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Fabrication and biocompatibility of nano-TiO_2/titanium alloys biomaterials

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Abstract

Using the process that titanium alloys were embedded by nanometer titanium dioxide powders and sintered in the high temperature furnace, the nano-TiO_2/titanium alloys biomedical material was fabricated out. The particle size of TiO_2 particles on the surface of Ti alloy was mainly 50–90 nm. The experimental results indicated that the films of nanocrystalline titanium oxide powders on the surface of Ti alloy were with an excellent biocompatibility. By cultivation in the simulated body fluid (SBF) for 7 days, the Ca phosphates were deposited on the specimen surface; and n (Ca)/n (P) atom ratio is about 1.6:1, which is similar to that of HA and human bone.

Keywords: Nanoparticles; Biomaterial; Simulated body fluid (SBF); Biocompatibility

1. Introduction

As biomedical materials, titanium and titanium alloys are superior to many materials such as stainless and pyrolytic carbon and so on, in terms of mechanical properties and biocompatibility. However, titanium and titanium alloys are still not sufficient for prolonged clinical use because the biocompatibility of these materials must be improved. Hence, the development of surface modification is a real necessity for the biomedical community. Titanium with a biocompatible coating such as HA has been successfully studied in recent years [1–7]. Titanium alloys are used for dental and orthopedic implants for its superior compatibility, which is attributed to the oxide film formed on its surface [1,2]. The surface modification recently becomes active in the field of implants, such as hydroxyapatite coating by plasma spraying or electrophoretic deposition [3–5], electrochemical deposition of Ca phosphates, basification treatment, sol-gel and anodized dielectric film [6–18]. In this research, we adopted nanometer titanium dioxide powders as the raw material, and embedded titanium alloys to sinter. By this way, a new biomaterial, the nano-TiO_2 biocompatible coating on the surface of titanium alloys, was fabricated out successfully. The method is a simple and adaptable technique for surface modification of the titanium alloys.

2. Experimental processing

Ti–2Zr–2Nb alloy ingots were carried out in a 25 Kg vacuum induction furnace by melting and casting. The ingots were machined into many specimens with a size of $20 \times 20 \times 8$ mm. Before sintering, specimens were polished and then rinsed by distilled water and acetone, subsequently degreased by hydrofluoric acid (5%), and washed by absolute alcohol and dried. Nanometer titanium dioxide powders were prepared by hydrolysis of titanium-tetrabutoxide with ethanol. The powder particle size of TiO_2 in the structure of anatase-type is mainly between 5 and 10 nm, as shown in Fig. 1. Titanium alloy specimens were embedded

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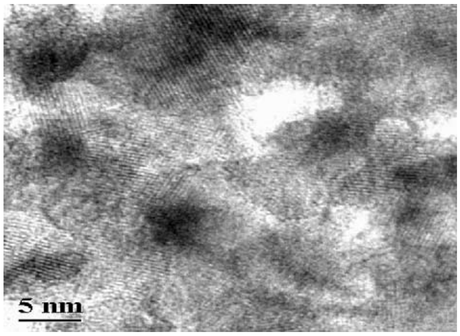

Fig. 1. HREM image of nano-TiO_2 particles synthesized.

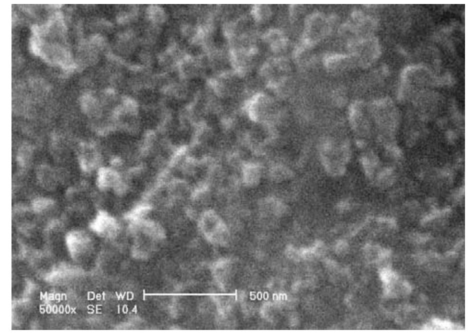

Fig. 2. The SEM micrograph of nano-TiO_2 coating.

by nanometer TiO_2 powders and sintered at 600 °C for 1 h, and annealed at 500 °C for 6 h in order to eliminate the residual stress of nano-particle-TiO_2 layer.

The microstructure evaluation and phase analysis of the single TiO_2 crystal nano-particles and sintered specimen surface were performed with a Philips Tacnai F20 high-resolution transmission microscopy (HREM), Philips XL30 TMP scanning electron microscopy (SEM), and X-ray diffractometry (Philips X' pert TMD). The specimens were cultivated in simulated body fluid (SBF) to test biocompatibility and bioactivity. Table 1 is the ion concentration of simulated body fluid and blood.

