Titanium Dioxide/Graphene Oxide Composite Coatings on Ti6Al4V Substrate for Improved Corrosion

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Abstract

Titanium and its alloy are widely used in the field of orthopedic implants for its excellent mechanical properties, biocompatibility. However, Ti6Al4V as implant could be corroded by body fluids, releasing toxic elements and causing physiological harm and other issues. To solve this problem, titanium dioxide/graphene oxide composite coating was prepared on Ti6Al4V by sol-gel method. The samples were characterized by scanning electron microscopy, X-ray diffraction and Fourier transform infrared spectroscopy. The electrochemical test was used to evaluate the corrosion property of the coating. The results show that the microcracks on the surface of Ti6Al4V are effectively covered by GO/TiO_2 film and are relatively dense. The phase composition of the film layer is mainly TiO_2, GO phase. According to the results of electrochemical corrosion analysis, the corrosion resistance of GO/TiO_2 composite film in simulated body fluid (SBF) are significantly improved compared with Ti6Al4V matrix.

Keywords

Ti6Al4V; Surface Modification; Sol-gel; Graphene Oxide.

1. Introduction

With the aging problem increasing, the demand of orthopedic and dental implant extending rapidly. Titanium and its alloy[1,2] are considered as the most ideal implant, which have gained significate attention duo to its appropriate properties like advanced strength, high biocompatibility, corrosion resistance, non-toxicity, wear resistance and low Yong's modulus. However, titanium and its alloys lack the anti-bacterial and osseointegration ability[3]. For optimal orthopedic implant, it is necessary to have good osseointegration. Furthermore, it is also need to have sufficient antibacterial properties. Biofilm formation and poor bone bonding are the main reasons, which result in the implant failure [4]. Therefore, it is crucial to improve the ability of titanium and its alloy to defend bacterial infection and integrate with bone tissue by surface modification[5].

To solve the problems metioned above, many approach of surface modification have been developed like ion implantation, chemical vapor deposition (CVD), microarc oxidation, anodic oxidation and sol-gel[6]. It has been shown that surface modification is one of the most efficient ways to endow the surface of titanium and its alloy with antibacterial activity in period of initial bacterial adhesion[7]. Among these methods, sol-gel method.

Sol-gel method[8] is a soft chemical method used for the preparation of alloy surface coatings, which has many advantages such as environmental friendliness, low temperature synthesis, uniform coating and controllable composition structure. The coatings all have the advantages of high thermal stability, similar thermal expansion coefficient and low cost to titanium-based alloys, so the method is expected to be widely used in the preparation of corrosion protective coatings for titanium alloys[9].

Grapheneoxide (GO)[10] is a two-dimensional carbon material rich in hydroxyl, carboxyl and epoxy groups. In recent years, because of its strong mechanical strength and good biocompatibility and other excellent properties, its performance and application in the field of biomedical research has been one of the hot spots[11]. Some studies have shown that the presence of GO on titanium implants can promote biommineralization and bone regeneration[12].

In this paper, a different concentration of solution of oxygenated stonemolene (GO) mixed with titanium dioxide (TiO_2) was prepared, which was supported on Ti6Al4V by dipping and pulling method.

2. Materials and Methods

2.1 Preparation of Samples

Experimental reagents: ethyl orthosilicate, sodium chloride, anhydrous alcohol, acetone, tetrabutyl titanate, N,N-dimethylformamide, concentrated nitric acid, concentrated sulfuric acid, drugs from Beijing Chemical Plant.

Ti6Al4V plate was cut into square sample (10 mm × 10 mm × 5 mm). The sample was polished with 400 #, 800 #, 1000 #, 1500 # and 2000 # sandpapers, ultrasonically cleaned with acetone, ethanol and deionized water for 30 min subsequently.

Graphene oxide (GO) preparation: In this work, graphene was prepared by the traditional Hummers method[13]. Ordinary graphite powder is mixed with sodium nitrate in ice water bath and concentrated sulfuric acid. After stirring well, add potassium permanganate to the mixture. After a period of reaction, hydrogen peroxide is added to reduce the remaining potassium permanganate. After the bubbles disappear, wash with diluted hydrochloric acid. Finally, after filtration, washing, centrifugation, ultrasound, freeze-drying standby.

