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Review article

Recent developments in graphene based metal matrix composite coatings for corrosion protection application: A review

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Abstract

Metallic coatings are considered as an important material which is utilized in a variety of protective applications due to its lightweight, tough and chemical resistive surface. Rising industrial demands for high performing coatings led the researchers to improve the properties of conventional metallic coatings for corrosion protection and other applications. Graphene based metal matrix composite coatings is a widely studied subject nowadays on account of its ability to protect metal substrates against deterioration in the corrosive environment. The addition of graphene as nanofillers into the metal matrix not only improves corrosion performance but also mechanical and tribological properties. In this present review, the effect of incorporation of graphene as reinforcement on corrosion behaviour of different metal matrix coatings when applied on different metal substrates has been presented. Electrochemical codeposition is used as main technique to deposit these composite coatings as thin film on metal surfaces. Major issues related to graphene nanosheets agglomeration, graphene-matrix interactions and controlling of electrodeposition process parameters are also discussed in detail.

1. Introduction

Metal matrix composite coatings (MMCs) are being used extensively in research and industrial purposes due to their peculiar mechanical, chemical and barrier properties. This type of coating is constituted by a metal or metal alloy matrix containing nanofillers of metal oxides, carbides or other organic materials as a secondary phase. Secondary phase materials incorporated into the metal matrix are generally in the form of ultrafine/nanoparticles or nanowires whose properties can influence the resultant properties and applications of fabricated coatings [1]. Most commonly used nanofillers in metal matrix nanocomposite coatings are ceramic nanoparticles such as SiC, Cr_2O_3, Al_2O_3, ZrO_2, TiO_2 and CeO_2 [2]. These nanoparticles embedded in the metal matrix fills in micro holes and crevices and forms a superior passive layer that resists the initiation and growth of defect corrosion, thus improving the corrosion resistance of the coating [3].

The final coating composition, microstructure and morphology are closely related to the deposition process parameters and composition of electrolytic bath mixture which can influence the corrosion performance of the coatings. Moreover, the tendency of the nanoparticles to agglomerate when mixed with metal matrix could generate voids at the reinforcement/matrix interface which can adversely affect the corrosion behavior of the underlying metal and gives cracking upon loading consequently deteriorating the surface properties of the composite film [4]. One of the ways to deal with the aforementioned issue is to incorporate carbon nanomaterials at the place of oxide nanofillers in the metal matrix which makes the coating thinner and improves its corrosion resistance. Nowadays the most popular choice of many researchers working in the field of anticorrosion coatings is graphene due to its extraordinary properties such as high impermeability, large surface area and high chemical resistance.

Various deposition processes have been described in the literature to form graphene based metal matrix composite coatings such as electrophoretic deposition [5], chemical vapor deposition (CVD) [6], electroless deposition [7], cold spraying [8] and electroplating. All of these deposition techniques were employed to achieve composite coatings with improved adhesion, good uniformity, high deposition rate, good reproducibility and low cost. Most of the results obtained proved that the presence graphene nanoplatelets not only increases the corrosion resistance but also hardness and wear resistance of the MMC coating/substrate system. Although, the addition of appropriate graphene percentage in the metallic matrix to generate high performing anticorrosive coatings directly depend on the metal/graphene suspension and on the deposition parameters employed. Moreover, the corrosion protection mechanism in MMC coatings consisting of graphene is generally due to barrier effect and creation

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of tortuous pathways to the electrolyte [9].

Numerous research articles have been reported in the literature on fabrication of graphene based composite coatings containing graphene nanolayers, but only limited review papers are available on the state of art in this area [10-12]. According to web of science, 2220 research articles has been published in this field when searched with keywords “graphene metal coating”. Figure 1 illustrates the trend of publications in graphene based coatings over the last 10 years from 2008 to 2019.

