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Structure and visible photocatalytic activity of nitrogen-doped meso-porous TiO_2 layer on Ti6Al4V substrate by plasma-based ion implantation

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Abstract: The nitrogen-doped porous TiO_2 layer on Ti6Al4V substrate was fabricated by plasma-based ion implantation of He, O and N. In order to increase the photodegradation efficiency of TiO_2 layer, two methods were used in the process by forming mesopores to increase the specific surface area and by nitrogen doping to increase visible light absorption. Importantly, TiO_2 formation, porosity architectures and nitrogen doping can be performed by implantation of He, O and N in one step. After implantation, annealing at 650 ℃ leads to a mixing phase of anatase with a little rutile in the implanted layer. By removing the near surface compact layer using argon ion sputtering, the meso-porous structure was exposed on surfaces. Nitrogen doping enlarges the photo-response region of visible light. Moreover, the nitrogen dose of 8×10^{15} ion/cm^2 induces a stronger visible light absorption. The photodegradation of rhodamine B solution with visible light sources indicates that the mesopores on surfaces and nitrogen doping contribute to an apparent increase of photocatalysis efficiency.

Key words: Ti6Al4V alloy; TiO_2 layer; nitrogen doping; ion implantation; structure; photocatalytic activity

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1 Introduction

TiO_2 is a widely used material for the degradation of organic pollutants due to its low cost, nontoxicity and high photocatalytic activity[1]. However, for TiO_2 film catalysts, a drawback encountered is associated with the rather large band-gap of 3.0−3.2 eV and thus only a small fraction of the solar spectrum is absorbed[2−3]. Therefore, considerable efforts have been made to extend the photoresponse of TiO_2-based systems further into the visible-light region[4−6]. Doping is an effective method to enhance the visible light absorption. Moreover, the recent reports revealed that nitrogen is an idea candidate among the doping species such as the transition metals and nonmetals[7−8]. To incorporate nitrogen in TiO_2, many strategies are used, such as ion implantation[9], magnetron sputtering[10] and sol-gel [11]. Ion implantation is the most straightforward approach. To overcome another drawback of the lower surface area of TiO_2 film, the porosity architectures were proposed [12−13]. Several studies reported the nitrogen doping by ion implantation[2, 9]. However, there was lack of information on the application of the pores by implantation to photocatalytic field.

In this work, the nitrogen-doped meso-porous TiO_2 layer was fabricated on Ti6Al4V substrate by plasma-based ion implantation. To increase the photodegradation efficiency of TiO_2, two methods were used in the process by forming mesopores to increase the specific surface area and by nitrogen doping to increase visible light absorption. Helium implantation was used to construct the porous structure. TiO_2 was formed by oxygen implantation. Doping was performed by nitrogen implantation.

2 Experimental

Commercial Ti6Al4V alloy was used as the substrate material. Before implantation, the samples with dimensions of 10 mm×10 mm×5 mm were mechanically ground and polished to a mirror-finish. The

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implantation was carried out in a home-made DLZ−01 installation at a base pressure of 3×10^{-3} Pa and a working pressure of 0.1 Pa. The plasma was generated by radio frequency. The implanting temperature was measured by an infrared thermometer and kept at approximately 350 ℃ for helium implantation, and the temperature of oxygen and nitrogen implantation was lower than 180 ℃. In order to achieve a thick porous layer closer to the surface, helium at −10, −30 and −50 kV was implanted into the titanium substrate subsequently and the corresponding doses were 6×10^{17}, 3×10^{17} and 3×10^{17} He/cm^2, respectively. Based on our previous work[14], the voltage of −30 kV and dose of 4×10^{17} O/cm^2 were applied for oxygen implantation. The nitrogen doping with doses of 4×10^{15}, 8×10^{15} and 12×10^{15} N/cm^2 was performed by implantation at −30 kV.