Anhydrous ethanol, butyl titanate and acetylacetone were mixed into A beaker and magnetically stirred at room temperature for 30 min to obtain solution A. Solution B was obtained by mixing anhydrous ethanol, 2 % nitric acid and distilled water evenly. Solution B was slowly added to solution A under stirring conditions, and then TiO_2 sol was obtained by magnetic stirring at room temperature for 2 h. After aging for 24 h, Then 0.02 g/L^{-1},0.04 g/L^{-1} and 0.08 g/L^{-1} GO was added, and the sol state used for final impregnation and lifting was obtained by stirring evenly. Finally, Ti6Al4V was impregnated and pulled in the prepared GO/ TiO_2 sol at a rate of 2 cm/min^{-1} (the process was repeated 6 times). The impregnated and pulled samples were dried for 2 h in an oven at 100° C and calcined for 1 h in a Muffle furnace at 500 °C. The calcined sample was rinsed with deionized water and anhydrous ethanol and then dried to obtain the sample GO/TiO_2. The sol dried at 90°C, and finally annealed at 450°C for 2 h and ground into powder for reserve.

2.2 Surface Characterization

The chemical components of the coating were analyzed by X-ray diffractometer (x-ray diffraction, XRD) with Cu ka as a radiation source with the scan range from 20 to 80°. Surface morphologies and elements distribution of the coating was investigated by scanning electron microscopy (scanning electron microscope, SEM). The surface wettability of the coating was evaluated by dropping 2 ml droplets on the surface of samples, then the water contact angle was analyzed by relevant software.

2.3 Electrochemical Testing

The corrosion experiment was carried out at 36.5 ± 0.5 °C with an electrochemical workstation (CHI600E, Shanghai Chenhua Instrument Co., Ltd.) in the SBF solution. A three-electrode system was employed in the electrochemical tests, with the saturated calomel electrode served as the reference electrode and the platinum sheet as the auxiliary electrode, the sample with working area of 1 cm2 as the working electrode. The anti-corrosion property was measured by polarization curve spectrum and electrochemical impedance spectrum.

3. Results and Discussion

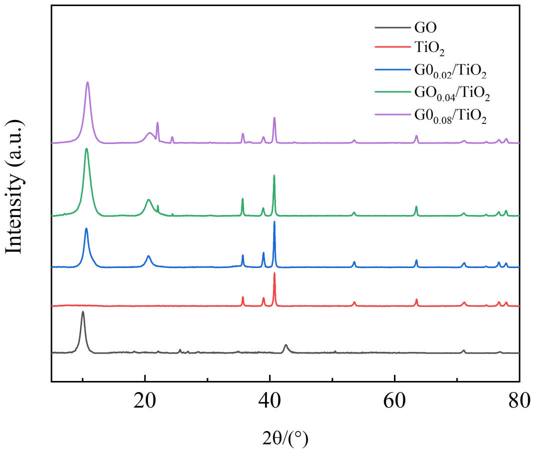

Fig.1 X-ray Diffraction patterns of different coatings

Fig. 1 shows the XRD test results of GO, TiO_2, and GO/TiO_2. GO diffraction peaks appear at 10° and 26.4° (Fig. 1), both corresponding to the (002) crystal face of graphite [14]. Compared with raw graphite, the reasons for the diffraction peak at 10° are: (1) Oxygen-containing functional groups are inserted around the graphite oxide sheet, and the hydrophilicity of these functional groups makes it easier for water molecules to enter the graphite oxide sheet. Graphene oxide is obtained by the graphite oxide sheet shedding, and the increased crystal face spacing is also caused by this factor; (2) Oxygen-containing groups, such as hydroxyl and carboxyl groups, diffuse around graphene oxide and increase the spacing between crystal faces in a certain sense at the spatial level [15]. As can be seen from Fig. 1, the curves of pure TiO_2 and GO/TiO_2 show obvious characteristic peaks of anatase type TiO_2, and 25.3° corresponding (101), 37.8° corresponding (004) and 48.0° corresponding (200) crystal faces can be obtained by comparison with PDF cards [16].