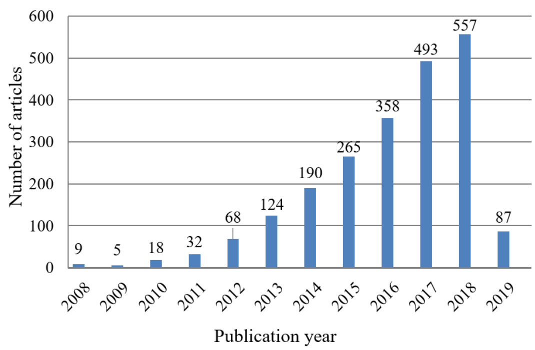

Figure 1. Record of graphene metal coatings showing number of research articles published since year 2008 (source: web of science, accessed on 09/02/2019).

In this short review, we discuss about the different types of metal matrix composite coatings embedded with graphene and graphene oxide nanosheets to improve their anticorrosion performance. Corrosion protection mechanisms involved in each type of coating electrodeposited on different substrate materials has been explained concisely. Moreover, a separate section is added at the end of the article focusing on agglomeration problem and possible remedies for multilayered graphene in metal matrix. The authors of this review article hope that the information provided will help future researchers and academicians to fabricate high performing graphene based metal matrix composite coatings with outstanding corrosion resistance potential.

2. Graphene films and coatings for anticorrosion application

Graphene is a two-dimensional carbon nanomaterial having thickness as small as one atom thick with densely packed hexagonal lattice structure. Graphene possesses outstanding properties of high mechanical strength, chemical inertness, high electrical and thermal conductivity, impermeability, and high optical transparency under ambient conditions [13]. These unique properties of graphene make it suitable for a wide variety of applications in different areas of science and engineering such as energy storage, electronic devices, sensors, photonic devices, advanced composites, coatings etc. [14]. Depending upon the area of application graphene can be fabricated in different forms such as graphene nanoplatelets (GNPs), graphene nanoribbons (GNRs) graphene oxide (GO) and single layered/multi-layered films [15].

Because of its high surface area and hydrophobic nature, graphene in anti-corrosion field is utilized either in the form of films or coatings to prevent the base metal surface from deterioration. Graphene film forms a thin impermeable passive layer on the surface of the metal and prevents penetration of oxygen or water molecules. These films are synthesized by CVD method on copper or nickel surfaces and can be transferred to other surfaces by mechanical transfer method [16]. Figure 2b shows graphene film formed by CVD on pure copper foil with visible graphene nanosheets edges. Sometimes pure graphene nanoplatelets are functionalized with coupling agents such 3-aminopropyltriethoxysilane (APTES) to increase covalent bonding with the base metal surface and applied as coating [17]. To reduce the cost of coatings, graphene is often replaced with reduced graphene oxide mixed with chemicals and deposited as a coating film via dip coating or spin coating process [18]. Ultrathin graphene films can reduce metal corrosion rate up to tens or even a hundred times. Although graphene coating is very thin, its anticorrosion effect is equivalent to at least five layers of conventional organic coatings.

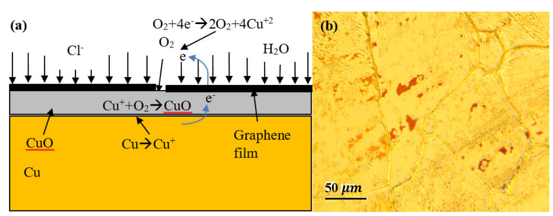

Figure 2. (a) Corrosion protection mechanism of copper foil deposited with pristine graphene film by CVD method (b) Optical microscope image showing grain boundaries and incomplete coverage areas on surface of copper foil.