3. Result and discussion

The HREM image of nano-TiO_2 particles synthesized with the size of 5–10 nm is shown in Fig. 1. Fig. 2 shows the SEM micrographs of the coating. It is indicated in Fig. 2 that the particle size of TiO_2 particles of coating layer on Ti alloy matrix after sintering is about 50–90 nm. The oxide film synthesized is very thin (<3 μm), which is anatase-type TiO_2 after analyzed by XRD as shown in Fig. 3. Because titanium surface is oxidized easily in the air at room temperature, so a thin TiO_2 film with a size of 3–7 nm has been formed on the Ti matrix surface before sintering. While nano-TiO_2 particles is covered on the Ti matrix surface, the covered nano-TiO_2 particles are contacted with thin TiO_2 film, as shown in Fig. 4(a). Since nanometer effect, the free energy of the system, which contains nano-TiO_2 particles and nano-TiO_2 film, is very high at sintering temperature. In order to decrease the energy of the system, nano-TiO_2 particles begin to grow and connect with thin TiO_2 film on the surface of Ti matrix.

Because titanium dioxide powders are covered on the surface, titanium alloys are oxidized continuously by the diffusion of oxygen, and the small nano-TiO_2 particles begin to conglomerate and grow up. So the coating and substrate are well knitted at the sintering temperature, as shown in Fig. 4(b). At the same time, the heating temperature is not too high, which can prevent nano-TiO_2 particles from growing up too large. Finally, nano-TiO_2 particles (50–90 nm) coating layer (about 3 μm)/Ti biomaterial is carried out. However, the particle size will be 4–6 μm if specimens are enwrapped by ordinary commercially titanium dioxide powders.

Theoretically speaking, nanometer materials possess more excellent characteristics than ordinary materials. To test the biocompatibility of nano-TiO_2/titanium alloys, we dipped the materials in the simulated body fluid to cultivate. After 7 days, specimens were taken out of SBF, washed and observed surface morphology (Fig. 5). From Fig. 5 it was found that the Ca phosphates were deposited on the surface of specimens. The Ca/P deposition layer was constituted of cyathiform polygon calcium phosphate with irregular nanometer circles like honeycomb. The energy spectrum (Fig. 6) shows that n (Ca)/n (P) atom ratio is about 1.6 : 1, which is very similar to that of hydroxyapatite (HA). It can be concluded that nanometer TiO_2/titanium alloys possess favorable biocompatibility.

The presence of nano-TiO_2 particles layer on the titanium alloy matrix represents excellent biocompatibility and bioactivity. So the calcium phosphates can be easily deposited on the surface of nano-TiO_2 particles. The crushability strength of TiO_2 particles layer on the surface of the titanium alloy matrix was about 1060 MPa, which was carried out by Sansi-801 MTS system. Since TiO_2 is a ceramic phase with a high melting temperature, the interface of nano-TiO_2/titanium alloys is very stable at room temperature and elevated temperatures. Analogous to the tailoring of these films through control of pH and electrochemical cell potential [19–21], the encounter during annealing causes variations in the stable oxide forms. Previous studies have specifically noted the potential toxicological benefits of low vanadium oxide content of titanium implant materials [19,20], and hence the impact of the oxides

Table 1
Ion concentration of simulate body fluid and blood

Ion		Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	Cl^-	HPO_4^{2-}	SO_4^{2-}
Concentration/ mM	Blood	142.0	5.0	2.5	1.5	27.0	103.0	1.0	0.5
	SBF	142.0	5.0	2.5	1.5	4.2	148.5	1.0	0.5

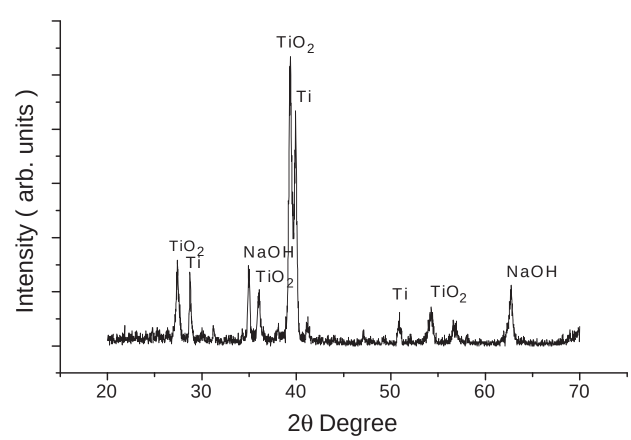

Fig. 3. XRD pattern of nanometer TiO_2 coating.