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Fretting corrosion response of boride coated titanium in Ringer's solution for bio-implant use: Elucidation of degradation mechanism

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ABSTRACT

Fretting corrosion of boride coated commercially pure titanium (CpTi) is investigated in Ringer's solution using open circuit potential (OCP) method. Coating is synthesized at 850, 910 and 1050 °C for 1, 3 and 5 h. Upon fretting, borided specimens exhibited lower galvanic coupling than bare and correspondingly the wear loss. TiB_2 + TiB and/or TiB_2 thickness plays a significant role in determining the fretting resistances. Passivation/repassivation is attributed by TiO_2/B_2O_3 and TiO_2 formations in borided and bare CpTi respectively. Study revealed that suppression of summation of synergistic and corrosion components improved the fretting performance of coated CpTi. Boriding of CpTi has enhanced the biocompatibility response.

1. Introduction

For many years, metallic based load bearing bio-implants such as hip and knee joints are found to suffer due to tribocorrosion which causes health issues such as inflammation, Arthrofibrosis, discoloration and reduction in their service life of implant [1–10]. In this context, the demand for the improvement of tribocorrosion resistance of the newly developed coatings/metallic materials have been increased significantly [1–5], as it is highly required to repair the bone damages. Amongst other, fretting corrosion is one of the frequently observed tribocorrosion issues [2], where the implanted articulating/contacting surfaces or orthopedic joints undergo micro-motion (~50–300 µm) due to the regular activities of patients [2]. Such implant portions in the total hip joint prosthesis are the femoral neck/stem head (made of metal based/ceramic contacts) and femoral stem/bone interface [2,11–13], and in case of knee joints are stem/bone contacts, bearing surfaces of Morse tapers, and femoral lateral condyle/tibia lateral condyle [9,10,14]. The fretting corrosion of hip implant modular junction has been investigated by simulating the femoral neck and head contacting surfaces using Ti-6Al-4V and Co-Cr-Mo respectively in simulated bovine calf serum [2]. The contacting surfaces of hip femoral head bore (made of stainless steel) and cone taper interface (made of Ti-6Al-4V or stainless steel) have been studied for fretting corrosion in 0.9% NaCl aqueous solution [8]. A retrieval study has addressed the role of femoral head size (28–36 mm) with the contact of femoral stem on the fretting corrosion behavior of different materials (metals and polymers). It suggests that the taller femoral head (36 mm) suffers a greater corrosion than the smaller head (28 mm), which may adversely affect the articulations [12]. A systematic report on the retrieved Co-Cr femoral components of total knee arthroplasty has shown that fretting corrosion is one of the prevalent failure mechanisms among different types [9].

Compared to other metallic bio-implant materials, titanium and its alloys are identified as the suitable materials for more than decades especially for the load bearing bio-implant uses. It is due to their good biocompatibility, excellent corrosion resistance (self-healing behavior upon surface damage), reasonable mechanical properties (low elastic modulus value, ~60–110 GPa close to human bone ~20–40 GPa, and strength-to-weight ratio), and economically feasible [15]. Naturally formed amorphous TiO_2 layer (~4–6 nm thickness) offers better corrosion resistance than other metallic bio-implants [16]. However, the passive layer exhibits a poor wear resistance even with soft tissues, during implanting into the patient, due to its poor mechanical properties [17,18] and eventually exposes the underlying metal surface causing its accelerated corrosion. To achieve the increasing tribocorrosion resistance of titanium based bio-implants; the material researchers need to find an alternative ways such as coatings.

Developments of the several surface modification methods, for coating resistant to tribocorrosion, have been evolved. It includes plasma spray [19], thermal oxidation [20,21], anodization [22], chemical and electrochemical methods [23], thin film methods [4], and thermochemical diffusion coatings (Boriding, nitriding, etc) [24].

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Amongst these, boriding has received much interest in the direction of bio-implant applications, as it is considered to be a simple, cost-effective and ability to produce coating with high hardness over the complex shapes [25,26]. Pack boriding process produces boride composite layer (thickness of ~5–50 µm) with high hardness on the metal surface upon heat treatment between 800 to 1100 °C as function of soaking time [27,28]. Main advantage of the boride coating on titanium are good adherence (due to the formation of long TiB whiskers perpendicular to the Ti surface), and the comparable thermal expansion coefficients (For TiB_2-8.1 × 10^{-6}, TiB-8.5 × 10^{-6}, and Ti-8.6 × 10^{-6}/°C) which avoids the stress at the interface of coatings [28]. So far, the boride coating of Ti and its alloys have been investigated for boron kinetics [29], the improvement of properties like mechanical (hardness, wear resistance, etc) [30] and corrosion behavior [24,26]. Research focus on the *in-vitro* fretting corrosion of boride coated titanium is very scarce.

Corrosion and wear resistance of any metallic/coated bio-implants are much needed properties to ensure biocompatibility during its long service life. In light of the above, the present manuscript aims to evaluate the fretting corrosion of boride coated CpTi in Ringer's solution (a simulated body fluid). Fretting corrosion is investigated by open circuit potential measurement. Study includes the understanding of corrosion resistance under fretting condition, repassivation behavior, wear damage mechanism, and biocompatibility response of boride coating. Surface features of the fretted area are unveiled by the scanning electron microscope (SEM) and EDAX (Energy Dispersive X-Ray Analyzer). The oxide formed on exposure of the coated surface to Ringer's solution is probed by X-ray photoelectron spectroscopy (XPS). Biocompatibility of the boride coating is also evaluated.