X-ray photoelectron spectroscopy (XPS) was performed on a PHI 5700 ESCA spectrometer with an Al K_α (1 486.6 eV) source operated at 13 kV and 300 W. The cavity structure was characterized by a JEM−2010 transmission electron microscopy (TEM). Phase structure was investigated by glancing X-ray diffraction (GXRD) with a fixed incident angle of θ=1°. The surface topography was observed with a scanning electron microscopy (SEM) using a field emission microscope (S−4800 model, from Hitachi, Japan). The UV-Vis absorption spectra were obtained by UV-Vis spectrophotometry (TU−1901) with an integrating sphere attachment for their diffuse reflectance in the range of 200−800 nm. Photocatalytic activities were evaluated by measuring the removal rate of rhodamine B in aqueous solutions. And the photodegradation rate was determined by measuring the intensity change of the absorption spectra of rhodamine B solution before and after visible light illumination from Xe light instead of sun rays.

3 Results and discussion

Fig.1 shows TEM images of the implanted layer on Ti6Al4V substrate. Helium bubbles with several nanometers are formed by implantation (Fig.1(a)). After implantation of helium, subsequent oxygen implantation leads to an apparent increase in the size of previous helium. Bubble growth is related to the following reasons. First, collision cascades by oxygen implantation induce Ostwald mechanism, i.e. collision decomposes the small bubble and makes this fresh helium move to big bubble, thus the big bubbles are enlarged. Second, the hot peak by oxygen implantation offers a driving force and contributes to moving and gathering of helium. It is also found that the bubble size almost does not change by nitrogen implantation. The reason for this is that the process time is too short for nitrogen implantation compared with that for helium and oxygen implantation.

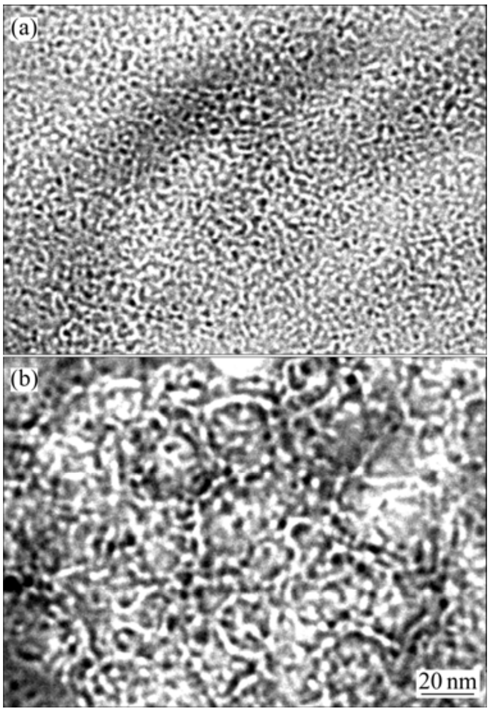

Fig.1 TEM images of implanted layer on Ti6Al4V substrate implanted with helium(a) and helium and oxygen(b)

It is well known that anatase possesses excellent catalytic activity, especially for the mixing phases of anatase with a little rutile. However, oxygen implantation does not lead to anatase in the implanted layer, thus subsequent annealing treatment is necessary to obtain the expected phase structure. Fig.2 shows GXRD patterns of helium and oxygen implanted titanium samples annealed in air at different temperatures. While the annealing temperature ascends to 650 ℃, the expected mixing structure of anatase with a little rutile forms in the implanted layer.

