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ScienceDirect

Acta Biomaterialia 4 (2008) 553–559

Acta BIOMATERIALIA

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Apatite formation on alkaline-treated dense TiO_2 coatings deposited using the solution precursor plasma spray process

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Received 23 August 2007; received in revised form 29 October 2007; accepted 19 November 2007
Available online 26 December 2007

Abstract

A dense titania (TiO_2) coating was deposited from an ethanol-based solution containing titanium isopropoxide using the solution precursor plasma spray (SPPS) process. XRD and Raman spectrum analyses confirmed that the coating is exclusively composed of rutile TiO_2. SEM micrographs show the as-sprayed coating is dense with a uniform thickness and there are no coarse splat boundaries. The as-sprayed coating was chemically treated in 5 M NaOH solution at 80 °C for 48 h. The bioactivity of as-sprayed and alkaline-treated coatings was investigated by immersing the coatings in simulated body fluid (SBF) for 14–28 days, respectively. After 28 days immersion, there is a complete layer of carbonate-containing apatite formed on the alkaline-treated TiO_2 coating surface, but none formed on the as-sprayed coating.
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Keywords: Solution precursor plasma spray process; Titania coatings; Apatite; Alkaline treatment; Simulated body fluid

1. Introduction

Metallic materials (stainless steel, Co- and Ti-based alloys) are often used as orthopedic and dental implants in clinical practice because of their excellent mechanical properties such as high strength, ductility and toughness [1]. However, their near-bioinertness and dangerous metallic ions release are still major problems in clinical applications. For these reasons, the modification of biomaterials surface properties, which support bioactivity and corrosion resistance, is one of the key objectives in the design of orthopedic/dental implants. In recent years, there has been increasing interest in the formation of a bioactive surface layer on Ti and its alloy, which will induce apatite formation in the living environment or simulated body fluid [2–8]. Alkaline treatment of the Ti alloy has been widely used to induce bioactive apatite formation in simulated body fluid [2–7]. However, the effort to form a bioactive apatite layer on high concentration (10 M) NaOH-treated stainless steel in simulated body fluid at a temperature of 37 °C was not successful [2]. Therefore, it is desirable to deposit a bioactive surface layer on stainless steel to increase its bioactivity.

The bioactivity of TiO_2 gel, powder and films has been investigated recently. Li et al. [9] showed that titania gels form apatite on its surface in simulated body fluid, indicating that Ti–OH groups are able to induce apatite nucleation. Kasuga et al. [10] reported the apatite formation on TiO_2 powders in simulated body fluid after photoexcitation on the powders using Hg lamp and the apatite formation is due to the abundant negatively charged Ti–OH groups on the TiO_2 surface induced by the light-illumination. The apatite-formation ability of TiO_2 film was also investigated by Wu et al. [8] and Lin and Yen [11]. Besides the bioactivity of TiO_2, it was also reported that the titanium oxide film on the Ti surface can act as a chemical barrier against release of metal ions from the implant and thus greatly improve the in vivo corrosion resistance of the Ti implant [12]. Since the corrosion resistance is known to

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1742-7061/$ - see front matter Published by Elsevier Ltd. on behalf of Acta Materialia Inc.
doi:10.1016/j.actbio.2007.11.008

increase with the thickness of the oxide layer [13,14], a thick TiO_2 layer is desired to increase the corrosion resistance.

Recently, a solution precursor plasma spray (SPPS) process has been developed for the deposition of highly durable 7YSZ thermal barrier coatings with low thermal conductivity [15,16] as well as the deposition of dense, hard coatings [17]. In the SPPS process, liquid-precursor solutions are injected directly into the plasma jet. The atomized droplets undergo a series of physical and chemical reactions prior to deposition on the substrate as a coating. The SPPS method for the deposition of ceramic coatings offers several advantages over the conventional coating/thin film deposition methods, such as high-rate deposition of thick coatings, compositionally graded coatings, and deposition of nanostructured coatings. These advantages and the potential to deposit a wide range of ceramics (oxides and non-oxides) make the SPPS method technologically attractive.

