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Abstract

Titania (TiO_2) coatings were produced using the high velocity oxy-fuel (HVOF) technique on Ti-6Al-4V substrates. The titania feedstock powder exhibited nanostructured morphology, formed by a successive agglomeration of individual nanostructured titania particles (spray-drying) smaller than 100 nm. The resulting coatings were dense (porosity <1%) and exhibited rutile and anatase as phases with percentages of ~75% and ~25%, respectively. These coatings were heat-treated in a H_2/N_2 environment at 700°C for 8h. During the heat-treatment nanostructured titania fibers were formed on specific surface regions of the coatings. The nanofibers formed by this "chemical or reaction-based texturing" exhibited diameters of 50-400 nm and lengths in the order to 1-5 μm. It is thought that engineering these surfaces at nano and micro-scales may lead to interesting applications of titania coatings related to cell attachment/growth (for biomedical applications).

Introduction

Enhanced Biocompatibility of Nanostructured Materials

It has been demonstrated that nanostructured ceramics, such as, alumina, titania and HA exhibit higher osteoblast cell proliferation and adhesion (in vitro) when compared to their conventional counterparts [1]. Webster et al. [1] explained this better performance of the nanostructured material as the effect of the nanotexture of these materials on the adsorption of the adhesion proteins like vitronectin and fibronectin. These types of proteins mediate the adhesion of anchorage-dependent cells (such as osteoblasts) on substrates and coatings [1]. These adhesion proteins are initially adsorbed on the surface of an implant almost immediately upon its implantation in the human body. When the osteoblast cells arrive at the implant surface they "see" a protein-covered surface that will connect with the transmembrane proteins (integrins) of the osteoblast cells. It is important to point out that these proteins, such as vitronectin and fibronectin, exhibit nanosized lengths and structures. It is interesting to note that the surface of a nanostructured material (nanosized grains) will exhibit nanocharacteristics, like nanoroughness, whereas, the surface of a conventional material (microsized grains) will exhibit microcharacteristics. It was proven that the interaction or the adsorption of a nanosized protein (e.g., vitronectin and fibronectin) to a nanotextured surface will be more effective than that provided by a microtextured one [1]. Therefore engineering biomaterials containing nanotextured regions on their surfaces seems to be an interesting method to improve the adhesion of the osteoblast cells, contributing to a better long-term performance of the implanted material.

Engineering Nanotexture on Titania Surfaces

Yoo et al. [2, 3] were able to produce nano titania fibers on the surface of sintered titania (rutile). These nanofibers were formed on titania surfaces in a H_2/N_2 environment at 700°C for 8 h. The nanofibers formed by this process exhibited diameters of 15-50 nm and lengths of 1-5 μm. These results open interesting possibilities. Titania is also a biomedical material [1], therefore this process could be an asset to engineer specific nanotextured zones on titania surfaces, which may enhance the bioperformance of this class of biomaterial.

Biocompatible Titania Thermal Spray Coatings

Hydroxyapatite (HA) air plasma sprayed coatings have been employed for many years in hip-joint implants in order to promote the osteointegration of the bone tissue to the metallic implant (usually Ti-6Al-4V) [4]. Despite the success of this application, there are problems associated with HA coatings, which generally come from the low mechanical performance and dissolution of the HA coatings by the human body [5]. As an alternative to HA, titania coatings have been engineered to provide high mechanical performance and good biocompatibility [6]. These HVOF-sprayed coatings made from a nanostructured titania feedstock exhibited superior mechanical performance and biocompatibility when compared to air plasma sprayed HA coatings [6]. The goal of the present work was to perform a preliminary study by employing the technique developed by Yoo et al. [2, 3] to investigate the possibility of engineering an array of nanotextures on the titania coating surface. It is believed that this array of nanotextures, if correctly engineered, could enhance the biocompatibility of the coating surface by improving the adhesion and proliferation of the osteoblast cells, i.e., a stronger adsorption strength between the adhesion proteins (e.g., fibronectin) and the titania surface. Therefore the objective of this was to verify if these nanofibers could be developed on the surface of these HVOF-sprayed titania coatings made from a nanostructured feedstock by using the technique developed by Yoo et al. [2, 3].

