Perspective—Electrodeposition of Graphene Reinforced Metal Matrix Composites for Enhanced Mechanical and Physical Properties: A Review

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Electrodeposition of graphene reinforced metal matrix composites for enhanced mechanical and physical properties: A review

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Abstract. Graphene, a two-dimensional material consisting of carbon sheets with exceptionally superior mechanical, electrical and thermal properties, presents itself as an effective second phase reinforcement option for composites and functionally graded materials. Although polymer matrix composites reinforced with graphene have been explored extensively, metal/graphene composite is a comparatively new field of research. This perspective article reviews electrochemical deposition as a strategy to fabricate well-dispersed metal/graphene composites for their potential to enhance mechanical and physical characteristics. The recent state of the art research works has been discussed along with the challenges that are being encountered and their possible solutions.

1. Introduction

The 2010 Noble prize in physics for the successful isolation of graphene layer from graphite crystals through mechanical exfoliation opened up new avenues in the field of 2D materials \cite{1}. The excellent mechanical and physical properties of this newly discovered material rendered it suitable for reinforcements or fillers in composite materials having a wide range of applications. Till date, CNTs are the most dominant carbon material used as a filler as it has been well established as reinforcement for mechanical and physical property enhancement \cite{2}. Recently, graphene has started occupying the space because of economic viability with similar intrinsic properties as compared to CNTs. Moreover, the larger surface area of graphene makes it a better load distributing reinforcement. The present works demonstrating the improvement in tensile strength, Young’s modulus, hardness, as well as electrical and thermal conductivities establishes the enormous potential that graphene reinforced MMCs possess \cite{3}. The expanding but limited number of research work in this particular field is due to the technological difficulty encountered during the processing of graphene-MMCs as
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compared to polymer matrix composites. The vander-Waals forces present between the graphene rings make it difficult to get dispersed in the metal matrix, thus resulting in agglomerates. The poor affinity of graphene towards metals makes it challenging to obtain active interfaces. Besides, the high temperature (>873 K) employed to fabricate various MMCs has a damaging effect on the graphene layer and its properties. Thus, the fabrication process has a significant bearing on the property improvement of graphene-metal composites.

Graphene reinforced MMCs (with metals such as Al, Mg, Cu, Ni, etc.) have been prepared through various processing routes such as powder metallurgy, chemical deposition, molecular level mixing, sol-gel method, electrodeposition, etc. [4, 5, 6, 7]. The powder metallurgy route sometimes fails to prevent the agglomeration of graphene, thus limits the creation of interfaces between matrix and reinforcement. Also, the high temperature employed in this process leads to oxide formation, hence impairs the purity of the matrix metals. The need of vacuum for techniques like chemical deposition makes it economically expensive and challenging to operate. Thus, electrochemical deposition acts as an alternate method for efficient distribution of graphene and co-deposition in metal matrix owing to the stable dispersion of graphene in aqueous solution. This bottom-up approach has gained popularity recently as it offers better control over the output parameters like grain size, reinforcement distribution, and thickness of deposition. The process necessitates an electrochemical cell and a power source for the passage of current through the anode and cathode. The co-deposition of the composite commences through the reduction of metallic particles on the cathode. This easy, cost-effective technique being a low-temperature process preserves the intrinsic properties of graphene during the preparation of the composite. By altering the input parameters like current density, solution concentration, pH, electrode distance [8], etc. the nature of deposition can be easily regulated. It is also possible to effectively control the crystallographic structure and surface properties like roughness and hardness by the application of pulse current waveform. Moreover, electroforming, which is based on the principle of electrodeposition, can be utilized as a one-step process to fabricate complex and intricate parts consisting of the graphene/metal composite. The alternate layered structures of metal and graphene or graded deposition are the other possibilities offered by the electrochemical deposition process.

