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Multilayered TiAlN films on Ti6Al4V alloy for biomedical applications by closed field unbalanced magnetron sputter ion plating process

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ABSTRACT

Ti6Al4V alloy has been widely used as a suitable material for surgical implants such as artificial hip joints. In this study, a series of multilayered gradient TiAlN coatings were deposited on Ti6Al4V substrate using closed field unbalanced magnetron sputter ion plating (CFUBMSIP) process. Taguchi design of experiment approach was used to reveal the influence of depositing parameters to the film composition and performance of TiAlN coatings. The phase structure and chemical composition of the TiAlN films were characterized by X-ray diffractometry (XRD) and X-ray photoelectron spectroscopy (XPS). Mechanical properties, including hardness, Young's modulus, friction coefficient, wear rate and adhesion strength were systematically evaluated. Potentiodynamic tests were conducted to evaluate the corrosion resistance of the coated samples in Ringer's solution at 37 °C to simulate human body environment. Comprehensive performance of TiAlN films was evaluated by assigning different weight according to the application environment. S8, deposited by Ti target current of 8 A, Al target current of 6 A, bias voltage of −60 V and nitrogen content with OEM (optical emission monitor) value of 45%, was found to achieve best performance in orthogonal experiments. Depositing parameters of S8 might be practically applied for commercialization of surgical implants.

1. Introduction

Medical implants, such as orthopedic implants, odontological implants and trauma products etc., have been widely used to ameliorate the lives of patients by reducing the pain and restoring function to the otherwise functionally compromised structure [1,2]. Titanium alloys, stainless steel (SS), and cobalt-based alloys are commonly used for implant applications. Particularly, Titanium alloys are the most widely used implant materials due to their high specific strength, good corrosion resistance and biocompatibility [3]. However, current surgical implants such as artificial hip and knee joints undergo degradation after 10–15 years of use [4]. This degradation is mainly attributed to wear and corrosion failures. The release of metal ions, even in small amounts, may cause local irritation of the tissues surrounding the implant. It has been demonstrated that the corresponding cell and tissue responses are affected not only by the chemical properties of the implant surface, but also by its physical and mechanical properties [5].

Surface treatment of medical implants is a feasible and promising way to overcome the problem of ion release and to improve the biological, chemical, and mechanical properties [6]. Muraleedharan and Meletis [7] conducted ion nitriding of pure titanium and Ti6Al4V at low pressure by intensifying the glow discharge. A surface layer of TiN followed by a Ti_2N layer and an interstitial nitrogen diffusion zone was developed on Ti6Al4V resulting in a higher wear, corrosion and wear-corrosion resistance. Zreiqat et al. [8] modified the surface of Ti6Al4V with zinc, magnesium (Mg) and alkoxide-derived hydroxy carbonate apatite (CHAP) by ion beam modification. Experimental results indicated that surface modification with CHAP or Mg contributed to successful osteoblastic function and differentiation at the skeletal tissue–device interface. Pohrelyuk et al. [9,10] developed nitride coatings on Ti6Al4V alloy by thermodiffusion treatment and evaluated the corrosion resistance in simulated body fluids at 36 °C and 40 °C. Results show that nitride coatings improve anticorrosion properties of alloy and corrosion resistance of alloy increases with the content increase of TiN phase in nitride coating. Kwok et al. [11] deposited hydroxyapatite (HA) coatings on Ti6Al4V by cathodic electrophoretic deposition (EPD) and carbon nanotubes (CNTs) were also used to reinforce the HA coating for hardness enhancement. Gordin et al. [12] treated a superelastic Ni-free Ti-based biomedical alloy in surface by the implantation of nitrogen ions. A titanium-based nitride was formed on the substrate surface and the friction coefficient was reduced and corrosion resistance was improved significantly. Liu et al. [13] implanted silver ions on Ti6Al4V by plasma immersion ion implantation (PIII) technique. Experimental results revealed that the nanohardness and elastic modulus of coated samples were increased and the friction coefficient was reduced from 0.78 to 0.2. Panjwani et al. [14] coated ultra-high molecular weight

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polyethylene (UHMWPE) thin film onto Ti6Al4V alloy specimens using dip coating method. This coating shows low coefficient of friction and high wear durability for the tested conditions. Besides, PVD [15], CVD [16], plasma spraying [17], and laser surface treatment [18,19] have also been widely used in surface treatment of medical implants.

Titanium–aluminum-nitride (TiAlN) film, owing to the superiorities such as high hardness, excellent oxidation, corrosion and wear resistance, has been attracting more and more attentions for biomedical applications in recent years [20]. Yang et al. [21] prepared TiAlN coatings with different Al concentrations on Ti6Al4V substrate by reactive magnetron sputtering. Remarkable improvement in erosion performance was observed and attributed to a good combination of high hardness and toughness. Kim et al. [22] compared and analyzed the effects of TiN and TiAlN coating layers on the wear performance of Ti6Al4V by a cathodic vacuum arc ion plating technique. It was demonstrated that TiAlN coating was superior to TiN from the viewpoint of wear resistance. Subramanian et al. [23] deposited TiN, TiON, and TiAlN onto CP–Ti substrates by direct current (DC) reactive magnetron sputtering method and assessed the surface electrochemical corrosion in simulated body fluid and cytotoxicity. The corrosion testing revealed that TiAlN coating had highest corrosion resistance. Microstructural and mechanical properties were also systematically investigated by the same group [24]. Yildiz et al. [25] investigated wear and corrosion behavior of plasma nitriding, TiAlN film by closed field unbalanced magnetron sputter ion plating process (CFUBMSIP) and Al_2O_3 coating on Ti6Al4V using plasma spray method, respectively. Al_2O_3 exhibited best wear performance while TiAlN film achieved highest corrosion resistance. Besides, two different parameters of DC bias and pulse were compared and pulsed films were more effective than biased films in terms of fatigue resistance [26]. However, the influence of process parameters such as the sputtering currents, reactant gas flow, and bias voltage on microstructure, mechanical properties and corrosion performance is still worthy of further investigation.

