Tribocorrosion behavior of Nb coating deposited by double-glow plasma alloying

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Abstract

Titanium and titanium alloys are considered as good implant materials, but their poor tribocorrosion resistance limits further development. In this study, niobium coating (DG-Nb) was deposited on TA3 pure titanium (Pure Ti) by double-glow plasma alloying aiming to improve the tribocorrosion resistance of Pure Ti. The properties of the samples were characterized by using X-ray diffraction (XRD), scanning electron microscope (SEM). Open circuit potential (OCP) and coefficient of friction (COF) tests were used to examine the tribocorrosion performance. The results showed that DG-Nb can largely enhance the tribocorrosion resistance of Pure Ti in Ringer’s physiological solution.

1. Introduction

The recent development of medicine and materials has promoted the utilization of implant materials, including stainless steel, cobalt-chromium alloy, organic polymer, magnesium alloy, magnesium matrix composite, nickel-titanium shape memory alloy and titanium alloy [1–4]. In the case of stainless steel, it exhibits good fatigue strength and ductility, but has poor healing rate after implantation, prone to pitting corrosion and gap corrosion, and poor wear resistance. Undesirably, nickel and chromium release carcinogenic elements, which can cause series health risks. Cobalt-chromium alloy can bear large loads and displays good corrosion resistance, however, both metals possess known cytotoxicity. Organic polymers, although show low elastic modulus, are close to human bone, and have no stress shielding, reports have shown that they have poor mechanical properties and small load. Magnesium alloys and magnesium matrix composites have good biocompatibility, but poor mechanical properties and corrosion resistance, as well as fast biodegradation rate. The yield and tensile strength of nitinol alloy are high, as well as strong corrosion resistance. Titanium and titanium alloys have good biocompatibility. Ti6Al4V, a commonly used biomaterial, has toxic elements Al and V, while pure titanium is non-toxic and has strong corrosion resistance. Although pure titanium is considered as a good medical material, it has poor tribocorrosion properties [5].

Tribocorrosion is the phenomenon of material loss caused by chemical or electrochemical reaction between the surface material and the surrounding medium during the relative sliding of the friction pair [6]. In the face of poor abrasion resistance of pure titanium, surface modification technology can improve abrasion resistance. Common preparation methods include CVD, PVD, electrochemical oxidation, chemical conversion membrane, etc. The hardness of the coating obtained by electrochemical oxidation is much higher than that of the substrate. For chemical conversion films, their thin and lack of wear resistance makes them unsuitable for this occasion. Double-glow plasma alloying is a technique to prepare alloy coatings. Figure 1 presents the basic principle of double-glow plasma surface alloying technology. Under vacuum condition, there are three electrodes, one anode (vacuum furnace shell), two cathodes, namely source cathode (target) and sample cathode (substrate). There is a set of DC power supply between anode and source pole, and between anode and sample pole. After switching on the power supply, the argon ion (Ar\(^+\)) produced by glow discharge bombards the source...
cathode under the action of electric field, which promotes the alloy elements to be sputtered and deposited on the surface of the sample cathode. On the other hand, under the action of electric field, Ar\(^+\) bombards the workpiece to produce diffusion channels such as lattice defects, and heats the workpiece to the temperature of alloying to form a surface modified layer with special properties\([7]\). The coating prepared by double-glow plasma alloying not only has a good binding force, but also produces a transition layer, which is suitable for biological coating preparation \([8]\).

Reports have displayed that silver exhibits bactericidal effects, but if silver content in the coating is too high, cell damage can occur. Gold’s desirable non-toxicity is hindered by its high cost, softness, and easy of in body accumulation, which cannot undergo degradation. Niobium (Nb), known as the life metal, has relatively stable chemical properties in body fluids and is non-toxic \([9]\). Besides, it has a low friction coefficient \([10]\) and is a more suitable coating component.

In this paper, niobium coating was permeated on the surface of TA3 pure titanium by double-glow plasma alloying technology. The surface structure and chemical composition were analysed by scanning electron microscope (SEM), X-ray diffractometer (XRD) and energy dispersive spectroscopy (EDS). The tribocorrosion behavior was examined under Ringer’s physiological solution.

