Iranian Journal of Pharmaceutical Sciences
Winter 2008: 4(1): 17-22
www.ijps.ir

Original Article

Sol-Gel Derived Titania Coating on Titanium Substrate

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Abstract

The synthesis of titania via sol-gel method has been widely studied. In the present work, titania was deposited onto a titanium substrate via sol-gel method. Different processing parameters such as the repetition number of dipping/heat treatment process and dipping time have been studied to obtain the homogenous titania coating. Phase and microstructural evaluation of the powder and coating samples were performed, using X-ray diffraction and scanning electron microscopy. The particle size distribution of the powder was measured by zetasizer instrument. Based on the results obtained in this work, both rutile and anatase phases formed after the heat treatment at 600 °C. In addition, the thickness and the morphology of the coatings were found to be influenced by the repetition number of process.

Keywords: Anatase; Coating; Nano powder; Rutile; Sol-gel.
Received: December 6, 2007; *Accepted:* January 15, 2008

1. Introduction

New biomaterials are being constantly developed to respond to the need for better mechanical properties and biocompatibility. In the recent years, the synthesis of bioceramic films on the selected metal surfaces has been attracting considerable attention, as a result of the successful combination of the good mechanical properties of metals and the good chemical stability of ceramic films. A titania film is a well-known material used in a wide variety of applications such as catalysts, sensors and solar cells [1-5]. Recently, the use of this material has been extended to medical applications, for example, as a modifier of surface of orthopedic and dental implants and artificial heart valve [6]. Many investigations have demonstrated that these films have good blood compatibility [4].

Titania exists in three polymorphs: Rutile, anatase and brookite. Rutile is considered as a stable form of titania. Anatase is metastable and converts to rutile at temperatures between 400 and 1200 °C which can be accompanied by grain growth. Titania has different properties depending on its polymorphs. The temperature of anatase to rutile transformation depends on the particle size. For small particle sizes (<50 nm), anatase seems to be more stable and transforms to rutile at 700 °C [3, 6, 7].

A number of techniques have been reported for the synthesis and formation of nanocrys-

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talline titania films. These include the sol-gel processing, the ion beam enhanced deposition (IBED), the plasma immersion ion implantation (PIII) and the vacuum plasma spraying (VPS) [6, 15]. The sol-gel technology is a low temperature method for the film preparation via chemical routes. Its principal advantages are the control of surface morphology and composition [8]. Previous studies on the surface modification of titanium alloys with titania have indicated that the sol-gel derived TiO_2 films have good bioactivity. These films can play an important role in the nucleation of hydroxyapatite and other calcium phosphate phases, not only at *in vitro* but also at *in vivo* conditions [4, 8]. This bioactive behavior is attributed to the presence of hydroxyl groups. The resulting Ti-OH bonds promote the interactions with bone cells by providing the sites for the Ca and P nucleation [9-14].

2. Materials and methods

The sol-gel process started with the preparation of a TiO_2 sol. To produce a TiO_2 sol, titanium propoxide ($Ti(OCH_2CH_2CH_3)_4$, Aldrich, UK) was hydrolyzed within an ethanol-based solution, containing diethanolamine [$(HOCH_2CH_2)_2NH$, Aldrich, UK] and distilled water. This mixture was stirred at room temperature for 24 h at 500 rpm and then at 60 °C for 72 h (200 rpm). The molar ratios of diethanolamine/Ti and water/Ti were 1 and 2, respectively. The titania solution was devided in two parts. One part was used for the titania powder preparation, whereas the rest was left for coating process.

For the titania powder preparation, the titania gel was dried at 150 °C and heat treated at 600 °C for 1 h. For the coating process, the disc samples of commercially pure Ti (cp Ti) were sequentially polished with abrasive papers (400, 600, 800, 1000 and 1200 grit) and washed in acetone and ethanol. The Ti substrates were dipped into titania gel with a rate of 1 cm/min. To increase the thickness and homogenous distribution of coatings, the samples experienced several dipping/heat treatments. The details of the repetition number of dipping/heat treatment process and dipping time in the solution are summarized in Table 1. After drying at 60 °C for 10 min., the samples were heat treated at 600 °C for 1 h. X-ray diffraction (XRD, Siemense diffractometer) and scanning electron microscopy (SEM, Philips, XL30) were used for the phase and microstructural characterizations of the titania powder and the coated samples. The particle size distribution of the powder was measured by zetasizer instrument (Zetasizer, Malvern Instrument, Co, 3000 HAS).

