PREFACE

During the last decade, there has been extensive use of titanium and its alloys for biomedical applications. Titanium and its alloys have modulus of elasticity lower than other metallic biomaterials such as stainless steels and Co-Cr alloys. In general, elastic moduli of β-type titanium alloys is much lower than those of α and (α + β) type titanium alloys. Among titanium alloys, developed for aerospace applications, Ti-6Al-4V was the first titanium alloy to be used as biomedical implants. However, some health issues have been reported to be associated with the release of vanadium and aluminium ions from Ti-6Al-4V alloy. Another disadvantage is the mismatch of modulus of elasticity of Ti-6Al-4V (~120 GPa) with that of human bone (~30 GPa), that creates stress shielding effect between the implant and human bone, causing excessive bone resorption and loss of bone. Consequently, non-toxicity of implant and its low elastic modulus are the two crucial requirements for a suitable titanium bio-implant. Much of the research of biomaterials has been focused on reducing elastic modulus of materials for biomedical applications. Alloying of titanium with non-allergic beta stabilizing elements such as Nb, Zr, Mo, Ta and Sn shows possibility of controlling modulus of elasticity through various heat treatments. Beta titanium alloys, in addition to low elastic modulus also possess adequate mechanical properties and wear resistance.

Titanium and its alloys are in much demand for bio-medical applications because of their good corrosion resistance, specific strength and biocompatibility. Improved corrosion resistance of such titanium alloys is due to formation of a stable passive oxide layer at the surface. The electrochemical and physicochemical properties of the passive oxide layer play a vital role in the process of osseointegration and biocompatibility of

titanium implants. Corrosion is one of the main challenges for ensuring stability and biocompatibility of metallic implants.

Both corrosion as well as fatigue failure in most of the materials occurs from the surface; therefore, through surface modification, the performance of metallic materials can be effectively improved. Several researchers have worked on improving lifetime of titanium implants through surface modification. In commercially pure titanium, a nanocrystalline layer was developed by ultrasonic shot peening (USSP) technique and was found to cause significant improvement in its fatigue life and surface hardness. Many researchers have found USSP a potential process for enhancing hardness, corrosion resistance and fatigue resistance through inducement of large amount of compressive residual stresses as well as grain refinement in the surface region of materials. This process can be controlled to produce rapid nanostructuring and gradient microstructure in short duration with high energy of impacts.

The present investigation deals with the influence of heat treatments on the microstructure, hardness, tensile behaviour and elastic modulus of the near-β Ti-13Nb-13Zr alloy. It also presents the effect of USSP treatment on surface microstructure modification, corrosion behaviour, low cycle fatigue and in-vitro biocompatibility of the alloy. This thesis comprises of eight chapters.

Chapter 1 presents brief introduction along with literature review on the properties and applications of the Ti-13Nb-13Zr alloy. It also presents the details of grain refinement processes in metals/alloys. USSP improves both fatigue and corrosion resistance of titanium alloys. The objectives of the present investigation are listed at the end of this chapter.

Chapter 2 presents details of the material, Ti-13Nb-13Zr alloy, and the procedure of its characterization before and after heat treatment. The alloy Ti-13Nb-13Zr was procured from Baoji Kedipu Shaanxi, China, as rod of 30 mm diameter. It was cut into pieces of 110 mm length and pieces were longitudinally sectioned into two halves, to be machined into cylindrical shape of 12 mm diameter, for machining of cylindrical fatigue test samples. The cylindrical blanks were subjected to two different solution treatment temperatures and quenched at different temperatures. Three different heat treatments were given. Two samples were solution treated at 900°C (above β transus~735°C) for 1 hour, one was quenched in water at room temperature (25°C) and the other in alcohol maintained at sub-zero temperature (-30°C), and these are designated as 900WQ and 900SZQ, respectively. The third sample was solution treated at 660°C and quenched in water and designated as 660WQ.The microstructure is characterized before and after ultrasonic shot peening (USSP) treatment. The procedures of characterization like optical microscopy, scanning electron microscopy, transmission electron microscopy, electron probe micro-analysis and X-ray diffraction are described. The procedures of the measurement of elastic modulus of the heat-treated samples, evaluation of surface roughness and microhardness are also described. Test procedures for electrochemical corrosion by potentiodynamic polarization, electrochemical impedance spectroscopy and static immersion tests inside Ringer's solution are presented. The procedure of conducting low cycle fatigue tests is described. The methods used for biocompatibility study through cell proliferation and cell adhesion tests are described.

