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Thermal oxidation of CP-Ti: Evaluation of characteristics and corrosion resistance as a function of treatment time

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ABSTRACT

Commercially pure titanium (CP-Ti) samples were subjected to thermal oxidation (TO) treatment at 650 °C for 8, 16, 24 and 48 h. The morphological features, structural characteristics, microhardness and corrosion resistance in Ringer's solution of thermally oxidized samples were compared with that of the untreated one, to ascertain the suitability of thermally oxidized sample as a bio-implant. The thickness, morphological features and phase constituents of the oxide film formed during thermal oxidation (TO) exhibit a strong dependence on the treatment time. Samples oxidized for 48 h lead to the formation of oxide grains along with a thick oxide film consisting of rutile and TiO phase. Samples oxidized for 24 h lead to the formation of oxide grains with thinner oxide layer at the grain boundary. Almost a 3 fold increase in hardness is observed for samples oxidized for 48 h compared to that of the untreated sample. Based on the corrosion protective ability, the untreated and thermally oxidized samples can be ranked as follows: {TO 48 h}>{TO 16 h}>{TO 8 h}≈{TO 24 h}>untreated. From corrosion protection point of view, TO for 48 h is a promising surface treatment and it can be a suitable alternative to the untreated CP-Ti as a bio-implant.

1. Introduction

Titanium and titanium alloys are widely used as bio-implant materials, particularly for orthopedic and osteosynthesis applications due to their low density, excellent biocompatibility, corrosion resistance and mechanical properties [1–4]. One of the important reasons for choosing these materials is their ability to develop a naturally formed passive oxide layer, typically of 4–6 nm thickness, which is comprised of either amorphous or poorly crystallized non-stoichiometric TiO_2. This passive oxide layer is highly stable and its neutral behaviour in corrosive medium provides excellent corrosion protection. However, the stability of the passive oxide layer could be altered under *in vivo* conditions. Mu et al. [5] have identified accumulation of metal ions on adjacent tissues when the implants were retrieved for analysis. The main reason for this occurrence is due to the inferior mechanical properties of the native forms of TiO_2 films that can be disrupted at very low shear stresses, even by rubbing against soft tissues [6]. Due to the inherent property of the titanium and its alloys, the passive oxide layer could subsequently form upon reaction with the local environment. However, the wear debris and the metal ions released during fracture of the passive layer could cause adverse tissue reactions. Fretting and sliding wear conditions could also lead to fracture of the passive oxide layer [7–10]. Under extreme conditions, the effects of fretting and sliding wear might lead to loosening and eventual failure of the implant, causing suffering to the patients and warrants re-surgery. The above limitations preclude the use of Ti and its alloys for articulating surfaces.

To meet the challenging demands and, to circumvent the problems due to the poor mechanical property of the naturally formed oxide films on titanium implants, numerous surface modification methods such as, chemical treatment (acid and alkali treatment) [11,12], electrochemical treatment (anodic oxidation) [13], sol–gel coatings [14], chemical vapour deposition [15], physical vapour deposition [16], plasma spray deposition [17], ion implantation [18], thermal oxidation [19], etc. have been explored. Among them, thermal oxidation (TO) was found to be a cost-effective method to deliberately generate a barrier oxide layer of relatively higher thickness (~20–30 μm) on titanium compared to the naturally formed oxide layer (typically of 4–6 nm). TO treatment of titanium is aimed to produce *in situ* ceramic coatings, mainly based on rutile, in the form of a thick, highly crystalline oxide film, which is accompanied by the dissolution of oxygen beneath them. The thermally formed oxide layer enables an increase in hardness, wear resistance and corrosion resistance of titanium and its alloys [20–24]. However, the improvement in these functional properties becomes limited when the treatment temperature and time are increased beyond a certain limit. TO treatment of titanium ≥800 °C and for prolonged time duration results in thickening of the oxide layer, which eventually spalls-off from the surface [25,26]. Dearnley et al. [26] have studied the oxidation behaviour of the CP-Ti at 800 °C for 36 h. They have reported that the

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developed thicker TiO_2 layer (~25 μm) fails along the oxide-oxygen diffused zone interface which is supported by the formation of many cracks on the oxide layer. The large volume ratio of rutile to Ti (1.73) [27], large lattice mismatch and the large difference in coefficient of thermal expansion between rutile and titanium are considered to be responsible for the spallation of the oxide layer from the substrate [28]. Hence, it is important to optimize the treatment temperature and time so as to prepare an adherent, homogeneous and thick surface oxide layer, preferably with rutile structure so that an improvement in hardness, wear resistance and corrosion resistance could be realized. In this perspective, the present paper aims to study the effect of treatment time (viz. 8, 16, 24 and 48 h) on the thermal oxidation of CP-Ti at 650 °C to optimize the treatment condition. Corrosion resistance is an important property of a biomaterial as it determines the biocompatibility of the material. The corrosion resistance of TO titanium in simulated body fluids has been reported in the literature [20,29]. However, there are limited results available on the corrosion resistance of CP-Ti thermally oxidized as a function of treatment time, which is rather limited. Hence, the corrosion resistance of TO CP-Ti in Ringer's solution (simulated body fluid environment) was also evaluated to identify the optimum treatment time.

