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In vitro bioactivity of plasma-sprayed TiO_2 coating after sodium hydroxide treatment

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Abstract

TiO_2 coatings were deposited on titanium alloy substrates by atmospheric plasma spraying using commercial TiO_2 powders. A chemical treatment method was employed to induce bioactivity on the TiO_2 surface. The as-sprayed TiO_2 coatings were immersed in 10M sodium hydroxide solutions at 60 °C for 24 h and then soaked in simulated body fluids (SBF) for a period of time to investigate the formation of apatite on the sample surface. Field-emission scanning electron microscopy was used to observe the surface morphologies and the phase composition of the as-sprayed coating and apatite were analyzed by X-ray diffraction and Fourier transform infrared spectroscopy. Our results show that the as-sprayed coatings are composed of rutile, anatase and a small quantity of Ti_3O_5. After the NaOH treatment, carbonate-containing hydroxyapatite can be induced to form on the surface during the SBF immersion test.

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Keywords: TiO_2 coatings; Plasma spraying; Sodium hydroxide treatment; Simulated body fluid; Apatite

1. Introduction

Plasma-sprayed bioactive hydroxyapatite coatings have been used widely as valuable bone-repairing materials [1]. In recent years, plasma-sprayed titanium coatings [2] and wollastonite coatings [3] have been found to form a biologically active bonelike apatite layer on the surface in simulated body fluid (SBF) immersion tests or in vivo experiments. However, deleterious ions released from many biomaterials and artificial implants cause concerns [4]. TiO_2 coatings are widely used in many optical, electronic, and tribological applications [5–7]. They have also recently demonstrated promising in vivo corrosion behavior acting as a chemical barrier against release of metal ions from biomedical implants [8,9]. The excellent biocompatibility of TiO_2 ceramics and thin films has also been recognized. T. Kasuga, et al. indicated the formation of apatite on compacted TiO_2 powders in simulated body fluids [10]. The bioactivity of TiO_2 powders and sol−gel-derived TiO_2 films has been examined by many researchers [11,12]. However, the use of plasma sprayed TiO_2 coatings as bioactive (bone conductive) materials has not been explored extensively. In our previous work, plasma-sprayed TiO_2 coatings were shown to possess better mechanical properties than other biomaterials coatings. The bonding strength with the Ti alloy substrate was found to be higher than 40 MPa while good biocompatibility was also observed [13].

Surface treatment has been used to increase the surface bioactivity of some materials, and the methods include chemical treatment [14], laser treatment [15], ion injection surface modification [16], and so on. Since Branemark first reported their application, titanium and titanium alloys have

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been widely used as implant materials, and their bioactivities are believed to be linked to TiO_2 [17]. Kim et al. first introduced alkali and heat treatments to improve the bioactivity [18]. Further research indicated that apatite was formed on the surface of pure titanium, including NaOH-treated and NaOH-heat-treated substrates [19]. In our previous works, bone-like apatite could be induced on the surface of plasma-sprayed titanium coatings treated with NaOH in simulated body fluid immersion tests [2]. After the materials were implanted into a dog femur, new bone was found to form on the surface of the NaOH-treated implant surface [20]. However, the titanium oxide layer formed on the surface of the titanium or titanium coatings is so thin that ion release from the materials is a concern thereby shortening the lifetime of the implant. The purpose of this work is to obtain a relatively thick TiO_2 coating by plasma spraying followed by the inducing of surface bioactivity using the NaOH treatment. Introduction of surface bioactivity (bone conductivity) to plasma-sprayed TiO_2 coatings which are generally recognized to have excellent biocompatibility and corrosion resistance as well as high bonding to titanium alloys makes them more superior than many current biomedical coatings.

2. Experimental details

Commercial titanium alloy (Ti6Al4V) blocks of 10 × 10 × 2 mm were employed as substrates. Prior to plasma spraying, all the substrates were sandblasted with brown corundum. A commercial TiO_2 powder (Wuhan, China) agglomerated by the spray drying method was used as the feedstock in the plasma spray experiments. The coatings were prepared by an atmospheric plasma spraying system, including a Sulzer Metco F4-MB plasma gun mounted on an ABB S3 robot. The main spraying parameters are listed in Table 1.