Experimental Procedure

Nanostructured Titania Feedstock and HVOF Spraying

The nanostructured titania feedstock employed in this work (VHP-DCS (5-20 μm), Altair Nanomaterials Inc., Reno, NV, USA) exhibited a nominal particle size range from 5 to 20 μm. The feedstock powder was thermally sprayed via the HVOF technique using an oxy-propylene based torch (Diamond Jet 2700-hybrid, Sulzer Metco, Westbury, NY, USA). The coatings were deposited on Ti-6Al-4V substrates that had been grit-blasted to roughen the surface before spraying. Initially during HVOF spraying (before coating deposition), the velocities and temperatures of the titania particles in the spray jet were measured using a diagnostic tool (DPV 2000, Tecnar Automation, Saint Bruno, QC, Canada). The diagnostic tool is based on optical pyrometry and time-of-flight measurements to measure the distribution of particle temperature and velocity in the thermal spray jet. A total of 5000 particles were measured at the centerline of the thermal spray jet, where the particle flow density was the highest. The particle detector was placed at the same spray distance as used when depositing the coatings, i.e., 20 cm from the torch nozzle. During the spraying process on the Ti-6Al-4V substrates a cooling system (air jets) was applied to reduce the coating temperature, which was monitored using a pyrometer. The maximum surface temperature was approximately 240°C.

Nano and Microstructural Characterizations

The nanostructural and microstructural features of the feedstock and HVOF-sprayed coating were evaluated via scanning electron microscopy (SEM).

Phase Content

X-ray diffraction (XRD) (Cu Kα radiation) was used to determine the phases present in the titania feedstock and coating. A 2θ diffraction angle ranging from 20-60° (using a step size of 0.05° and step time of 2.5 s) was employed. A general model, developed by Berger-Keller et al. [7], for the quantitative XRD analysis of the volume percent of anatase in rutile-anatase mixtures was used based on the formula $C_A = 8I_A/(13I_R+8I_A)$; where C_A is the concentration of anatase (in volume), I_A is the intensity of the (101) anatase peak and I_R the intensity of the (110) rutile peak.

Heat Treatment

The as-sprayed coatings were heat-treated at 700°C for 8 h in a flowing 5% H_2/95% N_2 atmosphere.

Results and Discussion

Nanostructure of the Feedstock

When analyzed at high magnification it is possible to observe the nanostructured features of the feedstock (Fig. 1). Each microscopic feedstock particle is formed by agglomeration via spray-drying of innumerous individual nanosized particles of titania. All individual nanosized particles of titania exhibit a diameter not larger than 100 nm. Therefore it is confirmed that this feedstock is nanostructured.

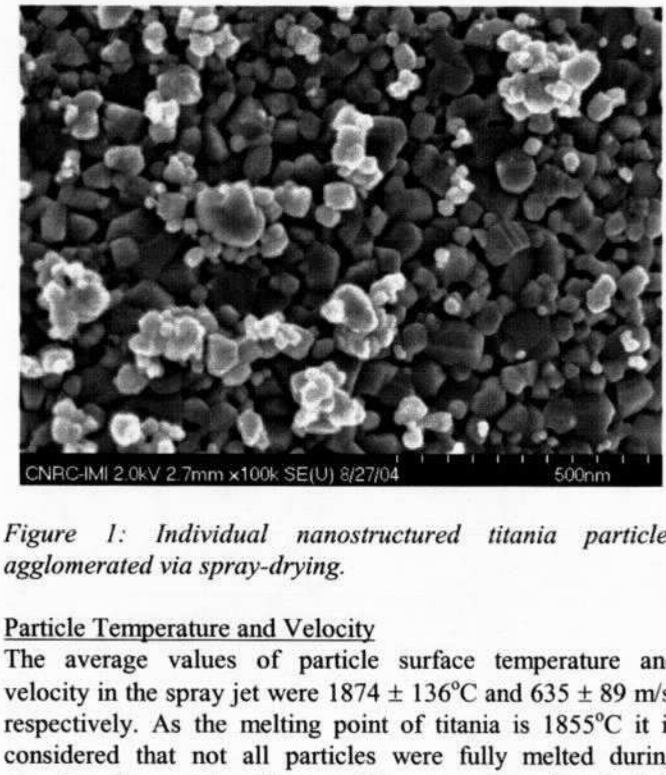

Figure 1: Individual nanostructured titania particles agglomerated via spray-drying.

