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Mutifunctional arc ion plated TiO_2 photocatalytic coatings with improved wear and corrosion protection

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ABSTRACT

An arc ion plating (AIP) system was used to deposit anatase TiO_2 thin films with photocatalytic and antimicrobial properties. This study aims to evaluate the properties and performance of such films, including surface hardness, adhesion, abrasive wear resistance and corrosion protection. The experimental results show that film hardness and scratch adhesion reach maximum values of 679.6 HV and 21.2 N, respectively. Film quality is strongly influenced by the degree of crystallinity, which is in turn affected by both deposition time and oxygen partial pressure. The wear resistance of the TiO_2 coatings can be closely correlated to the film adhesion, however all films impart significantly higher resistance to abrasive wear than that of the uncoated surface. On the other hand, TiO_2 coatings on stainless steel give rise to an increased (less negative) corrosion potential and decreased corrosion current in a sodium chloride solution. Overall, AIP-TiO_2 film can however provide satisfactory protection for stainless steel.

1. Introduction

The discovery by Fujishima et al. [1,2] of a photosensitive anatase TiO_2 electrode that triggers hydrogen formation opened a new era of using the anatase polymorph of TiO_2 as a photocatalytic material to initiate formation of superoxide ions (O_2^-) and hydroxyl radicals (OH) [3] to degrade organic contaminants, as well as providing an antimicrobial function. More recently, photocatalytic TiO_2 was synthesised in the form of thin films, to take advantage of its functional properties over a wide range of substrate materials; as a result, commercialized products such as self-cleaning glass, air cleaning lamp, wiperless windshield etc, have been demonstrated. A considerable amount of research has been performed on the development of antimicrobial anatase TiO_2 thin films [4,5], to demonstrate novel manufacturing procedures [6–10], and to evaluate photocatalytic and antimicrobial properties in more detail [8,9,11]. Additionally, sophisticated ion beam assisted deposition (IBAD) of TiO_2 on stainless steel [12] and easily prepared sol–gel TiO_2 thin films on nickel–titanium shape memory alloy [13] have been shown to be effective in providing corrosion resistance against specific environments as well as inherent biocompatibility.

Increasingly for successful commercial application, new functional coatings are required to possess multi-functionality. Rutile TiO_2 for example is, as an optical coating, able to exhibit controlled refractivity, as well as providing sufficient mechanical strength [14–17]. TiN hard coatings used for decorative purposes and tribological applications are able to provide controlled color, particularly with the appropriate addition of alloying elements, as well as satisfactory wear resistance. Evaluating more thoroughly the protection performance of anatase TiO_2 coatings is important for the commercial diversification of functional applications. Such films could take further steps towards real service if the wear and corrosion protection capabilities are better understood.

An arc ion plating technique commonly employed for ceramic hard coating deposition was chosen to deposit anatase TiO_2 for photocatalytic and antimicrobial purposes in previous studies [8,9,11]. This led to the idea of using an anatase TiO_2 thin film as an antimicrobial coating, while benefiting from its ceramic nature, i.e. hardness and chemical inertness to perform synergistically as a protective coating. This study aims to evaluate the protection performance of such antimicrobial coatings, including surface hardness, film adhesion, abrasive wear resistance and corrosion protection to determine whether such films are able to compete as protective hard coatings with conventional tribological films, i.e. ceramic nitrides, such as TiN, CrN and their numerous derivatives.

2. Experimental procedure

A typical AIP system is used in this study and details were described in previous studies [8,9,11]. During deposition, oxygen was admitted

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Table 1
Coating conditions used to produce TiO_2 films in this study

Coating parameter		Value			
Fixed parameters	Cathode material	Ti (purity: 99.99%)			
	Cathode voltage (V)	20			
	Cathode current (A)	90			
	Substrate bias voltage (V)	0			
	Operating pressure, P_t (Pa)	0.50			
Deposition time changed	Deposition time, t_d(min)	15	30	60	90
	Oxygen partial pressure, PO_2 (Pa)	$0.50_{at\ PAr=0}$			
	Film thickness (μm)	2.00	2.50	5.00	7.50
	Cross-sectional morphology	Featureless	Columnar grain	Columnar grain	Columnar grain
	Crystal structure	Poor crystalline rutile	Major anatase + minor rutile	Major anatase + minor rutile	Major anatase + minor rutile
Oxygen partial pressure changed	Oxygen partial pressure, PO_2 (Pa)	$0.15_{at\ PAr=0.35}$	$0.25_{at\ PAr=0.25}$	$0.35_{at\ PAr=0.25}$	$0.50_{at\ PAr=0}$
	Deposition time, t_d(min)	30			
	Film thickness (μm)	2.65	2.65	2.60	2.50
	Cross-sectional morphology	Featureless	Fine Columnar grain	Columnar grain	Columnar grain
	Crystal structure	XRD amorphous	Very poor crystalline rutile	Major anatase + minor rutile	Major anatase + minor rutile

into the deposition chamber to react with titanium ions that were emitted from a titanium cathode surface via arc spots. AISI 304 stainless steel was used as the substrate material and substrates were cut to different shapes for microstructural analysis and measurement. They were polished and cleaned prior to coating. The coating conditions are shown in Table 1. The deposition time and oxygen partial pressure were changed systematically, to reveal their effects on film microstructure and properties. A MAC-MXP3 X-ray diffractometer (XRD) was used to identify the crystal structure of the deposits, using Cu Kα radiation with voltage of 40 KV, current of 30 mA, range of 2θ from 20 to 45° and step size of 4°/min. A Hitachi S-4800 field emission gun scanning electron microscope (FEGSEM) was used to observe cross-sectional morphology of the deposits.