In the present study, a series of gradient TiAlN multilayer coatings have been deposited on Ti6Al4V substrate via CFUBMSIP process and the schematic of film composition is presented in Fig. 1. It consists of Ti layer, TiN layer as well as TiAlN layer and the height in Fig. 1 is not to scale to the thickness of each layer. The crystallographic structures and chemical composition of deposited films were investigated by X-ray diffractometry (XRD) and X-ray photoelectron spectroscopy (XPS), respectively. Mechanical properties and corrosion performance related to the durability of surgical implants were evaluated by a series of experiments. Finally, optimum depositing parameters were decided based on the comprehensive performance of TiAlN films.

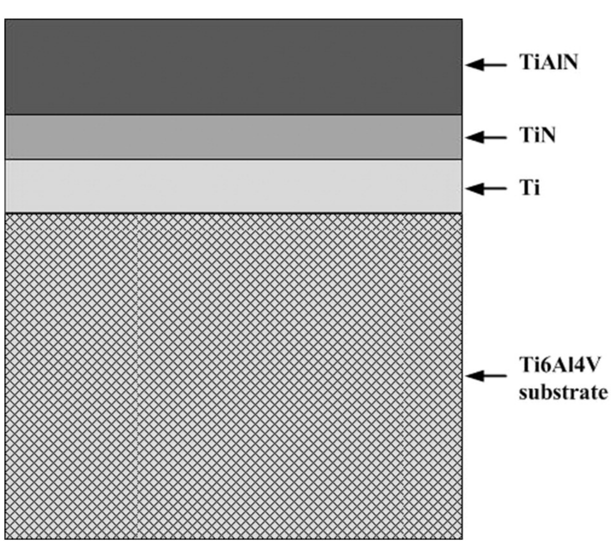

Fig. 1. The schematic representation of multilayered TiAlN film composition on Ti6Al4V substrate (not to scale).

Table 1
Factors and levels in Taguchi design of experiments for TiAlN films.

Level	Deposition parameters		
	Al target current (A)	Bias voltage (−V)	OEM (%)
1	2	50	45
2	4	60	55
3	6	70	65

2. Experimental

2.1. Taguchi design of experiments

Taguchi design of experiments method is widely useful in evaluating the performance of a process with quantitative responses. This method is an active statistical method despite traditional one-factor-at-a-time approach. The inputs are changed and correspondingly the output observed which can lead to process improvement instead of passive approach, which is totally time-consuming and excessive in cost [27]. Therefore, Taguchi method was applied to study the relationship between the deposition parameters and the characteristics of the TiAlN coatings. The film composition was mainly determined by the target sputtering current, reactant gas flow and bias voltage [28]. The nitrogen flow was controlled by a closed-loop optical emission monitor (OEM) of which the principle was to detect the optical emission of the metal plasma excited by magnetron sources during the reactive sputtering process. In this study, the plasma intensity of Ti_2^+ ions emitted during the reactive sputtering process was used to determine the OEM value [29]. Therefore, the sputtering current of Ti target was set as a constant of 8 A for stable and precise control of OEM. Sputtering current of Al target (A), bias voltage (B), and OEM value (C) were selected as factors for Taguchi design of experiments and each parameter had three levels. For full factorial experiments with 3 factors and 3 levels, 27 trails should be conducted to investigate the influence of each factor and level. However, according to Taguchi method, an orthogonal array of $L_9(3^3)$ can be selected and only 9 trails should be carried out. Table 1 lists the schedule of the orthogonal experiment of $L_9(3^3)$. It should be pointed out that a higher OEM setting corresponds to a lower flow rate of nitrogen taking part in the reaction. Thickness (T), friction coefficient (f), wear rate (r), critical load (L_c), hardness (H), Young's modulus (E), corrosion potential (E_{corr}) and corrosion current (I_{corr}) are taken as the index points to evaluate the coatings performance under different factors and levels.

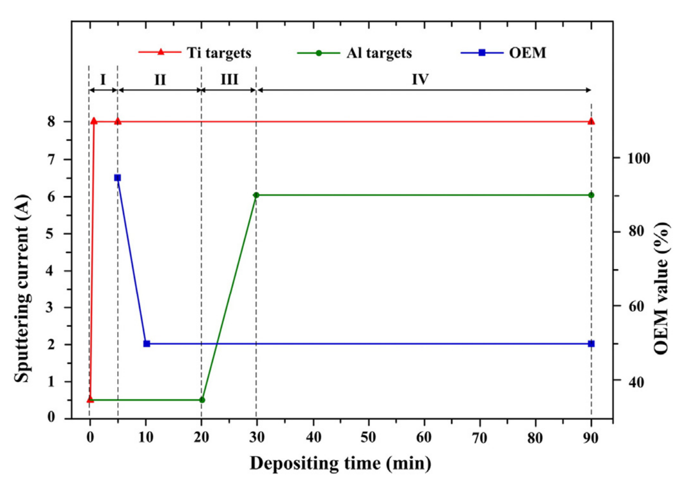

Fig. 2. Schematic diagram of depositing process for multilayered TiAlN film on Ti6Al4V alloy by CFUBMSIP (using S8 as an example).