2. Current status

In recent years, graphene (Gr) and its derivatives such as graphene oxides (GO) and reduced graphene oxides (RGO) have been lucrative ultra-thin reinforcement options for MMCs because of their ability to induce high strength, high chemical inertness and improved tribological properties in the matrix of composites. The electrodeposition of metal/Gr composite has broadly taken two routes; one uses GO as the source material in the electrolyte solution while the other utilizes Gr directly with the help of some dispersant to attain stable dispersion in the solution. While graphene itself is difficult
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to disperse in aqueous solutions because of its hydrophobic nature, the hydrophilicity of GO makes it conducive for uniform dispersion in the electrolyte carrying metal ions. The hydrophobicity of graphene contributes towards cluster formation, hence the agglomeration in the solution. The solvation free energy of the cluster becomes lower than the solvation free energy of individual solutes combined because of the large volume-to-surface area ratio of the cluster. Also, the driving force for cluster formation increases with increasing temperature [9]. Hence, R. Cui et al. [10] has utilized dispersant of polymeric surfactant for dispersion of commercially available multi-layered graphene. The Cu/Gr composites, thus obtained with varying percentages of graphene, were found to have a homogenous distribution of graphene with enhanced wear resistance, thermal conductivity, and arc ablation resistance. The addition of surfactants may induce heterogeneous impurities in the matrix, which can inhibit the inter-facial interaction between the graphene and the matrix. R.T Mathew et al. [11] made use of graphene layers without dispersant but provided the solution with mechanical stirring of around 1150 rpm. Along with varying graphene concentration, they undertook the experiment of varying current densities. The addition of graphene not only led to the modification of crystallographic growth direction but also the grain refinement of deposits as demonstrated in Figure 1.

The Cu/Gr composites demonstrated a very high yield strength with comparable electrical conductivity to pure copper. A higher current density was found to be suitable for strong and effective graphene reinforcement, thus an increase in the yield strength. Similarly, Li et al. [12] carried out the preparation of Al/Gr composite by dispersion of graphene nanplatelets with the help of magnetic stirring at a speed of 250 rpm. The composite thus electrodeposited demonstrated a massive 11-fold reduction in the friction coefficient value under the dry sliding condition as compared to the pure Al coating. The fabrication of microsystems viz., micro-cantilever and micro-mirror consisting of metal/Gr composite through electrodeposition eliminate the drawbacks of machining processes such as residual stress induction, thermal damage, difficulty in controlling the precision and accuracy, etc. The enhanced properties of the composite render an added advantage. Li et al. [13] employed both ultrasonication and mechanical stirring for the effective dispersion of graphene sheets in a nickel sulphamate electrolytic bath. The grain refinement and hindrance to dislocation movement provided by the metal-Gr interface lead to 2.7-fold enhancement in the Vickers hardness and 1.4-fold in Young’s modulus, respectively. The combination of mechanical stirring and ultrasonic agitation in 3 consecutive cycles was implemented in the research work carried out by Toosinezhad et al. [14]. The electrodeposited Co-Gr composite manifested a 3 fold increase in micro-hardness than that of pure cobalt.

The other route of fabrication that has been followed by researchers is the use of graphene oxide (GO) instead of graphene in the solution. In the first step, a metal-GO composite is formed, which then gets reduced at the cathode to form a metal-Gr composite. The hydrophilicity of GO makes it well suited for electrodeposition in aqueous solution. The oxygen-containing functional groups make it easy for GO
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| Current Density | 300 mA cm⁻² | 600 mA cm⁻² | 900 mA cm⁻² |
|----------------|-------------|-------------|-------------|
| Pure Cu        | ![image](a)  | ![image](b)  | ![image](c)  |
| Cu-5 Gr        | ![image](d)  | ![image](e)  | ![image](f)  |
| Cu-10 Gr       | ![image](g)  | ![image](h)  | ![image](i)  |
| Cu-20 Gr       | ![image](j)  | ![image](k)  | ![image](l)  |
| Cu-50 Gr       | ![image](m)  | ![image](n)  | ![image](o)  |

**Figure 1.** Grain refinement with increased concentration of graphene and current density. Reprinted from [11] with permission from Elsevier.