Large number of scientific articles are available in literature proving graphene as a good corrosion resistant material which can impede corrosion process on metal surface. Most of these experiments in literature are conducted in simulated conditions of weather, for shorter duration of time and at room temperature [19]. However, in real corrosive environmental conditions, graphene contributes to localized galvanic corrosion on account of its high electrical conductivity in the presence of an electrolyte [20]. Furthermore, pure graphene coatings are highly susceptible to surface defects upon extended exposure to corrosive media leading to localized corrosion of metal substrate as shown in Figure 2a. Also, the implementation of pristine graphene for large scale anticorrosion application is still in development stages because of failure to fabricate economical and sizable graphene sheets with least defects and adhesion reliability on the substrate surface.

One way to deal with these shortcomings is to incorporate graphene or graphene oxide nanosheets into metal matrix coatings as nanofillers. However, poor dispersibility of graphene nano-layers in metal matrix can severely restrict the formation of consistent graphene metal composite film.

3. Corrosion protection mechanisms in graphene based MMCCs

Graphene based metal matrix coating provides corrosion protection to the base metals through combination of different mechanisms. This includes the formation of strong physical barrier that resists the diffusion of corrosive agents; sacrificial cathodic protection; active corrosion inhibition; and reduction of electrochemical reactions in the coating layers via high ionic resistivity at the coating-metal interface as shown in Figure 3 [21].

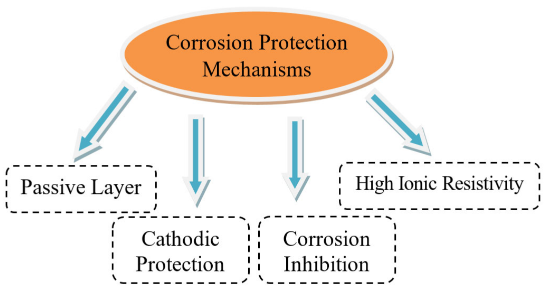

Figure 3. Schematic diagram showing different corrosion protection mechanisms of metal matrix nanocomposite coatings embedded with metal oxide nanofillers.

The first mechanism involves the creation of a physical impermeable barrier on substrate surface by metal matrix and graphene layers which give extra protection against penetration of oxygen and water molecules. Surface passivation can also be achieved by formation of corrosion products that fills up all micro-cracks and voids isolating the substrate from the corrosive environment [22]. In cathodic protection method, the coating behaves like anode and sacrifices itself thereby protecting the cathodic base metal. The sacrificial ability of the coating not only depends upon the type of metal deployed as matrix material but also on the corrosion by-products [23]. Corrosion inhibition is another mechanism in which active inhibitors are stocked and dispensed as soon as a corrosion defect point appears in the coatings. To impart this corrosion inhibition ability, MMNCs are generally embedded with conductive polymers that cover the defects by forming an oxide layer. Nowadays, several new generation conductive polymers with superior redox properties have been developed such as polyaniline, polypyrrole, Poly(3,4-ethylenedioxythiophene) and polyindole to mitigate the propensity of corrosion in metals. However, the methods to fuse these inhibitors into coating systems are complex and restricted with technological and economic problems. One way to overcome this problem is to design self-healing nanocomposite coatings by combining the active inhibitors with traditional metallic coatings [24].

4. Electrodeposition process for graphene based MMCCs

Electrodeposition is a material coating galvanostatic technique widely used in research and industrial applications due its versatility and ability to form superior quality nanofilms and coatings with varying compositions on intricate shapes. Electrodeposition is a promising technique in preparation of corrosion resistant films and coatings made from carbonaceous materials such as nanotubes and graphene [25]. However, these coatings can be deposited advantageously only on conductive substrates and has numerous applications vowing to its superior properties. For graphene based metal coatings, the electrolytic suspension in this process is prepared by mixing graphene/graphene oxide nanosheets, metal compounds and isopropyl alcohol or water as a solvent [26]. These suspensions are directly deposited on substrate meshes and other conductive substrates as shown in Figure 4.