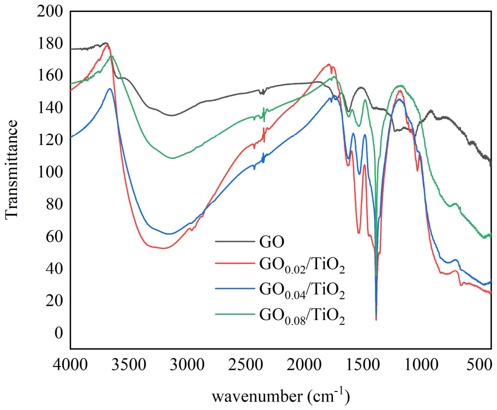

Fig. 2 The FT-IR spectra pattern of different samples

As shown in fig. 2, the hydroxyl group at 3 425 cm^{-1} responds[17]. The characteristic absorption peaks of GO appear at 1 126 and 1 046 cm^{-1}, corresponding to C-O-C and C-O respectively. In the low frequency region of 486 cm^{-1}, a wide absorption band appears, which belongs to the Ti-O-Ti bond, and moves slightly towards the higher wave number with the addition of GO, indicating that Ti-O-Ti and Ti-O-C bond in the composite material, that is, there is a hydroxy-hydroxy-Go functional group on the surface of TiO_2 The chemical interaction between the two cells. The above analysis indicated that the GO/TiO_2 composite material was successfully prepared. It can be seen from Figure 2 that the characteristic peak at 3 425 cm^{-1} belongs to the stretching vibration absorption peak of hydroxy -OH. The absorption peaks of C-H are found at 2 923 and 2 848 cm^{-1} [40]. The absorption peak in the double bond expansion vibration region is at 1 623 cm^{-1}, corresponding to the double bond C-C, and the absorption peak at 1 406 cm^{-1} corresponds to the C-OH bond.

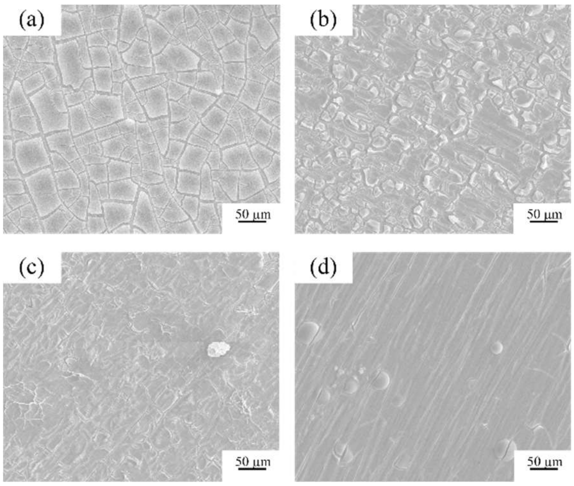

Fig.3 The SEM image of samples with different concentration of GO (a) 0 g/L (b) 0.02 g/L (c) 0.04 g/L (c) 0.08 g/L

Fig. 3 shows the SEM morphology of GO/TiO_2 composite coating. As can be seen from Fig. 3 (a), the titanium dioxide coating without graphene oxide admixture contains numerous cracks. This is due to the evaporation of organic solvents in the coating during the drying process, as well as the mismatch in thermal expansion coefficients between the surface titanium dioxide ceramic film and the substrate during heat treatment. With the rise of graphene oxide doping in the titanium dioxide sol, it is evident that the cracks in the coating show a decreasing trend. The introduction of GO can prevent TiO_2 from agglomerating in the coating matrix, so the composite of GO and TiO_2 can be used as coating fillers, which is conducive to the dispersion of fillers, increase the steric resistance between graphene sheets and reduce the crack of the TiO_2 coating. Therefore, the electrochemical test below will use the sample with a GO doping concentration of 0.08 g/L.

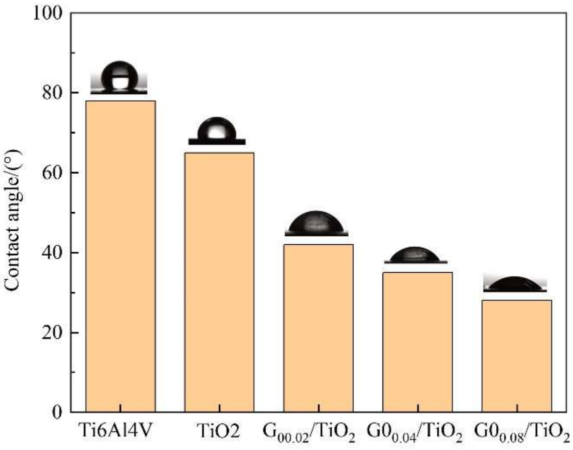

Fig. 4 Contact angle of different samples

Fig. 4 shows the contact angles of different sample surfaces. The results show that the contact angles of Ti6Al4V, TiO_2 coating, $GO_{0.02}/TiO_2$ coating, $GO_{0.04}/TiO2$ coating and $GO_{0.08}/TiO_2$ coating are 78°, 65.6°, 42.2°, 35° and 28°, respectively.