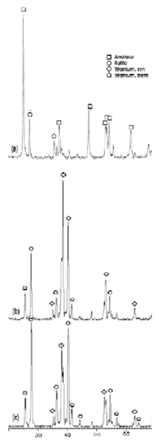

Figure 1. The XRD pattern of the TiO_2 powder and coatings after heat treatment at 600°C. (a) TiO_2 powder; (b and c) TiO_2 coating for the samples (# 5) and (# 4), respectively.

3. Results and discussion

3-1- XRD analysis

The crystal structure of the TiO_2 powder and the coatings were characterized using XRD. Figure 1 (a-c) shows the XRD patterns of the TiO_2 powder and coatings after heat treatment at 600 °C. The traces of anatase and rutile phases can be identified in these patterns. It can be deducted that heat treatment

Table 1. The details of coating process of titania.

Sample number	1	2	3	4	5	6	7
Dipping time in the solution (min.)	-	1	1	1	2	3	4
repetition number of dipping/heat treatment process	-	2	3	4	2	2	2

at 600 °C lead to form the highly crystalline titania phases. It is thought that this phase distribution can improve the likelihood of bone-like apatite nucleation [10, 13].

Figures 1b and 1c present the phase transformation from anatase to rutile with increasing the repetition number of heat treatment. For instance, for the sample 4, which was heat treated 4 times, the peak intensities of the rutile phase increased severely in comparison with the sample 5, which was heat treated 2 times.

3.2. Size and morphological analysis

Figure 2 shows the particle size distribution measured in different media containing pure ethanol, pure methanol, pure distilled water and hexamethaphosphate-added distilled water. The three ultrasonic agitation time were studied during zetasizer experiment in the optimum media (hexamethaphosphate-added distilled water) (Figure 3). An average particle size of 135 nm was measured using an agitation time of 15 min. Figure 4 illustrates the SEM photograph of the powder sample after the heat treatment at 600 °C at high and low magnification. The agglomerates shown in this figure are composed of very small grains of about 100 nm. Taking into account the SEM images and the particle size distribution, it seems the agglomerates seen in SEM direct observation are well dispersed during the zetasizer sample preparation.

3.3. SEM analysis

3.3.1. The effect of repetition number of dipping/heat treatment process

The effect of the repetition number of dipping/heat treatment process on the surface morphology was also investigated (Figure 5). As shown in this figure, the increasing of repetition number of dipping/heat treatment process enhanced the homogeneity and the number of titania particles formed on the

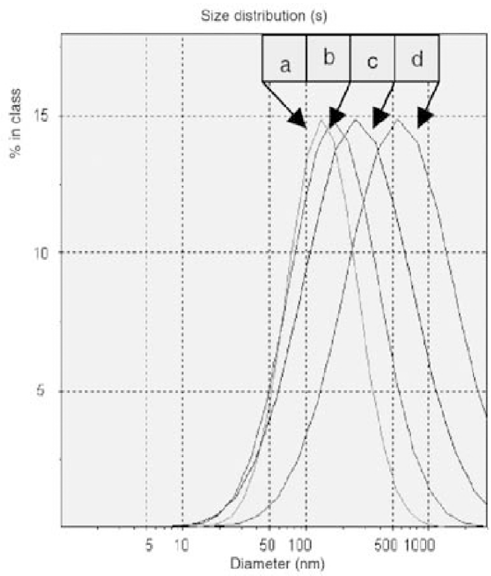

Figure 2. Particle size distribution of powder sample in different media: (a) hexamethaphosphate-added distilled water, (b) pure ethanol, (c) pure methanol, (d) pure distilled water.

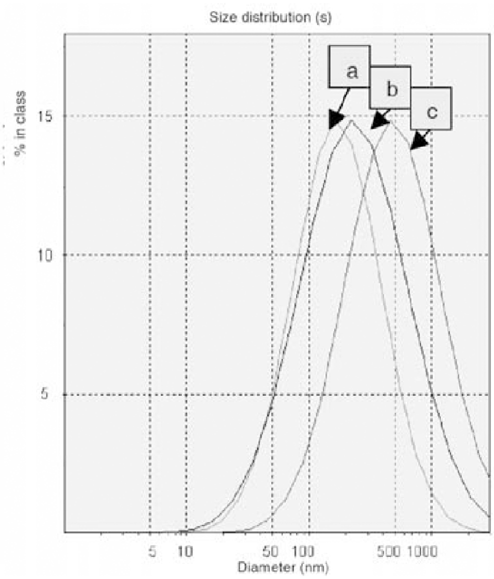

Figure 3. Particle size distribution of powder sample prepared at different ultrasonic times: (a) 15 min., (b) 10 min., (c) 5 min.

