

Table of Contents

	<u>Page No.</u>
List of Figures	xix
List of Tables.....	xxvii
Abbreviations	xxix
Symbols.....	xxxiii
PREFACE	xxxvii
Chapter 1.....	1
Introduction And Literature Review	1
1.1 Biomaterials.....	1
1.2 Titanium and Titanium Alloys	2
1.3 Biomedical Applications of Titanium Alloys.....	7
1.4 Impact of Microstructural Modification on Mechanical Properties	10
1.5 Importance of Elastic Modulus	20
1.6 Effect of USSP on Microstructure.....	23
1.7 Corrosion Behaviour	24
1.8 Fatigue Behaviour	28
1.9 Osseointegration	31
1.10 Scope of The Present Investigation	35
1.11 Objectives of the Present Investigation	36
Chapter 2.....	37
Material and Experimental Details.....	37

2.1 Introduction.....	37
2.2 Material	37
2.3 Ultrasonic Shot Peening Treatment	38
2.4 Microstructural Characterization	39
2.5 Mechanical Properties.....	41
2.6 Electrochemical Corrosion Measurements	44
2.7 Bioactivity Tests	46
Chapter 3	49
Elastic Modulus and Tensile Behaviour	49
3.1 Introduction.....	49
3.2 Microstructural Characterization	49
3.3 Microhardness.....	53
3.4 Elastic Modulus	53
3.5 Tensile Properties.....	54
3.6 Discussion.....	57
3.7 Conclusions.....	61
Chapter 4	63
Microstructural Characterization and Microhardness variation after USSP treatment.....	63
4.1 Introduction.....	63
4.2 Microstructural Characterization	63
4.3 Surface Roughness.....	69

4.4 Microhardness	71
4.5 Residual Stress.....	73
4.6 Discussion.....	74
4.7 Conclusions	78
Chapter 5.....	81
Effect of USSP on Corrosion Resistance	81
5.1 Introduction	81
5.2 USSP Treatment	81
5.3 Corrosion Properties.....	82
5.4 Weight Loss in Static Immersion tests	89
5.5 Chemical Analysis by XPS	93
5.6 Discussion.....	96
5.7 Conclusions	104
Chapter 6.....	105
Effect of USSP on Low Cycle Fatigue Behaviour.....	105
6.1 Introduction	105
6.2 Microstructure	106
6.3 Roughness.....	107
6.4 Microhardness	108
6.5 Residual Stress.....	109
6.6 Low Cycle Fatigue Behaviour.....	110
6.7 Discussion.....	120

6.8 Conclusions.....	126
Chapter 7	127
Influence of USSP and Subsequent Stress Relieving on Biocompatibility and Cell Response.....	127
7.1 Introduction.....	127
7.2 Sample Preparation	128
7.3 Osseointegration	128
7.4 Wettability test.....	130
7.5 Cell Culture.....	132
7.6 MTT Assay	135
7.7 Discussion.....	136
7.8 Conclusions.....	140
Chapter 8	141
Summary and Suggestions for Future Work	141
8.1 Introduction.....	141
8.2 Summary	141
8.3 Suggestions for Future Work.....	145
Bibliography	146
List of Publications	173
International Conferences.....	173

List of Figures

<u>Figure No.</u>	<u>Figure Caption</u>	<u>Page No.</u>
Figure 1.1 (a)	The hcp (alpha) and bcc (beta) structure of titanium.	
	(b) Categories of titanium phase diagrams formed with different alloying additions.	3
Figure 1.2	Key microstructural phases observed in various types of microstructures in a wide range of titanium alloys.	5
Figure 1.3	Biomedical applications of titanium alloys.	8
Figure 1.4	Laser shock peening process.....	16
Figure 1.5	Shot peening process.	17
Figure 1.6	Schematic of (a) ultrasonic shot peening instrument, (b) chamber assembly, and (c) principle of ultrasonic shot peening.	18
Figure 1.7	Stress shielding phenomenon.....	20
Figure 1.8	Elastic modulus of currently used biomedical alloys.	21
Figure 1.9	Bright field TEM micrographs with related SAED patterns taken at depths of (a) 5 μm and (b) 20 μm from the surface of the alloy Ti–6Al–4V following USSP with 3 mm balls.	23
Figure 1.10 (a)	TEM micrograph and, the corresponding (b) SAED pattern of Ti-Nb-Zr-Fe alloy after 60 minutes of SMAT treatment by 8 mm steel shots.	24
Figure 1.11 (a)	Cyclic polarization curves of β solution treated specimens with different cooling conditions of Ti–13Nb–	