to get dispersed uniformly in the electrolyte solution. The reduced graphene from GO replaces some of the metal ions and grows in its stead. The change in the growth direction of the metal deposition because of graphene incorporation improves the properties like thermal conductivities [15]. **The grain refinement due to the**
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graphene reinforcement also contributes towards an improvement in the anti-wear performance [16]. The research work carried out by Pavithra et al. [6] has successfully attempted the composite electrodeposition of Cu/Gr by dispersion of GO in the electrolytic solution containing copper ions. The emphasis has been on the improvement of mechanical properties like strength and hardness of the composite fabricated through pulse electrodeposition. The research clearly shows pulse reverse electrodeposition (PRED) as having an edge over DC electrodeposition in terms of the uniform distribution of graphene in the Cu matrix. Figure 2 demonstrates the grain refinement and uniform distribution of graphene with different current waveforms. Altering of the duty cycle results in a uniform, smooth deposition with minimal chances of hydrogen embrittlement. The forward cycle of the pulse current waveform enables the mass deposition while the reverse cycle removes the excess graphene and hydrogen at the cathode, thereby controlling the grain growth. Whereas, in the case of DC electrodeposition, rapid deposition and growth happen at the most active nucleation sites because of the continuous supply of current. Several factors associated with pulse deposition like on time, off time, frequency of pulse, makes it feasible to optimize the parameters to obtain uniform microstructural structures. Moreover, the enhanced deposition rate in case of graphene-MMC electrodeposition can be attributed to an increase in deposition current observed in current-transient curve. The uniform and compact morphology as a result of graphene incorporation leads to enhancement in property like corrosion resistance [17].

![Figure 2](https://mc04.manuscriptcentral.com/jes-ecs/Journal-of-The-Electrochemical-Society.png)

Figure 2. (a), (b) & (c) FIB images of as-deposited and polished surface of PRED Pure Cu, DC Cu-Gr and PRED Cu-Gr. (d) (e) & (f) represent the annealed PRED Pure Cu, DC Cu-Gr, PRED Cu-Gr respectively. Reprinted from [6] with permission from SpringerNature.

Electrodeposition, thanks to its versatility and low-temperature application, finds
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A place in hybrid processes for fabrication of layered composite as well as functionally graded materials (FGM). Layered composites consisting of alternating layers of different materials have been found to possess enhanced and unique mechanical properties. The dislocation obstruction at the interfaces is accountable for such improvement, and the strength enhancement takes place with a reduction in the layer spacing and width. The fabrication of layered composites has been undertaken by various processes but has not been able to address the limitations of scalability and production on an industrial scale. The combination of electrodeposition with a method like roll-based transfer process has demonstrated the potential to overcome these limitations. Kim et al. [18] successfully synthesized Cu/Gr layered composite by replacing the vacuum deposition method with electrodeposition, thereby reducing the time and cost. A smaller grain size of copper was obtained through the electrodeposition process compared with the evaporative techniques. This, along with the hindrance provided by the interfaces to the movement of dislocations, contributed towards an enhanced strength of the layered composite. Multilayered composite of Cu-Gr-Ni has also been fabricated through this hybrid process involving electrodeposition. The uniform distribution of graphene on the copper foil is attributed to the electrodeposition process which resulted in the strengthening and toughening of the same due to load transfer and interfacial strength [19]. Functionally graded metal/Gr composite is another possibility that has been realized by the electrochemical deposition method in an economically superior way. A minor variation of the duty cycle in pulse electrodeposition can generate varying degrees of reinforcement content in the metal matrix. Zhang et al. [20] successfully fabricated corrosion-resistant functionally graded Ni/Gr material with a variation of duty cycle in the range of 0.4-0.8. At a relatively higher duty cycle (0.8-0.6), the anodic dissolution of metal is faster than the particle velocity; thus, a higher percentage of metal deposition and lower graphene content is obtained. With a gradual decrease in the duty cycle up to 0.4, the short on-time makes it difficult for the metals to nucleate. Longer off-time enhances the chances of graphene being embedded in the metal matrix. A higher percentage of graphene provides a higher number of sites for nucleation and inhibits grain growth, thereby resulting in finer grains. But too low a duty cycle results in a distortion of the lattice because of much higher nucleation rate as compared to the growth rate. The corrosion resistance of FG Ni/Gr was found to be best followed by that of uniform Ni/Gr composite in a saline environment.

3. Future needs and prospects

The damaging effect of high-temperature processes towards graphene sheets and the economically expensive nature of vacuum methods made researchers look towards electrodeposition as an alternate method for processing of metal matrix composites reinforced with graphene. Initially, the focus was on metal/GO deposition, which subsequently gets reduced to metal/Gr composite because of the numerous oxygen-containing functional groups that make it easy to get dispersed in aqueous solution.

