Applied Surface Science 355 (2015) 593–601

Contents lists available at ScienceDirect

Applied Surface Science

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

Plasma sprayed rutile titania-nanosilver antibacterial coatings

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ARTICLE INFO

Article history:
Received 5 February 2015
Received in revised form 19 July 2015
Accepted 21 July 2015
Available online 26 July 2015

Keywords:
Titania
Antibacterial
Plasma spray
Silver
Low content

ABSTRACT

Rutile titania (TiO_2) coatings have superior mechanical properties and excellent stability that make them preferential candidates for various applications. In order to prevent infection arising from bacteria, significant efforts have been focused on antibacterial TiO_2 coatings. In the study, titania-nanosilver (TiO_2/Ag) coatings with five different kinds of weight percentages of silver nanoparticles (AgNPs) were prepared by plasma spray. The feedstock powders, which had a composition of rutile TiO_2 powders containing 1–10,000 ppm AgNPs, were double sintered and deposited on stainless steel substrates with optimized spraying parameters. X-Ray diffraction and scanning electron microscopy were used to analysize the phase composition and surface morphology of TiO_2/Ag powders and coatings. *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) were employed to examine the antibacterial activity of the as-prepared coatings by bacterial counting method. The results showed that silver existed homogeneously in the TiO_2/Ag coatings and no crystalline changed happened in the TiO_2 structure. The reduction ratios on the TiO_2/Ag coatings with 10 ppm AgNPs were as high as 94.8% and 95.6% for *E. coli* and *S. aureus*, respectively, and the TiO_2/Ag coatings with 100–1000 ppm AgNPs exhibited 100% bactericidal activity against *E. coli* and *S. aureus*, which indicated the TiO_2/Ag coatings with more than 10 ppm AgNPs had strong antibacterial activity. Moreover, the main factors influencing the antibacterial properties of TiO_2/Ag coatings were discussed with grain size and the content of silver as well as the microstructure of the coatings.

1. Introduction

Titania coatings are the materials highly appropriate to be employed as self-cleaning surfaces, wastewater treatment and disinfection, protective coatings and biomaterials because of their excellent stability, nontoxicity, superior mechanical properties, good biocompatibility and low cost [1–3]. The emergence of infectious diseases in general poses a serious threat to public health worldwide, especially with the emergence of antibiotic-resistant bacterial strains [4]. Therefore, increasing attentions has been focused on developing TiO_2 coatings with antibacterial properties in order to reduce the frequency of infections and diseases resulting from bacteria [5].

The well-known TiO_2 polymorphs are rutile, anatase and brookite. The structure of rutile (tetragonal, space group $P4_2/mnm$) is made of chains of TiO_6 octahedra that share a vertex along the *c*-axis, and rutile is the most thermodynamically stable phase of the three polymorphs [6]. Moreover, rutile is known as an anti-wear and anti-corrosion material with excellent mechanical properties [7,8]. It has been reported that rutile layers could decrease the levels of bioreactivity and improve biocompatibility [9]. Therefore, titania coatings were tentatively prepared by using rutile powders.

There are many methods that have been used for the preparation of TiO_2 coatings, including sol–gel [10], chemical vapor deposition (CVD) [11], physical vapor deposition (PVD) [12], atmospheric plasma spraying (APS) [13] and suspension flame spraying [14]. Among these techniques, APS is a particularly appropriate technique because a large area of TiO_2 can be easily deposited without any special requirements, such as vacuum pressures or reactive atmospheres [6].

Extensive effort has been made to develop the antibacterial TiO_2 coatings. Heidenau et al. reported a study of the antibacterial as well as the biocompatible potential of different metal ions includes Ag^+, Zn^{2+}, Co^{2+}, Al^{3+} and Hg^{2+} in TiO_2 coatings [15]. Zhao et al. fabricated antibacterial nano-structured titania coating incorporated with silver nanoparticles on titanium implants [16]. Recently, researchers have focused on the modification of TiO_2

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http://dx.doi.org/10.1016/j.apsusc.2015.07.147
0169-4332/

coatings with different antibacterial agents such as Ag, Cu, Zn and Au [5,17–19]. Among these materials, silver has long been known to exhibit strong bactericides and has attracted increasing attention because of other benefits such as a broad antibacterial spectrum including antibiotic-resistant bacteria, non-cytotoxicity at suitable doses, satisfactory stability, and smaller possibility to develop resistant strains [20–22]. So it is possible to fabricate antibacterial TiO_2 coatings by introducing silver nanoparticles into the rutile powders. But nanoscale Ag could enter human bodies, tissues or even cells, and becomes toxic to human cells at higher levels, Vik et al. pointed that the maximum silver concentration released in vitro should be no more than 10 ppm [23]. Therefore, it is significant to prepare TiO_2 coatings with excellent antibacterial property and suitable AgNPs doses. But there are limited studies that consider the effect of silver concentration on antibacterial property in the plasma sprayed TiO_2/Ag coatings.

In this work, titania coatings with different amounts of silver nanoparticles were deposited on stainless steel substrates by plasma spray with a optimized spraying condition. The TiO_2/Ag coatings, which were denoted as T1, T2, T3, T4 and T5, were prepared by using rutile TiO_2 powders containing 1 ppm, 10 ppm, 100 ppm, 1000 ppm and 10,000 ppm AgNPs, respectively. The feedstock powders were prepared by mechanically mixing TiO_2 powders sintered at 1300 °C and AgNPs powder, followed by sintering and crushing the mixtures to make silver nanoparticles homogeneously distribute on the surface of rutile powders. The objective of this work is to investigate the effects of composition on antibacterial property for a material with minimum amount of silver nanoparticles (AgNPs) as well as maintain the excellent antibacterial property.

