Wear 305 (2013) 8–13

Contents lists available at SciVerse ScienceDirect

Wear

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

Tribological characterization of biocompatible HAp-TiO_2 coatings obtained by high velocity oxy-fuel spray

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ARTICLE INFO

Article history:
Received 21 January 2013
Received in revised form
13 May 2013
Accepted 27 May 2013
Available online 2 June 2013

Keywords:
Ceramics
Thermal spray coatings
Biotribology
Wear testing

ABSTRACT

Bioceramic coatings have been employed for many years to improve the biological, and consequently the mechanical, properties of bone implants. However, only a few studies have focused on wear behavior, which has been considered of secondary importance compared to other properties. The present study demonstrates that contrary to this assumption, it is important to guarantee the integrity of the coatings during and after implantation, a process that subjects the surface to high wear. Reciprocating ball-on-flat tests were performed to characterize the wear properties of HAp-TiO_2 coatings, which have previously been shown to present other good mechanical and biological properties. An alumina ball was used as counterface and the tests were conducted at 37 °C immersed in Hank's solution, to simulate physiological conditions. Three loads were employed: 5 N, 10 N and 15 N. The results show a clear advantage of more compact coatings, with a lower percentage of amorphous phases, since they present a higher friction coefficient. That could indicate, according to the literature, better implant fixation and a lower wear rate, and thus ensure the integrity of the coating.

1. Introduction

Bioactive and biocompatible coatings have been employed for many years to improve the biological behavior of bone prostheses (dental, hip and shoulder implants, etc.) [1]. The requirements of such coatings include good cell behavior on their surface and optimal mechanical behavior [2,3], in order to guarantee the stability of the coating under physiological conditions. The most commonly evaluated properties are adherence (using the bond strength test or scratch test) [1], shear strength [4] and fracture toughness [5], whereas other properties, such as the wear behavior of coatings, receive less attention. Although there are many studies of the tribological behavior of joint coatings at the wear surface of the joint [6,7], there are very few which report these kinds of test for bone–implant interface coatings, and the majority of these focus on fretting, i.e. micro-movements of the device with respect to the bone due to differences in the elastic response of the two materials [8,9]. However, coatings are subjected to considerable wear from the time the implant is placed into the bone until it is completely stabilized [10]. Following implantation, coating debris may be present between the coating itself and the surrounding bone tissue [10]. Although some studies have reported that these particles are innocuous and even improve mechanical interlocking and fixation [11], other studies have concluded that this debris could interfere in osseointegration [12]. In fact, any lack of coating integrity that may arise could provoke contact between the bone and metallic substrate and the consequent migration of metallic ions [13] and loss of direct bonding between tissue and implant [14].

The most extensively employed materials – industrially at least – to produce biocompatible coatings are ceramics; usually hydroxyapatite and normally obtained by plasma-spraying [1]. Hydroxyapatite presents good biocompatibility because of its similitude to bone [15], but it lacks good mechanical properties [16]. Specifically, and according to studies conducted on the tribological behavior of hydroxyapatite, it is evident that it is very susceptible to wear [8]. In recent years, many options have been considered to improve the mechanical behavior of hydroxyapatite coatings. Examples include the use of interlayers between substrate and coating [17], heat treatments [18] or its combination with other compounds such as carbon nanotubes [19] or ceramics (SiO_2 for instance) [20].

In this study, two approaches are employed to obtain biomedical coatings and to study their wear behavior. One of them is to mix hydroxyapatite powder with titania powder, which shows better mechanical properties in general and better wear behavior in particular. The other consists of substituting plasma-spraying by high-velocity oxy-fuel (HVOF) spraying. Both options have been

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http://dx.doi.org/10.1016/j.wear.2013.05.009

shown to have a positive influence on mechanical behavior in general [20]. The goal of this study, however, is to evaluate the influence of the two approaches on tribological behavior, in order to ensure that the coating behaves correctly and detect possible negative consequences.

2. Experimental method

2.1. Coatings obtention and characterization

The raw material was a mechanical mixture of TiO_2 (rutile) powder (20 wt%), supplied by Sulzer-Metco, and hydroxyapatite powder (80 wt%), obtained from Plasma-Biotal Ltd. The mixture was thermal-sprayed onto a previously grit-blasted Ti6Al4V substrate using a Sulzer-Metco DJH 2600 HVOF system. Powder characterization was as reported elsewhere [20].

Four sets of conditions, detailed in Table 1, were considered: T_0V_0, T_0V_1, T_1V_0 and T_1V_1, where T is the theoretical temperature of the beam the particles travel in and V is their velocity; and where 0 corresponds to a lower level and 1 to a higher level of either parameter.