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But these also absorb a large number of metal ions and form agglomerations before co-depositing into the metal matrix. Hence, it can espouse a great deal of porosities, void, and roughness in the composite deposit that can impair the mechanical as well as physical properties of the composite. Moreover, due to incomplete reduction and retention of oxygen molecules, the reduced Gr from GO has inferior properties compared to graphene produced by other methods [21, 22]. Mai et al. [23] undertook a surfactant-free electrodeposition process to fabricate GO/metal composite with increased wear resistance. The surfactant-free colloidal solution prepared using ethylene diamine tetra acetic acid (EDTA) forms anionic complexes with copper ions and repels the negatively charged GO ions. The electrostatic repulsion keeps the GO ions in suspension. Anionic surfactant, sodium lauryl sulphate was also utilized in order to obtain a uniform coating of Cu/Gr composite having enhanced corrosion resistance [24]. Later, the attention shifted to Gr instead of GO dispersion in the plating solution. It not only gives better control over the properties of the metal/Gr composites but also the density of the composite is anticipated to improve due to the direct forming technique. The hydrophobicity of graphene sheets leads to their agglomeration, as discussed in the previous section. The entanglement and agglomeration of graphene sheets impact the anti-corrosive property of the fabricated composites. Hence, various anodic, as well as polymeric surfactants, have been added to the solution in order to ensure the uniform dispersion of graphene sheets or nanoplatelets. Mechanical stirring has also been employed to keep the graphene in the solution phase.

Ultrasonic agitation can be a way forward in the direction of effective dispersion. Very recent research by Zhang et al. [25] has taken the first step in this direction through the ultrasonic electrodeposition of Ni/GO composite. The ultrasonic energy imparted not only helped in the uniform dispersion of GO but also contributed towards the enhancement in mechanical properties. Optimization of the ultrasonic power was crucial for obtaining a uniform distribution of graphene in the metal matrix. The friction coefficient of the composite also diminished with an upsurge in the ultrasonic power. The implementation of ultrasonic power in electrodeposition can be taken to the dispersion of graphene sheets in the plating solution. The deposition of higher density and uniformity with further enhancement in properties would be feasible due to the direct forming of metal/Gr composite. Another advanced electrodeposition process, namely jet electrodeposition, presents the possibility of a high-velocity deposition which can effectively disperse the second phase particles upon the substrate. Ji et al. [26], in a recent work, demonstrated the Ni/Gr composite by using GO because of its hydrophilicity. The high-velocity impingement of solution onto the cathode facilitates a reduction in the double layer thickness, which in turn increases the limiting current density. To avoid the incomplete reduction-related issue prevalent with GO deposits, a separate high-velocity feeding system for graphene can be developed along with the jet assembly for the electrolyte solution. The judicious control of the jet parameters and the feeding system can lead to an improvement in graphene composition in the matrix as well as the properties of the composite. Magnetic field assisted
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electrodeposition of Ni-graphene composite has been the latest addition to this advanced fabrication domain. The addition of Co$_7$Fe$_3$ magnetic powders in the electrolyte along with graphene by Zhang et al. [27] resulted in a uniform distribution of reinforcement. The incorporation of CoFe in the matrix led to increased roughness along with higher amount of hydrocarbon absorption. The improvement in corrosion resistance can be associated with the barrier action of air pockets provided by absorbed hydrocarbons.

The aim of improving the mechanical and physical properties through graphene reinforcement in the metal matrix depends on the optimum concentration of graphene/GO in the matrix. While a low graphene composition leads to grain growth along the low energy index plane, a high concentration induces galvanic interaction between the metal and graphene. Both ends of the concentration scale cause a reduction in the corrosion behaviour. When GO is utilized as the dispersed phase in the solution for its subsequent reduction to graphene, the resulting composition of graphene in the matrix is dependent on the GO concentration. With an increase in concentration, there is an increase in graphene composition, but too high a concentration leads to agglomeration and significantly decreased surface area of graphene [28]. Moreover, the concentration of graphene in the metal matrix has been found to influence the morphology of the composite. The morphologies such as honeycomb or cauliflower structures greatly impart corrosion resistance. Hence, even though various researchers have pointed towards an increase in wear/corrosion resistance of electrodeposited metal/Gr composites, the optimum concentration of Gr required needs to be investigated extensively. Also, the methods and parameters to control the composition precisely need to be studied extensively with a focus on the electrochemical deposition process. There is no conclusive theory yet regarding the wear mechanism explaining the wear properties of metal/Gr composite. Although it is established that graphene helps in preventing the oxidation of metal at the expense of its own oxidation, the microstructural evolution of the metal matrix at the friction interface due to graphene reinforcement is not known correctly. Hence, in order to get a clear picture of the tribological behavior, a more comprehensive microstructural and chemical investigation needs to be undertaken.

