ARTICLE IN PRESS

Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Effect of deposition parameters on properties of TiO_2 films deposited by reactive magnetron sputtering

Bo Wang[a,b], Shicheng Wei[b,*], Lei Guo[b], Yujiang Wang[b], Yi Liang[b], Binshi Xu[b], Fusheng Pan[a], Aitao Tang[a], Xianhua Chen[a]

[a] College of Materials Science and Engineering, Chongqing University, Chongqing 400045, PR China
[b] National Key Laboratory for Remanufacturing, Academy of Armored Forces Engineering, Beijing 100072, PR China

ARTICLE INFO

Keywords:
TiO_2 films
Reactive magnetron sputtering
Structure
Corrosion
Antifouling

ABSTRACT

TiO_2 films were grown onto unheated 5083 aluminum alloy substrates by reactive magnetron sputtering from a pure Ti target in Ar-O_2 gas mixture in different power, bias voltage, Ar/O_2 ratio and deposition time at room temperature. The effects of different deposition parameters on the structure and properties of TiO_2 films were investigated systematically by field emission scanning electron microscope (FESEM), atomic force microscope (AFM), X-ray diffractometer (XRD), X-ray photoelectron spectroscopy (XPS), nanoindentation tests, electrochemical tests and antibacterial tests. The results show that power and bias voltage are two main factors to affect the structure and properties of TiO_2 films during the sputtering process. XRD results show that anatase phase is the main phase of the film, and the enhanced content of anatase phase with the increase of sputtering power and bias voltage. Nanoindentation tests exhibit that higher H/E (Hardness/Modulus) ratio can be achieved by depositing TiO_2 film. And the corrosion resistance and antifouling property are all improved after depositing TiO_2 film. 2# sample shows the optimal corrosion resistance, E_{corr} and I_{corr} are −0.27388 V and 3.7232 μA/cm^2, respectively. 1# sample exhibits excellent antibacterial property, the d ensity of bacteria is only 217 cell / mm^2, which is 484% higher than that of uncoated matrix.

1. Introduction

Recently, TiO_2 coatings have been attracting much more attention due to their high chemical stability, low cost, non-toxic, excellent optical and electrical properties, outstanding hydrophilcity and hydrophobicity properties [1–3]. As a consequence, TiO_2 coatings have been widely used in self-cleaning, antifogging, antibacterial, biomedical materials, photocatalysis and other fields [4–6]. Nowadays, TiO_2 coatings can be prepared by many different ways, such as Sol-Gel [7,8], Micro-arc oxidation (MAO) [9,10], Chemical vapor deposition (CVD) [11,12], Pulsed laser deposition (PLD) [13,14], hydrothermal method [15,16] and magnetron sputtering [17,18]. Among these methods, magnetron sputtering presents obvious advantages in reproducibility, homogenous thickness, high mechanical durability, good adhesion to the substrate, easy-controlling film structure and composition, industrial processes applicable to mass-production-scale deposition [19,20]. However, the structure and properties of TiO_2 films can be affected by many different parameters during the sputtering process, such as sputtering power, bias voltage, reactive gases pressure, deposition time, deposition temperature, target-substrate distance and so on [21,22]. Hence, great efforts have been made to investigate the effects of different deposition parameter on structure and properties of TiO_2 films, and explore the optimum deposition parameters to improve the properties of TiO_2 films [23–28]. However, most studies are focus on the effects of only one magnetron sputtering deposition parameter at high temperature on the structure and properties of TiO_2 films, for example, photocatalysis properties. Few of studies paid attention to the effect of multi-factors coupling on the structure, corrosion behavior and antibacterial properties of TiO_2 films at room temperature. By Taguchi method, multi-factors can be designed to estimate the effect of multi-factors coupling on the structure and properties of TiO_2 films, optimize the deposition parameters. In fact, with the sustainable development of energy and economy, the research on TiO_2 films deposited by magnetron sputtering at room temperature has been drawn much more attention because of it can not only reduce the cost, but also expanded the application range deposited at room temperature.

Therefore, in the present work, the properties of TiO_2 films depositing by reactive magnetron sputtering on 5083 aluminum alloy with different deposition parameters at room temperature have been

* Corresponding author.
E-mail address: wsc33333@163.com (S. Wei).

http://dx.doi.org/10.1016/j.ceramint.2017.05.139
Received 23 February 2017; Received in revised form 19 April 2017; Accepted 18 May 2017
0272-8842/

Table 1
Experiment parameters of TiO_2 films.

Parameters	Value			
Substrate	5083 aluminum alloy			
Target	Ti (99.95%); 70 mm diameter			
Gas	Ar (99.995%); O_2 (99.995%)			
Base pressure	1×10^{-4} Pa			
Substrate temperature	Room			
Substrate rotate vertical axis	1 rpm			
Code	**Control factors**	**Level 1**	**Level 2**	**Level 3**
A	Power (kW)	3	5	8
B	Bias voltage (V)	60	80	100
C	Ar/O_2 ratio (%)	20	27	33
D	Deposition time (h)	2	3	4

investigated. The main purpose of the study is to explore the optimal deposition parameter and to find the corrosion resistance and antibacterial mechanism of TiO_2. The studies will be helpful for the future development of the high anticorrosion and antifouling TiO_2 films.