2. Materials and methods

2.1. Preparation of titania-nanosilver coatings

Commercial rutile titania powders (99.99 wt.%, Jing Rui New Material Co. Ltd) and silver nanoparticles (99.5 wt.%, Aladdin Chemistry Co. Ltd) were employed as powders for the resulting coatings. The mean particle size of TiO_2 and Ag powders was in the range of 10–40 μm and 60–120 nm, respectively. The process of manufacturing feedstock powders included three steps: (a) sintering the original TiO_2 powders in a muffle furnace to increase the bonding strength and make organic binder volatilize, the sintering system was presented in Table 1; (b) wet milling the sintered TiO_2 and Ag powders for 4 h in a ball mill; (c) sintering the mixed powders for 1 h at 800 °C in argon atmosphere. The sintered powders were then crushed and separated by 200 mesh screens. The powders with a size less than 200 mesh were used as feedstock material for plasma spray. In order to investigate the effect of the compositions in TiO_2/Ag coatings on antibacterial properties, titania powder mixed with five different kinds of weight percentages of silver powders were deposited with a proper spraying condition. The TiO_2/Ag coatings, denoted as T1, T2, T3, T4 and T5, were prepared by using TiO_2 powders containing 1 ppm, 10 ppm, 100 ppm, 1000 ppm and 10,000 ppm AgNPs, respectively. The TiO_2 coatings were also sprayed under the same conditions for comparison and denoted as T0.

Table 1
Sintering system of titania powders.

Temperature (°C)	Heating rate (°C/min)	Time (min)
0–400	8	50
400–600	5	60
600–800	4	50
800–1000	3.3	60
1000–1100	2.9	35
1100	0	120
1100–1300	2.5	80
1300	0	60

Table 2
Spray parameters of titania-nanosilver coatings.

Current (A)	Voltage (V)	Powder feed rate (rpm)	Spray distance (mm)	Ar (slpm)	H_2 (slpm)	Angle of feed power (°)
600	60	22	100	32	12	90

Stainless steel was used as substrate and machined into samples of 20 mm × 50 mm × 1 mm. Prior to the coating process, the surface of stainless steel substrates was thoroughly cleaned, degreased, and grit-blasted with corundum in order to produce a rough surface for good bonding. Atmospheric plasma spray system (APS-2000, Sulzer Metco, Switzerland) was applied to fabricate the TiO_2/Ag coatings. Coating samples, with thickness of about 40 μm, were deposited onto the stainless steel substrates by APS. The spray parameters adopted in our work were listed in Table 2.

2.2. Specimens analyses

Scanning electron microscopy (SEM, JSM-6510, JEOL, Japan) was employed to observe surface morphology of the TiO_2/Ag and TiO_2 powders and as–prepared coatings. The elemental distribution of specimens was observed by energy-dispersive X-ray spectrometry (EDS, ADD0076, INCAx, UK). X-Ray diffraction (XRD, Ultima IV, Rigaku, Tokyo, Japan) with CuKα radiation was used to examine the phase compositions of the plasma sprayed coatings. X-ray photoelectron spectroscopy (XPS, MICRO-LAB 310F, Thermo Scientific, UK) was employed to study the surface atomic composition and chemical state of silver on the surface of T5 coatings. All binding energy values were determined by calibration and fixing the C1s line to 285 eV. The sample was also examined with an Al Ka X-ray source after being etched 10 s.

The amount of silver in TiO_2/Ag coatings was quantified by optical emission spectrometry (ICP-OES, 700series, Agilent Technologies, USA) as following: titania/silver powers were scraped off from TiO_2/Ag coatings surface and weighed ($M_{coatings}$), then dissolved in nitric acid solution. After the measurement of silver concentration (C_{silver}) in acid solution by ICP-OES, the silver in the coatings can be expressed as the value of ($C_{silver} \times V_{nitric\ acid}$)/$M_{coatings}$ [4].

2.3. Antibacterial test

The antibacterial efficacy of the TiO_2/Ag and TiO_2 coatings were examined by counting method in the dark using *Escherichia coli* (*E. coli*, ATCC 25922) and *Staphylococcus aureus* (*S. aureus*, ATCC 25923). The coating specimens were sterilized by autoclave at 121 °C for 30 min after being cleaned in ethanol and deionized water. A volume of 100 μl of each strain (10^8 cfu (colony forming units)/ml) was dripped onto the surface of the samples. The specimens with the bacterial solution were incubated at 37 °C for 48 h in a Constant Temperature Incubator and 5 ml sterile water was placed near each specimen to maintain high humidity (RH > 90%). The bacteria from the surface of specimens were recovered in accordance with the National Standard of China (GB/T 18204-2000). After incubation at 37 °C for 48 h, the specimens' surfaces were scoured with sterile cotton swabs, washed-off with sterilized phosphate buffer solution (PBS), and transferred into centrifuge tube. The centrifuge tube was shaken drastically for 5 min in order to make the bacteria enter into PBS thoroughly. The harvested bacterial solution was diluted in a sterilized PBS. These dilution series were then inoculated onto a standard agar medium and cultured