The as-sprayed coatings were ultrasonically cleaned in acetone and deionized water, and then were immersed in 10M NaOH aqueous solutions at 60 °C for 24 h. After washing in deionized water, the as-sprayed and NaOH-treated coatings were soaked in SBF to investigate their bioactivities. The ion concentrations of the SBF are nearly equal to those of human blood plasma, as shown in reference [13]. The SBF was buffered at PH 7.4 at 37 °C with trimethanol aminomethane and hydrochloric acid. After soaking in SBF for two and four weeks, the samples were taken out, rinsed with deionized water, dried, and then inspected or tested using various methods.

Table 1
Plasma spraying parameters

Ar gas flow (slpm*)	40
H_2 gas flow (slpm)	12
Arc current (A)	600
Arc voltage (V)	70
Spraying distance (mm)	100

*slpm: standard liter per minute.

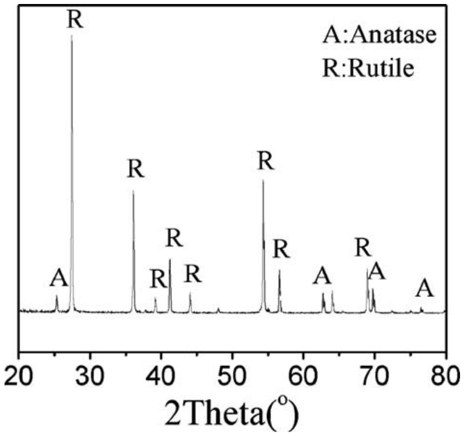

Fig. 1. XRD pattern of TiO_2 powders.

The phase characterization of the coatings before and after SBF tests were conducted by X-ray diffraction (XRD) employing a JAPAN-RICOH diffractometer equipped with a Ni-filtered Cu K_α radiation ($\lambda = 1.5418$ Å) source. In the thin film X-ray diffraction (TFXRD) experiments, the glancing angle of the incident beam was fixed at 2°. A few micrograms of the Ca-P layer formed on the coating in SBF were scraped off. This was mixed with KBr and pressed for structural analysis using Fourier transfer infrared (FTIR) spectroscopy using a Bio Rad FTS-185. The surface morphologies, cross-sectional microstructures, and composition of the as-sprayed and NaOH-treated coatings were examined by field-emission scanning electron microscopy (FE-SEM) and energy-dispersive X-ray spectrometry (EDS) using a JEOL JSM-6700F SEM and electron probe X-ray microanalysis ($EPMA-8705QH_2$, Shimadzu, Japan). The surface compositions of the TiO_2

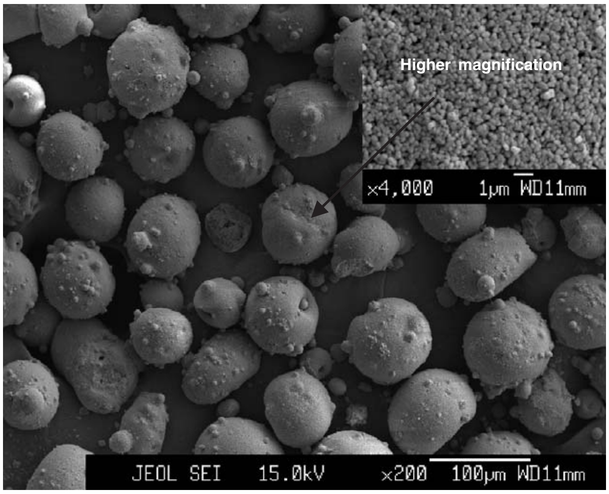

Fig. 2. SEM image of spray-dried TiO_2 powders.