2. Experimental procedures

TiO_2 thin films were prepared on 5083 aluminum alloy substrates by reactive magnetron sputtering, with a base pressure of 1×10^{-4} Pa. A metallic Ti target with 70 mm diameter (purity 99.95%) was sputtered in a reactive gas atmosphere containing argon (Ar, purity: 99.995%) and oxygen (O_2, purity: 99.995%) at a total pressure about. The Ar/O_2 ratio was range from 4:1 to 1:1 in the experiments. There are four influential process parameters: power, Ar/O_2 ratio, bias voltage, and deposition time. Therefore, Taguchi method [4,29] was used to design the experiment parameters. Each parameter was assigned at 3 levels, as shown in Table 1. An L_9 (3^4, with 4 columns and 9 rows) orthogonal array was applied, and it is shown in Table 2. According to the following results and calculating by Orthogonality Experiment Assistant II software, the sputtering power and bias voltage are the key factors to affect the properties and structure of TiO_2 films. And the following analyses are all based the two main factors.

The matrix (5083 aluminum alloy) should be ultrasonically cleaned in acetone, ethanol and deionized water for 10 min, separately. Then they dried in nitrogen atmosphere. Before depositing experiment, the target was pre-sputtered for 15 min to remove the surface impureness. After film growth, the samples should allow to cool down to room temperature before being retrieved for each characterization.

Surface morphologies and microstructure of TiO_2 thin films were analyzed by a field emission scanning electron microscope (FESEM, JEOLJSM-6500F) using an accelerating voltage of 20 kV with equipped with an oxford INCA Energy 350 dispersive X-ray spectrometer (EDS). The surface topography was characterized by an atomic force microscope (AFM, SPM-9700) in tapping mode. The particles size of TiO_2 films were counted by an image-pro-plus software. Phase analysis were performed with a Rigaku D/MAX-2500PC X-ray diffractometer (XRD) using a Cu Kα X-ray source in grazing incident mode with incidence beam angle of 1°. The diffraction scanning angle ranges from 20° to 80° at a scanning rate of 0.03°/s. The chemical composition and chemical binding states of TiO_2 thin films were analyzed by X-ray photoelectron spectroscopy (XPS, Escalab 250Xi).

Mechanical properties (Hardness and Elastic modulus) of films were measured by nano-indentation (MTS NanoII) in continuous stiffness mode. And the load rate was 10 nm/s with a 1 nm amplitude modulation at 45 Hz. Penetration depth was lower than one tenth of the film thickness in order to minimize the substrate influence on the measured properties. For each specimen, at least 10 indents were performed to calculate the average.

In order to evaluate the corrosion behavior of TiO_2 thin films, the electrochemical experiments were taken out. Electrochemical impedance spectroscopy (EIS) was used to measure the corrosion behavior of TiO_2 thin films immersed in 3.5% NaCl solution. The samples for electrochemical measurements were mounted in epoxy resin with a square area of 10×10 mm^2. The experiment was carried out on a ZAHNERIM6 electrochemical working station. A conventional three-electrode system was used. The coated sample as the working electrode, the counter electrode is the platinum sheet, and a saturated calomel electrode as the reference electrode. The frequency interval ranged from 100 kHz to 10 mHz, the potential scanning rate was 1 mV/s. And all the experiments were taken out at room temperature. The electrochemical results were analyzed by ZSimpWin version 3.21software. And the results of E_{corr} and I_{corr} were calculated by Cview-2 software.

The antibacterial test was carried out in the laboratory. *Escherichia coli* (*E. coli*) bacteria from Chinese academy of Science, -Institute of Oceanology was selected to estimate antifouling property of TiO_2 films. A Luria-Bertani (LB) medium (including 10*g* L^{-1} peptone, 5 g L^{-1} yeast extract, 10*g* L^{-1} NaCl and 1000 mL distilled water) was used to culture *E. coli*. Then *E. coli* was inoculated into the liquid LB medium and cultured at 37 °C for 12 h. And the process of centrifugation was necessary to separate the bacterial body from the liquid LB medium. Bacteria were diluted and suspended in 0.1 M phosphate buffer saline (PBS, 8 g L^{-1} NaCl, 0.2 g L^{-1} KCl, 1.44 g L^{-1} Na_2HPO_4, 0.44 g L^{-1} KH_2PO_4 and 1000 mL distilled water) to 10^7 cells mL^{-1} for the following experiments. Above all the media should be sterilized at 121 °C for 0.5 h before inoculation. The process of inoculation and the following experiments were all carried out on an Aietech superclean bench after 1 h of ultraviolet sterilization. Then the samples with TiO_2 films were exposed to 10^7 cells mL^{-1} *E. coli* solution at 37 °C for 24 h. After that, the samples were washed by PBS and mounted by 5 wt% glutaraldehyde for 30 min, then immersed in 1 µg mL^{-1} 4, 6-diamidino-2-phenylindole (DAPI) for fluorescence dye. Finally, the dye samples were observed by fluorescence microscope at a magnification of ×100. The images of density of bacteria were analyzed by an Image-pro-plus 6.0 software. The hydrophilicity of TiO_2 thin films was estimated by measuring the contact angle at room temperature. An OCA15pro contact angle meter was used for measuring the contact angle. For each specimen, at least five different positions were performed to calculate the average.

Table 2
The sample number.

Code	Control factors			
	A	B	C	D
1#	1	1	1	1
2#	1	2	2	2
3#	1	3	3	3
4#	2	1	2	3
5#	2	2	3	1
6#	2	3	1	2
7#	3	1	3	2
8#	3	2	1	3
9#	3	3	2	1

3. Results and discussion

3.1. Film microstructure and morphology

The SEM images of TiO_2 films in different process parameters are shown in Fig. 1. And the pictures from (a) to (m) are corresponded with the sample from 1# to 9#, respectively. It can be seen clearly that the surfaces are covered with grain-liked structures and distributed unevenly. There are two main kinds of morphologies: spherical shaped particles (smaller size) and dipyramidal-liked (larger size) particles. The average size of spherical shaped particles is 18.2 nm, from 8.6 nm