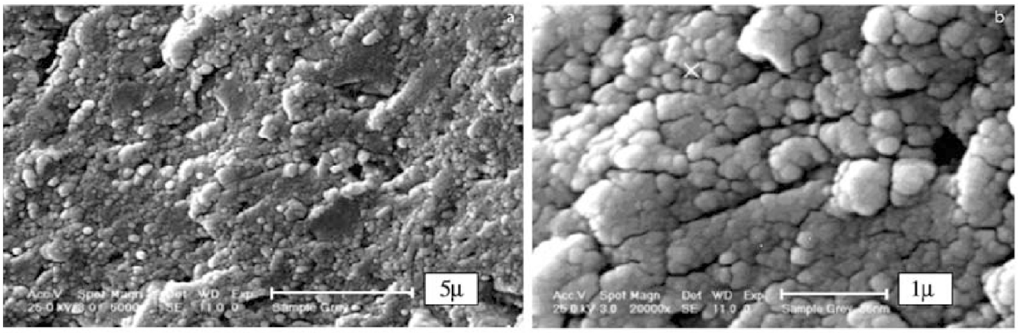

Figure 4. SEM micrograph of the TiO_2 powder after heat treatment at 600 °C, a) × 5000, b) × 20,000.

surface of titanium. Taking into account the results of XRD analyses, it seems that the size of primary particles (Figure 5-b) has not affected by the repetition number of dipping/heat treatment process. For the samples quadruply dipped/heat treated (Figure 5-d), the small rutile particles appeared between the big primary particles.

The cross sectional view of the samples, doubley and triply dipped/heat treated are presented in Figure 6. Using a repetition number of dipping/heat treatment process 3 times led significantly to increase the thickness of coatinng. The thickness of coatings attained to several micrometers for these samples. There is no obvious discontinuity between the deposited coatings and the underlying substrate. It can be concluded that the TiO_2 coatings are adhered to the Ti substrate.

3.2.2. The effect of dipping time

Figure 7 displays the SEM morphologies of the samples experienced different dipping time. The samples (#5, #6 and #7) were heat treated at 600 °C for 1 h. These images reveal that with the increase of dipping time the grain size diminishes. It can be due to the activation of more sites for the nucleation of new titania resulting to a more homogenous coating.

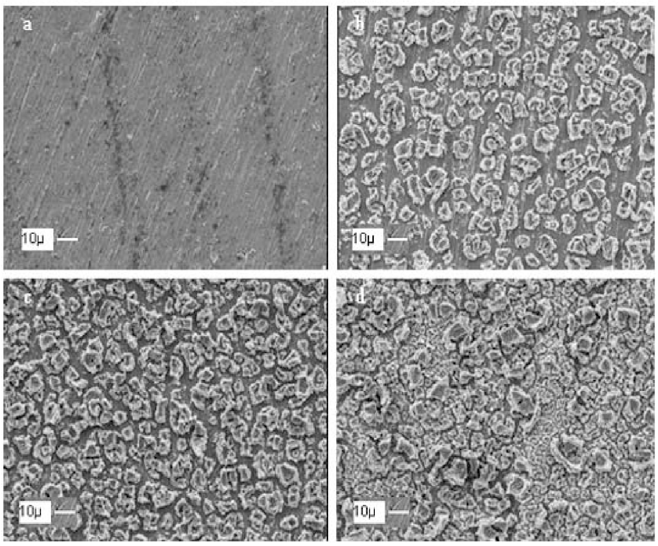

Figure 5. SEM micrographs of the samples: (a) uncoated sample, (b) doubley, (c) triply, (d) quadruply dipping/heat treated (at 600 °C).