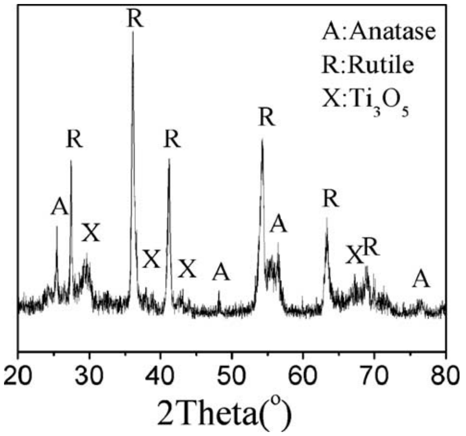

Fig. 3. XRD pattern of as-sprayed TiO_2 coating.

coatings before and after NaOH treatment were determined by Auger electron emission spectroscopy (AES) using a FISONS, MICROLAB-310F. The surfaces of TiO_2 coatings before and after NaOH treatment were carefully cleaned by deionized water and dried at 100°C before the AES analysis.

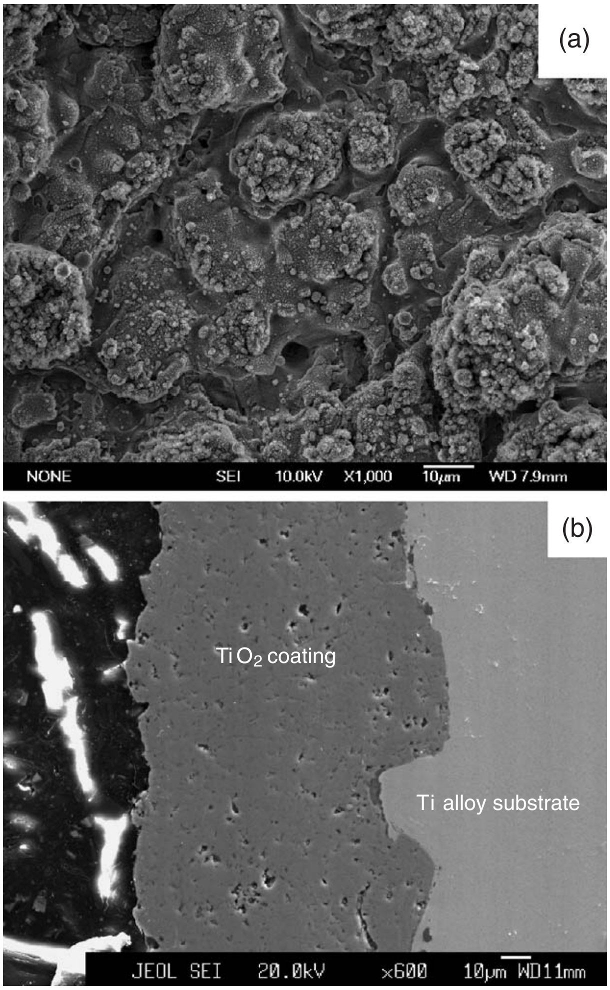

Fig. 4. Morphologies of as-sprayed TiO_2 coating: (a) surface, (b) cross section.

3. Results and discussion

The XRD pattern of the TiO_2 powders shown in Fig. 1 reveals that the rutile content in the original powder is about 95%. Fig. 2 shows the SEM image of the spray-dried powders. The shape of the spray-dried powders was similarly spherical having sizes of 30 to 70 µm. The higher magnification analysis of the spray-dried particles indicates that the size of the original powder is about 0.3 µm.

Fig. 3 depicts the X-ray diffraction pattern acquired from the plasma-sprayed TiO_2 coating. It can be seen that the as-sprayed coating is primarily composed of the rutile phase and a small amount of anatase and TiO_{2-x} (most of them is Ti_3O_5). The deoxidization of TiO_2 is due to the cooling rate of the molten or partially molten droplets being in excess of 10^6 K/s and low oxygen partial pressure during plasma spraying [21]. It is well known that the rutile phase is a stable phase from the viewpoint of thermodynamics whereas the anatase phase is a metastable phase and will be transformed to rutile at about 1100K [22]. During plasma