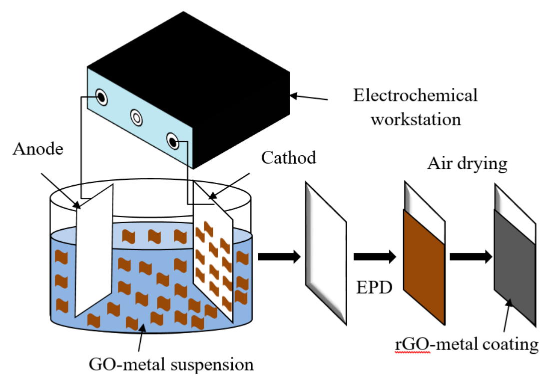

Figure 4. Schematic illustration showing electropherotic deposition of reduced Graphene Oxide - metal composite coating on metal substrate.

A variety of galvanostatic electrodeposition techniques can be employed to fabricate graphene composite coatings such as direct current (DC), pulsed direct current (PDC) and pulsed reverse current (PRC). In the conventional direct current electroplating, current density(I) is the only variable parameter whereas in pulse current electroplating ON-time (T_{ON}), OFF-time (T_{OFF}) and peak current (IP) are the three independent variable parameters [27]. In pulse current method, the duty cycle (γ) corresponds to the percentage of total ON-time of a cycle and is given by [28]:

$$\gamma = \frac{T_{ON}}{T_{ON}+T_{OFF}} = T_{ON} \times F \quad (1)$$

where F is frequency, defined as the reciprocal of the cycle time (T):

$$\gamma = \frac{1}{T_{ON}+T_{OFF}} = \frac{1}{T} \quad (1)$$

Electrodeposited layers formed by addition of graphene nanosheets in metal matrix are thin smooth, homogeneous and exhibits extraordinary properties of large surface area, high thermal stability and good electrical conductivity. The process also enabled the fabrication of graphene nanocomposites by combining graphene with other carbonaceous materials or conductive polymers forming novel nanocomposites coatings with enhanced properties [29]. Though several latest improvements have been achieved for pristine graphene using electrodeposition process to form films and coatings but still many problems are associated with defects in the coatings are not solved. Another challenge in employing this technique is graphene-based nanocomposite materials having mixture of materials with different electrochemical properties consequently affecting the quality of final coatings.

5. Graphene-metal matrix composite coatings

Graphene composite coatings are widely applied in various areas such as automobile industries, ship building industries, metallurgical industries etc. due to superior properties such as smooth texture, enhanced corrosion performance and better solderability. Graphene nanosheets provide extra protection to the base metal by forming stable impermeable barrier in the metal matrix that resists the diffusion of corrosive agents [30]. In case of graphene oxide (GO), reduced graphene oxide (rGO) is formed during electrodeposition process on the cathode from GO-metal suspension [9]. However, rGO layers in the matrix gives less resistance compared to pure graphene due incomplete removal of oxygen functional groups. Many authors in the literature have reported enhancement of corrosion properties due to the addition of graphene in pure metal matrix.

Nickel is widely used by many researchers as a matrix metal for preparing composite coatings on various metallic substrates because of its high corrosion and abrasion resistance as well as considerable micro-hardness. Additionally, insertion of graphene particles in nickel matrix can further boosts its structural, chemical and barrier properties. The most convenient method of depositing Ni-graphene (Ni-G) based composite coatings on metallic substrates is electro-codeposition due to its remarkable benefits such as low processing cost, high deposition rates, uniform thickness and microstructure controlling [31]. Several research articles have been published dealing with corrosion resistant Ni matrix composite coatings reinforced with graphene on different metal substrates. The phenomenal corrosion properties of graphene as reinforcing medium in nickel matrix were demonstrated by Szeptycka et al. [32]. Low concentration Watts-bath containing nickel ions, graphene particles and organic additives were employed to electro-deposit Ni-G composite coatings. Corrosion resistance testing of coated samples was conducted in 0.5 M NaCl solution by voltammetry method. The results obtained suggested that the addition of graphene particles in plating bath gives better corrosion resistance to the Ni-G composite coated samples than pure Ni plated samples. Moreover, the mixing of organic compounds resulted in compressive stresses in coating layers which also assisted in improvement of corrosion behavior. Likewise Jabbar et al. [33] described briefly the fabrication of Ni-G composite coatings by electrochemical co-deposition process at various deposition temperatures. Coating microstructure, composition and surface morphology were characterized by SEM, XRD and EDS. Electro-chemical properties of deposited coatings were studied by polarization and EIS tests. Experimental results showed that the composite coating layers created exhibited high corrosion resistance at 450°C temperature with coarse surface, refined grains and high microhardness. Furthermore, it was observed that the film thickness was increased with increasing deposition temperature.

