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Nano Graphene Oxide Embedded Hydroxyapatite Coating on AZ91D Mg Alloy at Various Voltage for Bone Implant Application

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Abstract: Magnesium (Mg) and its alloys have been widely explored for biomedical applications as future biodegradable implant materials. Furthermore, a facile plasma electrolytic oxidation (PEO) technique was used to create biodegradable hydroxyapatite (HA) and nanographene oxide (nGO) coating on AZ91D Mg alloy. However, Mg and its alloy are vulnerable to the physiological environment, resulting in an untimely loss of mechanical power. Other than that, the coating factor for clinical application, such as HA, has barriers in hardness, strength, and wear resistance. This paper focuses on the physical properties and surface morphology of HA/nGO coating on AZ91D Mg alloy through PEO coating to solve the problem. The AZ91D Mg alloy was coated with HA/nGO using the PEO method at constant HA/nGO concentration and coating time, with variable voltages (115V, 230V, 345V, and 460V). Surface morphology analysis, elemental composition analysis and surface roughness, and were evaluated. Finally, the effect of a particular voltage level on the surface roughness at the constant coating time of 10 minutes indicates the surface roughness values of 1.6667 µm at 345V were obtained and demonstrate that HA/nGO samples are well disseminated at 345V coating compared to the other voltages.

Keywords: *Magnesium, HA, Graphene, PEO*

1. Introduction

Mg has now been intensively researched as prospective biodegradable implant material with adequate mechanical characteristics that are similar to human bone [1]. However, the quick corrosion of Mg in physiological settings has resulted in a premature loss of the implant's mechanical strength [2]. To reduce the early degradation rate of biodegradable Mg alloys, surface modification is necessary. Plasma Electrolytic Oxidation (PEO) coating is one of the most cost-effective and straightforward ways of producing a ceramic coating (calcium phosphate) on Mg alloy, which can improve corrosion resistance, wear resistance, and bonding strength. HA is the most often utilized calcium phosphate, and its biocompatibility has been well researched and proven [3]. Aside from biocompatibility and acceptable mechanical qualities, an ideal implant for bone tissue creation should be capable of responding to certain biological signals expressing and encouraging cell attachment, differentiation, proliferation, and, eventually, tissue regeneration [4]. Because of its excellent electrical conductivity, great mechanical strength, excellent biocompatibility, light density, and high stability, nGO can be employed as a potential reinforcing agent [4].

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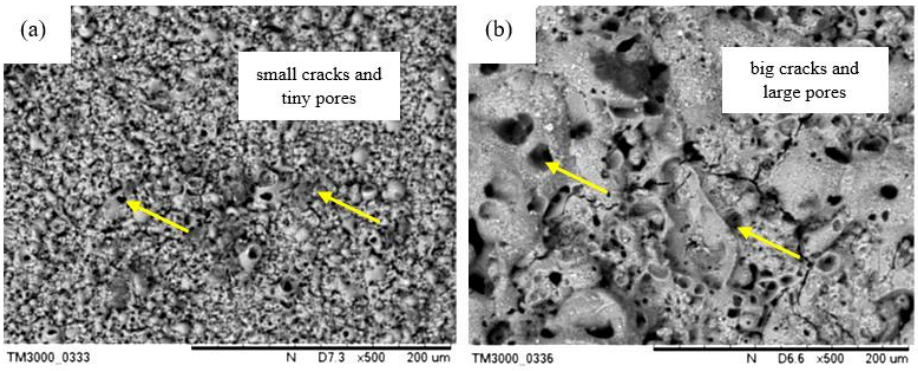

Fig. 1. SEM morphology of sample with (a) 345 V and (b) 460 V.

PEO processes create hard and sticky ceramic surfaces on magnesium substrates, and several factors, including pH, current density, voltage, and duration, have been shown to influence these surfaces [3]. The bioactive HA and nGO composite coating on the Mg alloy substrate was synthesized using a simple one-step PEO method in the presence of a standardized phosphate electrolyte. Electrochemical pressure tests have also been performed between the coatings and the ground of the Mg alloy to characterize the microstructure, phase composition, and powder coating using Xray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), scanning electron microscopy (SEM), and surface roughness [4].

In this study, the effect of voltage on the thickness and surface roughness of the HA/nGO coating layer on AZ91D has been explored and the evaluation of the HA/nGO coating layer microstructure on the AZ91D Mg alloy was also studied.

