JOURNAL OF THE MECHANICAL BEHAVIOR OF BIOMEDICAL MATERIALS 4 (2011) 756–765

available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/jmbbm

Research paper

Nanomechanical and nanotribological properties of bioactive titanium surfaces prepared by alkali treatment

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ARTICLE INFO

Article history:
Received 26 March 2010
Received in revised form
2 July 2010
Accepted 10 July 2010
Published online 17 July 2010

Keywords:
Alkali-heat treatment
Sodium titanate
Bioactivity
Elastic modulus
Hardness
Nanoscratch

ABSTRACT

Alkali-heat treatment (AHT) is a simple and practical method to make titanium surfaces bioactive. Hydroxyapatite nucleates on Ti when in contact with body fluids due to the presence of a thin sodium titanate film produced by the AHT. This method was proposed more than a decade ago and it has been widely investigated at varied scopes. However, there is still little information about the mechanical properties of this film. In this work, the tribo-mechanical behavior of films produced by alkali treatment (AT) and AHT on Ti is investigated using instrumented indentation technique. The films were also characterized by TF-XRD, SEM, EDS and *in vitro* bioactivity tests. Analytical methods were employed to obtain the mechanical properties of the film from instrumented indentation data. The heat treatment subsequent to the alkaline processing increased the film elastic modulus from 1.7 GPa to 2.8 GPa, the hardness from 12 MPa to 20 MPa and the critical load for scratch test from 1.5 mN to 5.5 mN. Despite the overall improvement in the film bioactivity and tribo-mechanical behavior, the AHT elastic modulus is only 2% of the pristine Ti whereas hardness is less than 1%. This information must be considered for implant design purposes.

1. Introduction

Titanium is a bioinert material regarding the body surroundings and is commonly used as artificial dental and orthopedic replacements (Liu et al., 2004; Niinomi et al., 2004; Park and Kon Kim, 2000). Among the several existing methods to make titanium surfaces bioactive (Chu et al., 2002; de Jonge et al., 2008; Liu et al., 2004), the alkali-heat treatment (AHT) is a simple and practical one, proposed by Kim et al. (1996) more than one decade ago. In this process, the Ti surface is submitted to a chemical treatment by using alkali solutions, namely sodium hydroxide, in which native surface oxides and (mainly) metallic species are converted to form a hydrogel film. Subsequent heat treatment in air at 600 °C dehydrates the hydrogel film, stabilizing it as amorphous sodium

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doi:10.1016/j.jmbbm.2010.07.005

titanate containing a small fraction of crystalline phase (de Souza et al., 2010a; Liu et al., 2004; Kim et al., 1996, 1997a). Afterwards, other modified AHT protocols (combined with water or calcium chloride treatments) were proposed and have been examined to improve the titanium surface bioactivity (Fujibayashi et al., 2001; Kizuki et al., 2009; Takemoto et al., 2005, 2006; Uchida et al., 2002).

According to the mechanism described by Takadama et al. (2001a,b), at the implant site, the AHT titanium surface interacts with the physiological body fluids nucleating hydroxyapatite (HA). This situation can be nicely reproduced *in vitro* by using simulated body fluid (SBF) solutions (Kokubo and Takadama, 2006; Müller and Müller, 2006; Resende et al., 2008). The formed HA is similar to the natural apatite that constitutes the bone mass, so that it behaves as an interconnection between the implant and osseous tissues (Kim et al., 1997a, 2003; Liu et al., 2004; Takadama et al., 2001a,b; Yamaguchi et al., 2009). The potentiality and interest of this method can be illustrated by the commercialization and clinical use in Japan of an artificial total hip joint processed by AHT (Kizuki et al., 2009; Yamaguchi et al., 2009). In addition, the alkali treatment is currently employed in association with other techniques in order to produce bioactive Ti devices (Jonásová et al., 2004; Rakngarm et al., 2008; Takemoto et al., 2006).