Several attempts have been made to ameliorate the surface properties of Ni-G based hybrid coatings either by melding with metallic particles or manipulating deposition parameters such as duty cycle, bath composition, current density, frequency and temperature. Such an attempt was made by Seza et al [34] to enhance the corrosion and mechanical properties of Ni-Al_2O_3/Y_2O_3/G composite coatings by varying the duty cycle on low carbon steel specimens during electro-plating process. The amount of co-deposited particles on the surface increased with increase in duty cycle at constant frequency of 1000Hz. This resulted in improved microhardness of nanoparticles which in turn acted as dislocation barriers providing extra corrosion protection. Yu et al. [35] made an unsuccessful attempt to enhance corrosion performance of Ni-graphene composite coatings by inducing N_2H_4 in plating electrolytes. The idea was to immobilize the Ni ions in $NiSO_4$ solution to restrain agglomeration of graphene particles. Though the coatings composed with N_2H_4 had well dispersed graphene particles formed can intact layer but exhibited poor corrosion resistance compared to neat Ni coatings on account of the evolution of surface defects such as cracks and roughness. Ding et al [36] proficiently fabricated a novel self-cleaning super hydrophobic Ni-G composite coatings by electrodeposition method followed by treatment with myristic acid. Micrographs of deposited films revealed that microstructure consisted of hierarchical micro-nano structure of nickel and graphene particles. The fabricated super-hydrophobic coatings exhibited excellent anticorrosion performance, long term durability and self-cleaning ability after chemical alteration with myristic acid. Additionally, the coated surface exhibited magnificent super-hydrophobicity with water contact angle (CA) of 160.4 ± 1.5°. Whilst the use of graphene as a secondary phase material promote the corrosion resistant properties of the Ni-G composite coatings, it should be noted that the generation of micro/nano defects in Ni layer can lead to accelerated galvanic corrosion of the base metal

[37]. Hence, for the protection of ferrous-based substrates and alloys sacrificial zinc-based coatings are chosen over nickel-based coatings.

Kumar et al. [38] electrodeposited a highly corrosion resistant zinc-Graphene (Zn-G) hybrid coatings on mild steel substrate. Introduction of graphene particles into zinc matrix resulted in formation of hillock structure on the surface of coatings with minimum surface defects and shortened grain sizes which delayed the formation of micro pits as compared to pure Zn coated surface. The average thickness of deposited composite film was 62 nm. The corrosion performance of the synthesized coatings was studied by Tafel curves and EIS spectra. Zn-G coatings exhibited a considerable improvement in corrosion behaviour in terms of reduced corrosion current and corrosion rate due to alteration in the texture as confirmed by XRD. A new sort of zinc-graphene oxide (Zn-GO) hybrid coatings was also successfully processed by Li et al. [39] using pulsed electrodeposition employing choline chloride (ChCl)/ urea based deep eutectic solvent (DES). Usage of ChCl:2urea DES facilitated the electrodeposition process by dispersing GO sheets homogeneously which acted as preferential nucleation sites. Electrochemical behaviour of Zn-GO showed superior corrosion resistance and higher stability than pure Zn coatings. Apart from zinc, one of the commonly used pure metal coatings for anticorrosion application is Sn. Presently; Sn is widely applied in beverage can coatings and food packaging. Literature indicates that Sn and graphene can be utilized favorably for corrosion protection. Berlia et al. [40] determined the electrochemical properties of Sn-graphene composite coatings which were electrodeposited on mild steel substrates. Inclusion of graphene particles into pure Sn coatings suggested the change in surface morphology and enhancement of polarization resistance with simultaneous decrease in corrosion rate. Also, equivalent circuit for EIS data showed a reduction in double layer capacitance for Sn-G coatings. Similarly, a new two-step method was adopted by Yang et al. [41] to coat hybrid graphene-tin oxide (G-SnO_2) on aluminum alloy specimens. The composite coating films were synthesized by self-assembly method followed by hydrothermal heat treatment processing to reduce brittleness. The absolute corrosion protection efficiency (CPE) of deposited film was up to 99.7%, demonstrating that the G-SnO_2 coating significantly enhances corrosion performance in extreme corrosive environment.

