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Hydrothermal Fabrication of Iodine Doped Titanium Oxide Films on Ti Substrate

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Abstract**—**Titanium oxide films with different morphologies have for the first time been fabricated through hydrothermal reactions between a titanium substrate and iodine powder in water or ethanol. SEM revealed that iodine supported titanium (Ti-I_2) surface shows different morphologies with variable treatment conditions. The mean surface roughness (R_a) was increased in the different groups. Use of surfactant has a role to increase the roughness of the film. The surface roughness was in the range of 0.15 µm-0.42 µm. Furthermore, the electrochemical examinations showed that the Ti-I_2 surface fabricated in alcoholic medium has high corrosion resistance than in aqueous medium.

Keywords**—**Corrosion, Hydrothermal, Surface roughness, Titanium oxide.

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I. INTRODUCTION

TITANIUM and its alloys have become the premier choice for biocompatible dental and orthopedic implant materials [1], [2]. Chemistry and topography of the implant surface mainly influence the biocompatibility, implant-bone integration and long-term stability of the implant. The metallic titanium surfaces are covered by a very thin native oxide films (3-8 nm) on exposure of the metal to air [3], [4]. Titanium oxide thin films show attractive properties, such as chemical durability, biocompatibility and photo response. Thick TiO_2 films can be obtained by oxidation of titanium metal using oxidants or under anodization. Also, numerous approaches the sol-gel, sputtering, chemical solution methods, solvothermal method etc. [5] have often been used as methods for fabrication of TiO_2 thin film in order to change the implant surface topography or chemically modifying the surface layer creating optimized surface layers for different applications. Surface properties, including micro-topography, chemistry and wettability are important factors affecting the quality of bone healing by influencing the biological responses of bone-interfacing implants [6]-[10]. Furthermore, the surface roughness, corrosion resistance and antibacterial properties of the material surfaces are very important factors for the biocompatibility and long-term durability of the implant. Corrosion adversely affects the biocompatibility of a material due to the toxic effect of the corrosion product [11]. If the corrosion resistance is high, the release rate of metallic ions is low. Therefore, it is important to evaluate the corrosion resistance and hence the electrochemical behavior of the metallic material when used in biomaterial applications. Bren et al [12] work confirms that surfaces with nano-scale roughness have greater influence over osteoblast differentiation than micro-scale roughness. Keller et al [13] showed that osteoblast attachment to titanium is directly related to surface roughness.

Here we report for the first time that TiO_2 films with different morphologies can be grown through hydrothermal reactions between titanium substrate and iodine powder in aqueous or alcoholic medium with/without any organic templates. The surface properties and corrosion resistance of the different surfaces were evaluated.

II. MATERIALS AND METHODS

Commercially pure Ti plates grade 2 (20 mm × 10 mm × 2 mm) were abraded with 220 to 800 grits SiC paper and chemically pickled with a mixture of HNO_3, HF and water in the ratio1:3:6 by volume, respectively. Prepared specimens were hydrothermally heated at 200ºC for 2 h with iodine powder in water or ethanol with/without the aid of surfactants. Oxides films were grown under different conditions, addition of 2% I_2 (1) aqueous solution, (2) ethanolic solution, (3) aqueous solution with 1 g cetyltrimethylammonium bromide (CTAB), (4) ethanolic solution with 1 g CTAB, (5) aqueous solution with 1 g sodium bis(2-ethylhexyl) sulfosuccinate (NaAOT) and (6) ethanolic solution with 1 g NaAOT, respectively.

The morphology of the resulting films was investigated by a scanning electron microscopy (SEM). The crystalline structure of films grown in different media was identified by X-ray diffraction (XRD, Rigaku, Japan). The surface roughness of the specimens was quantified using a Surftest Formtracer (Surftest SV-402, Mitutoyo Instruments, Tokyo, Japan). A 2 µm diamond stylus was used to determine the center line average roughness (R_a) along a length of 10 mm. Three individual measurements, between which the distance was 200 µm, were made for each specimen to obtain accurate data regarding the surface roughness. The potentiodynamic polarization behavior of specimens was recorded in the scanning range of - 0.1 to + 0.5 V (vs. Ag/AgCl, KCl satd) at a scanning rate of 2 mV/s. All electrodes were immersed into the Hanks Balanced Salt

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solution for 20 min to study the corrosion behavior of different Ti samples.

III. RESULTS AND DISCUSSION

X-ray diffraction (XRD) analyses were performed to analyze the phases of fabricated films. The peak intensities reflect the total scattering from the each plane in the phase's crystal structure, and are directly dependent on the distribution of particular atoms in the structure. Thus intensities are ultimately related to both structure and composition of the phase. Fig. 1 shows the representative XRD patterns of films grown in different media. They exhibit the presence of titanium peaks in all sample groups. No any peaks of titanium oxide were observed which seems to be attributed to thin oxide layer with a low crystallinity of TiO_2 layer. The heights of the titanium peaks are slightly different in all groups which suggest that the formed films were different in thickness [14]. No evidence of iodine and iodine containing species are reflected in the spectra probably due to the minute amounts of the dopant which is below the detection limit of the XRD technique. Similar results were reported by Bagwasi etal [15].