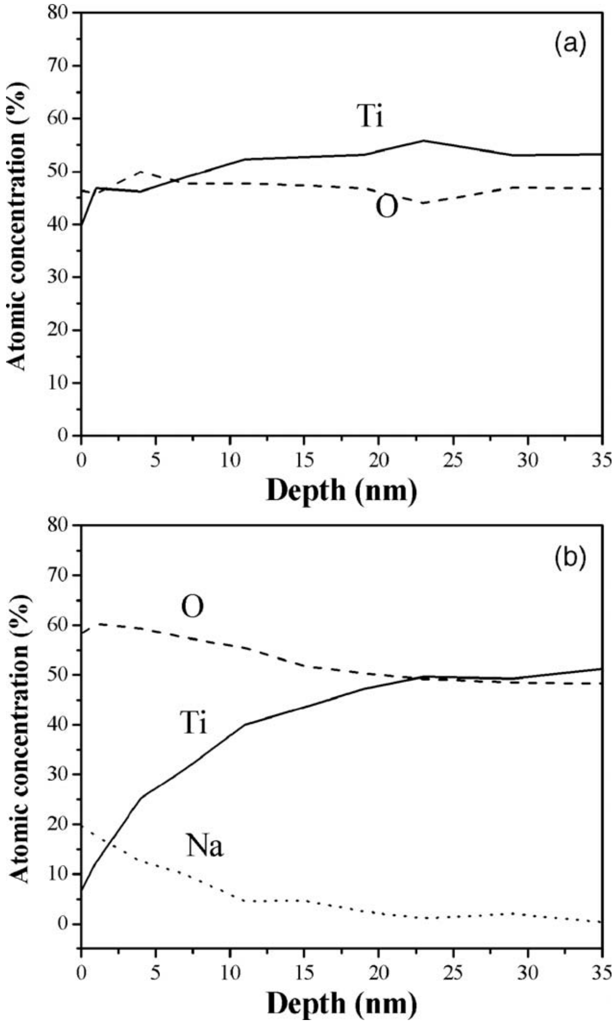

Fig. 5. AES depth profiles of TiO_2 coating: (a) as-sprayed, (b) treated by NaOH solution.

