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Corrosion behavior of titanium boride composite coating fabricated on commercially pure titanium in Ringer's solution for bioimplant applications

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ABSTRACT

The boriding of commercially pure titanium was performed at 850 °C, 910 °C, and 1050 °C for varied soaking periods (1, 3 and 5 h) to enhance the surface properties desirable for bioimplant applications. The coating developed was characterized for the evolution of phases, microstructure and morphology, microhardness, and consequent corrosion behavior in the Ringer's solution. Formation of the TiB_2 layer at the outermost surface followed by the TiB whiskers across the borided CpTi is unveiled. Total thickness of the composite layer on the substrates borided at 850, 910, and 1050 °C for 5 h was found to be 19.1, 26.4, and 18.2 μm respectively which includes <3 μm thick TiB_2 layer. The presence of TiB_2 phase was attributed to the high hardness ~2968 $Hv_{15\ gf}$ of the composite coating. The anodic polarization studies in the simulated body fluid unveiled a reduction in the pitting corrosion resistance after boriding the CpTi specimens. However, this value is >0.55 V_{SCE} (electrochemical potential in in-vivo physiological environment) and hence remains within the safe region. Both the untreated and borided CpTi specimens show two passive zones associated with different passivation current densities. Among the CpTi borided at various times and temperatures, a 3 h treated shows better corrosion resistance. The corrosion of borided CpTi occurred through the dissolution of TiB_2.

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1. Introduction

Surface modification is a proven alternative to minimize the surface damage of metallic materials including bioimplants. Titanium and its alloys are extensively preferred bioimplants due to their low density, excellent corrosion resistance, and acceptable biocompatibility. The Ti based bioimplants, however, suffer from the poor fretting corrosion and sliding wear resistance when subjected to the two body contact such as in the hip and knee joints [1–3]. The naturally formed passive oxide layer on the titanium is easily removed from the contact zone, due to poor mechanical properties of the oxide, and as a result fresh metallic surface is exposed to the physiological fluid [4]. This increases corrosion of metals/alloys and subsequent release of metallic ions (such as Ti, Al and V from Ti–6Al–4V alloy) along with the wear debris to the physiological fluid. A number of surface modification techniques and processes such as plasma based, laser based and assisted, thermal oxidation, organic and inorganic coatings, diffusion coatings have been developed to overcome the inferior tribological resistance of the titanium and its alloys [4–9]. Over the past several years, boriding, a diffusion based coating method has been increasingly used to improve the tribological and corrosion behavior of metallic materials. Titanium borides (TiB_2 and TiB) have shown the remarkable properties such as low electrical resistivity (similar to metals), high melting points, high hardness and excellent wear, and corrosion resistance [10,11]. Boriding of the titanium, therefore, can be an extremely viable method to improve its tribological behavior. Interestingly, TiB_2 and TiB coatings can be developed in-situ on the surface of titanium by heating the Ti specimen encapsulated by the mixture containing boron source, an activator, and filler material. The coating by reinforcement of the borides (a non-diffusive ex-situ method) performed on the surfaces of several metals/alloys in which coating adherence may be lost can, thus, be avoided. The other important reason for choosing the boride coating is the comparable thermal expansion coefficient of TiB_2/TiB and Ti, which may ensure much less thermal stresses and so the distortion at the interface. The coefficients of thermal expansion of TiB_2, TiB, and Ti are 8.1×10^{-6}, 8.5×10^{-6} and 8.6×10^{-6}/°C respectively. The undesirable thermal mismatch between Ti matrix and several other ceramics such as Ti_5Si_3, CrB, B_4C, SiC, and TiC is reported to cause high residual stresses that degrade the coating–matrix interface [12–14].

The boriding by thermochemical diffusion process (namely pack boriding) has been extensively investigated on the ferrous substrates for various industrial applications. The pack boriding is a very simple

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and cost effective process compared to the liquid and gas boriding methods [15–17]. Recently, boriding process has been attempted on the titanium and its alloys for orthopedic implant applications [10, 18–20]. It is reported that the TiB and TiB_2 intermetallic phases formed under the different boriding conditions have average hardness of 850 and 3300 Hv. The boriding process involves diffusion of boron (B) atoms from the high concentration boron region (source) to a low or no boron region (sink such as titanium) through the surface defects at elevated temperatures >800 °C. Boride coating on the titanium and its alloys has been reported to enhance the wear resistance and showed a low coefficient of friction against the sapphire ball when subjected to sliding under the dry and lubricated conditions [10,11, 21]. The growth kinetics of boriding process on the surface of titanium has been studied by Sarma et al.; they have shown that the growth of TiB_2/TiB greatly governed by the β-transition temperature and subsequent B diffusion in the α and β phases differs significantly [22]. Tikekar et al. have showed that the boriding at ~900 °C for 24 h (near β transition temperature) produced a higher coating thickness (~60 μm) than the samples borided at 850 °C (~28 μm) or at >1050 °C (~50 μm) for 24 h [23].

