CHAPTER 4

CONCLUSIONS

In the present investigation, the Ti surface was modified in two different ways namely (i) Formation of TNPA using two different type of electrolyte: (a) aqueous and (b) organic with varying concentration of HF between 0.1 M to 0.2 M at the constant voltage of 40 V for 1 h and (ii) TNTA using organic with 0.26 M NH$_4$F at the constant voltage of 50 V for 2.5 h.

To enhance the bioactivity of TNPA, alkali treatment was carried out with 5 M NaOH for 30 min and annealed at 450 °C. The bioactivity of TNTA was enhanced by incorporation of Sr and Zr ions by simple dip coating method. The specimens were then immersed in Hank’s solution for different durations (3, 5 and 7 days) to find out the HAp forming ability. FE-SEM, ATR-FTIR, TF-XRD, XPS, AFM and electrochemical corrosion studies were performed to study the nature of surface morphology, topography, existence of characteristic functional groups, compositional analysis of elements, phase composition and corrosion behaviour of TiO$_2$ nanopore and nanotube arrays before and after in-vitro immersion in Hank’s solution. The contact angle measurements were done to study the wetting behavior of the specimens. The conclusions are summarized below.

TNPA

- During anodization in a mixture of 0.15 M HF with 0.13 M glycerol for 1 h at 40 V, the color of the Ti changed from blue to whitish green and pink swiftly. The color change is due to the increase in oxide film thickness.
• The average pore diameter was found to be 84 and 64 nm respectively for organic and aqueous electrolytes at 40 V in the optimum fluoride ion concentration of 0.15 M.

• The length of the nanopores are found to be 0.075 µm and 0.1 µm in aqueous and organic electrolytes respectively.

• The heat treatment of the as prepared amorphous TNPA resulted in crystalline anatase structure as evidenced from the TF-XRD patterns.

• The nature of electrolyte and electrolyte concentration employed for anodization played an important role in altering the pore diameter and length.

• The surface morphological and elemental composition studies showed the growth of HAp layer on alkali heat treated TNPA by in-vitro immersion in Hank’s solution.

• The contact angle measurements showed that the alkali heat treated TNPA was hydrophobic in nature.

• The potentiodynamic polarization studies showed that the alkali heat treated TNPA after 7 days of immersion exhibited higher corrosion resistance than the UT samples.

**TNTA**

• During anodization in a mixture of 0.26 M NH₄F and 14.5 M ethylene glycol for 2.5 h at 50 V, the colour of the Ti sheet was changed from grey to pale green to blue.

• The I-t curves revealed that the following steps were involved in the formation of nanotube arrays: (1) growth of oxide layer
on the surface of Ti due to the interaction of $O^{2-}$ and $Ti^{4+}$, (2) dissolution of oxide layer, (3) overlap of the two process i.e oxide layer formation and dissolution which in turn formed pits on the surface and (4) development of pores from the pits and finally, the pores were transformed into tubes.

- The average tube diameter and wall thickness were found to be 110 and 15 nm respectively and the average inter tube diameter (distance between the centre of the adjacent tubes) was found to be 128 nm.

- It was clear from the cross sectional FE-SEM images of TNTA, that, the tube structures were formed with a length of approx. 2.1 µm.

- The morphological studies revealed that the nanotube morphology is retained with small reduction in the tube diameter after the complete incorporation of Sr ions over the TNTA tube walls.

- The FE-SEM images of TNTA after 7 days of immersion, revealed the presence of HAp particles, white globular in shape and the corresponding EDS spectrum showed the peaks of Ca and P which confirmed the HAp formation over the modified specimens.

**Sr-TNTA and Zr- TNTA**

- Similar morphology was not seen in the case of Sr-TNTA and Zr-TNTA. Instead, a trabecular bone like morphology and thick flake like morphology were observed for Sr-TNTA and
Zr-TNTA respectively. This may be due to the incorporation of Sr and Zr ions which were adsorbed over the entire surface.

- The ATR-FTIR results of TNTA, Sr-TNTA and Zr-TNTA revealed the well-defined phosphate and carbonate peaks, which confirmed the HAp formation on the surface after immersion in Hank’s solution.

- The TF-XRD patterns of TNTA, Sr-TNTA and Zr-TNTA revealed the characteristic HAp peaks after immersion in Hank’s solution for 7 days.

- Contact angle measurements showed super wettability for TNTA, whereas Sr-TNTA and Zr-TNTA specimens showed hydrophilic behavior.

- The roughness measurements exhibited micro roughness for TNTA, Sr-TNTA and Zr-TNTA specimens.

- Potentiodynamic polarization studies showed that the current density was minimum for the Sr-TNTA after 7 days of immersion in Hank's solution, which suggested the higher corrosion resistance of the specimen.

- Electrochemical impedance spectroscopic measurements revealed two time constant behavior, indicating the inner barrier and outer porous layer after 3 days of immersion in Hank’s solution, whereas the appearance of third time constant behavior revealed the resistance provided by the newly formed HAp layer after 5 and 7 days of immersion in Hank’s solution.
From the above observations, we can conclude that the Sr-TNTA exhibited higher corrosion resistance and enhanced *in-vitro* bioactivity when compared to other specimens. The corrosion resistance of the TNTA, Sr-TNTA and Zr-TNTA specimens were found to be in the order as follows:

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\text{Sr-TNTA} > \text{Zr-TNTA} > \text{TNTA}
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Hence, the TNTA with Sr ions is projected to have an immense potential in clinical medicine, especially as a bone implant material to provide improved corrosion resistance and enhanced bioactivity.

The future direction of this work focuses on the *in vivo* studies of TNTA with and without the incorporation of Sr and Zr ions into TNTA specimen. The implants will be implanted into the rats for 4 weeks. X-rays will be taken for the rats before and after the implantation of the specimens. The SEM-EDAX and TEM will be taken before and after the implantation of the specimens into the rats to understand the cell structure of the tissue over the implant surface. The implant samples will be removed from the rats after 4 weeks. Histological studies will be carried out for the control, TNTA, Sr-TNTA and Zr-TNTA at 4 weeks after implantation.