13Zr alloy in Ringer’s solution; (b) Polarization curves of Ti-13Nb-13Zr and Ti-15Mo in aerated Ringer’s solution.....	26
Figure 1.12 (a) Stress controlled fatigue (S-N) curve and, (b) Strain- controlled fatigue data of of Ti-7.5Mo, Ti-13Nb-13Zr, Cp-Ti, and Ti-6Al-4V alloy in their cast condition	29
Figure 1.13 Cell cultured on Cp-Ti samples (a) for three days, USSP treated for 30, 60, 90 and 120 seconds; followed by stress relieving, (b) for 1, 2 and 3 days, USSP treated for 45 minutes and annealed.....	33
Figure 2.1 Schematic representation of Ultrasonic shot peening set-up	38
Figure 2.2 Ultrasonic velocity gauge for elastic modulus measurement.....	41
Figure 2.3 Geometry of tensile test sample.	42
Figure 2.4 Geometry of LCF test sample.	43
Figure 2.5 Test samples suspended in Ringer’s solution for static immersion test.....	45
Figure 3.1 Heat treatment outline for the alloy Ti-13Nb-13Zr.....	49
Figure 3.2 Optical microstructures of the Ti-13Nb-13Zr alloy in different conditions (a) AR, (b) 660WQ, (c) 900WQ and (d) 900SZQ. Magnified views are shown in the insets.....	50
Figure 3.3 XRD patterns of the Ti-13Nb-13Zr alloy in different conditions.....	51
Figure 3.4 Variation of microhardness in different conditions.....	53
Figure 3.5 Elastic modulus of Ti-13Nb-13Zr alloy in different conditions, measured by ultrasonic testing	54

Figure 3.6 Typical stress-strain curves of Ti-13Nb-13Zr alloy in different conditions.....	55
Figure 3.7 SEM fractographs of tensile tested samples with different conditions: (a) AR, (b) 660WQ, (c) 900WQ and (d) 900SZQ, showing dimple morphology	56
Figure 4.1 (a) Optical, (b) SEM, and (c) TEM micrographs of the Un- USSP (900WQ) sample.....	64
Figure 4.2 TEM micrographs of (a) of α' (hcp) and (c) β (bcc) phases, along with respective SAED patterns shown in (b) and (d)..	65
Figure 4.3 XRD profiles of the Un-USSP and USSP treated specimens (used for corrosion study).....	66
Figure 4.4 XRD profiles of the Un-USSP and USSP treated specimens (used for low cycle fatigue study).	66
Figure 4.5 Typical TEM micrographs with respective SAED patterns, of the different conditions: (a) Un-USSP showing twins and dislocations, (b) USSP30, (c) USSP60, and (d) USSP120.....	68
Figure 4.6 Variation of average surface roughness with duration of USSP.	70
Figure 4.7 SEM images of the (a) Un-USSP, (b) USSP30, (c) USSP60 and (d) USSP120 specimen showing surface cracks.....	71
Figure 4.8 Microhardness variation along the depth of the Un-USSP and USSP treated samples.....	72

Figure 4.9 SEM micrographs of the (a) USSP120, (b) USSP240, and (c) USSP360 samples, showing depth of modified layer on the longitudinal mid-section of the specimens.	72
Figure 4.10 Surface residual stress of the Un-USSP and USSP treated specimens.....	73
Figure 5.1 Potentiodynamic polarization curves of the Un-USSP and USSP treated samples.	83
Figure 5.2 Nyquist diagrams of the Un-USSP and USSP treated Ti- 13Nb-13Zr specimens.....	86
Figure 5.3 Equivalent circuit diagram for the fitting of EIS data.....	86
Figure 5.4 Bode diagrams (a) log-log plot of $ Z $ vs. freq. and (b) log- log plot of phase angle vs. freq., of Un-USSP and USSP treated specimens. The experimental data are shown by the symbols and the simulated data are shown as the solid lines.....	87
Figure 5.5 Weight change in the Un-USSP and USSP treated samples after static immersion in Ringer's solution, at room temperature.	90
Figure 5.6 Corrosion rate of the Un-USSP and USSP treated samples after 35 weeks of immersion in Ringer's solution.....	90
Figure 5.7 SEM images along with EDS of the (a) Un-USSP, (c) USSP30, (e) USSP60, and (g) USSP120 samples after 35 weeks of immersion in the Ringer's solution.	92
Figure 5.8 Typical XPS survey data of the USSP30 and Un-USSP specimens.....	93

Figure 5.9 High resolution XPS showing Ti 2p, Nb 3d, Zr 3d, Ca 2p, P 2p, and O 1s of the Ti-13Nb-13Zr alloy, in the USSP30 and Un-USSP condition.	94
Figure 5.10 Schematic illustration of the passive layer and associated compressive residual stress in different conditions (a) Un- USSP, (b) USSP30, and (c) USSP120 samples.....	95
Figure 6.1 XRD peaks of the Un-USSP, USSP240 and USSP240-SR samples.	106
Figure 6.2 Variation of hardness across the depth of Un-USSP, USSP240 and USSP240-SR samples.	108
Figure 6.3 Residual stress as a function of depth in USSP240 and USSP240-SR samples.	109
Figure 6.4 Cyclic stress response curves of (a) Un-USSP, (b) USSP240 and (c) USSP240-SR samples.....	111
Figure 6.5 Fatigue hysteresis loops for first cycles in the Un-USSP, USSP240 and USSP240-SR conditions.	112
Figure 6.6 Coffin-Manson plot for the Un-USSP, USSP240 and USSP240-SR samples.	113
Figure 6.7 Fatigue life cycles for the Un-USSP, USSP240 and USSP240-SR conditions, at different total strain amplitudes.	114
Figure 6.8 SEM micrographs showing fracture surface of Un-USSP, USSP240 treated and USSP-SR samples, at different total strain amplitudes.....	116