Particle Temperature and Velocity

The average values of particle surface temperature and velocity in the spray jet were 1874 ± 136°C and 635 ± 89 m/s, respectively. As the melting point of titania is 1855°C it is considered that not all particles were fully melted during spraying, i.e., semi-molten particles were also deposited in addition to the fully molten ones. Therefore part of the original nanostructure of the feedstock is embedded in the coating microstructure as already shown in other references [6, 8].

Phase Structure of the Coating

The XRD pattern of the nanostructured titania feedstock is found in Fig. 2. Almost all feedstock structure exhibits anatase as the main phase, with a very minor content of rutile. The XRD pattern of the coating shows two phases, rutile and anatase (Fig. 3). Anatase transforms irreversibly to rutile at temperatures from 400 to 1000°C, therefore the anatase phase found in the coating probably represents the semi-molten particles embedded in the coating microstructure. The particles that were fully molten probably represent the rutile phase in the coating microstructure. According to calculations based on the XRD pattern, the percentage (in volume) of anatase phase in the coating is 25%.

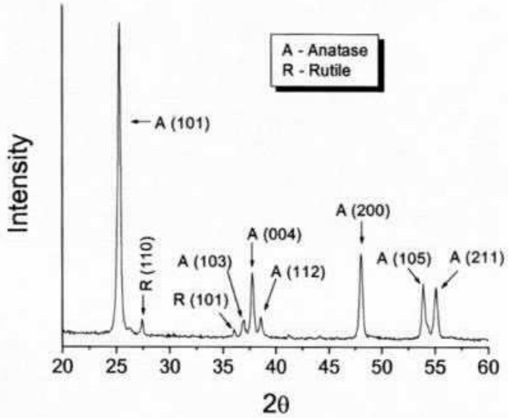

Figure 2: XRD pattern of the nanostructured titania feedstock powder.

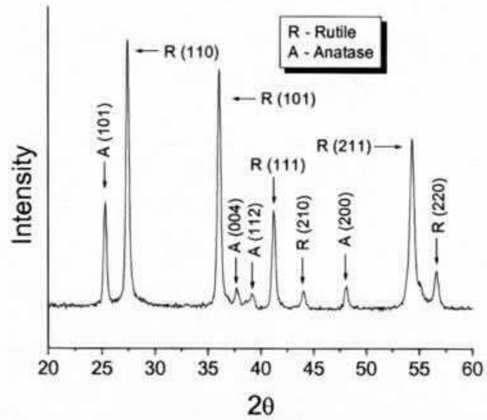

Figure 3: XRD pattern of the HVOF-sprayed titania coating produced from the nanostructured feedstock.

Nanostructured Titania Fibers

Figure 4 shows the nanofibers formed on the coating surface after the heat treatment. It is interesting to notice that different types of nanofibers were formed. Some nanofibers exhibit straight boundaries, like sharp blades (Fig. 4b), however, nanofibers with carved boundaries are also found (Fig. 4c). Round and thin nanofibers were also observed (Fig. 5).

To this point there are no solid studies to explain this phenomenon of nanofiber formation on the surface of the titania coatings. According to Yoo et al. [2, 3], the nanofibers formed on the surface of bulk titania were the result of an etching process, i.e., not a deposition process.