The sample surface wettability is mainly determined by the surface structure, chemical composition. The TiO_2 coating applied on Ti6Al4V surface using sol-gel resulted in an increase in the wettability of the samples due to the increase in the surface roughness of the samples caused by the large number of cracks generated during evaporation and heat treatment. The hydrophilicity of the coatings showed an upward trend with the rise of GO doping. This is because the appropriate amount of GO doping is conducive to the separation of photogenerated carriers and improve the hydrophilic properties of the film. On the other hand, the GO layer contains a large number of hydrophilic groups, which can be fully dissolved and stably stored in organic solvents, which has a certain effect on the enhancement of hydrophilicity.

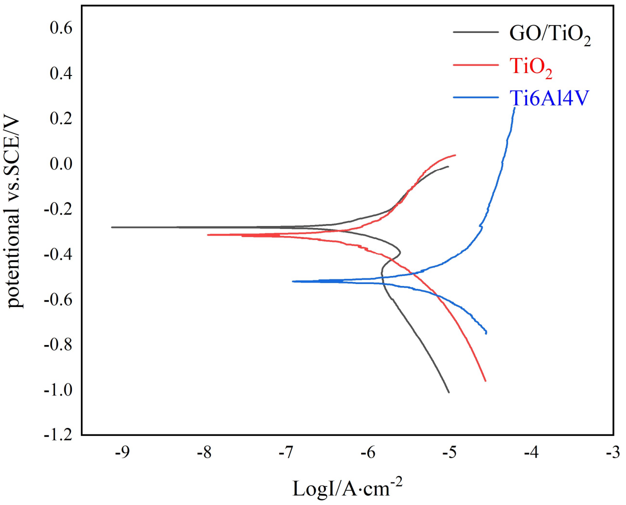

Fig. 5 The polarization curves of different samples

Table 1. Electrochemical parameters of different coating

Group	EOCP/V	Ecorr/V	Icorr/Acm^{-2}
Ti6Al4V	-0.565	-0.518	3.076×10^{-6}
TiO_2	-0.243	-0.213	9.161×10^{-7}
$GO_{0.08}/TiO_2$	-0.189	-0.228	9.072×10^{-7}

Corrosion resistance is one of the crucial factors for evaluating implants. Effective corrosion resistance can prevent the release of metal ions from the implant matrix during corrosion reaction in organism, thereby avoiding implant failure caused by inflammatory reactions. Fig. 9 shows the polarization curve and EIS spectra of Ti6Al4V, TiO_2 and GO/TiO_2 immersed in SBF solution. The electrochemical parameters in Table 1 were obtained by analyzing the polarization curves. Compared with substrate, the self-corrosion current (Icorr) of the TiO_2 coating and GO/TiO_2 coating is 9.161×10^{-7} A/cm^2 and 9.072×10^{-7} A/cm^2, respectively, both of which are lower than 3.076×10^{-6} A/cm^2 of Ti6Al4V. The self-corrosion voltage (Ecorr) of the GO/TiO_2 coating also shifts towards the positive axis. The analysis of electrochemical parameters revealed that the corrosion resistance of the GO/TiO_2 coating is superior. This is due to the doping of GO, which makes the cracks in the TiO_2 coating less visible, reducing the contact area between the corrosive medium and Ti6Al4V. On the other hand, GO in the composite coating also complicates the diffusion path of corrosive ions, affecting the charge transfer between the corrosive medium and substrate. Ultimately enhancing the corrosion resistance of the coating.

4. Conclusion

In this paper, a solution of GO mixed with TiO_2 was prepared, which was supported on Ti6Al4V by dipping and pulling method, and GO doped TiO_2 was obtained.

(1) The addition of GO significantly reduces the cracks in the coating, and due to the hydrophilicity of GO, the hydrophilicity of the coating has been improved.

(2) Through the data analysis of electrochemical impedance spectrum and potentiodynamic polarization curve tested in SBF solution, it can be confirmed that the corrosion resistance of different samples is ordered as: GO/TiO_2> TiO_2> Ti6Al4V. Therefore, the GO/TiO_2 composite film has excellent corrosion resistance.

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