Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 22(2012) s120−s126
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Photocatalytic activities of N doped TiO_2 coatings on 316L stainless steel by plasma surface alloying technique

WANG He-feng[1], SHU Xue-feng[1], LI Xiu-yan[2], TANG Bin[3]

1. Institute of Applied Mechanics and Biomedical Engineering, Taiyuan University of Technology, Taiyuan 030024, China;
2. Department of Physics and Optoelectronics, Taiyuan University of Technology, Taiyuan 030024, China;
3. Surface Engineering Institute, Taiyuan University of Technology, Taiyuan 030024, China

Received 9 July 2012; accepted 23 August 2012

Abstract: Nitrogen doped titanium dioxide (N-TiO_2) coatings were fabricated by oxidation of the TiN_x coatings in air. TiN_x coatings were prepared on stainless steel (SS) substrates by plasma surface alloying technique. The reference TiO_2 sample was also deposited by oxidation of the Ti coatings in air. The as-prepared coatings were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and ultra violet-visible absorption spectroscopy (UV-Vis). The formation of anatase type TiO_2 is confirmed by XRD. SEM measurement indicates a rough surface morphology with sharp, protruding modules after annealing treatment. The band gap of the N-doped sample is reduced from 3.25 eV to 3.08 eV compared with the undoped one. All the N-doped samples show red shift in photoresponse towards visible region and improved photocurrent density under visible irradiance is observed for the N-doped samples. The photocatalytic activity was evaluated via the photocatalytic oxidation of methylene blue (MB) in aqueous under visible light irradiation. The results reveal that the N-doped samples extend the light absorption spectrum toward the visible region. The degradation rate of N-TiO_2 is 20% in visible irradiation for 150 min.
Key words: TiO_2; N doping; photocatalysis; stainless steel; plasma alloying

1 Introduction

Stainless steel (SS) can be used in hospitals, public, food industries and kitchen appliances [1,2]. The existing and breeding of microorganism on the surface of SS products do not meet health criteria. With sustainable improvement of the people's living level, public awareness on safety during food and medicine processing has been rapidly raised. It is crucial to improve the antibacterial properties of SS. One of the promising routes to this end is to deposit a protective ceramic coating on the metal surface. For example, medical metals were coated with silver or copper, which are strong antibacterial metal elements [3−5].

There were many studies trying to prepare antibacterial stainless steel surfaces by coating, ion implantation, chemical synthesis process, etc. [6−8]. However, the surface modifications would fail in a short time due to dropping off of the antibacterial coatings and then would not provide enough antibacterial functions during utilizations of these coatings. Meanwhile, it is difficult to maintain antibacterial effect simultaneously with good wear and corrosion resistance. Therefore, how to enhance the antibacterial capability of the stainless steel surface and not influence its base performance degradation is needed.

TiO_2, a well known biomaterial, has potential applications including as an antibacterial coating for sterilizing biomedical metallic implants, hospital equipments and as self-cleaning surfaces for use in architecture [9,10]. At the same time, TiO_2 possesses low friction, high wear resistance, excellent corrosion resistance and good biocompatibility [11,12]. However, TiO_2 can only be activated by irradiating with ultraviolet (UV) light due to its high band-gap energies. Therefore, the modification of TiO_2 to render its sensitivity to visible-light became one of the most important goals to

Foundation item: Projects (51171125, 11172195) supported by the National Natural Science Foundation of China; Project (20110321051) supported by the Shanxi Province Programs for Science and Technology Development, China; Project (2011-038) supported by the Shanxi Province Foundation for Returned Overseas Scholars, China; Project (2010081016) supported by the International Scientific and Technological Cooperation Foundation of Shanxi Province, China
Corresponding author: SHU Xue-feng; Tel: +86-351-6010540; +86-13834600938; E-mail: shuxuefengtyut@163.com

increase the utility of TiO_2. For this purpose, doping or combining TiO_2 with various metal or non-metal ions has been considered [13,14]. The TiO_2 doped with non-metals has drawn great attention due to their nontoxic feature. Many attempts have been made in the direction of N, C, or anion-doped TiO_2 photocatalysis because it has good potential for the utilization of solar energy [15−18]. Since ASAHI et al [16] reported that N-doping significantly improved the photocatalytic reactivity of TiO_2 films toward organic molecules under visible light illumination. The most feasible and successful approach among these anions seems to be N-doping.