Cobalt (Co) coatings are treated as good alternative to nickel and chromium coatings because of its low friction, superior wear resistance and less toxicity. Graphene Oxide-Cobalt Oxide (GO-CoO_2) composite coatings were fabricated by pulsed electrodeposition method from a plating bath containing cobalt sulphate particles and GO nanosheets. The addition of GO nanosheets resulted in enhancement of corrosion properties, tribological properties and grain refinement. Cobalt ions also favored in formation of smooth texture of surface and increase in hardness [42]. Hard trivalent chromium-Cr(III) based coatings are being developed because of its low toxicity, high mechanical and corrosion resistance. However, to mitigate the problem of pores and micro-cracking, the surface morphology of the coating is altered by changing deposition parameters or by incorporation of secondary phase nanoparticles. Rekha et al. [43] illustrated how incorporation of graphene nanoparticles in chromium based coatings enhances its corrosion resistant properties. Chromium-graphene (Cr-G) composite coatings were prepared by electrodeposition using Cr(III) and graphene plating bath. Furthermore, formic acid and chemically synthesized zinc oxide nanoparticles were added into electrolytic bath to scale down the cracks in coatings and provide extra corrosion protection to the base metal. Polarization and EIS studies revealed that the addition of graphene nanoparticles led to changes in microstructure of the coatings which subsequently enhanced the corrosion efficacy compared to pure Cr(III) based coatings.

Copper coatings can be considered as a good replacement to traditional zinc-based coatings due to its high electrical and thermal conductivities. Cu coatings are highly corrosion resistant and are specifically used in chloride-containing surroundings such as sea locations. However, pure copper coating properties can be increased further by infusing suitable nanoparticles in the matrix. Raghupathy et al. [45], investigated the effects of GO particles on microstructure, morphology and corrosion conduct of GO-Cu composite coatings. Highly corrosion resistant and compact coatings were produced by electrodeposition of electrolytic bath containing GO into Cu particles. The possible mechanism of improved corrosion behavior was related to recovery of passivation at defected sites induced by refined texture and strong impermeability of GO nanosheets to copper ions and diffusion oxygen molecules in the chloride bath. Additionally, GO-Cu hybrid coatings exhibited long term electrochemical stability when exposed to Cl^- ions indicating its potential for everlasting applications.