### 2. Materials and methods

The matrix consists of TA3 pure titanium (Pure Ti), in which one part was a square specimen 15 mm \(\times\) 15 mm \(\times\) 4 mm in size; the other part was a round specimen 50 mm \(\times\) 4 mm in size (for tribocorrosion test). All samples were polished by sandpapers of 320, 400, 600, 1000 and 1400 grit until no obvious scratches were observed. Then pure titanium was polished to a mirror surface by silica suspension. After ultrasonic washing and drying in anhydrous ethanol, the samples were sealed in anhydrous ethanol to prevent oxidation. The composition of Pure Ti was: 0.21 wt% Fe, 0.01 wt% C, 0.01 wt% N, 0.001 wt% H, 0.21 wt% O and the remaining was Ti.

Nb target for double-glow metal was prepared by powder metallurgy 99.99% pure. The target material was disk-shaped with diameter of 100 mm and thickness of 5 mm. Impurities and adsorbed oxides were removed from the target material’s surface, which was repeatedly roughened and ground, and then placed in anhydrous ethanol for ultrasonic cleaning and cold air drying.

The niobium coating (DG-Nb) was permeated on the surface of Pure Ti by double-glow plasma alloying technology. The parameters of double-glow plasma alloying technology are summarized in table 1.

| Source Voltage (V) | Cathode Voltage (V) | Working Pressure (Pa) | Pole Spacing (mm) | Holding Time (h) |
|-------------------|---------------------|----------------------|-------------------|-----------------|
| 800               | 450                 | 36                   | 18                | 3               |


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![Figure 1. The basic principle of double-glow plasma surface alloying technology.](image)

Table 1. The parameters of double-glow plasma alloying technology.

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parameters of XRD were as belows: tube voltage: 40 KV; tube current: 150 mA; source: CuKα; scanning range (2θ): from 10° to 90°; scanning speed: 5° min⁻¹; step by step scanning.

The tribocorrosion behaviours of Pure Ti and DG-Nb were examined by Reciprocating tribocorrosion meter (Wuhan Coster Instrument Co., Ltd and Lanzhou Hua-hui Instrument Technology Co., Ltd). Friction ball choose a 6 mm diameter GCr15 steel ball; The normal loads were 2 N; The tests were carried out with soaking duration of 5 min, sliding duration of 10 min and soaking duration after sliding of 5 min The reciprocating length was 5 mm; the friction frequency was 1 Hz; the experimental temperature was 36.5 ± 1 °C. The tribocorrosion medium was Ringer’s physiological solution. The Ringer’s physiological solution was composed of NaCl (8.61 g l⁻¹), CaCl₂ (0.49 g l⁻¹) and KCl (0.30 g l⁻¹). The pH value was 6.2. The samples were kept as a working electrode with an exposed area of 19.635 cm². The saturated calomel electric reference electrode and graphite electric reference electrode were used in tribocorrosion equipment. During the tribocorrosion test, the curves of open circuit potential and friction coefficient before, during and after wear were recorded. The electrochemical impedance spectra of different samples before and after tribocorrosion were also measured. The frequency range of impedance spectrum measurement was 10⁻² Hz ~ 10⁵ Hz, and the amplitude of disturbance signal was 10 mV. The sample’s surface was washed immediately after tribocorrosion tests and dried for later use to avoid remaining physiological solution adsorbed on the sample surface and interference for subsequent analysis and tests. Moreover, 3D Measuring Laser Microscope was adopted to measure the size of the frayed surface.

3. Results and discussion

3.1. Microstructure of DG-Nb

As shown in figure 2, DG-Nb has uniform and compact surface without obvious defects because of the continuous bombardment of the sample surface by spherical plasma, possibly. The plasma constantly bombards the surface of the modified layer and the areas with poor binding to the matrix fall off, while those with good binding possess constant atomic deposition that grow into particles, thus showing uniform undulation and sag morphology. During Nb deposition, Ar⁺ bombardment with high energy density not only helps the surface
temperature of the workpiece to rise to about 800 \sim 1000 ^\circ C, but also forms a certain number of vacancy and dislocation channels, which is conducive to accelerating the internal diffusion of Nb elements. The surface of DG-Nb is mainly composed of 83.04 wt.% Nb and 16.96 wt.% Ti, confirming that Nb concentration on the matrix surface is relatively high.

