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Graphene Coating on Non-Ferrous Metals – A Review

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***Abstract*: Graphene has been speculated to be seen as the vital building block of several objects. Since its inception there has never been a setback of limitations to it's capabilities. Graphene owns distinguished properties such as resistance to chemicals, lubricity, highest mechanical strength, thermal stability and so on. This has lead to a series of researches and findings after its discovery. The crucial part of application is by making it an element of support to other compounds, thereby overcoming their defects. Here we have reviewed about the various methods of graphene coating on metals and their key portions of improvisation along with their after effects.**

***Keywords*: Enter key words or phrases in alphabetical order, separated by commas.**

1. Introduction

Graphene is a single layer of carbon atom placed with carbon-carbon bond length of 0.142 nanometers. They have been observed to have an honeycomb structure under the transmission electron microscope (TEM). It has a sp2 orbital hybridization making it stable and as the strongest element ever discovered. The thermal conductivity is as high as 5300 $W \cdot m^{-1} \cdot K^{-1}$ and a melting point close to 4125k. As a zero band semiconductor their electrical conductivity is high along with the lowest resistivity of $10^{-6} \Omega \cdot cm$. Having these unexceptional properties it has many other properties such as impermeability to every element except water, resistance to action of chemicals, anti-bacterial characteristics, large specific surface area and also being eco-friendly. An element of such high qualities can definitely put to use in a variety of places starting from reducing wear/scratch resistance, providing lubricity, preventing reactions from environment and even to prevent fouling and microorganism growth in various fields [1]-[7]. The production of graphene by various methods is still a fraction of the demands, hence there also thrives the research of minimal usage of graphene over other elements to enhance their performance. This lead to process of coating graphene on several materials. Here we mainly deal with metals like copper, aluminum, brass and so on. Though the main objective of a coating is to prevent the material from damage, several coatings used prior to graphene had harmful effects on the environment. Coatings such as hexavalent chromium (Cr (VI)), tributyltin (TBT), cadmium (Cd), Cobalt (Co) and copper (Cu) served to be harmful to the human environment and are currently banned. In the regard of coating graphene over metals to increase, we have a review of the property of lubricity, wear resistance and corrosion resistance properties along with the best suitable process parameters.

2. Methodology

A. Graphene coating techniques

Different coating techniques has been employed to develop graphene layer on metals. The techniques used based on our study are

- Chemical vapor deposition
- Physical vapor deposition
- Electrophoretic deposition
- Spray coating
- Bar coating
- Rapid thermal processing

B. Graphene coating on copper by chemical vapor deposition

CVD is a high temperature deposition process commonly used for the production of high quality grapheme coatings using a variety of precursor as carbon source. Different experiments were done to improve the tribological properties of copper by coating grapheme by chemical vapor deposition technique. The graphene coating showed better corrosion resistance than bare copper. graphene coating on Cu is less corrosion susceptible as compared to coatings that were mechanically transferred to an Al surface, probably due to the galvanic corrosion in the presence of small concentration of graphitic materials. The efficiency of the corrosion inhibition could be further enhanced by depositing graphene coating with higher purity in order to achieve an improved homogeneous coating structure and thereby avoid the possibility of galvanic corrosion [8]-[12]. Graphene coating was developed on copper and aluminium for the comparing the behavior of coating properties. The results showed that graphene coated copper had better corrosion resistance than graphene coated aluminium. Multiple graphene layers were developed on copper and test results showed better corrosion resistance than single layer graphene. Corrosion was retarded and arrested locally by transferring an extra graphene layer over the in situ grown graphene. When graphene was coated by chemical vapour deposition and electrophoretic deposition, the CVD coated graphene reduced corrosion rate more than EPD coated graphene. Graphene coating deposited by CVD method was found to be multilayered, graphitic and much adherent to Cu compared to partially reduced GO coating deposited by EPD. Both CVD-graphene and EPDGO coatings inhibited the corrosion processes of Cu, but the former reduced the corrosion rate of Cu by an order of magnitude than the latter. Graphene coating on copper (Cu) is shown to increase the resistance of the metal to electrochemical degradation by one and half orders of magnitude. The impervious and inert graphene layer protects the Cu film from electrochemical degradation. the graphene film acts as an impermeable ionic barrier to significantly improve the corrosion resistance of copper. The deposited graphene layers proved capable in enhancing corrosion protection of pure metals. It was found that the graphene affected the investigated metals differently; primarily slowing the anodic dissolution reactions for Ni and the cathodic reduction reactions for Cu [14]-[16]. These preliminary, yet reproducible results indicate that graphene can provide a barrier to metal dissolution from the metal substrate to the environment.

The effects of the AO irradiates on monolayer and multilayer graphene films coated Cu foil were investigated It was experimentally confirmed that the multilayer graphene have a better anti-oxidation than monolayer graphene after AO irradiation.An investigation on the early stages of corrosion of graphene-coated copper monoand polycrystalline substrates was done. Corrosion was not seen in the copper single crystal due to the graphene coating. For polycrystals, despite the graphene protection, the corrosion was enabled due to the intercalation of the electrolyte in the graphene/copper interface. Observed rate of corrosion in case of the graphene-protected polycrystal was noticeably high. It was demonstrated that a low temperature graphene coating technique by the surface wave plasma -CVD process as an efficient oxidation resistive barrier of Cu foil. a single layer of chemical vapor deposition (CVD) grown graphene transforms the Cu surface into a near ideal adhesionless contact surface when subject to nanoindentation, leading to a higher load bearing capacity as well as a near ideal Hertzian contact behavior. nanoindentation measurements show a significant stiffer response for Cu/graphene coated thin film than for bare Cu [17]-[19]. Cu covered with more graphene layers has less friction at the same normal force before the rupture of graphene layers.