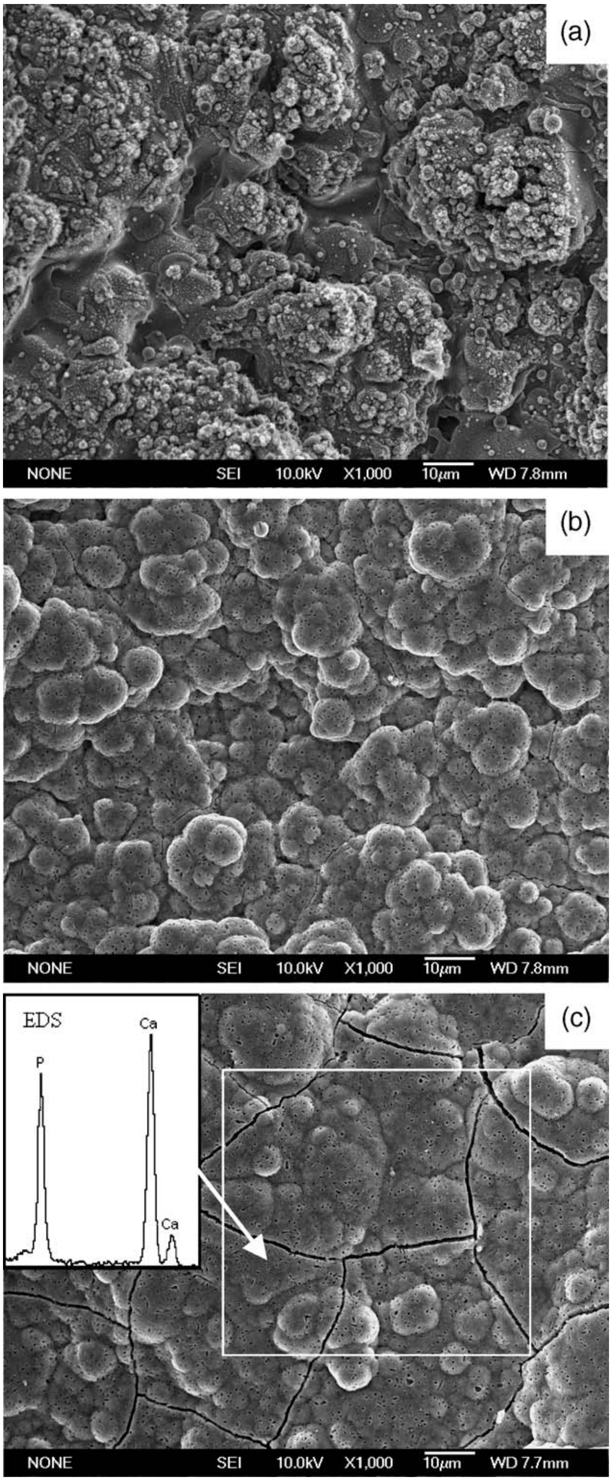

Fig. 6. Surface morphologies of TiO_2 coatings after SBF immersion: (a) as-sprayed after immersion for four weeks, (b) treated by NaOH and immersion for two weeks and (c) treated by NaOH and immersion for four weeks.

spraying, the powders are heated and accelerated and then projected onto the substrates, followed by flattening, rapid cooling and solidification. Hence, most powders are melted in the plasma flame. The metastable anatase phase can be partly retained due to the rapid cooling process. Some researchers have also reported that the TiO_2 coatings produced by plasma spraying consist mainly of the rutile phase with a low fraction of anatase phase, despite the crystalline structure of the initial powders [22,23].

The surface and cross sectional morphologies of the as-sprayed coating are displayed in Fig. 4. The as-sprayed coating exhibits a rough surface with some pores and the porosity is about 6% by Archimedes method. Excellent adhesion is observed between the TiO_2 coatings and Ti-6Al-4V substrate (Fig. 4b) and the bonding strength is about 38 MPa based on a tensile adhesion test (ASTM C 633-79).

The change in the surface chemistry after NaOH treatment is evaluated by AES depth profiling analysis, and the AES depth profiles of the TiO_2 coatings before and after NaOH treatment are shown in Fig. 5. The surface of the as-sprayed coating is composed of Ti and O (Fig. 5a). After NaOH treatment, Na is also found (Fig. 5b). The results indicate the formation of a sodium titanate layer on the TiO_2 coating after NaOH treatment.

Fig. 6 shows the surface views of the as-sprayed and NaOH-treated TiO_2 coatings after soaking in SBF for two and four weeks. In Fig. 6b, it can be seen that the surface of the NaOH-treated TiO_2 coating after SBF immersion for two weeks is completely covered by porous ball-like particles. The surface morphology is very different from that of the as-sprayed coating. After a longer immersion period, micro-cracks resembling those on a tortoise shell appear on the newly formed layer (Fig. 6c). After four weeks of SBF immersion, the entire surface of the NaOH-treated TiO_2 coating is covered by white crystals visible to the naked eyes. The EDS analysis corresponding to the features shown in Fig. 6c indicates that the newly formed layer on the surface of NaOH-treated titania coating is composed of calcium and phosphate. The EDS quantitative analysis gives a Ca to P ratio of around 1.53 that is nearly equal to the composition of hydroxyapatite (Ca/P=1.67). In contrast, the surface of the as-sprayed coating without NaOH treatment retains the original morphology after immersion in SBF for four weeks (Fig. 6a).

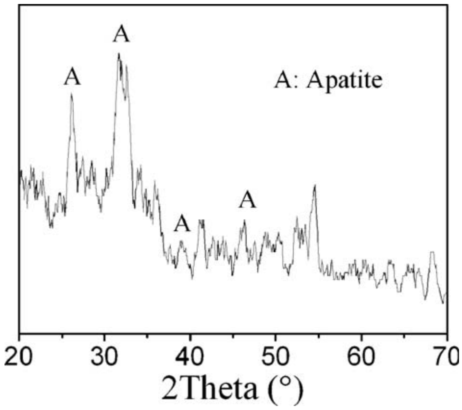

Fig. 7. TFXRD pattern of NaOH-treated TiO_2 coating soaked in SBF for four weeks.