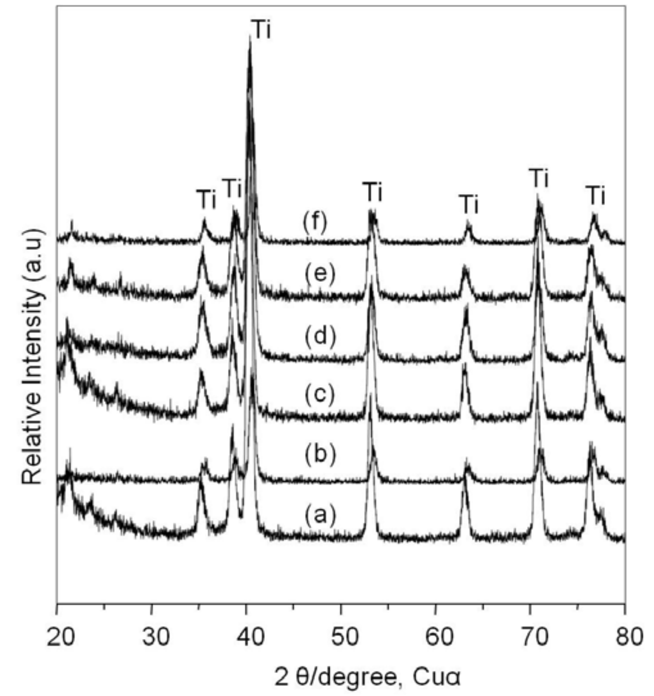

Fig. 1 XRD patterns of I-doped TiO_2 at different hydrothermal treatment conditions (a) 2% I_2 aqueous solution (b) 2% I_2 ethanolic solution (c) 2% I_2 aqueous solution with 1g CTAB (d) 2% I_2 ethanolic solution with 1g CTAB (e) 2% I_2 aqueous solution with 1g NaAOT (f) 2% I_2 ethanolic solution with 1g NaAOT

A range of different nanostructures were fabricated on titanium plate by hydrothermal technique using iodine powder in aqueous or alcoholic medium. The morphology of the resulting films was investigated by a scanning electron microscopy (SEM). Fig. 2 shows the SEM images of titanium oxides films with different morphologies. The surface showed noticeable changes as the treatment medium is different. The oxide film shows uniform surface morphology in aqueous medium (fig. 2 a) while in alcoholic medium further irregularities was observed (fig. 2 b). It was observed that the addition of surfactants in the treatment medium accelerates the rate of reactions which produces the dense and granular morphology of the films (fig. 2 c-f). When CTAB or NaAOT was introduced to the reaction system, more abundant and rough surfaces were produced on the substrates. It has been proven that this hydrothermal modification technique can be extended to other metallic substrates such as that of the titanium alloy, stainless steel and nitinol, implying the utility of this technique for generating nanostructured metallic implants for biomedical applications [16].

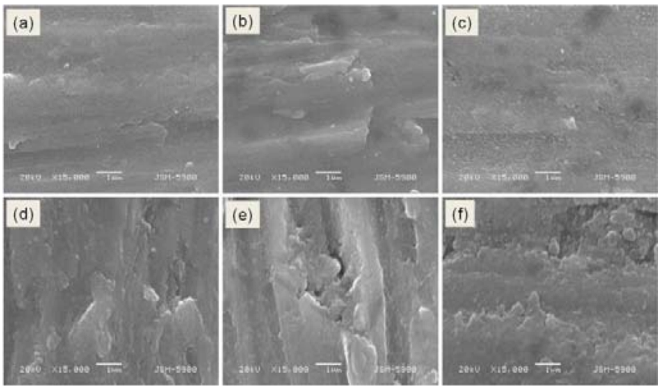

Fig. 2 Various TiO_2 films grown under different conditions at 200ºC (a) 2% I_2 aqueous solution (b) 2% I_2 ethanolic solution (c) 2% I_2 aqueous solution with 1g CTAB (d) 2% I_2 ethanolic solution with 1g CTAB (e) 2% I_2 aqueous solution with 1g NaAOT (f) 2% I_2 ethanolic solution with 1g NaAOT

The surface of titanium became much rougher after hydrothermal treatment. Fig. 3 shows the surface roughness diagram of different titanium oxide surfaces fabricated hydrothermally in iodine powder in water or ethanol with/without surfactants. The roughnesses of the surface oxide film in the first two sample groups were almost same value. Using surfactant in the hydrothermal treatment the roughness markedly increased. This markedly changed in the surface roughness is due to the variation in the size and topography of the surface oxide film which is in agreement with SEM results. The highest average roughness (Ra) ~0.41 µm was obtained than the other sample groups. It is known that substrates with smoother surfaces are more likely to result in the formation of thicker fibrous encapsulation than are those with rougher surfaces [14].