In this research, the deposition of a TiO_2 coating on a stainless steel substrate using the solution precursor plasma spray process is presented. The bioactivity of as-sprayed and alkaline-treated coatings in simulated body fluid (SBF) was investigated and characterized.

2. Experimental procedure

The TiO_2 coatings were deposited using the direct current (DC) plasma torch (Metco 9MB, Sulzer Metco, Westbury, NY, USA), which was attached to a six-axis robotic arm. Argon and hydrogen are used as the primary and the secondary plasma gases, respectively. Nitrogen is used as the solution-precursor atomizing gas. The feedstock precursor used here was an ethanol-based solution containing titanium isopropoxide (97 wt.%, from Alfa Aesar). The coatings were deposited on the grit-blasted (Al_2O_3 grit of #30 mesh size), plasma preheated (preheating temperature ~200 °C) 304 stainless steel disk substrates (25 mm diameter, 3 mm thickness).

The as-sprayed TiO_2 coatings were ultrasonically washed in acetone and rinsed in deionized water, and then were immersed in 5 M NaOH solutions at 80 °C for 48 h. After washing in deionized water, the as-sprayed and NaOH-treated coatings were soaked in the simulated body fluid (SBF) solution made according to the recipe by Kokubo [18]. The SBF ion concentrations are nearly equal to those of the human blood plasma, as shown in Table 1. After soaking in SBF solutions for 14–28 days at 36.5 °C, the samples were taken out, and rinsed with deionized water.

The crystalline phase composition of all the samples was carried out using X-ray diffraction, XRD (Cu Kα radiation, D5005, Bruker AXS, Karlsruhe, Germany). The XRD patterns were collected in a 2θ range from 20° to 80° with a scanning rate of 2° min^{-1}.

Raman instrument (Renishaw™ Ramascope 2000. Renishaw, Gloucestershire, UK), using an Ar-ion 514 nm wavelength laser, was also used to identify the coating phase composition before and after SBF test.

The chemical composition and the binding state of elements in the as-deposited and NaOH-treated coating surface were characterized by X-ray photoelectron spectroscopy (XPS, VG Scientific ESCALAB Mark II) using the Mg Kα X-ray source and pass energy of 60 eV. All the spectra were calibrated at the C 1s binding energy (284.8 eV). Survey scans were performed up to 1100 eV at 1 eV s^{-1}. The data analysis was performed with CasaXPS software. The relative sensitivity factors were selected from the Scofield element library in CasaXPS.

An environmental scanning electron microscope (ESEM 2020, Philips Electron Optics, Eindhoven, the Netherlands) and a JEOL JSM-6335F field emission scanning electron microscope (FESEM) were used to characterize the coating microstructure.

3. Experimental results and discussion

3.1. Microstructure and phase composition of as-sprayed coating

In the SPPS process, 25 coating scans over the stainless steel substrate were carried out to produce the coating. Fig. 1 shows the SEM photographs of the surface and polished cross-section of the as-sprayed TiO_2 coating. Fig. 1a shows the coating is characterized by a rough surface with fully melted splats. The diameter of the splats range from 1 to 5 μm, whereas the splat diameters in a typical air plasma spray (APS) coating are in the range of 50–100 μm [19]. The area of the splats is two orders of magnitude smaller than those in APS coatings. The finer splats size can improve the contact between splats [16]. The polished cross-section (Fig. 1b) shows the as-sprayed TiO_2 coating is quite dense with a uniform thickness of ~30 μm. There are no coarse splats boundaries, which are always present in conventional APS coatings. It should also be noted that there are no horizontal or vertical cracks in the coating.

Table 1
Ion concentration of SBF

	Ion concentration								
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}	SO_4^{2-}	pH
SBF	142.0	5.0	1.5	2.5	147.8	4.2	1.0	0.5	7.4
Blood plasma	142.0	5.0	1.5	2.5	103.0	27.0	1.0	0.5	7.2–7.4