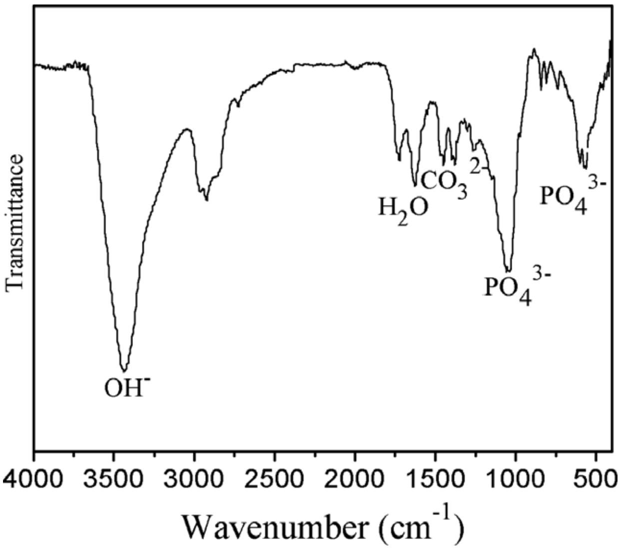

Fig. 8. FTIR spectrum of NaOH-treated TiO_2 coatings soaked in SBF for four weeks.

The thin film X-ray diffraction pattern acquired from the Ca-P layer on the NaOH-treated TiO_2 coating soaked in SBF for 4 weeks is exhibited in Fig. 7. The peaks corresponding to the crystalline apatite phase are observed in the TFXRD pattern. The peaks of the apatite crystallite were very broad, indicating that the apatite layer consists of superfine crystalline and/or defective structure grains [24]. Fig. 8 shows the FTIR spectrum of the NaOH-treated TiO_2 coating soaked in SBF for four weeks. The bands at 560–600 cm^{-1} and 1030–1090 cm^{-1} represent the characteristic peaks of the PO_4^{3-} group [25]. The band at around 1650 cm^{-1} can be assigned to absorbed H_2O characteristic of precipitates in aqueous solutions. The OH^- absorption around 3500 cm^{-1} is observed in the FTIR spectrum. The bands between 1400 and 1550 cm^{-1} indicate the presence of the CO_3^{2-} group [26]. The results obtained from TFXRD and FTIR suggest that the newly formed layer on the NaOH-treated TiO_2 coating is composed of carbonate-containing hydroxyapatite (bone-like apatite).

The mechanism of apatite formation on the surface of NaOH-treated coating in the SBF is similar to that on NaOH-treated titanium. TiO_2 reacts with the NaOH solution to form sodium titanate. The sodium titanate releases Na^+ ions via exchange with the H_3O^+ ions in the SBF to form Ti–OH groups on its surface. Li et al. suggested that OH groups on ceramic surfaces were effective in inducing the formation of an apatite layer [27]. The Ti–OH groups can form negative charges in the SBF solution and immediately combine with the positively charged Ca^{2+} ions in the SBF to form amorphous calcium titanate. This calcium titanate layer combines with phosphate ions in the SBF to form amorphous calcium phosphate and then the calcium phosphate transforms into apatite [28]. Once the apatite nuclei are formed, they spontaneously grow by consuming calcium and phosphate ions from the SBF solution. The calcium phosphate phase that accumulates on the surface of the NaOH-treated TiO_2 coatings is initially amorphous (a-CaP). It later crystallizes to a carbonate-containing hydroxyapatite (bone-like apatite) structure by incorporating carbonate anions from the solution with the a-CaP phase [29].

4. Conclusion

TiO_2 coatings were deposited on Ti-6Al-4V substrates using atmospheric plasma spraying. The as-sprayed coating is primarily composed of the rutile phase and a small amount of anatase and TiO_{2-x} (most of them is Ti_3O_5). The porosity of the as-sprayed coating is about 6% and the bonding strength between coating and titanium alloy substrate is about 38 MPa. After NaOH treatment, carbonate-containing hydroxyapatite (bone-like apatite) can be formed on the surface in SBF immersion tests. In contrast, no hydroxyapatite can be observed on the surface of the as-sprayed coating without NaOH treatment under the same SBF immersion conditions. Our results show that bioactivity can be induced on plasma-sprayed TiO_2 coatings by the NaOH solution treatment. The formation mechanism includes the formation of sodium titanate on the surface of the NaOH-treated TiO_2 coatings, followed by the release of $Na^+$from the sodium titanate via exchange with the H_3O^+ ions in the SBF to form the Ti–OH groups thereby inducing apatite precipitate on the surface of the treated TiO_2 coating.

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