Most of the studies on TiB_2/TiB coatings are aimed to investigate the kinetics of boron diffusion and evaluation of physical and microstructural properties. Attempts are also made to establish the biocompatibility of boride coatings. An in-vitro test on the plasma processed titanium boride coatings on α-Ti matrix has demonstrated good cytocompatibility compared to that of the untreated titanium specimens, indicating boride coated titanium a strong candidate for the biomedical applications [24]. A favorable cell growth rate on the plasma sintered composite TiB_2–Ti within the 48 h duration along with an excellent blood compatibility with a low hemolytic level (<0.12) has been demonstrated [25]. From the literature it appears that the due attention has rarely been given to understand or study the corrosion behavior of TiB_2/TiB coating on titanium and its alloys. Needless to mention, the corrosion is an important criterion to establish the biocompatibility of a newly proposed implant material or modification thereon (such as boride coating) and deserves extensive investigations. Among a few earlier studies, Covino et al. have focused on the corrosion of pure TiB_2 ceramic in the acid solutions and compared the performance of TiB_2 made from the various routes such as press and sintered (PAS) and an electro deposition process [26]. The study concluded that the PAS titanium diboride corrodes at the rate 50 to 100 times higher than that of the electrodeposited and does not passivate in sulfuric acid solution. A relatively recent study has evaluated the corrosion performance of a sintered TiB_2 mixed with the nickel powder (as a sintering additive) in 3.5% NaCl solution. The study showed protection to the TiB_2 by the formation of passive film at 25 and 45 °C but the resistance of the film is reduced with further increase in the temperature of solution up to ~65 °C. The corrosion attack was found concentrating along the nickel rich grain boundaries [27]. In most of such studies, the current density associated with the passive region of a TiB_2 is reported to be in the order of 10^{-3} A/cm^2 or higher indicating pseudo passivation. The corrosion behavior of a pure and sintered TiB_2 is shown to influence by the porosity present in the specimens or the segregation along the grain boundaries [27]. However, no corrosion studies, to the best of our knowledge, appear in the literature on TiB_2/TiB composite coatings fabricated on the titanium or titanium alloys developed by the pack boriding method. The corrosion behavior of such coated specimens may actually differ largely from those described earlier [26,27] where TiB_2 is coated by the other methods (ex-situ) due to obvious reasons. The corrosion study of the borided titanium in SBF solution is thus necessary in order to establish its biocompatibility for the bioimplant application.

The present study, thus, aimed to develop the boride composite coatings on CpTi by using a pack boriding process. It was performed at temperatures in the range 850 to 1050 °C for varied soaking durations such as 1, 3 and 5 h (hours). Corrosion studies on the fabricated coatings were made in the Ringer's solution using the open circuit potential (OCP), anodic polarization, and the electrochemical impedance spectroscopy (EIS) techniques. The dissolution behavior of the boride coating was also investigated and compared with the untreated titanium by performing the long term exposure at OCP in the Ringer's solution; analysis of the post exposure solution was done for measuring the metal/B ion emission using the ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy). The study also includes the coating characterizations for the phase analysis by the X-ray diffraction (XRD) technique and Boron accumulation in TiO_2 passive film by X-ray photoelectron spectroscopy (XPS). The coating morphology was investigated by the scanning electron microscope (SEM), mechanical properties by the microhardness tester, and coating roughness by the surface profilometer.

2. Materials and methods

2.1. Materials

A commercially pure titanium, CpTi (wt.%: N-0.01; C-0.03; H-0.01; Fe-0.20; O-0.18 and Ti-balance) was used as a base substrate for the coating development. The CpTi in the form of a rod of 20 mm diameter was cut in the disks of 3 mm thick for the fabrication of coatings and subsequent corrosion and other characterizations. Prior to boriding, the specimens were polished using SiC abrasive papers ranging from 100 to 2/0 grades followed by cleaning with the distilled water. Thus polished substrates were ultrasonicated in acetone to remove the contaminants from the surface of the substrate. A mixture consisting of 50% boron source (B powder, Merck), 15% of an activator ($NaCO_3$, Merck) and 35% of filler (charcoal activated, Merck) (in wt.%) was used for boriding the polished CpTi specimens.

2.2. Boriding process

The boriding was performed by encapsulating the polished and cleaned CpTi specimens into the above-mentioned boriding mixture in a sealed alumina crucible. Sealing is required to prevent the oxygen ingress into the mixture, which otherwise may interrupt the titanium boride formation by forming a TiO_2 layer in preference to boride. The boriding process was carried out at temperatures 850, 910, and 1050 °C with varied soaking periods (1–5 h) in an argon environment. After the completion of pre-decided soaking periods, the borided CpTi specimens were furnace cooled to room temperature. The borided specimens were then cleaned by the ultrasonication in acetone to remove the loosely adhered boriding mixtures and these samples were used for the further characterizations.

2.3. Coating characterizations

The coating on the CpTi specimen was characterized for phase evolution, microhardness, microstructure, and surface morphology. The XRD analysis was performed using a Cu-Kα source (λ—1.5426 A°) for the phase identification in both the untreated and borided CpTi specimens using D8 Discover, Bruker make X-ray diffractometer. The SEM and energy dispersive X-ray analysis (EDAX) (Nova Nano SEM 430 make) were used to investigate the coating morphology, thickness, and composition at the cross section of the borided specimens. The microhardness and surface roughness (a 2D surface profilometer) measurements were carried out using the Leica and Tayor Hobson 2 makes respectively. Adhesion test of the coating (TiB_2) was carried out by a Rockwell C diamond indenter (120° angle, 200 μm radius) using computer controlled scratch tester (Model TR101, DUCON). The specimen was mounted on the test table and slid at a speed of 0.2 mm/s. The load on the indenter was increased at a rate of 2 N/mm to know the critical load (as per the ASTM standard C1624-2010) for the coating damage. The change in the slope of the normal load versus displacement

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