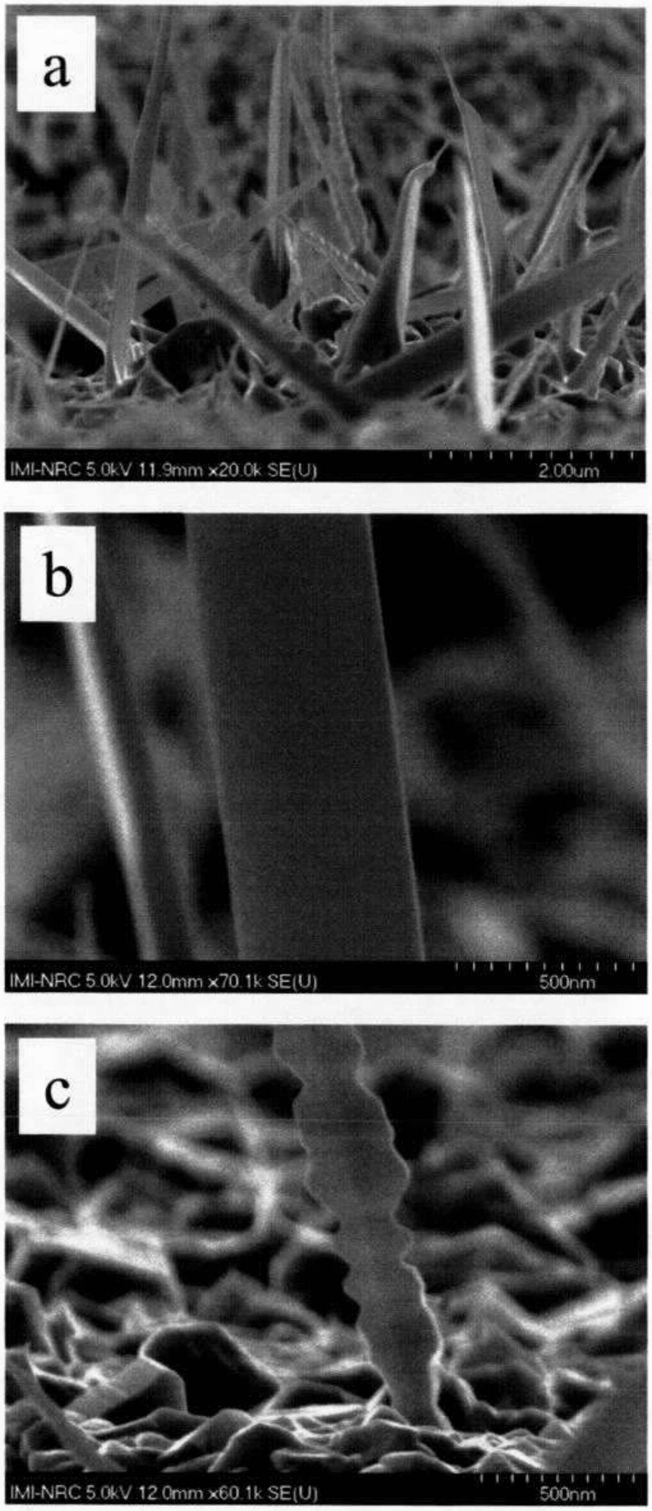

Figure 4: (a) General view of the nanofibers formed on the surface of the titania coating after heat treatment (700°C/8 h – H_2/N_2 atmosphere); (b) high magnification view of a nanofiber; (c) a nanofiber and the coating surface.

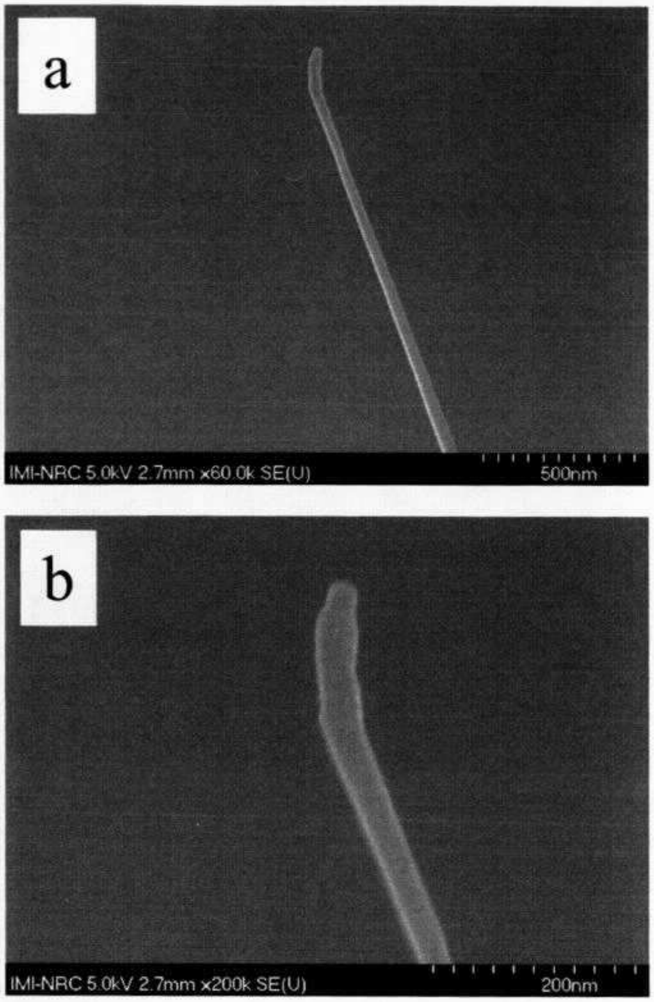

Figure 5: (a) Round and thin nanofiber formed on the surface of the titania coatings after heat treatment (700°C/8 h – H_2/N_2 atmosphere); (b) tip of the nanofiber.