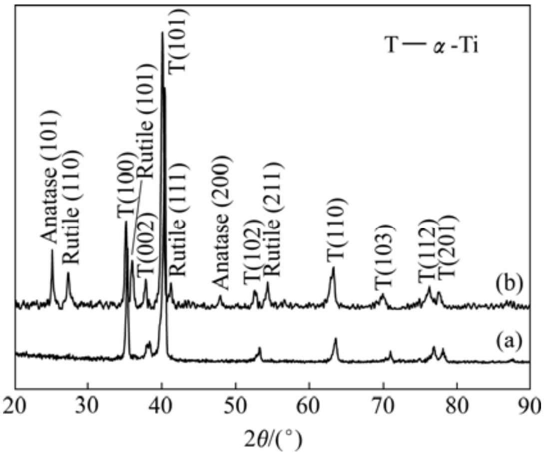

Fig.2 GXRD patterns of helium and oxygen implanted titanium samples annealed in air at different temperatures: (a) 630 ℃; (b) 650 ℃

Our previous work revealed that helium bubbles distributed under the surface[15]. In order to employ the pores for photodegradation, the bubbles should be exposed on surfaces. Here, argon ion sputtering was used to remove the near surface compact layer of the implanted sample and the pores form on the surface in Fig.3. The pores size was enlarged into several hundred nanometers due to the increase in bubble size by annealing and argon ion sputtering.

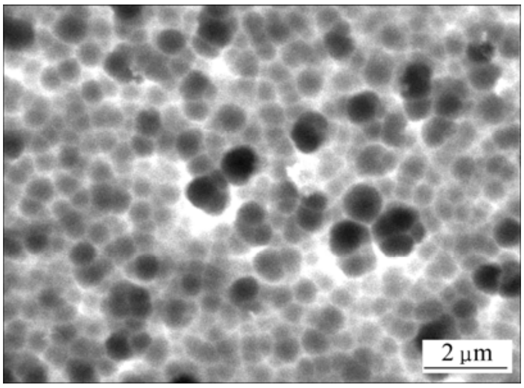

Fig.3 SEM image of mesoporous surface of sample implanted at −10, −30, −50 kV, 6×10^{17}, 3×10^{17}, 3×10^{17} He/cm^2, −30 kV, 4×10^{17} O/cm^2, −30 kV, 4×10^{15} N/cm^2, annealed at 570 ℃ and sputtered by argon ion

For the doped samples, the nitrogen chemical states were characterized and shown in Fig.4. The broad N 1s peaks consist of three different peaks at 396.8, 398.7 and 400.4 eV by deconvolution. The observed peak at 396.8 eV is attributed to atomic *β*-N and proves the presence of Ti—N bonds formed when N replaces O in TiO_2 crystal lattice[2]. The peak at 398.7 eV is due to the nitrogen in N-Ti-O environment[16] and the peak at 400.4 eV is assigned to *γ*-N from molecularly adsorbed nitrogen containing compounds onto the surface of samples[17]. For the nitrogen doping dose of 8×10^{15} ion/cm^2, *β*-N amount is higher than that for the nitrogen dose of 4×10^{15} and 12×10^{15} ion/cm^2.

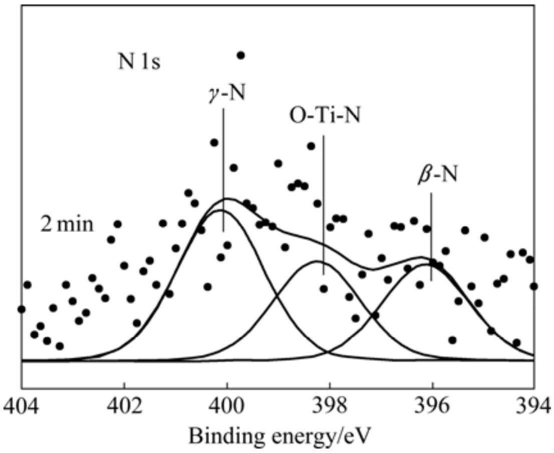

Fig.4 N1s spectra of doped nitrogen of mesoporous TiO_2 layer

Fig.5 shows UV-Vis absorption spectra of the samples with and without doped nitrogen. Nitrogen doping induces an apparent increase in the visible-light absorption in the region of 400−600 nm. Furthermore, for the nitrogen dose of 8×10^{15} ion/cm^2, the photo-response of visible-light is stronger than that of the sample implanted with nitrogen doses of 4×10^{15} and 12×10^{15} ion/cm^2. This result also proves that the nitrogen doping dose should not be very high to improve the visible-light absorption.