2. Methodology

The PEO method was used to create an oxide layer on 1 mm × 1 mm × 1 mm Mg alloy. The samples were manufactured, and a couple of operations were accomplished which is a mounting, polishing, and PEO coating process. The Mg was mounted with epoxy resins and polished with emery paper #1000. The DC power supply QRP-60H15D was used to apply various voltages (115, 230, 345, 460 V) to the samples during the PEO process at ambient temperature for 10 minutes. The sample served as an anode, while the stainless-steel plate served as a cathode, in the PEO operation. 54 g/L Na_3PO_4, 5 g/L $CaCo_3$, 2 g/L NaOH, 2 g/L HA, and 2g/L nGO are used to make the electrolyte. The coated samples were then dried in an oven for 24 hours before being processed further. The surface roughness of the sample after coating was tested using the CS-3100 machine. Each analysis was carried out three times, in three different horizontal directions. The arithmetic average roughness was calculated using Ra. Eq. (1) was used to get the entire surface roughness average.

$$Ra = \frac{Ra_{(1)} + Ra_{(2)} + Ra_{(3)}}{3} \quad (1)$$

SEM was utilized to examine the surface morphology and thickness of the coated sample, and EDS was employed to evaluate the elemental composition of the HA/nGO coated sample microstructure.

3. Result

Fig. 1 shows the SEM micrograph images of the samples treated in HA/nGO-based solution with different values of voltage. The coating layer was formed as soon as the application of voltage. The formation of coating covered with nGO and granules could be observed clearly as the voltage increased. As can be seen, the HA/nGO coating shown in **Fig. 1** (b) with the larger voltage shows the bigger formation of micropore on the surface, whereas the coating with lower voltage (a) shows the lesser amount and size of the micropore shape [5].

Furthermore, the surfaces of both samples had a porous shape due to the rapid solidification of molten oxides around micro-discharge channels in the electrolytes [6]. Fattah [7] also concurred, stating that the evolution and features of the discharging sparks during the PEO process, which are closely tied to the conductivity of the electrolyte, impact the creation of porous structure and modify the surface morphology and thickness of the coatings. It can be concluded that the larger the fractures created, the higher the voltage of the HA/nGO PEO coating.

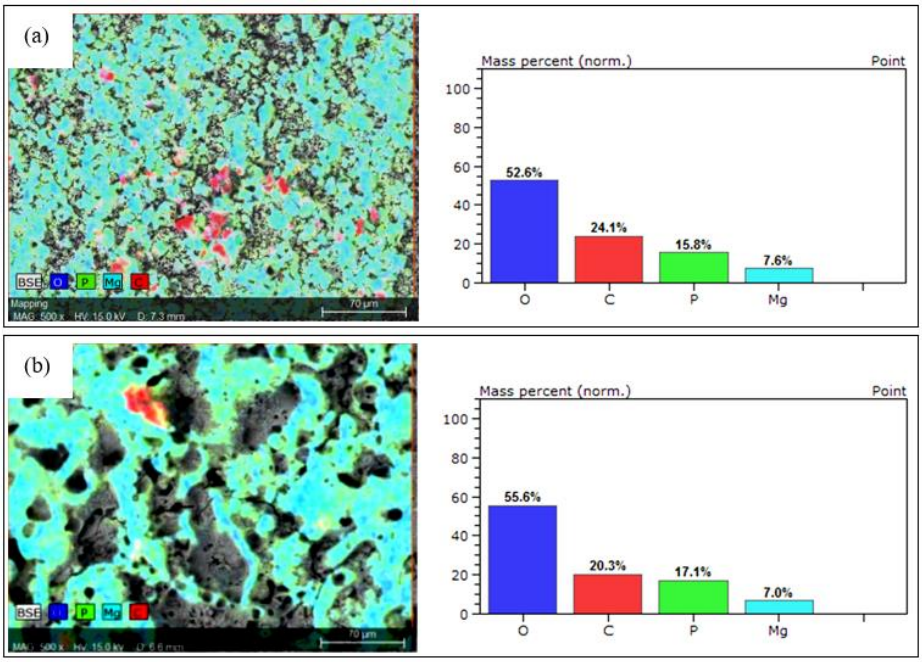

Fig. 2. Distribution of composition by colors and percentage of (a) 345V and (b) 460V coated samples.

The elemental composition was studied in **Fig. 2** by the composition and percentage of the coated samples that were treated for 345 and 460 V. The HA/nGO coatings are mostly composed of oxygen, Mg, phosphate, and carbon. The magnesium elements come from magnesium alloy substrates. The oxygen element comes from the electrolyte and nGO, the phosphate element comes from HA and sodium phosphate, and the carbon element comes from nGO. This suggests that the Mg alloy substrate and electrolyte had an important role in the creation of the HA/nGO coating [8]. Furthermore, PEO coatings have crystalline and amorphous phase component species derived from both metal and electrolyte [9].