The cross-section of the coating was analyzed by scanning electron microscopy, with a JEOL JSM-5310 apparatus, after being cut, grinded, polished and sputtered. Thickness and porosity were calculated from the obtained micrographs using the Matrox Inspector software. Hardness was measured using a Vickers indentor with a Matsuzawa MXT-CX microhardness tester at 300 gf.

The crystalline phases of the coating were analyzed by X-ray diffraction with a Siemens D500 X-ray diffraction Bragg-Brentano type $\theta/2\theta$ apparatus, using Cu$K_{\alpha 1+2}$ radiation with $\alpha_1 = 1.54060$ and $\alpha_2 = 1.54443$ at 40 kV and 30 mA. Rietveld calculations were also made with scraped off coatings after conducting another slower measurement, adding 30% by weight of Al_2O_3 as standard mixed with the coating.

2.2. Tribological tests

Reciprocating ball-on-flat tests were performed with a Plint TE67/R tribometer (Phoenix Tribology Ltd., UK) in accordance with the standard ASTM G133-05(2010), employing at least two different samples and conducting four different assays per load and set of conditions. The duration of the sliding test was 1 h; long enough to reach a stable friction coefficient regime. A 10 mm diameter alumina ball was used as counterface, and all the tests were performed under physiological conditions (immersed in Hank's solution at 37 °C). The frequency of the reciprocating motion of the flat sample and the stroke length were fixed for all tests at 1 Hz and 12 mm, respectively. In addition to the friction coefficient, the wear coefficient was calculated. According to the wear coefficient definition [21], k (mm^3/N m) is defined by Eq. (1):

$$K = V/S.P \quad (1)$$

Table 1
Spraying conditions.

	80%HAp–20%TiO_2			
	T0V0	T_0V_1	T_1V_0	T_1V_1
O_2 (l/min)	253	240	278	265
Propylene (l/min)	81			
Compressed air (l/min)	203	264	203	264
Oxygen/propylene	3.65	3.65	3.96	3.96
Number of layers	5			
Distance (mm)	220	200	240	200

where V corresponds to volume loss in mm^3 (obtained by confocal microscopy, see Section 2.3.1.), S to the total sliding distance (43.2 m) and P to the normal applied load (N).

2.3. Track observation

2.3.1. Confocal microscopy

After the different assays, the samples were observed using a confocal technique with a Leica DCM3D microscope, in order to evaluate volume loss during sliding as a measure of the wear resistance of the coating.

2.3.2. SEM observation

In order to analyze the surface of the track and determine whether the remaining surface had been damaged, as well as to identify the dominant wear mechanisms, the samples were gold-sputtered to make them conductive, then observed using a JEOL JSM-5310 scanning electron microscope.

3. Results and discussion

3.1. Phase identification

The XRD results listed in Table 2, as well as the representative XRD spectrum shown in Fig. 1 (case T_1V_1, the differences between the four cases are not evident visually) show that the main crystalline phases of the coatings are the initial ones: hydroxyapatite and rutile. The anatase and α-TCP phases appeared in smaller amounts (not indicated in the figure to avoid confusion). The amounts of amorphous phase were identified via Rietveld calculations (Table 2), thereby determining that the largest amount appeared under the T_1V_0 condition, followed by T_0V_0 and T_0V_1, with T_1V_1 presenting the lowest quantity of amorphous phase. This relation between the amounts of amorphous phase in each of the cases is given by the respective residence times of the particle and the beam temperature. T_1V_0 presents the highest percentage of amorphous phase due to its highest residence time and highest beam temperature, followed by T_0V_0, which has the second longest particle residence time. T_0V_1 and T_1V_1 have the lowest residence times – lower for T_1V_1 than for T_0V_1 – and hence the lowest percentages of amorphous phase.

3.2. Microstructural analysis

Analysis of the microstructure is essential to gaining an understanding of the wear mechanism of the material. SEM micrographs can be observed in Fig. 2, and the thicknesses values in Table 3 allow comparison between cases, since no significant differences capable of influencing wear behavior were found by ANOVA for this value.

Mere observation of the cross section of the coatings shows T_1V_1 to be the case with the most compact and homogeneous structure, with a very low porosity and almost no detectable cracks. The highest hardness value of this case is easily explained by its lowest amount of amorphous phase and the lowest porosity. In contrast, the T_0V_0 case presents the most porous and heterogeneous cross section of the four, with the lowest hardness,

Table 2
XRD results. Quantification of the phases present.

	HAp (%)	Rutile (%)	Anatase (%)	α-TCP (%)	Amorphous+not considered
T_0V_0	49.2	9.8	1.3	11.2	28.5
T_0V_1	48.9	10.4	1.2	16.7	22.8
T_1V_0	44.8	8.7	1.3	10.9	34.3
T_1V_1	53.4	10.7	1.5	20.3	14.1