
TABLE OF CONTENTS

	Page No
List of Figures	I–X
List of Tables	XI–XII
Preface	XIII–XVII
CHAPTER 1	1–37
Introduction and Literature Review	
1.1 Historical Development of Titanium and its Alloys	1
1.2 Crystal Structure and Phase Stability of Titanium and its Alloys	3
1.2.1 Alpha (α) Stabilizers	4
1.2.2 Beta (β) Stabilizers	5
1.2.3 Neutral Elements	5
1.3 Classification of Titanium Alloys	5
1.3.1 Commercially Pure Titanium (α -alloys)	6
1.3.2 Near- α Alloys	7
1.3.3 β Alloys	9
1.3.4 α + β Alloys	10
1.3.4.1 Microstructure of Alloy Ti–6Al–4V (α + β Alloy)	11
1.3.4.1.1 Fully Lamellar Microstructure	12
1.3.4.1.2 Fully Equiaxed Microstructure	12
1.3.4.1.3 Bi-modal (dual phase) Microstructure	13
1.4 Surface Modification Techniques	15
1.4.1 Laser Shock Peening	15
1.4.2 Conventional Shot Peening (SP)	16

1.4.2.1	Air Blast Shot Blasting (ABSP)	17
1.4.3	Ultrasonic Shot Peening (USSP)	18
1.4.4	High Energy Shot Peening	21
1.5	Effect of USSP on Microstructure	21
1.6	Effect of USSP on Corrosion	24
1.6.1	Electrochemical Corrosion	24
1.6.2	High Temperature Oxidation	27
1.6.3	Hot Corrosion	27
1.6.3.1	High Temperature Hot Corrosion	28
1.6.3.2	Low Temperature Hot Corrosion	29
1.7	Effect of USSP on Fatigue	32
1.8	Scope of Investigation	36
1.9	Objectives of the Present Study	37

CHAPTER 2 **38–49**

Material and Experimental Methods

2.1	Introduction	38
2.2	Material	38
2.3	Ultra Sonic Shot Peening (USSP) Treatment	39
2.4	Microstructural Characterization	40
2.4.1	Optical Metallography	41
2.4.2	Scanning Electron Microscopy (SEM)	41
2.4.3	Transmission Electron Microscopy (TEM)	42
2.5	X-ray Diffraction (XRD)	43
2.6	Roughness Measurement	43
2.7	Hardness Testing	43
2.8	Stress Relieving Treatment	43
2.9	Potentiodynamic Polarization	44
2.10	Hot Corrosion	44
2.10.1	Salt Composition and Procedure of Salt Coating	44

2.10.2	Weight Gain Measurement	46
2.11	Tensile Tests	47
2.12	Low Cycle Fatigue (LCF) Tests	47
 CHAPTER 3		50–70
Surface Nanostructuring of Ti–6Al–4V Through Ultrasonic Shot Peening		
3.1	Introduction	50
3.2	Microstructure Characterization	50
3.2.1	Optical Microscopy	51
3.2.2	Scanning Electron Microscopy	52
3.2.3	Transmission Electron Microscopy	55
3.3	XRD Analysis	60
3.4	Surface Roughness	63
3.5	Microhardness Profile	64
3.6	Residual Stress	65
3.7	Discussion	66
3.8	Conclusions	69
 CHAPTER 4		71–82
Effect of Ultrasonic Shot Peening on Electrochemical Corrosion Behavior of Ti–6Al–4V Alloy		
4.1	Introduction	71
4.2	Electrochemical Corrosion	71
4.2.1	Corrosion Behavior	72
4.2.2	SEM and EDS Analysis	75
4.3	Discussion	78
4.4	Conclusions	82
 CHAPTER 5		83–124
Effect of Ultrasonic Shot Peening on Hot Corrosion Behavior of Ti–6Al–4V Alloy		

