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Surface characterization and corrosion behavior of silanized magnesium coated with graphene for biomedical application

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HIGHLIGHTS

- Graphene oxide (GO) coatings of Mg was prepared by multi-step coating process.
- FTIR and Raman spectra showed the presence of silane and graphene on Mg surface.
- The corrosion resistance properties were studied by using polarization and EIS.
- GO layers on Mg provided superior corrosion protection compared to silanized samples.

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ABSTRACT

We here report the use of thin layers of graphene oxide (GO) as a protective coating that inhibits corrosion of underlying magnesium (Mg) metal. In order to coat the GO layer, Mg surfaces were hydroxylated with NaOH solution followed by silanization with dipping in 3-aminopropyltriethoxysilane (APTES) solution and subsequent coating with GO. Here, electrochemical methods were employed to study the corrosion behavior of Mg by coating graphene on it using multi-step coatings. Potentiodynamic polarization measurement determined that the graphene coating effectively inhibited the metal from corrosion. Electrochemical impedance spectroscopy (EIS) measurements suggested that graphene film on metal surface protect the metal from oxidation. This was as a result of impermeability of GO coatings to ions diffuse of oxidizing gas and corrosive liquid solution.

1. Introduction

Magnesium and its alloys are very attractive candidate materials for several applications such as transportation industry, electronic industry, aerospace field, mobile phone, and so on [1]. Such rapid increase of Mg use is mainly due to its lightweight with favorable strength-to-weight ratio. Recently, the study of biocompatible, biodegradable, osteoconductive implant materials is popular in the field of biomaterials and corrosion protection engineering [2,3]. Mg and its alloys are also beneficial for various implant applications because they could reduce the risks associated with permanent metallic implants, such as restenosis, thrombosis, physical irritation, potential inflammatory responses, and inability to adapt to the growth and changes of the human body [4]. Unfortunately, Mg and its alloys are highly susceptible to corrosion in physiological environments, which is one of the critical factors limiting their further application. Impurities and second phases act as active cathodic sites causing local galvanic acceleration of corrosion of the matrix [5]. Corrosion of base metal represents tremendous problem that has spurred global search for cost effective and environment friendly alternatives of current corrosion-inhibiting technologies.

The corrosion resistance of Mg and its alloys can be improved by making appropriate surface treatment. Accordingly, a broad range of surface modification techniques, including chemical

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conversion coatings, electrodeposition, polymer plating, anodic oxidation, physical vapor deposition and chemical vapor deposition, have been adopted to improve the corrosion performance of Mg and its alloys [6–10]. Among the different techniques, silane based anti-corrosive coatings for Mg and its alloys have been proven to be effective, inexpensive and environment friendly [11,12]. Silane coupling agents react with water (hydrolysis) to form a silanol group (SiOH) that permits attachment to hydrated metal surfaces (metal-OH) via formation of Si—O—metal bonds [13,14]. Silanization can increase film thickness, thereby providing better adhesion for primer than bare metal. In addition, silanization could provide free amine group on the surface of a substrate.

GO, a layered material with oxygen-containing groups, such as hydroxyl, epoxide, carboxyl and carbonyl functional groups, is hydrophilic which readily disperses in water to form stable suspension [15,16]. Further, amine functional groups have been proven to be a good candidate as anchor groups of molecular adsorbents on graphene. Several experiments have demonstrated that graphene can effectively protect the metal substrates from corrosion. Prasai et al. [17] have shown that a coating of graphene inhibits the rate of corrosion of copper and nickel, on which graphene is grown by chemical vapor deposition (CVD). An et al. [18] reported a reduced GO reinforced composite coating prepared by electrophoretic deposition (EPD) on the surface of stainless steel.

The present work reports an innovative method to produce graphene layer as anti-corrosive coating on pure Mg by means of combined methods of hydroxylation, silanization and dip coating, simultaneously. The free $-NH_2$ groups from silane covalently interact with functionalized graphene sheets via dip coating process. The silane and graphene layers were investigated by Fourier transform infrared (FTIR) and Raman spectroscopy. The anti-corrosion properties of the coating were assessed by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements.