Figure 6.9 SEM micrographs showing fracture surface morphology of Un-USSP, USSP240 treated and USSP240-SR samples, at different total strain amplitudes.	117
Figure 6.10 TEM images of Un-USSP sample, fatigue tested at $\pm 0.70\%$ strain amplitude showing; (a) α' laths with twinned region identified by (b) double diffraction spots in SAED pattern.....	118
Figure 6.11 TEM images of USSP240 sample, fatigue tested at $\pm 0.70\%$ strain amplitude showing α' laths having (a) twin variants PT (primary twins) and ST (secondary twins) (b) enlarged view of red marked area and (c) corresponding SAED pattern along the $[1\bar{2}1\bar{3}]_{\alpha'}$ zone axis indicating cross twins identified as two twin variants of the $\{1\bar{1}01\}$ twinning system.....	118
Figure 6.12 TEM images of USSP240 sample fatigue tested at $\pm 0.70\%$ strain amplitude having α' laths with (a) dislocation tangles (b) SAED pattern along the $[1\bar{2}1\bar{3}]_{\alpha'}$ zone axis (c) twin-twin intersection.....	119
Figure 6.13 TEM images of USSP240-SR sample fatigue tested at $\pm 0.70\%$ strain amplitude having α' laths (a) twinned region (b) enlarged view along with (c) SAED pattern along the $[2\bar{4}2\bar{3}]_{\alpha'}$ zone axis.....	119
Figure 7.1 Contact angles formed by distilled water droplets, applied on the surface of the Un-USSP, USSP and USSP-SR samples.....	131

Figure 7.2 Cell culture images of on the various Un-USSP and USSP samples after 2 days of incubation. Blue color: nuclei staining; red color: actin cytoskeleton filaments staining.133

Figure 7.3 Cell culture images of on the various Un-USSP and USSP samples after 4 days of incubation. Blue color: nuclei staining; red color: actin cytoskeleton filaments staining.134

Figure 7.4 Cell culture images of on the various USSP-SR samples after 2 days of incubation. Blue color: nuclei staining; red color: actin cytoskeleton filaments staining.134

Figure 7.5 Cell culture images of on the various USSP-SR samples after 4 days of incubation. Blue color: nuclei staining; red color: actin cytoskeleton filaments staining.135

Figure 7.6 Histograms showing relative cell viability measured for the Un-USSP, USSP and USSP-SR conditions. The absorbance of the control for the second day culture was used as a reference for all the samples in this experiment.136

List of Tables

<u>Table No.</u>	<u>Table Caption</u>	<u>Page No.</u>
Table 1.1	Some α , $\alpha+\beta$, β titanium alloys and their tensile properties.....	4
Table 1.2	Tensile properties of main metallic biomaterials in annealed condition.....	10
Table 1.3	The basic difference between SP and USSP	19
Table 2.1	Chemical composition of the Ti-13Nb-13Zr alloy (wt%).....	37
Table 2.2	Processing parameters of USSP.....	38
Table 2.3	Test matrix for LCF tests.	44
Table 3.1	Different phases and their volume fractions in different conditions.	52
Table 3.2	Tensile properties* in the as-received and different heat- treated conditions.	55
Table 3.3	Effect of the different processes and heat treatments on modulus and other tensile properties* of the alloy Ti- 13Nb-13Zr, reported earlier	60
Table 4.1	Designations of the USSP treated specimens.....	64
Table 4.2	Calculated crystallite size and mean micro-strain of the USSP treated specimens.....	67
Table 4.3	Surface roughness* of the Un-USSP and USSP treated specimens.	70
Table 5.1	Designations of the USSP treated specimens.....	82

Table 5.2 Electrochemical parameters of the Un-USSP and USSP treated specimens extracted from polarization plots fitted in the Tafel regions.	84
Table 5.3 EIS data simulation for the Un-USSP and USSP treated specimens.....	87
Table 5.4 Surface composition from XPS spectra of Un-USSP and USSP30 sample.....	94
Table 6.1 Surface roughness* of the Un-USSP, USSP240 and USSP240-SR treated specimens.	107
Table 6.2 Fatigue life of the specimens USSP treated for different durations at $\Delta\epsilon_t/2=\pm 0.70\%$	110
Table 6.3 LCF parameters calculated from Coffin-Manson plot for the Un-USSP, USSP240 and USSP240-SR conditions.....	113
Table 6.4 Low cycle fatigue data in Un-USSP, USSP240 and USSP240-SR conditions of samples at different total strain amplitudes.	114
Table 7.1 Wettability of the Un-USSP, USSP and USSP-SR samples.	130