C. *Graphene coating on copper by electrophoretic deposition*

The Electrophoretic deposition is an environment friendly process. Unlike CVD, the EPD process does not destroy the microscopic properties of a metal substrate due to its deposition at room temperature. Direct deposition of graphene on metal substrate is not possible due to its poor dispersion in aqueous and non-aqueous solutions. EPD is a colloidal forming process where electrostatically charged colloidal particles in a stable suspension are deposited (as loose homogeneous compact or film) onto an oppositely charged electrode by the application of DC electric field. To further densify the deposits to eliminate porosity, a post EPD treatment (heat treatment) is usually required [6]. The process can be applied, in general to any solid in particulate form with small particles (<30 µm) and to colloidal suspension.

The deposition by EPD also results in partial reduction of GO. EPD-GO was found to be better at a suspension concentration of 2 mg/ml and operating temperature of 5v and 10s with a coating thickness of 400 nm. This had an advantage of lower temperature deposition, control of coating thickness, ease of coating, better coverage and high corrosion resistance [2]. To evaluate the oxidation behavior of monolayer and multilayer graphene coated Cu foil, the different layers graphene coated and uncoated Cu foil were tested in the AO irradiation environment. Around 40% of the observed area (region B) is severely oxidized and other area (region A) still keep initial stage, indicating some regions of underneath metal Cu are protected by the monolayer graphene.

D. *Graphene coating on copper by spray coating*

A two-step approach is required to prepare graphene nanosheet coatings, which is composed of a spray process of GO suspension followed by a low voltage electrochemical reduction process of the obtained GO nanosheet coatings. The tribological performance of the as-prepared electrochemically reduced graphene oxide nanosheet coatings (ERGO) on copper disk are evaluated by sliding against steel ball in humid air. When the normal load is less than 2.5N, the COF of copper is reduced to 1/6 its value, and the specific wear rate is reduced more than two orders of magnitude. These improved tribological performances are attributed to the presence of ERGO nanosheets in the sliding interface. They provide easy shearing, prevent direct contact of the two metallic sliding surfaces and reduce ploughing effect of hard asperities, effectively suppressing adhesive wear and abrasive wear, lead to low wear rate of copper disk [13].

E. *Graphene coating on aluminum*

The corrosion resistance of Aluminum is significantly increased with the introduction of graphene on the metal surface. The oxygen functional groups such as carboxyl, hydroxyl, epoxy, and carbonyl present in the GO sheets increases the interlayer distance between the GO sheets. The reduction in interlayer spacing is due to the removal of oxygen functional groups leads to the formation of graphene. Rhee et al. have deposited a graphene coating on Al by transferring CVD-grown graphene onto an Al substrate [20], [21]. Polyvinyl alcohol (PVA) is employed as a binder between Al and rGO because PVA can modify the surface of Al; moreover, it is a cheap, nontoxic, and water-soluble synthetic polymer. The effect of PVA on the interface between rGO and Al was investigated by comparing rGO/Al-p and rGO/Al-d. This result demonstrates that rGO may act as an effective corrosion barrier for Al. Furthermore, the corrosion resistance of Al can also be improved since the adhesion between Al and rGO is enhanced by PVA. Micro-arc-oxidation (MAO) featured as high productivity, ecological friendliness, economic efficiency, and its coating with excellent bonding onto the substrate, has been applied widely to light alloys such as aluminum. The addition of graphene particles could slow down growth rate of the voltage due to its good conductivity and breakdown voltage was decreased. Also, increased the MAO coating thickness and hardness. The corrosion resistance of the coating samples was improved with the addition of granphene particles, and the best result was presented in the G2 coating with 0.15 g/L granphene particles. After the salt-spray corrosion test for 530 h, the G2 coating were almost keptintact, and the mass gain was low as 1.5 mg/cm2[22]. GPTMS is a kind of coupling agent with epoxy, which is widely used in sizing agents, sealants and thermoplastic resin. The aluminum alloy sample was immersed in a silane hydrolysis solution with graphene oxide, and a gel film was deposited on the surface. After curing, a GPTMS/graphene coating with more than 10 μm thickness was obtained. The GPTMS/rGO coating showed quite good corrosion resistance, excellent adhesion force, relatively high micro-hardness and good thermal shock resistance. The covalent metallic-siloxane bonds (AlOSi) improved the adhesion force greatly. The laminate structure of graphene could increase the hardness and decline the brittleness at high temperature. EIS results confirmed a significant improvement of barrier property. In 3.5% NaCl solution the anodic current density of the aluminum alloy sample with GPTMS/rGO coating was reduced by several orders of magnitude compared with those of bare aluminum alloy sample or the sample with graphene film [23], [24].

3. Conclusion

The above stated discussions have been a clear source of facts to prove Graphene as a suitable coating material on non-ferrous metals to improve various properties. A wide range of application areas benefit and serve to show the immense depth of this multipurpose material. Also, the physical and chemical properties of Graphene along with various research have promoted unprecedented growth progress in the pursuit of protective coatings, some specific applications may be with pure Graphene coatings or Graphene enhanced composite coatings, the desired properties of Graphene can provide enhanced protective characteristics with minimal shortcoming. This literature review suggests a completely successful and helpful methodologies of graphene coatings. This will turn out to be most enhanced form of protective coating, while remaining safe to the environment.

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