Biodegradable magnesium alloy implants are extensively applied in biomedical applications because of its low density, biocompatibility and non-toxicity. However, poor corrosion resistance of magnesium limits its applications in human body. This limitation can be settled either by alloying of Mg or by surface modifications with other materials. Silicon oxide coating has been tested successful on Mg AZ31 alloy in reducing corrosion rate. But the performance of sole SiO_2 coatings was not satisfactory as a result of defect generation in the microstructure [49]. In another study [50] graphene coatings has also been reported as an effective method to inhibit corrosion in magnesium alloys. Rad and coworkers [51] fabricated two distinct novel coatings. One coating consisted of SiO_2 nanoparticles dispersed in GO matrix and another bi-layer nano-SiO_2/GO coating on magnesium alloy prepared by two steps process for orthopedic applications. In Bi-layer coating, nano-SiO2 was deposited by Physical Vapor Deposition (PVD) method as inner layer on Mg alloy surface and GO was deposited by dip coating as outer layer on previous SiO_2 coating surface. Corrosion test results revealed that both SiO_2/GO composite and SiO_2-GO bi-layer coatings considerably increased charge transfer resistance and reduced corrosion current density of Mg alloy. However, antibacterial test results proved that nano-SiO_2 bilayer coatings possess better antimicrobial activity against the S.mutans than SiO_2/GO composite coatings. Furthermore, the surface morphology of nano-SiO_2 inner layer confirmed the presence of pores and micro-cracks with significant increase in the total thickness of the bi-layer coatings.

6. Graphene-metal alloy matrix composite coatings

Metal alloy coatings are frequently used as a replacement for pure metallic coatings because of its superior wear resistance, mechanical properties and thermal stability. Addition of alloy particles in pure metal matrix coatings suppresses oxidation while improves luster and prevents formation of brittle phases in the matrix [52]. Several metal alloy coatings have been synthesized with graphene oxide nanoparticles as secondary phase material. Nickel and zinc alloys are commonly used metals alloys in coatings as these alloys are well known for its high corrosion and wear resistance but suffer severe degradation in aggressive environment due to dissolution of other metallic phases [53]. Recently, Rekha et al. [46,47] reported the electrochemical performance of GO/SnZn and GO/SnNi hybrid coatings on mild steel. The coatings were electrodeposited using an electrolytic bath containing GO particles, gluconate as complexing agent and sodium lauryl sulphate as surfactant. Corrosion resistance of both GO/SnZn and GO/SnNi composite coatings were improved with the increase in GO percentage. Microstructural investigations revealed that the addition of GO assisted in homogenous dispersions of Zn-phase and Ni-phase in alloy matrix resulting in uniform corrosion on the coating surface. Moreover, morphological characterization suggested that the compactness and smoothness of the coatings increased with increased percentage of GO. However, crystalline size and texture remained impassive for GO/SnNi and decreased for GO/SnZn coatings with the inclusion of GO. Karimi et al. [54] fabricated two composite coatings by adding GO and rGO in ZnNi alloy matrix by electrodeposition method on mild steel specimens. SEM characterization of hybrid coating showed poor dispersion of rGO in ZnNi bath solution. Tafel plots and EIS analysis revealed significant improvement in corrosion properties of both the coatings compared to coatings of pure ZnNi alloy matrix. However, the combined effect of deposition parameters on corrosion resistance and mechanism involved were not investigated in this study. Figure 5 shows the comparison of TAFEL polarization curves for different graphene-metal matrix hybrid coatings with graphene-metal alloy matrix hybrid coatings deposited on mild steel samples. It is clear from the graph that corrosion potential of graphene-metal alloy coated samples shifted towards anodic region compared to graphene-metal coated substrates indicating superior corrosion resistance.

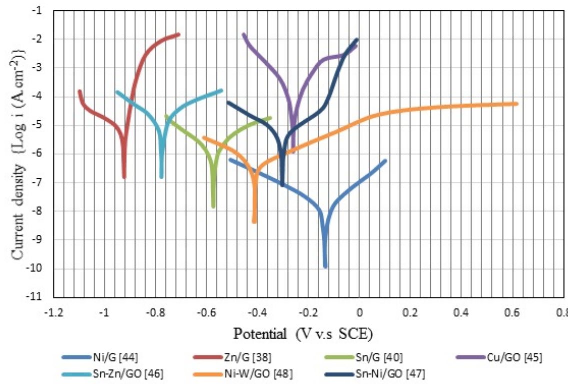

Figure 5. Tafel polarization curves of mild steel substrates coated with graphene metal matrix coatings and graphene metal alloy matrix coatings in 3.5% NaCl solution.