The cross-section morphology of DG-Nb can be observed in figure 3 with a dense structure, no obvious holes and cracks, and no peeling between layers. The coating is composed of a surface sedimentary layer and sub-surface diffusion layer. According to the distribution of Nb content with depth, the thickness of the sedimentary layer is about 1 \mu m and diffusion layer is about 1.5 \mu m. Hence, the preparation method is beneficial to achieve the alloy bonding between the modified layers and gradient distribution of comprehensive properties.

Figure 4 presents that the surface phase of DG-Nb mainly consists of Nb and \alpha-Ti. Additionally, a small amount of TiO is detected, which may be due to the rapid local oxidation or passivation of pure titanium caused by Nb rich surface layer. Nb and \beta-Ti are both body centered cubic structures, and the diffraction peaks are in the same position. During Nb deposition, the surface temperature of the workpiece rises to about 800 \sim 1000 ^\circ C. Furthermore, the reason for \beta-Ti formation is that under the action of accelerating electric field, \beta-stable elements Nb and Ar + collide with \alpha-Ti matrix surface causes a sharp increase in the workpiece temperature reaching the phase transition point of Ti. During the process \alpha-Ti with dense hexagonal structure transforms into \beta-Ti with body centered cubic structure. Subsequently, the cooling process allows part of \beta-Ti to be kept at room temperature. Combined with Nb element changes along the depth of Nb modified layer, the existence of Nb form in Ti gradually changes. Nb is enriched in the surface layer. As Nb content decreases, Nb exists in \alpha-Ti and \beta-Ti in the form of solid dissolved atoms.

Figure 4. XRD pattern of DG-Nb.

Figure 5. Evolution of OCP and COF of Pure Ti and DG-Nb during tribocorrosion tests.
3.2. Tribocorrosion behaviour

The change of friction coefficient (COF) and open circuit potential under 2 N load of Pure Ti and DG-Nb samples over time were presented in figure 5. After loading, the friction coefficient of Pure Ti matrix increases continuously with sliding time, and enters the stable wear stage under the lubrication of simulated body fluid. The friction coefficient fluctuates between 0.45 and 0.6, and the calculated average friction coefficient is 0.516. DG-Nb sample wear process can be divided into three stages. Stage I: DG-Nb sample experiences continuous
running-in stage during 1st minute. Stage II: wear stage and average friction coefficient is about 0.043, the surface of the Nb deposition is not worn through. Stage III: after 7 min wear, the friction coefficient increases slowly with sliding time, the friction coefficient of the continuous decline in surface caused by the gradient distribution of the surface of Nb element and comprehensive mechanical properties of gradient distribution. At this stage, the Nb sediment begins to peel off, and a cycle of sticking-shearing-disengagement and re-adhesion occurs between the Nb sediment and rubbing ball in the simulated body fluid environment. Then, the abrasion

Figure 7. The SEM and EDS of DG-Nb and GCr15 steel ball after tribocorrosion. (a), (b) DG-Nb; (c), (d) GCr15; (e), (f) DG-Nb; (g), (h) GCr15.
process occurs in the internal diffusion layer. During the whole corrosion wear process, the friction coefficient of DG-Nb sample is much smaller than that of the matrix. As shown in figure 5, five minutes before wear, different samples demonstrate a stable open-circuit potential indicating the formation of a stable and uniform passivation film in the solution. When normal loading is applied, the potential of different samples changes and moves in a more negative direction. This is due to micro defects such as dislocation density and residual internal stress on the worn surface increase after the surface passivation film is locally damaged under normal loading [11], and the exposed fresh metal has higher corrosion activity in the simulated body fluid environment. Simultaneously, the agitation of the friction process can accelerate the cathode reduction process, hence, the titanium corrosion reaction in the simulated body fluid is easier to carry out.