Recently, many investigations have been made to prepare N-doped TiO_2 coatings by oxidization of TiN_x [19−21], such as anodic oxidation of titanium nitride films prepared by electrophoretic deposition (EPD) [19], oxidization of TiN_x films deposited by reactive DC magnetron sputtering [20]. These show that oxidization of TiN_x films is a viable method to prepare N-doped TiO_2. The plasma surface alloying technique [22,23] is an effective and economical method to improve the surface performance of metals or alloys, such as micro-hardness, wear resistance, and oxidation resistance. The advantage of this technique is that a gradient diffusion layer can be obtained with enough thickness and good adherence between modified layer and the substrate [24].

In principle, N-TiO_2 coatings on metal substrate could be directly obtained by using the plasma surface alloying technique, in which titanium target is sputtered in $Ar/O_2/N_2$ mixture gas. Two key points should be taken into account. Firstly, oxygen would lead to “target poisoning”, which affects the stability of the process parameters and the deposition rate. Secondly, in glow discharge sputtering, the temperature of the substrate is higher than 800 °C, which would result in the formation of rutile-TiO_2 coatings, rather than the anatase-TiO_2 coatings with good photocatalytic properties.

Based on these considerations, the N-TiO_2 coatings were prepared by two-steps. Firstly, the TiN_x coatings on SS substrate were deposited by plasma surface alloying technique. All the resulted TiN_x coatings were subsequently annealed in air at 450 °C for 2 h to oxidize. The photocatalytic properties of the coatings were measured and discussed by combined theoretical and experimental results.

2 Experimental

2.1 Materials and methods

The 316L SS samples (d20 mm×5 mm) were ground with No. 80−1500 emery papers, and then polished with 0.3 and 0.05 μm alumina powders, respectively. Finally, the surfaces of samples were cleaned by ethanol and acetone.

The N-TiO_2 coatings were prepared by a two-step processing. Firstly, the TiN_x coatings were deposited on SS substrates by plasma surface alloying technique, in which titanium targets were sputtered in Ar/N_2 mixture gas. The sketch is shown in Fig. 1. The process parameters were as follows: the Ar/N_2 mixture gas pressure was 30−40 Pa ($V(N_2):V(Ar)=1:2$), the source voltage for supplying Ti elements was −1100 to −550 V, the distance from the source target to the substrate sample was 15 mm, the process temperature was 950 °C and the process duration was 3 h. All the resulted TiN_x coatings were subsequently annealed in air at 450 °C for 2 h to oxidize and crystallize the samples.

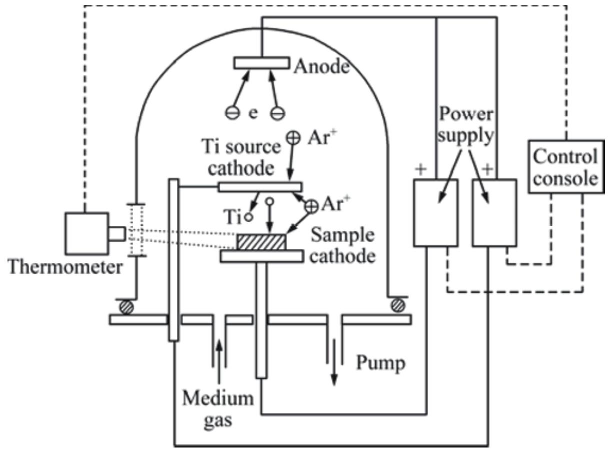

Fig. 1 Sketch of plasma surface alloying technique

2.2 Characterizations

The surface morphologies of the as-deposited and thermally oxidized coatings were examined using scanning electron microscopy (SEM). The composition was determined by X-ray photoelectron spectroscopy (XPS) with Al K_α X-ray as the radiation source. An X-ray diffractometer (XRD) with the 1.54 Å Cu K_α line as the excitation source was employed to examine the crystal structure of the coatings. The absorption spectra of the samples were collected by UV-Vis spectrophotometer (Shimadzu UV 2450 (Japan)).

2.3 Photocatalytic activity measurement

The surface photocatalytic activity of the samples was measured by photodegradation of MB with the initial concentration and volume of 2.0×10^{-5} mol/L and 30 mL, respectively. First, a piece was settled in aqueous MB in a glass beaker. Then, it was irradiated at room temperature by a halogen lamp (90 W, irradiation distance of 20 cm). The schematic diagram is shown in Fig. 2. It is better to make a visible photocatalyst that works under conventional visible light lamps. The degradation rate was measured by UV-Vis