is obtained after the addition of graphene in iron matrix. This can be attributed to the graphene high mechanical strength, surface area & 2D structure. As graphene has high aspect ratio amongst nanofillers, so low concentration of graphene can contribute to enhance properties. It has been also seen that higher concentrations of graphene in metal powder lead to agglomerations caused decline in properties. This response of hardness can be directly linked to the good exfoliation and uniform dispersion of graphene in iron powders. As can be distinctively seen that Fe/GNPs has shown highest increment of hardness which is about 41% increase than pure iron. Whereas other solvents have also shown some response in hardness enhancement as compared to pure iron.

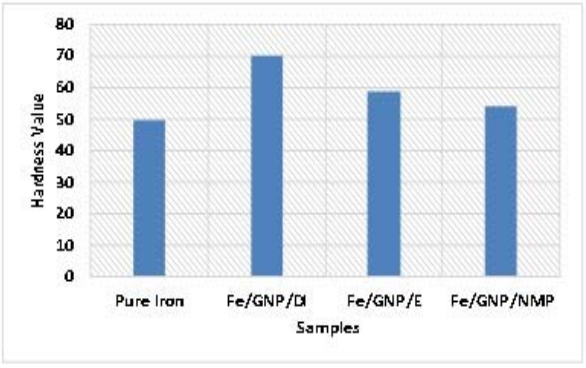

Figure-4. Hardness values of Fe/GNPs nanocomposite in different solvents.

As a consequence, increase in hardness is not up to expectation which could be possibly due to presence of graphene agglomerations, low graphene content and possible reaction of iron with graphene carbon at higher temperature during sintering. The results of hardness values have given direction that graphene dispersed in water would produce enhancement in properties and also it is confirmed that graphene is also contributing its reinforcing role in iron matrix.

Microstructural analysis

Figure-5 depicts the Fe/GNPs nanocomposites sintered nanocomposites SEM images processed in three solvents. As it can be evidently seen that graphene is present in between the grains and at the grains. Graphene is visibly observed in nanocomposite processed in DI water as compared to other solvents which is also confirmed by EDX results. Factors which affects the density and hardness are porosity due to low compaction pressure and graphene agglomerates evolved as big black spots.

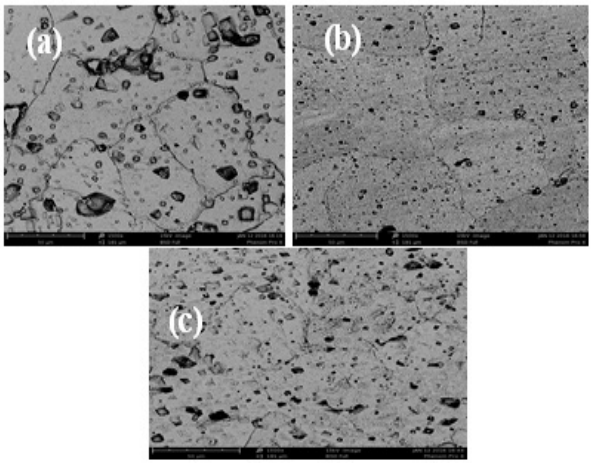

Figure-5. SEM micrographs of GNPs-Fe nanocomposites (a) DI Water, (b) Ethanol & (c) NMP.

CONCLUSIONS

Fabrication of Fe-0.1 wt% GNPs nanocomposite in different solvents by ultra-sonication, mechanical agitation and turbula mixing were successfully conducted. The results of density and hardness has clearly highlight the importance of graphene dispersion which could be attained by selecting suitable processing technique and solvent. Amongst DI water, Ethanol and NMP, water has shown maximum dispersion of graphene in iron powders which is due to good exfoliation of graphene in water. Water processed graphene iron nanocomposites has shown 41% increase in hardness as compared to other solvents. Higher properties would also be achieved by proper optimization of processing parameters and condition and will be investigated in future research work.

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