ABSTRACT

Human beings are likely to face serious problems caused by diseases, accidents and aging during their lifetime. In the past, physicians had a very limited number of material choices for implantation, to solve these medical problems. However, in the recent years, significant advances in science and technology of medical materials have altered the choices of physicians to develop new materials for the solution of the implantation problems.

Now-a-days, much attention has been focused on titanium for its use in medical and dental fields owing to its superior properties such as low density, high corrosion resistance and satisfactory biocompatibility. However, direct ossteointegration of such implant materials is one of the main goals of biomaterial research for dental and orthopedic applications. Hence, chemical, mechanical or biological treatments have been investigated to obtain a faster, better and durable bonding of implants with bone.

In recent years to improve ossteointegration, scientists have focused their attention on the interface interactions between the implant surface and the bone. In particular, many efforts have focused on the modification of a stable and thin oxide layer formed spontaneously on the surface of titanium. This stable oxide layer has been considered to be responsible for the titanium biocompatibility and for the ability of this material to ossteointegrate. However, when titanium is placed in-vivo, titanium oxide layer changes its properties because of the electrolytic nature of the body fluids, whose components are able to interact and bind to the oxide layer of the metal.
surface. In particular, titanium dioxide exhibits hydroxyl group formation which, in their deprotonated form, can bind calcium and phosphate, thus promoting ossteointegration properties. Therefore, the rate of ossteointegration can be modulated by tailoring the oxide layer properties before implantation. The introduction of new methods capable of changing the physicochemical and morphological properties of the oxide film can be a step forward towards developing a new generation of highly compatible surfaces suitable to induce a strong and durable bonding to the bone.

Hence, one of the strategies envisaged in this work is to modify the surface of titanium and its alloys by simple chemical treatment using hydrogen peroxide (H$_2$O$_2$) solution. The present work is aimed towards an effective H$_2$O$_2$ treatment on titanium and its alloys inorder to improve the corrosion resistance and biocompatibility in simulated body fluid (SBF) solution.

A very few reports are available on the surface modification of pure titanium using H$_2$O$_2$ and their surface characterization involving XRD, SEM and EDAX. However, the effect of concentration of H$_2$O$_2$ on titanium alloys, attempts on the bioactivity and corrosion behaviour of surface treated specimens in SBF solution have not yet been reported.

In the present investigation, pure titanium, Ti-6Al-4V and Ti-6Al-7Nb alloys were treated with various concentrations of H$_2$O$_2$ namely 5 wt.%, 15 wt.% and 25 wt.%. The bioactivity behaviors of the surface modified specimens were characterized by Raman Spectroscopy, Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Analysis (EDAX) and Fourier Transform Infrared (FTIR) spectroscopy. The in-vitro corrosion
behaviour of the specimens immersed in SBF solution was evaluated using various electrochemical techniques such as open circuit potential (OCP), potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).

The results of Raman spectroscopy revealed that the surface of Ti, Ti-6Al-4V and Ti-6Al-7Nb alloys of H₂O₂ and subsequent heat treated specimens, irrespective of concentrations, exhibited an anatase nature of the crystal structure, which is considered to be more essential for the bioactivity of the material.

The morphologies of H₂O₂ treated specimen exhibited different surfaces depending on the concentrations of H₂O₂, which were characterized using SEM-EDAX. The results revealed that 5 wt. % of H₂O₂ treated titanium showed numerous bright and dark contrasting spots indicating that the layer formed over the titanium surface was not plain but was made of a number of crests and troughs. In the case of titanium treated with 15 wt. % of H₂O₂, a porous titania layer was observed with uniformly networked pores covered the entire surface of the specimen. The SEM images of titanium treated with 25 wt.% of H₂O₂ exhibited cracked surface oxide layer.

The surface of Ti-6Al-4V alloy treated with 5 wt.% of H₂O₂ exhibited many white colored particles. The observed white colored particles were found to be vanadium as evinced from EDAX analysis. The treatment of Ti-6Al-4V alloy with 15 wt.% and 25 wt.% of H₂O₂ resulted in the formation of cavities, with the pore size in the sub-micrometer scale.

Ti-6Al-7Nb alloy treated with 5 wt.% of H₂O₂ exhibited some clusters of flower like particles over the surface and corresponding EDAX analysis showed the surface enriched with niobium. Ti-6Al-7Nb alloy treated
with higher concentrations namely 15 wt.% and 25 wt.% of H₂O₂ exhibited some traces of white particles.

In-vitro evaluation was carried out for the H₂O₂ treated specimens after seven days of immersion in SBF solution. The growth of apatite over the surface modified titanium alloys was confirmed using FTIR, SEM and EDAX analysis at each stage of the investigations.

The electrochemical corrosion studies revealed that there is an increase in potential in the nobler direction and a decrease in current density after seven days of immersion in SBF solution. Further, the electrochemical impedance spectroscopic studies were carried out to understand the layered structure of titanium and its alloys and its influence on the growth of apatite on these layers after H₂O₂ treatment. The obtained data were fitted using an equivalent circuit to reveal the nature of layer formed.

In conclusion, Ti and Ti-6Al-4V alloy treated with 15 wt. % of H₂O₂ showed the matured growth of calcium and phosphate layer over the surface as deduced from the SEM-EDAX images and also from EIS, the resistance values of the apatite layer formed was very high when compared to specimens treated with other concentrations of H₂O₂. However, H₂O₂ treated Ti-6Al-7Nb alloy exhibited only few globular like particles as observed from the SEM images. Moreover, the resistance values of the various layers formed was very low, indicating the poor bone bonding ability of the specimen. From the electrochemical studies, it was observed that the corrosion resistance of the Ti , Ti-6Al-4V and Ti-6Al-7Nb alloys treated with various concentrations of H₂O₂ was found to follow the order 15 wt.% > 5 wt.% > 25 wt.%; 15 wt. % 25 wt.% > 5 wt.% and 15 wt.% > 25 wt.% > 5 wt.%.