An FM-700 microhardness tester with Vickers indenter geometry was used to measure the surface hardness of the coated specimens according to ASTM E92-82 [18], using an indentation load of 100 g. A CSM Revetest Xpress scratch tester was used to evaluate film adhesion according to ASTM G171-03 [19]. A diamond indenter of Rockwell C geometry (of conical apex angle 120° ± 5° and hemispherical tip of 200 μm ± 10 μm radius) was used as the stylus, with a maximum load of 40 N applied incrementally over a scratch length of 10 mm. The critical load (L_c) for adhesion of the TiO_2 coating was determined by monitoring the acoustic signal and confirmed by optical microscopy after testing.

Abrasive wear resistance of the coated specimens was evaluated using a JuYen Ltd., CY-6347 Taber tester according to ASTM D4060-07 [20], with a rotation speed of 40 rpm at a load of 500 g. A CS-10 abrasive rubber wheel was employed as the counter face. Specimens were measured by weight in milligrams before (A) and after (B) 1000 rotation cycles, and wear index (I) calculated according to Eq. (1), where C describes the number of rotation cycles. The wear track of the tested specimens was examined using surface profilometry (Hommel werke GMBH, model T1000).

$$I = \frac{(A-B)\times 1000}{C} \tag{1}$$

An EG&G 263A potentiostat was used to perform potentiodynamic polarization tests in a 3.5 wt.% NaCl electrolyte according to ASTM G44-99 [21]. The electrolyte was de-aerated by sparging with pure nitrogen gas for 30 min. A saturated Ag/AgCl electrode was used as a reference (REF), with a platinum counter electrode (AUX) and anatase TiO_2 coated specimens inserted as the working electrode (WE). The potential scan range was set between −0.6 V and 0.6 V with respect to the reference and a scan rate of 10 mV/s was applied. The data collected was analyzed using PowerSuite software to determine the corrosion potential (E_{corr}) and corrosion current (I_{corr}) of each specimen.

3. Results and discussion

3.1. Coating microstructure

The cross-sectional morphology and associated X-ray diffraction pattern of the TiO_2-coated specimens obtained at different deposition times and different oxygen partial pressures have been given in previous publication [9], with each film thickness, film morphology and crystal structure summarized in Table 1. The deposited films reveal that a thick and columnar-grained structure was obtained for the deposited film using an extended deposition time. The increased anatase phase content corresponding to the appearance of a columnar-grained structure can be ascribed to the increased substrate temperature that is induced by continuing titanium ion bombardment during deposition [8].

When an oxygen partial pressure ≥0.35 Pa is employed, it only appears that the deposited films become crystalline, otherwise being X-ray amorphous. Corresponding to the change in crystal structure, the cross-sectional morphology of the deposited films exhibited columnar grains when deposition occurred at higher oxygen partial

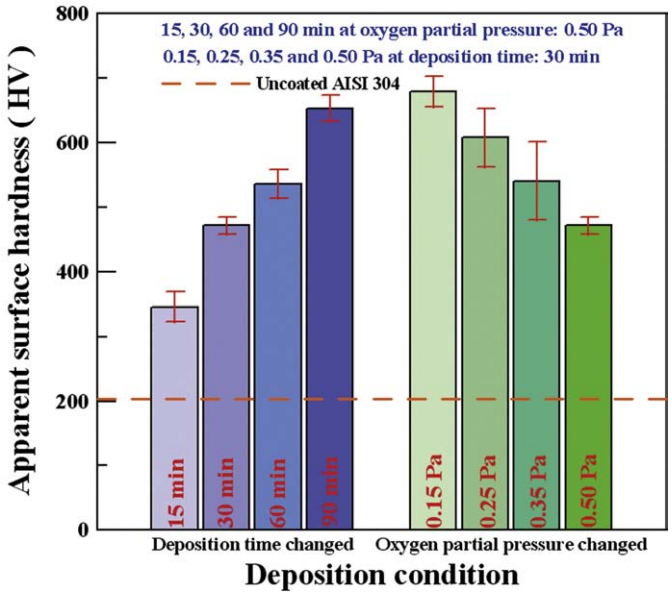

Fig. 1. Apparent surface hardness of the TiO_2 coated specimens deposited in different conditions. Dashed line indicates hardness of stainless steel substrate.