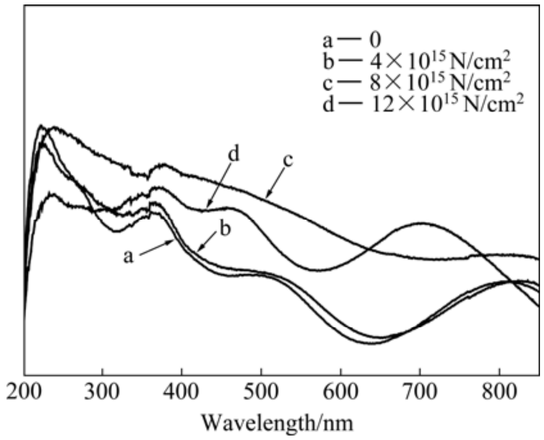

Fig.5 UV-Vis adsorption spectra of mesoporous TiO_2 layer with different nitrogen doses

The explanations for the increase in visible-light absorption by nitrogen doping are claimed to be in the band gap narrowing. At the beginning, the band gap narrowing is attributed to the hybridization of N 2p states with the O 2p-derived valence band. However, recent density functional theory (DFT) calculations indicate no band gap narrowing due to N doping rather than N 2p states forms localized states within the band gap just above the maximum valence band. Based on the XPS results, it can also be inferred that the increase in visible-light absorption is attributed to the band gap narrowing by the formation of the localized N 2p states caused by atomic *β*-N within the band gap. Moreover, the nitrogen doping dose of 8×10^{15} ion/cm^2 leads to more *β*-N, thus the visible-light absorption is stronger than that of other doses.

For different samples, the removal rate of rhodamine B as a function of irradiation time is shown in Fig.6. Nitrogen doping increases the removal rate, and the nitrogen dose of 8×10^{15} ion/cm^2 leads to a much higher removal rate because of the strong visible absorption. The mesoporous architecture further increases the removal rate and the increase factor reaches 2 after decomposition for 1 h.

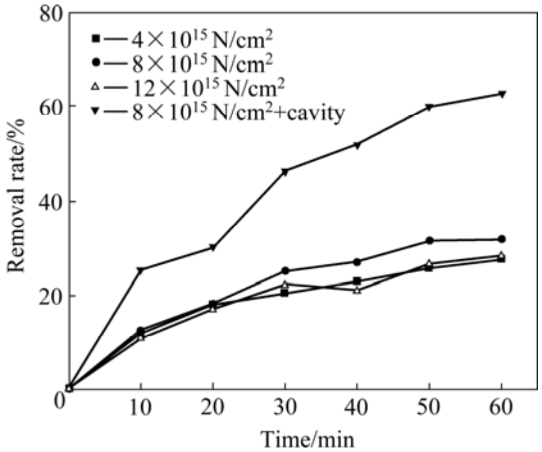

Fig.6 Effect of nitrogen doping dose on visible light-induced photodegradation rate of rhodamine B on Ti6Al4V samples

4 Conclusions

1) Plasma-based ion implantation of He, O and N into the Ti6Al4V substrate produces a nitrogen-doped mesoporous TiO_2 layer. After implantation, annealing at 650 ℃ forms a mixing structure of anatase and a little rutile.

2) Argon ion sputtering is employed to expose the pores on surfaces. Doped nitrogen presents as β-N, N-Ti-O and γ-N in the TiO_2 layer. Nitrogen doping enlarges the photo-response region of visible light and the nitrogen dose of 8×10^{15} ion/cm^2 induces a stronger visible light absorption.

3) The mesopores and nitrogen doping evidently increase the removal rate of rhodamine B with visible light source.

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