2. Materials and methods

2.1. Materials and coating preparation

The CpTi specimen with the chemical composition (in wt %) of N-0.01; C-0.03; H-0.01; Fe-0.20; O-0.18 and Ti-balance was used for the investigation. It was utilized as discs form with the dimensions of 20 mm diameter and 3 mm thick, obtained from 150 mm length cylindrical rod (Akshat steel, Mumbai, India). Prior to boriding, the specimens were ground by abrasive SiC emery papers (using 100 to 1200 grit sizes), ultrasonicated in acetone for 10 min followed by cleaning in distilled water and finally dried. Upon boriding, the surface finished CpTi specimens were packed with boriding mixture in the alumina crucible. Boriding mixture consist of 50 wt%-Boron powder (Boron source), 15 wt%-$NaCO_3$ (an activator) and 35 wt%-charcoal (as filler). Boride coatings of CpTi were carried out as function of temperature (850, 910 and 1050 °C) and soaking time (1, 3 and 5 h) in Ar gas atmosphere. Further, the details of boride coating preparations were explained elsewhere [26].

2.2. Coating characterization

Boride coatings were characterized using XRD for phase analysis, SEM equipped with EDAX for surface morphology of coating at cross section, composition and thickness, and Vickers method for microhardness measurement. The operating conditions for each characterization were discussed in our previous work [26]. The oxide layer properties of the bare and borided CpTi specimens after the exposure in Ringer's solution (for 24 h duration) were analyzed using XPS. Before the exposure, the specimens were polished using colloidal silica solution and ultrasonicated in acetone and distilled water for 10 min separately. The XPS used Al-kα (1486.6 eV) and Mg-kα (1253.6 eV) radiations (SPECS make, Germany) and at 1 × 10^{-9} Torr vacuum level. The obtained XPS spectra were deconvoluted using CASA XPS software and calibrated them with respect to C1s peak position (284.6 eV). The XPS data analysis was done using Shirley method for background correction and the combination of Gaussian/Lorentzian peaks for peak fitting protocol.

2.3. Fretting corrosion behavior and characterization

Fretting corrosion performance of CpTi specimens borided at different temperature (850, 910 and 1050 °C) and soaking time (1, 3 and 5 h) was investigated in Ringer's solution and compared them with the bare CpTi. Prior to tests, borided CpTi was surface finished using the colloidal silica solution (1 µm particle size) to remove the impurities/adsorbed coating mixture. The Ringer's solution was prepared by dissolving the (in g/L) 9-NaCl (Sodium chloride), 0.43-KCl (Potassium chloride), 0.20-$NaHCO_3$ (Sodium bicarbonate) and 0.24-$CaCl_2$ (Calcium chloride) in distilled water (pH-7.4). Fretting corrosion tests were carried out at room temperature (25 ± 2 °C) in normal air atmosphere using fretting corrosion set-up (Wear and friction Tech-make, Chennai, India). The detail of this set-up is described elsewhere [31]. The corresponding electrochemical response was measured by Potentiostat/Galvanostat frequency response analyzer, ACM Instruments-make, Bi-STAT model, USA. The test assemble adopted the ball-on-flat contact method with the reciprocating displacement of ~200 µm, as the actual precision at the contacting surfaces of orthopedic implants meet these condition. Various fretting parameters used in this investigation were: 3N-applied load, (having maximum Hertzian contact pressure of 500 MPa is close to the yield strength of 480 MPa and tensile strength of 550 MPa of Ti), and 5 Hz-oscillating frequency (more than the actual human walking/stride frequency of 1 Hz, keeping shorter experimental durations in view). Fretting corrosion behavior was monitored by OCP measurement as function of immersion time against 8 mm Alumina ball, having roughness of ~20 nm (G 10 grade, Salem specialty ball company Inc., USA). Alumina ball was used as a counterpart material to mimic the orthopedic implants, where the matting component (femoral head) is made of Alumina. The OCP measurement under fretting corrosion tests were considered as three different regions: before 'ON-Set' of fretting motion (allowed to stabilize the surface for 60 min duration), during 'ON-Set' of fretting motion (Fretting-ON, for 60 min) and after 'OFF-Set' of fretting motion (Fretting-OFF, for 30 min). In articulating surfaces of orthopedic implants, the electrode potential of Ti based materials varies depending upon surface damages occurred during the various activities of patients such as rest position (sitting/standing considered as before and after fretting), and walking action (assumed as during fretting). Thus, the OCP measurement is intended to mimic those conditions and monitor the fretting corrosion response in different regions such as before, during and after fretting regions. Fretting tests were repeated minimum 2–3 times to ensure the reproducibility. Surface morphology of the fretted worn out surface was examined by SEM-EDAX analysis and the fretted dimensions were analyzed by ImageJ software. Elemental mapping of fretted zone was analyzed using electron probe micro analyzer (EPMA), JEOL JXA 8230. The fretted depth was measured by 2D surface profilometer (Taylor Hobson 2 make, USA).

2.4. In vitro biocompatibility and cell morphology

In order to check the effect of boride coating of CpTi and its bare specimens in the *in vitro* arena, an initial cytotoxicity test was done. Biocompatibility of these specimens were evaluated using mouse fibroblasts L929 cell lines (NCCS, Pune) by MTT (3-(4,5-Dimethylthiazol-2-yl)-2,5- diphenyltetrazolium bromide) assay as per ISO-10993 standard [32]. The detailed experimental protocol has been given in supporting file (S-Experimental detail).