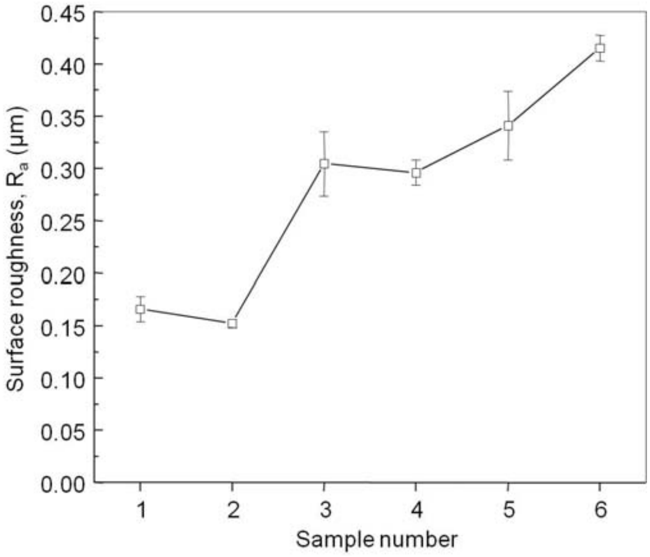

Fig. 3 Surface roughness of fabricated TiO_2 films on different conditions (1) 2% I_2 aqueous solution (2) 2% I_2 ethanolic solution (3) 2% I_2 aqueous solution with 1g CTAB (4) 2% I_2 ethanolic solution with 1g CTAB (5) 2% I_2 aqueous solution with 1g NaAOT (6) 2% I_2 ethanolic solution with 1g NaAOT (n=5 per group)

Measurements results of corrosion resistance of the oxidized titanium with hydrothermal treatment in aqueous or alcoholic iodine solution with or without surfactants measured after about 20 min of exposition in Hanks Balanced Salt Solution are shown in fig. 4. The values of corrosion potentials and corrosion current densities obtained for samples after treatment are comparable. Fig. 4 shows that the corrosion potential of samples using alcoholic iodine solution for hydrothermal treatment was higher than that of aqueous solution. The corrosion resistance is directly proportional to corrosion potential and inversely proportional to the current density. It follows that a low current density indicates a high corrosion resistance and consequently a low level of metals release, beneficial for the biocompatibility. The electrochemical evaluation methods represent fast and low cost techniques for material screening tests to gain knowledge about the materials biocompatibility. It is hypothesized that surface treatment methods such as surface thermal oxidation, hydrothermal treatment and so on will improve the corrosion resistance and decrease the ion release rate of rough surface effectively by increasing the thickness of surface protection film, improving its structural uniformity and facilitating the formation of ordered, compact surface protection film.

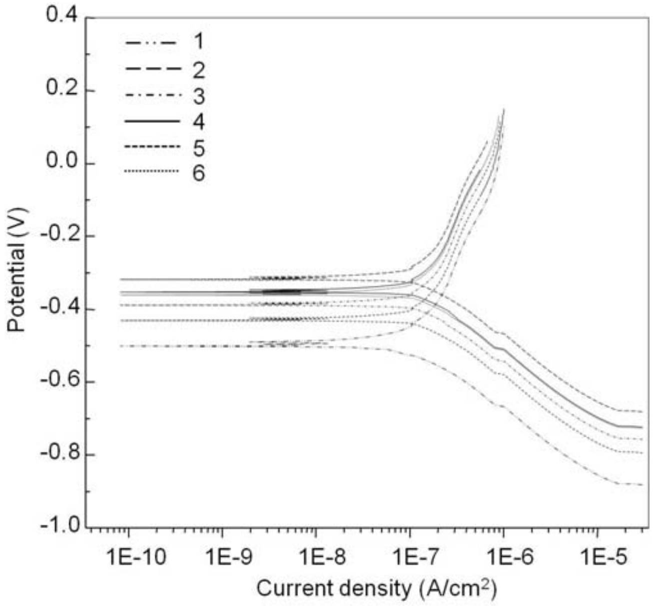

Fig. 4 Typical potentiodynamic polarization profiles for titanium specimen in various treatment conditions (1) 2% I_2 aqueous solution (2) 2% I_2 ethanolic solution (3) 2% I_2 aqueous solution with 1g CTAB (4) 2% I_2 ethanolic solution with 1g CTAB (5) 2% I_2 aqueous solution with 1g NaAOT (6) 2% I_2 ethanolic solution with 1g NaAOT

IV. CONCLUSION

In summary, we report the synthesis and characterization of TiO_2 films on titanium substrate using aqueous or alcoholic iodine solution. Fabricated oxide films showed different morphological structure with variation in surface roughness. Also, ethanolic treatment specimen show high corrosion resistance than aqueous treatment. Thus, treatment condition has important role on surface properties and chemistry of the materials. In future, iodine treated Ti material can be used as antibacterial biomaterial.

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