2. Materials and methods

2.1. Materials

All reagents were used as received. Reagent 3-aminopropyltriethoxysilane (APTES) (≥98%) from Sigma–Aldrich, Korea was used for organosilane treatment. Pure magnesium was purchased from magnesium company, Korea. Sodium hydroxide (ACS reagent, ≥97.0%) pellets were purchased from Sigma Aldrich, Korea.

2.2. Silanization of Mg

Pure Mg with dimensions of $2 \times 1.5 \times 0.4\ cm^3$ was used as the substrate. Substrates were polished with gradually finer SiC papers upto grit 2000. Samples were ultrasonically cleaned using acetone, dried in air, and then immersed in 5 M NaOH solution for 2 h to produce uniform hydroxide layer on Mg surface. The NaOH-activated Mg surface was referred as Mg—OH.

APTES solution was prepared by mixing 5% (v/v) silane, 90% (v/v) ethanol and 5% (v/v) water. The solution was stirred at room temperature for 1 h to allow hydrolysis to proceed. Hydroxylated Mg was chemically functionalized by immersing in hydrolyzed APTES solution at room temperature for 1 h to create a linkage between the silane group and the Mg surface. The samples were then dried in hot air and cured at 120 °C for 1 h. Samples coated with silane were denoted as Mg-silane.

2.3. Preparation of graphene oxide (GO)

Graphene oxide (GO) was prepared from purified graphite using modified Hummers' method [19]. Then the prepared GO powder was dispersed in 100 ml deionized water by ultrasonication for 1 h. The 50 ml of graphene suspension (0.5 mg/ml) was used for further coating.

2.4. Surface modification of silanized Mg with graphene

Mg-silane samples immersed in the graphene suspension were incubated at room temperature for 4 h with gentle shaking. Graphene coated samples were rinsed with water and dried. The resulting samples were denoted as Mg-silane-GO.

2.5. Characterization of samples

The surface morphology of samples was observed by field emission scanning electron microscope (FESEM, JEOL JSM-4800). Identification of functional groups was done by Fourier Transform Infrared spectroscopy (FTIR, Spectrum GX, Perkin Elmer, USA). Crystalline phase was evaluated by X-ray diffraction (XRD) using a Siemens D-500 diffractometer. Silane and GO layers and metal oxide formation were investigated by Raman spectroscopy (Nanofinder® 30, Tokyo Instruments Inc.) at an excitation wavelength of 487.55 nm (with exposure time of 30 s and laser power at 4.012 mW).

2.6. Evaluation of corrosion resistance

Electrochemical corrosion test and electrochemical impedance spectroscopy (EIS) measurements were carried out at 298 K using commercial saline as corrosive medium. Experiments were performed using three-electrode chemical cell (PAR STAT 2273) with an electrolyte volume of 200 ml. Mg samples with an exposed area of 1.13 cm^2 were served as working electrode, while Ag/AgCl (satd KCl) and Pt gauze electrode were used as reference and counter electrodes, respectively. Range of −0.5 to +0.5 V (vs Ag/AgCl, KCl satd) at a scan rate of 0.2 mVs^{-1} was used. Before electrochemical tests, the working electrode was immersed in the test solution at open circuit potential for 30 min to attain a stable state. EIS amplitude of 10 mV was used as imposing signal. The measurement frequency range was from 10,000 to 0.01 Hz. All EIS measurements were conducted on open-circuit potential, E_{corr}.

3. Results and discussion

3.1. Surface preparation of pure Mg

The process of producing graphene coating on the pure Mg surface involved several steps. The scheme of surface functionalization on pure Mg is shown in Fig. 1. Mg was treated with NaOH to generate abundant surface hydroxyl groups (—OH) by hydroxylation process that facilitated silane coating. The subsequent silanization step was proceeded with the hydrolysis of ethoxy ($-C_2H_5$) groups in APTES to form silanols (Si—O—H), which acted as reactive groups at the end of the molecule. The APTES silanols then started to condense with surface silanols, thereby self-assembling into a monolayer of APTES by lateral siloxane (Si—O—Si) network. In the siloxane structure, the self-assembled siloxane networks were oriented in such a way that the positively charged amine groups ($-NH_2$) are aligned away from the underlying Mg substrate. The Coulombic interaction between $-NH_2$ moieties and —COOH groups on GO ensured uniform film formation after dip coating [20]. This is called amidation reaction. Nucleophilic substitution reaction took