2. Experimental details

CP-Ti (grade-2) (chemical composition in wt.%: N: 0.01; C: 0.03; H: 0.01; Fe: 0.20; O: 0.18 and Ti: Balance) of 2 mm thickness was used as the substrate. The CP-Ti samples were mechanically polished using various grades of SiC paper, rinsed in deionized water and dried using a stream of compressed air. TO of samples was carried out in air in a rectangular furnace (LENTON make) at 650 °C for different periods of time viz. 8, 16, 24 and 48 h. The rate of heating was kept at 5 °C/min. in all the cases. After oxidation treatment the samples were allowed to cool in the furnace itself. The temperature employed for oxidation was fixed at 650 °C based on the available literature. Debonding and spalling of the oxide layer were noticed when the thermal oxidation of CP-Ti was done at temperatures higher than 800 °C and for longer time [25–27]. In view of this it was decided to fix the temperature not close to 800 °C but at 650 °C.

The phase constituents of untreated and thermally oxidized samples and the nature of the oxide film formed on the surface were determined by X-ray diffraction (XRD) (D8 DISCOVER, Brucker axs) using Cu–K_α radiation. The thickness of the oxide layer was determined using scanning electron microscopy (SEM). For measuring the thickness of the thermally oxidized layer, the cross-section of the treated sample was analyzed using SEM. The thermally oxidized sample was cut using a slow speed cutter (Buehler) using a very low load, followed by mounting and polishing using various grades of SiC paper and 0.3 μm alumina paste to a mirror finish, rinsed with deionized water, etched with Kroll's reagent for 10–15 s. Surface morphology of oxide was also assessed by SEM. The microhardness of the untreated and thermally oxidized samples was measured at the surface using a Leica VMHTMOT microhardness tester at a load of 200 gf applied for 15 s. Seven indentations were made on each sample and the values were averaged out.

The corrosion resistance of untreated and thermally oxidized samples was evaluated by potentiodynamic polarization and electrochemical

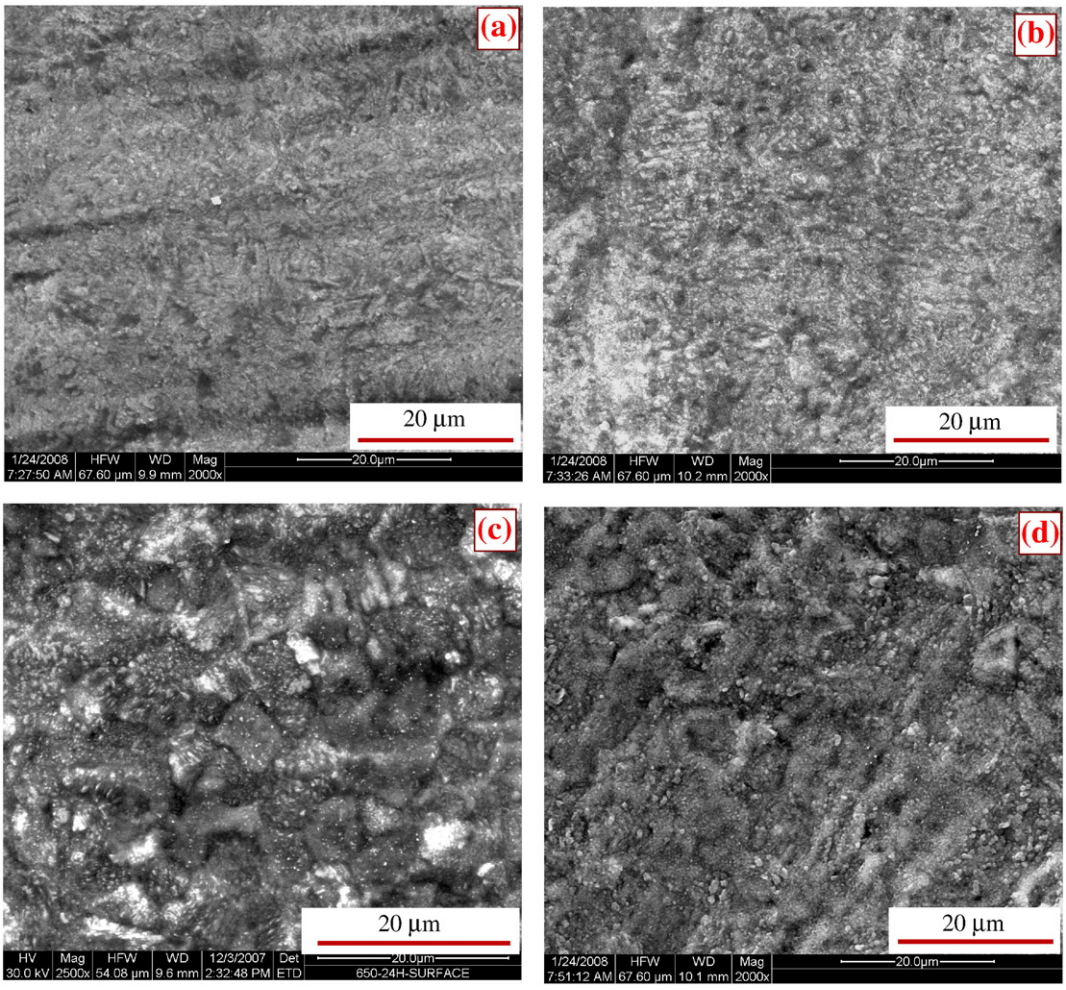

Fig. 1. SEM images of surface morphology of samples thermally oxidized at 650 °C for various time periods; (a) 8, (b) 16, (c) 24 and (d) 48 h.