5.1	Introduction	83
5.2	Visual Observations	84
5.3	Corrosion Kinetics	87
5.4	Characterization of Corrosion Products	95
	5.4.1 X-ray Diffraction Analysis	95
	5.4.2 SEM/EDS Analysis	99
	5.4.3 SEM/EDS Examination of Sectioned Hot Corroded Specimens	103
5.5	Electron Probe Micro-analysis (EPMA) of Sectioned Hot Corroded Specimens	109
5.6	Discussion	118
	5.6.1 Effect of 100%NaCl Salt Spray	119
	5.6.2 Effect of 75%Na ₂ SO ₄ +25%NaCl Mixed Salts Spray	121
	5.6.3 Effect of 90%Na ₂ SO ₄ +5%NaCl+ 5%V ₂ O ₅ Mixed Salts Sprayed	122
5.7	Conclusions	123

CHAPTER 6

Effect of Ultrasonic Shot Peening on LCF Behavior of Ti-6Al-4V Alloy 125-150

6.1	Introduction	125
6.2	Tensile Behavior	126
	6.2.1 Effect of USSP on Tensile Properties	126
	6.2.2 Fracture behavior of Tensile Tested Specimens	128
6.3	Low Cycle Fatigue Behavior	129
	6.3.1 Fracture Behavior of LCF Tested Specimens	134
	6.3.2 Deformation Behavior in LCF	141
6.4	Discussion	146
6.5	Conclusions	149

CHAPTER 7

151-154

Summary and Suggestions for Future Work

7.1	Introduction	151
7.2	Summary	151
	7.2.1 <i>Surface Nanostructuring</i>	151
	7.2.2 <i>Electrochemical Corrosion</i>	152
	7.2.3 <i>Hot Corrosion</i>	152
	7.2.4 <i>Low Cycle Fatigue Behavior</i>	153
7.3	Suggestions for Future Work	153
	REFERENCES	155–166
	LIST OF PUBLICATIONS	

Preface

Ti-6Al-4V alloy is used for wide applications such as chemical and aerospace industries due to high specific strength. It is also used in orthopaedic and dental bio-implants because of their excellent biocompatibility and corrosion resistance in physiological environments due to formation of protective oxide layer of TiO_2 . It has dual phase microstructure with primary α and transformed β . The Al is support to α phase however; V is β phase stabilizer element at room temperature.

Components of aerospace mostly fail due to fatigue. Fatigue failures of such structural components arise from cyclic loading and initiation of cracks from the surface. Low cycle fatigue (LCF) is an important property of these components, resulting from start-up and shut-down operation of turbine blades of aeroengine.

Turbine blades also encounter hot corrosion, resulting from the combustion of oil fuel and ingressed air, particularly in marine environment. A low grade of fuel contains sulfur, sodium, potassium, vanadium, lead, and molybdenum as contaminants. These impurities in the fuel following combustion in air lead to deposition of alkali metal sulfates on blade surface and cause hot corrosion. Sodium sulphate is a well-known corrosive agent, formed in the flame from sodium chloride or other sodium compounds and sulphur containing organic compounds, which are present in the almost any fuel.

Surface of the metals/alloys are modified by various processes such as, laser shock peening, conventional shot peening and ultrasonic shot peening (USSP). These techniques are useful in enhancing mechanical properties and corrosion resistance of the structural components. Therefore it is necessary to implement a process which is not only cost-effective but also produces a very high surface quality in successive process of manufacture. The grain

refinement and compressive residual stress in the surface region associated with USSP resist the process of crack initiation.

Ultrasonic shot peening is an innovative method to produce nanostructure on the surface of the metals/alloys with high frequency.

The present study deals with characterization of surface nanostructure, electrochemical corrosion and hot corrosion, and LCF behavior of ultrasonic shot peened alloy Ti-6Al-4V. The thesis comprises of seven chapters. Chapter-1 presents a brief introduction along with literature review on properties and applications of alloy Ti-6Al-4V. It also presents the details of grain refinement processes in metals/alloys. USSP improves both corrosion resistance and fatigue resistance of titanium alloys. The objectives of present investigation are listed at the end of this chapter.

Chapter-2 deals with details of the experimental procedure of USSP and characterization of the nanostructure in surface region of the alloy Ti-6Al-4V. In this chapter also present, the details of experimental methods used for electrochemical corrosion, hot corrosion, tensile test, low cycle fatigue test and study of deformation and fracture behavior.