Different impurities were found in the bulk titania samples, however, the role of these impurities on the nanofiber formation is not known. The fibers formed in this study seem to be a growth process and need to be further studied.

Yoo et al. [2, 3] also observed that differences in the sample density, grain size, sintering conditions and the control of gas flow rate during the H_2/N_2 treatment affect deeply the formation of the nanofibers. This is probably the reason why the nanofibers were formed in specific regions of the coatings, i.e., nanofibers were not observed throughout the coating surface. It was observed that the nanofibers formed in regions along or near the coating edges. Therefore for a massive production of nanofiber formation throughout the coating surface it is necessary to have an equilibrium of optimal microstructural and processing conditions.

Work is continuing in order to better understand the mechanisms that give rise to such behaviour and to find ways to promote a uniform distribution of nanofibers throughout the coating surface.

Conclusions

- The as-sprayed HVOF-sprayed titania coatings made from a nanostructured feedstock exhibited rutile and anatase as phases with percentages of 75% and 25%, respectively
- Nanofibers were formed on the coating surface after the as-sprayed coatings were heat treated at 700°C for 8 h in a H_2/N_2 atmosphere; a phenomenon equivalent to that observed by Yoo et al. [2, 3] in bulk titania.
- The nanofibers were produced (i) in specific regions of the coatings and (ii) exhibited different forms and shapes.
- To this point there are no strong scientific hypothesis to explain this phenomenon.
- It is thought that the formation of these nanofibers is the first step towards engineering nanotextures on the surface of these titania coatings, which may lead to an improvement of the bioperformance of these coatings.

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Lima, Rogerio

From: Akbar@matsceng.ohio-state.edu on behalf of Sheikh A. Akbar [Akbar@matsceng.ohio-state.edu]

Sent: Wednesday, June 22, 2005 11:43 AM

To: Lima, Rogerio

Subject: Re: International Thermal Spray Conference 2006

We do not have any problem with this idea. Make sure you include my student (Huyon Lee) as a co-author.

Best regards.

Sheikh
****
At 11:18 AM 6/22/2005, you wrote:

> Dear Sheikh,
>
> Once a year, every year, we (thermal spray researchers) have our main conference, the International Thermal Spray Conference (aka ITSC). In this conference thermal spray researchers from all over the world join together to show and discuss the latest advances in thermal spray science and technology. This conference is held in a city in North America, Europe or Asia. This year the ITSC 2005 was in Basel (Switzerland). Next year the ITSC 2006 will be held in North America (Seattle, WA) from May 15 to May 18. In 2007 the ITSC will be in Beijing, China.
>
> I would be delighted to present some of these nano TiO_2 rods results (on the TiO_2 coatings) that we have produced in the ITSC 2006 (15-18 May). This is the website of the conference: http://www.asminternational.org/itsc/
>
> I would like to know your opinion about that. I will have to submit an abstract before July 31st.
>
> Regards,
>
> Roger

Fabrication of Nanostructured TiO_2 Fibers on TiO_2 Coatings Produced from a Nanostructured Feedstock

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[b] Ohio State University (USA)

Titania (TiO_2) coatings were produced using the high velocity oxy-fuel (HVOF) technique on Ti-6Al-4V substrates. The titania feedstock powder exhibited nanostructured morphology, formed by a successive agglomeration of individual nanostructured titania particles (spray-drying) smaller than 100 nm. The resulting coatings were dense (porosity <1%) and exhibited rutile and anatase as phases with percentages of ~75% and ~25%, respectively. These coatings were heat-treated in a H_2/N_2 environment at 700°C for 8h. During the heat-treatment nanostructured titania fibers were formed on specific surface regions of the coatings. The nanofibers formed by this "chemical or reaction-based texturing" exhibited diameters of 50-200 nm and lengths in the order to 1-10 μm. It is thought that engineering these surfaces at nano and micro-scales may lead to interesting applications of titania coatings related to (i) cell attachment/growth (for biomedical applications) and (ii) photocatalytic properties. The possible mechanisms of nanofiber formation are discussed.