Chapter 3 presents the effect of three different heat treatments on modulus and tensile properties of the Ti-13Nb-13Zr alloy. The alloy was subjected to two different solution treatment temperatures and quenched at different temperatures. Elastic modulus was decreased with increase in the cooling rate, following the solution treatment. The

samples solution treated at 900° C and quenched at sub-zero temperature, contained α′′ martensite along with α′ and β phases and the elastic modulus was lowered. Among all the heat-treated samples, the one solution treated at 900°C and quenched in water, exhibited lowest elastic modulus of 60 GPa and adequate tensile properties for applications as bioimplants.

Chapter 4 presents the effect of USSP treatment on the microstructure modification, surface roughness, microhardness and residual stress of the material. The heat-treated alloy with low elastic modulus, and optimum mechanical properties was selected and given USSP treatments for different durations of 15 to 360 seconds. Microstructural changes were examined using XRD, SEM and TEM. The average surface roughness was found to increase with increase in the USSP duration. Microhardness was observed to be highest in the surface region, and gradually decrease towards the substrate. Microhardness and also the depth of modification increased with duration of USSP treatment. No phase transformation was observed due to USSP treatment, as confirmed through XRD. Nano size grains of 21, 13 and 12 nm were observed in the surface region of the alloy; after 120, 240 and 360 seconds of USSP duration.

Chapter 5 describes the effect of the USSP on corrosion behaviour of the Ti-13Nb-13Zr alloy in Ringer's solution by electrochemical impedance spectroscopy, potentiodynamic polarization and static immersion tests. The electrochemical study revealed reduction in corrosion of the USSP treated samples. Grain refinement and surface roughness were the two opposing factors controlling the corrosion behaviour. Besides refined grain size and the presence of surface compressive residual stresses, the appropriate USSP duration produced optimal corrosion resistance. There was maximum passivation from the 30 s of USSP treatment, and it decreased with an increase in the

USSP duration. The improvement in corrosion resistance from the USSP was due to grain refinement and the associated compressive residual stresses in the surface region.

Chapter 6 describes the influence of USSP as well that of stress-relieving 400°C for 1 hour (USSP-SR), on low cycle fatigue life of the Ti-13Nb-13Zr alloy, at room temperature. The results are discussed in terms of surface nano structuring and the compressive residual stress associated with the affected region. The gauge section of fatigue samples was subjected to USSP treatment uniformly, for different durations, by rotating the sample to ensure uniform peening along circumference of the gauge section for 4 minutes duration. Low cycle fatigue tests were conducted for non-USSP, USSP, and USSP-SR conditions under fully reversible (R = -1) axial loading, with triangular waveform, at total strain amplitudes of ±0.55%, ±0.60%, ±0.70%, ±0.80%, and ±0.90%, at a fixed strain rate of 0.005 s^{-1}. The microstructure and fracture morphology of the fatigue tested specimens are analyzed using scanning electron microscope. Low cycle Fatigue (LCF) tests were first conducted at ±0.70% total strain amplitude for the samples USSP treated for 120, 240 and 360 s of duration to find out the best fatigue life with respect to the peening duration. LCF life was increased considerably for all the specimens subjected to USSP treatment of 120-360 seconds but the optimum enhancement was seen in the specimen USSP treated for 240 s, in which fatigue life was enhanced nearly three times. Fatigue crack initiation in the un-treated and USSP-SR samples was found from the surface, whereas it was from subsurface in the USSP treated samples.

Chapter 7 deals with the in-vitro biocompatibility study of the alloy in non-USSP, USSP and USSP-SR conditions using cell proliferation and cell adhesion tests. Disc-shaped samples of 3 mm diameter and 2 mm thickness were prepared from the as heat-treated Ti-13Nb-13Zr alloy, with optimal elastic modulus and mechanical properties. MTT (4,5-di-methyl-thiazol-2-yl-2,5-diphenyl tetrazolium bromide) assay

was performed for checking cell proliferation/cell viability using a standard microplate absorbance reader. The increase in cellular activity increases the formation of formazan crystal, thereby increasing the absorbance value, which is directly proportional to the active cells. MG63 cells (10^4 cells/well) were seeded on the surface and after 48 h of incubation, relative cell viability was measured. A significant increase in cell proliferation is observed with increase in USSP duration. After 48 hours of incubation, there is about 1.6 times increase in cell viability of the MG-63 cells after 120 s USSP treatment, due to increased roughness and formation of nano-structures, with high positive potential. Improved cell viability in USSP-SR samples can be attributed to the increased osteoblast anchorage due to combined effect of roughness and formation of biocompatible oxide layer on the surface via stress-relieving treatment. A good amount of cell coverage can also be observed in fluorescence microscopy images of the USSP and USSP-SR samples compared to Un-USSP samples. It was observed from this study that USSP treatment on alloy surface significantly changed the surface architecture to nano level, which led to enhanced Osteoblast cell adhesion and proliferation.

Chapter 8 presents major conclusions drawn from the present investigation along with suggestions for the future work.