These EDS mapping findings show that elements are spread uniformly over the coating, however, there are specific places with a significant concentration of nGO in both samples, showing that nGO accumulates in these regions at a certain voltage. Furthermore, the presence of nGO factor (b) improved the corrosion resistance of the sample, which was consistent with Han's statement on the influence of corrosion resistance on AZ91D [10]. Furthermore, the presence of phosphate in the sample assisted in the modification of the mechanical and corrosion characteristics of Mg alloys [11]. Part of it, the percent of components in those samples revealed oxygen was still the most abundant, followed by phosphate, carbon, and finally Mg. The existence of carbon elements at 24.1% for 345V (a) and 20.3% for 460V (b) indicated that the HA/nGO was successfully coated on the samples.

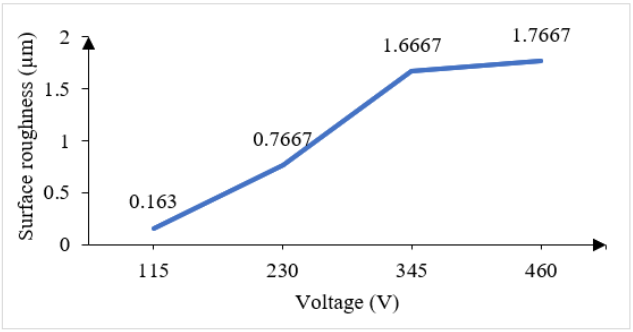

Fig. 3. Surface roughness value with different value of voltage.

The average arithmetic roughness, Ra, was used to determine the surface roughness. According to the results of the investigation, the value of surface roughness rose as the voltage of PEO coating increased, as shown in **Fig. 3**. The highest surface roughness measured was 1.7667µm at 460V, while the lowest was 0.163µm at 115V. Unfortunately, the sample coated with 115V and 230V was rejected because the roughness was not achieved at the commercial implantation, which is between 1-2µm [12]. In this situation, samples 345V and 460V produced the ideal range. The surfaces of metal implants that come into contact with the hard tissue should be in the ideal range to stimulate bone interaction with the materials and considerably accelerate mineralization.

Fig. 4 shows the SEM micrograph of cross-section morphologies of the samples. Previous research has identified three bands in the cross-section of the PEO-treated sample: the outside layer, the pore band, and the interior layer [13]. The outside layer and pore band were visible in PEO coating, as shown in **Fig. 4**, but the inner band was not visible due to its thinness and proximity to the magnesium alloy substrate. As the voltage increased from 345 to 460V, the thickness also increased from 42 to 74µm [14]. Therefore, the more the voltage applied, the more the thickness of the HA/nGO coating.

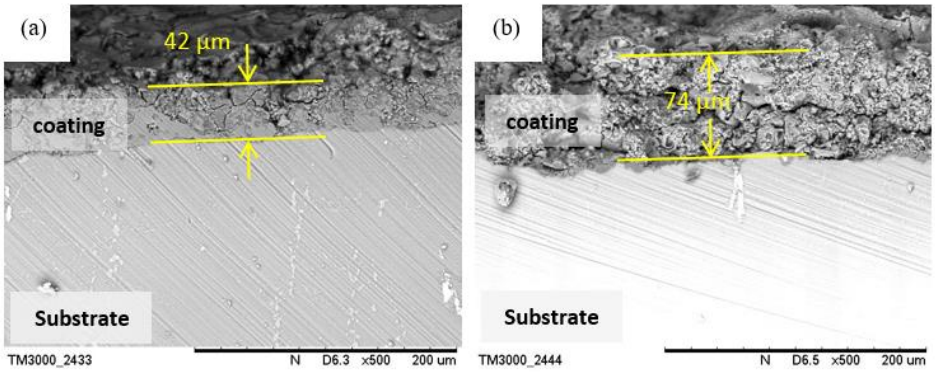

Fig. 4. SEM image of (a) 345V and (b) 460V on thickness.

This was demonstrated on the 345V sample, which has the smallest outer layer pore area and the narrowest pore band when compared to the 450V sample [15]. As a result, the integration of HA/nGO into the PEO coating increased the microstructure compactness of the coatings and reduced porosity, particularly in the 345V treatment, but not in the highest voltage 460V treatment.

4. Conclusion

The findings of investigations demonstrated the outcomes of a series of tests that displayed the physical characteristics of HA/nGO-coated magnesium alloy in terms of morphology and structural phases. A simple PEO approach was used to generate a HA/nGO coating on Mg substrates for biodegradable implants. The composite layer and HA/nGO components were successfully combined. The presence of HA/nGO in the electrolytes reduces the porosity of the coated samples. Operating with a variable parameter, such as voltages, influences surface morphology, as demonstrated by SEM and EDS data.

In addition, due to the considerable loss in bone-implant integrity, the evaluation of the surface texture of the coating concerning the roughness value was approved, yielding average surface roughness values of 1.6667µm at 345V. SEM and EDS data also show that the HA/nGO coated samples are better distributed at 345V. Overall, this study proved the potential safety of AZ91D magnesium alloy, which will improve the biomedical approach.

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