The goal of the heat treatment of the alkali-treated film on Ti is to improve the film–substrate adhesion and consequently improve the osseointegration, since the formed hydrogel on Ti is mechanically unstable, as qualitatively demonstrated by stuck–pull tests with adhesive tape (Kim et al., 1997a; Wei et al., 2002). After periods of *in vivo* implantation, mechanical tests were carried out by Nishiguchi et al. (1999) and Nishiguchi et al. (2001) in order to evaluate detaching and shear stresses of bones connected to Ti and Ti alloys. The authors reported that the implants with surfaces modified by AHT presented a higher performance in the mechanical tests cited above compared to the untreated implants and to the ones that were only alkali treated. These authors also reported that direct implant–bone connection, without any intervening fibrous tissues, was observed only in the AHT samples, which also achieved maximum fixation strength in earlier periods of *in vivo* implantation. Consequently, the AHT is an effective process to promote Ti osseointegration.

Notwithstanding, several works are devoted to characterize the AHT technique at varied scopes, and as described in the literature, the mechanical properties of the produced bioactive film needs a better description and interpretation in order to optimize the design of the body implants. In order to contribute to the understanding of the tribo-mechanical properties of alkali treated and alkali-heat treated modified Ti surfaces, the present work reports results about elastic modulus, hardness and nanoscratch tests obtained by the instrumented indentation technique.

2. Materials and methods

Samples of cp-Ti, grade 2 (N 0.03%, C 0.06%, H 0.005%, Fe 0.028%, O 0.132% in weight, with Ti being the balance), were cut in 1 cm × 2 cm × 0.2 cm plates. A mirror-like surface finishing was obtained with P600 SiC paper followed by 9 μm diamond paste and colloidal silica suspension mechanical polishing. The plates were successively washed with acetone, isopropyl alcohol and distilled water in an ultrasonic cleaner to eliminate any undesired surface contaminations.

The alkali treatment (AT) and alkali-heat treatment (AHT) were performed according to the protocol described by Kim et al. (1997a) and Liu et al. (2004), using 5M NaOH aqueous solution for 24 h at 60 °C. The alkali-treated samples (AT) were gently washed with distilled water and dried at 40 °C for 24 h. Selected AT samples were submitted to heat treatment (to become AHT samples) in atmospheric air at the rate of 5 °C/min until 600 °C. This temperature was kept for 1 h and then cooled until room temperature. At the same time, a Ti sample was maintained in the alkali solution for 72 h (named AHT-72 sample), and then heat treated according to the process described above, with the aim to produce thicker films for the hardness determination by instrumented indentation. In order to verify the effects of the heat treatment on the Ti substrate, the heating procedure used in the AHT samples was also performed in polished Ti under $5 \cdot 10^{-4}$ Pa vacuum pressure to minimize the oxide formation near the surface.

Untreated, AT and AHT samples were soaked in a simulated body fluid (SBF), prepared according to the Kokubo and Takadama (2006) recipe, at 36.5 °C, for 14 days, in order to verify the surface bioactivity.

Surface structural modifications were identified by Thin Film X-ray Diffraction (TF-XRD), using Cu K_α radiation with a glancing incidence angle of 1°. The scan velocity was 0.5°/min across the angular range of $20° \leq \theta \leq 60°$. The diffraction peaks were indexed according to the Inorganic Crystal Structure Database—ICSD) (FIZ Karlsruhe GmbH, 2008).

Hardness and elastic modulus profiles were obtained by instrumented indentation following the Oliver and Pharr (2004) method. The applied loads ranged from 0.14 to 300 mN in twelve successive loading/unloading cycles at increasing loads using a Berkovich diamond indenter. The nanoscratch tests were carried out with the Berkovich tip by the same instrumented indentation device. The ramping loads reached 10 mN, applied for 600 μm following the tip edge direction. The tip penetration profiles were monitored before, during and after the scratch test. The profiles during the loading and the elastic recovery were determined taking into account the original surface topography.

The modified surfaces and the scratch morphologies were analysed by scanning electron microscopy (SEM). Electron dispersive X-ray spectroscopy (EDS) was employed to observe the surface elemental composition.

3. Results

3.1. *Structural features, morphology and bioactivity*

The results in this section are presented in order to confirm that the produced films are bioactive. Fig. 1 presents TF-XRD patterns of the treated Ti samples, before and after the *in vitro* bioactivity tests. Fig. 1(a) shows patterns of Ti samples submitted to the AT and AHT. The untreated Ti, not shown