The surface morphology and energy dispersive spectroscopy of Pure Ti and GCr15 steel ball are shown in figure 6. A certain number of grooves are observed along the sliding direction from figure 6(a), which is a typical feature of abrasive wear. It was revealed that there are a large number of cracks and block-shaped spall pits (or pitting pits) on the surface of the matrix in figure 6(b), and Ti-Mo titanium alloy also has a similar surface appearance in phosphate-buffered saline [12]. The formation of grinding chips in the tribocorrosion process is a low-cycle fatigue process, and fatigue phenomenon promoting the generation of cracks, in which the matrix at the crack has high corrosion activity [13, 14]. The simulated corrosion of body fluids accelerates the initiation and propagation of cracks, and eventually leading to the shedding and peeling of abrasive particles, thus forming pitting pits [15]. The specific reaction formula is as follows:

\[ m \text{Me}(\text{OH}^-, \text{H}^+) + x \text{Cl}^- \rightarrow \text{MeCl}_x + m \text{H}_2\text{O}, \]

where, Me(OH\(^-\), H\(^+\)) represents the metal oxide film in solution, and MeCl\(_x\) is soluble chlorine salt.

The heat generated in the wear process increases the surface temperature of the wear mark, which promotes oxidation. According to the literature [13], the existence of brittle titanium oxide film is the main reason for poor tribocorrosion of titanium alloy. The formation and repair process of oxide film continuously accelerates the wear of titanium matrix. The obtained results show that the steel ball and Pure Ti adhere to each other during the tribocorrosion process, and the grinding chips adhere to the surface of the steel ball due to the wear and spalling of titanium. During adhesive wear, when the strength of the adhesive point is greater than that of the softer metal, the softer metal can be easily cut. The wear debris can transfer to the harder metal, so the wear of the out-of-phase friction pair can gradually become the wear of the in-phase metal, which is conducive to the aggravation of wear degree. Therefore, the wear mechanism of Pure Ti matrix in Ringer’s physiological solution is mainly abrasive wear, adhesive wear, pitting wear and oxidation wear.

The surface morphology and energy dispersive spectroscopy of DG-Nb sample and GCr15 steel ball were exhibited in figure 7. The wear trace morphology of DG-Nb sample is different from that of Pure Ti. The depth

Figure 8. 3D topographies and wear trace contour of different samples. (a), (b) Pure Ti; (c), (d) DG-Nb.
and width of the wear trace are obviously shallower, with slight scratches in local areas, indicating that DG-Nb sample significantly improves the wear resistance of Pure Ti in Ringer’s physiological solution. Although local destruction of surface oxide film structure, surface roughness and chemical composition of different wear areas of inhomogeneity is advantageous to the formation of micro galvanic corrosion, they accelerate the corrosion rate. However, in combination with the electrochemical impedance spectroscopy of seepage DG-Nb sample before and after wear excellent corrosion protection effect still remains, hence, more corrosion resistant Nb elements at different regions of surface oxidation film with good self-healing effect significantly reduces corrosion sensitivity. It can be deduced that the wear mechanism of Nb sample is mainly slight abrade and oxidation wear.

The 3D wear trace contour and wear trace contour curve of Pure Ti and DG-Nb sample are observed in figure 8. The calculation results of their wear amount are listed in table 2. According to the grinding trace contour curve, the grinding trace of Pure Ti matrix shows irregular zigzag shape, while that of DG-Nb sample is relatively flat and smooth. The rough surface contour allows increased contact area of corrosion liquid, thus accelerating the corrosion rate of metal. In combination with figure 8 and table 2, it can be seen that DG-Nb sample wear volume is only 5.34% of the matrix, and the specific wear rate is only 4.92% of the matrix. Meanwhile, during the whole tribocorrosion process, the friction coefficient of DG-Nb sample is much smaller than that of the matrix. It presents that Nb deposited layer has good antifriction effect.