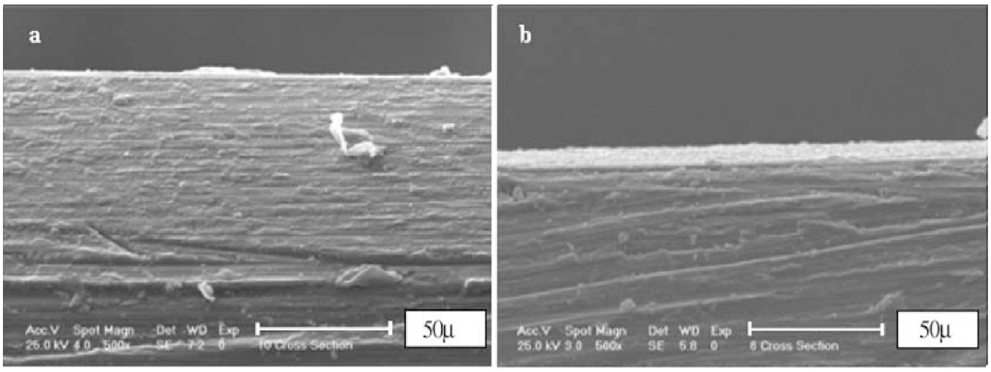

Figure 6. Cross sectional view of the coated samples: (a) doubley, (b) triply dipping/ heat treated.

4. Conclusion

The study of the titania powder and coating on titanium, prepared with the sol-gel process, disclosed the simultaneous presence of the rutile and anatase phases in the titania powder and coating, after heat treatment at 600 °C. Base on the zetasizer experiment results, the sol gel derived titania powder contained the particles with an average size of 135 nm. Accordingly, the agglomerates shown in the SEM images were well dispersed during the zetasizer experiment. Furthermore, the rutile characteristic peak intensities increased with the increasing of repetition number of dipping/heat treatment process. The homogeneity of titania microstructure

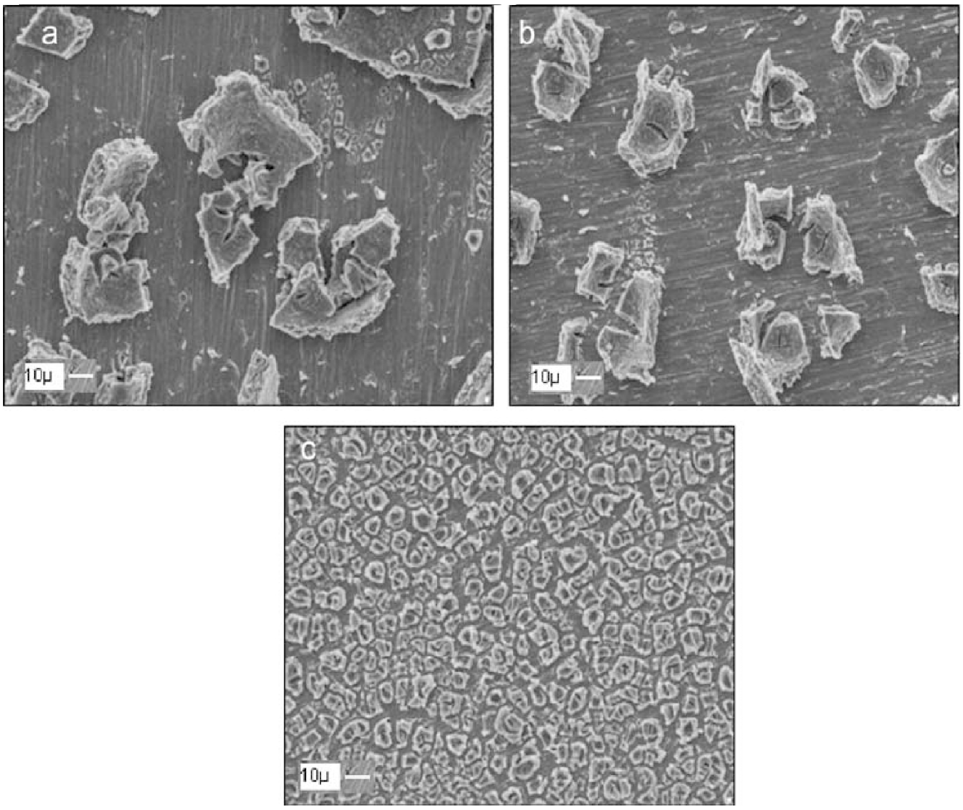

Figure 7. SEM images of coated samples with different dipping times: (a) 2 min., (b) 3 min., (c) 4 min.

enhanced with the repetition number of dipping/heat treatment process and dipping time.

Acknowledgments

The authors of this article acknowledge the support of the laboratory complex center of Islamic Azad University, Science and Research Branch, the kind help from the Geology and Mineral Discovery Institute for the Performance of the XRD analyses and the SEM laboratory of Tarbiat Modarres University.

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