The types of the current waveform used for the electrodeposition process carries a significant bearing not only on the deposition properties but also on the reinforcement distribution in the metal matrix. Though the use of a DC source leads to a faster rate of deposition, surface properties like roughness and uniformity get affected. The continuous application of current gives rise to a higher amount of grain growth at favorable nucleation sites. Researchers have lately focused on the application of pulse and pulse reverse current waveforms for composite electrodeposition using graphene as the reinforcement, as mentioned in the previous section. Pulse reverse electrodeposition offers an opportunity to optimize a large number of parameters like on-time, off-time, pulse width to precisely control the composite properties like density, uniformity, porosity, and the second phase particle composition. The forward cycle of the waveform facilitates the ion movement and deposition, while the reverse cycle helps in the removal
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Figure 3. Graphene concentration for different current waveform

of the excess metal ions or graphene particles/ platelets. The higher amount of graphene incorporation reduces the grain size as pulse current leads to the formation of a higher number of nucleation sites inhibiting grain growth. Electrodeposition using pulse reverse current has contributed towards the development of an emerging field, namely functionally graded materials (FGM). The difference in deposition properties and graphene composition with the application of different duty cycle makes it a suitable one-step fabrication method for FGMs. A higher duty cycle in the range of 0.8-0.6 offers prolonged forward cycle time during which the metal dissolution rate is faster than the particle velocity. Hence a lower amount of graphene could get incorporated in the metal matrix. Lowering the duty cycle up to 0.4 offers lesser on-time, thus more nucleation sites for the metal as well as graphene. The enhanced number of nucleation sites by graphene incorporation leads to finer grain size and compactness of the deposit. The FGM renders superior mechanical properties due to hindrance provided by the interface to the movement of dislocations. **Figure 3 shows schematically the dependence of graphene concentration in the metal matrix upon the type of current waveform and associated parameters like forward current**
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magnitude$(i_f)$, reverse current magnitude$(i_r)$, forward time period$(T)$ and reverse time period$(1-T)$.

The above discussions clearly show that the co-electrodeposition of metal and graphene for the fabrication of composites and more advanced materials like FGMs is a technologically feasible and economically favourable process. The research area needs further perusal and the combination of hybrid techniques in order to exploit its potential fully. Further, few more advancement in the electrodeposition of graphene and associated modification includes; usage of nanoporous graphene with single-atom nickel dopants as a catalyst for electrochemical hydrogen production [29], narrowing the two-dimensional interspacing of graphene oxide (GO) membranes without any impairment with the help of a facile electrophoresis deposition (ED) method [30], enhancement in the biofilm buildup in Bio-electrochemical system (BES) with the help of electrodeposited GO modified electrodes [31], electrodeposition of GO with the help of covalently linked electroactive monomer named carbazole (Cbz) [32], and so forth.

4. Conclusion

The applications of graphene as a 2D material encompasses diversified areas of research. Its role as a second phase reinforcement material has attracted researchers to utilize its efficacy in the form of its superior mechanical, electrical, and physical properties. This article has explored electrodeposition as a possible fabrication process for metal matrix composites reinforced with graphene. The effect of parameters viz., duty cycle, frequency, and current density on the deposition properties has been analysed. The mechanism behind the improvement in properties like strength, hardness, wear, and corrosion resistance has been discussed. The main challenges encountered in this method like uniform dispersion, selection of current waveform, and wear mechanism have been elaborated, and cutting-edge technologies like ultrasonic agitation and jet electrodeposition with a feeder system have been suggested as possibilities for further research.

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