The changes observed for electrochemical impedance spectroscopy before and after tribocorrosion of Pure Ti and DG-Nb samples were observed in figure 9. The scatter points are measured data and lines are fitting data. The equivalent circuit obtained by fitting also satisfies $Rs(Q_pR_p)(Q_cR_c)$ (figure 9). The equivalent circuit calculation parameters of EIS before and after tribocorrosion of Pure Ti matrix and DG-Nb sample are listed in table 3. In the equivalent circuit, $Rs$ represents the resistance of the Ringer’s physiological solution, which is in series with the two QR time constants. The first QR time constant contains $Q_p$ and $R_p$ in parallel, while the second time constant contain $Q_c$ and $R_c$ in parallel. $Rs$ is mainly manifested in the high frequency region of the electrochemical impedance spectrum. $R_s$ is the equivalent resistance of the porous passive film on the outer

![Figure 9](image-url)
surface. $Q_p$ is a constant phase angle element with porous passive film on the outer surface, which is mainly manifested in the high frequency region of the impedance spectrum. $R_q$ is the equivalent charge transfer resistance of the dense passivation film, which is mainly in the low and middle frequency region of the impedance spectrum. $Q_f$ is a constant phase angle element with dense passivation film. The passivation area on the surface of different samples before tribocorrosion is intact and dense. There are two distinct areas on the surface after tribocorrosion, namely, the passivation area outside the abrasion mark and the activation-passivation area inside the abrasion mark track. The entire tribocorrosion duration is relatively short, and the influence of passivation in the external area of the wear mark on the total impedance of the measurement system can be ignored, which mainly comes from the activation-passivation area inside the wear mark track [16]. In general, the larger the radius of capacitive reactance arc, the greater the charge transfer resistance of metal or alloy, so the corrosion resistance is better. Apparently, it can be observed that the capacitive reactance radius for different samples is: DG-Nb (after 2 N) > DG-Nb (before 2 N) > Pure Ti (before 2 N) > Pure Ti (after 2 N).

From table 3, it is known that, after tribocorrosion, the values of DG-Nb’s $R_p$ and $R_c$ increase, and the values of Pure Ti’s $R_p$ and $R_c$ decrease. According to the friction coefficient curve (figure 5), the SEM and EDS of DG-Nb after tribocorrosion (figures 7) and 3D topographies and wear trace contour of DG-Nb (figure 8), the wear of DG-Nb sample in the stable wear stage occurs in the diffusion layer. Nb content in the diffusion layer of Nb deposited layer is high, the surface film has a strong passivation ability in the tribocorrosion process. Thus, the reaction resistance of the inner and outer oxide layer displays a rising trend, especially the dense oxide film inside. It presents that the corrosion resistance of DG-Nb sample did not decreased after tribocorrosion, and the corrosion resistance DG-Nb is better than that of Pure Ti.

DG-Nb exactly enhances the tribocorrosion resistance of Pure Ti in Ringer’s physiological solution. The reasons for improved tribocorrosion resistance are as belows: (1) Good passivation ability of surface film; (2) Good antifriction effect of Nb deposited layer.

4. Conclusions

It was found that niobium coating was permeated on the surface of TA3 pure titanium by double-glow plasma alloying technology improves the tribocorrosion resistance of TA3 pure titanium. The specific conclusions are as follows:

Nb modified layer mainly consists of Nb, α-Ti, β-Ti and a small amount of TiO.

Before tribocorrosion, DG-Nb’s open circuit potential is 0.089 V higher than Pure Ti substrate. During tribocorrosion, the average friction coefficient of DG-Nb is lower than that of Pure Ti matrix. The wear volume of DG-Nb is only 5.34% of that of Pure Ti matrix, and DG-Nb wear rate is merely 4.92% of that of Pure Ti matrix. DG-Nb’s open circuit potential is always taller than Pure Ti substrate. After tribocorrosion, DG-Nb’s open circuit potential is 0.084 V more positive than Pure Ti. The corrosion resistance of DG-Nb before and after tribocorrosion are both better than that of Pure Ti. Therefore, DG-Nb has especially better tribocorrosion resistance than Pure Ti matrix.

Acknowledgments

This project was supported by Natural Science Foundation for Excellent Young Scientists of Jiangsu Province, China (Grant No. BK20180068), China Postdoctoral Science Foundation funded project (Grant No. 2018M630555), Opening Project of Key Laboratory of Materials Preparation and Protection for Harsh Environment, Ministry of Industry and Information Technology (Grant No. XCA20013-1).

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