Lately, Rahmani et al. [55] developed graphene based ZnNi tertiary nanocomposite coatings via pulsed electrodeposition process and investigated the influence of deposition parameters on microstructure and corrosion properties. The electrolytic bath for electrodeposition was prepared by adding 80wt% alumina, 5wt% yttria and 15wt% graphene nanoparticles in ZnNi sulphate. The resultant coatings displayed superior anticorrosion behaviour together with better wear resistance, high oxidation resistance and strong adhesion of coatings to substrates. Moreover, with the increase in the duty cycle and deposition frequency, the number of nanoparticles absorbed from the coating layer to substrate surface was increased by 1/vol%. Similarly, Yi et al. [48] deposited Ni-W/GO alloy hybrid coatings on C45 steel substrate by electrodeposition technique. The presence of GO sheets in Ni-W alloy matrix changed its surface morphology to uniform and compact coatings. Electrochemical results confirmed an improvement in corrosion resistance of the deposited coatings. This improved performance was linked to the formation of a strong physical barrier on the coating surface thus decreasing the metal- solution interaction.

7. Future challenges

The first major issue in employing graphene in metallic coating for anticorrosion application is commercial unavailability of low priced and defect free graphene in large quantities. Therefore, investigators are constantly working to develop defect free graphene from economical sources other than graphite so that the cost of graphene can be reduced [56]. The next problem is related with the compatibility of graphene nanosheets with metallic ions. Metal matrix coatings are commonly formed by electrochemical disposition or chemical process in which metal cations are reduced on cathode. Moreover, the graphene surface normally possesses negative charge. Now when the graphene nanoparticles are mixed with these reduced metal cations, graphene becomes unstable and starts coagulating in electrolyte solution. Consequently, the agglomeration of graphene nanosheets in the deposited coatings provides free passage of corrosion species to reach coating-metal interface [57]. Moreover, the final coating surfaces may generate thermal induced cracks during drying and subsequent sintering. However, this problem can be dealt by precise tuning of electrodeposition process parameters such as current, time and frequency to avoid graphene agglomeration and form smooth uniform coating surface. Safe disposal of remaining electroplating solution after completion of deposition process is also necessary to prevent environmental pollution.

8. Concluding remarks

In the present review paper, we have shown some aspects of the current state of development of graphene metal composite coating with improved corrosion performance. Some of the latest developments are centered on the improvement of corrosion properties by dispersions of graphene nanoparticles, changing process parameters in deposition process and addition of stabilizers between the metal matrix and the nanofillers.

Based on the analysis of literature review the following conclusions can be drawn:

1. Graphene filled metal matrix coatings containing well-dispersed graphene nanosheets in the matrix material not only improves barrier properties but also improves surface durability and wear properties.
2. The composition, quality and anticorrosion properties of the final coated structure formed electrodeposition largely depends upon the factors such as electrical conductivity of substrate, deposition time, concentration of graphene nanoparticles in suspension, dielectric constant and viscosity of suspension.
3. Pulsed current electrodeposition method yields better results against corrosion compared with non-pulsed current electrodeposition.
4. Corrosion properties of the coatings were improved up to addition of 1 wt% of multilayered graphene in the metal matrix and decreased thereafter.
5. No significant reduction in corrosion current density for metal alloy matrix coating was observed compared to pure metal matrix coatings even after addition of graphene nanofiller.
6. Most of the research is directed towards testing graphene based metallic coatings for improved performance on carbon steel substrates only.

While sufficient literature on graphene based metal matrix composite coating is available, investigators still believe that there exits room to further enhance the corrosion properties by tailoring the nanostructure of the coatings and get better understanding of coating interface interactions and their relationship with friction and wear.

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