Chapter-3 describes the effect of USSP on microstructure modification, surface roughness and microhardness. Solution treated samples of the alloy Ti-6Al-4V USSPed for different durations from 0.25 to 30 minute were examined for microstructural changes, and phase transformation. There was refinement of initial grains of $\sim 12 \mu\text{m}$ size into nano scale from USSP. It may be understood in terms of severe plastic deformation, twinning, intersection of twin systems, and further breakdown of submicron grains into nano grains. The average grain size of the samples USSPed for 5, 10, 15, and 30 minute was found to be 25 ± 3 , 20 ± 4 , 18 ± 4 and 16 ± 3 nm, respectively. The average grain size was found to decrease and Bragg peaks to broaden with increase in USSP duration. Microhardness and surface roughness increased with increase in peening duration.

Chapter-4 presents systematic study of electrochemical corrosion in Ringer solution. Polarization study was carried out for the samples USSPed for different durations from 0.25, to 30 minute in the Ringer's solution to examine the effect of USSP on corrosion resistance of this alloy. Surface morphology of the corroded samples was examined by SEM. The passive layer was analyzed by EDS. In general, corrosion resistance was improved by USSP up to the duration of 15 minute and there was maximum improvement in the specimen USSPed for 1 minute. However, corrosion resistance was drastically reduced due to USSP for long duration of 30 minute. Thus, corrosion behavior of the surface nanocrystallized specimen cannot be explained only in terms of the grain refinement, it is also affected by other factors like dislocation density, deformation, micro twinning, compressive residual stress, surface roughness and cracking.

Chapter-5 presents hot corrosion behavior of the alloy Ti-6Al-4V under salt covering of Type-1 and salt mixtures of Type-2 and Type-3, at 400, 500 and 600 °C. Specimens were subjected to cyclic heating and cooling for 100h. Surface morphologies of the corroded samples of non-USSPed and USSPed samples were characterized by SEM. Formation of the various oxides resulting from hot corrosion was characterized by EDS and XRD analysis. The elemental maps revealed variation of titanium, aluminium, vanadium, and oxygen in hot corroded samples of the both non-USSPed and USSPed specimens. Corrosion resistance was enhanced due to surface nanostructure both in air as well as in salt and salt mixtures at elevated temperatures of 400, 500 and 600 °C. Corrosion rate was found to be lower for the ultrasonic shot peened specimens as compared to those of the non-shot peened ones. Corrosion resistance of the sample exposed in Type-1 salt (100%NaCl) was found to be lowest among the three salt/salt mixtures. Corrosion resistance was observed to be higher in the Type-2 mixed salt (75%Na₂SO₄+25%NaCl) than that in the Type-3 mixed salt (90%Na₂SO₄+5%NaCl+ 5%V₂O₅). It was improved in USSPed samples due to formation of

double oxide layer. In general, corrosion kinetics was lower of the specimens subjected to USSP. The main corrosion products were characterized as TiO_2 , Ti_2O_3 , V_2O_3 , V_2O_5 and Al_2O_3 oxides on the corroded samples.

Chapter-6 brings out the effect of USSP on tensile behavior and low cycle fatigue (LCF) behavior of the alloy Ti-6Al-4V. Tensile results showed that yield and ultimate tensile strength continuously increased with increase in peening duration. Ductility decreased with increasing duration of USSP. Strain controlled LCF tests were conducted for the non-USSPed and 5 minute USSPed samples, at different total strain amplitudes ($\pm\Delta\varepsilon_t/2$) of $\pm 0.60\%$, $\pm 0.65\%$, $\pm 0.70\%$, $\pm 0.75\%$, $\pm 0.80\%$, $\pm 0.90\%$, and $\pm 1.0\%$. In general, fatigue life was increased with decrease in strain amplitude, as expected, for the both, non-USSPed as well as USSPed samples. However, the improvement in fatigue life of the USSPed samples was more prominent with lowering of strain amplitude. Fatigue life was observed to increase nearly by four times at the lowest strain amplitude. The increase in fatigue life observed in the present investigation may be attributed to delay in the process of crack initiation due to high surface compressive residual stresses and refinement of the surface grains to nanostructure by USSP. USSP produces compressive residual stress which reduces the effective tensile stress at the surface which is important for crack initiation and propagation of small cracks. The variation of cyclic stress with number of cycles, so called cyclic stress response, showed pronounced cyclic softening to a stress below the yield stress at all the strain amplitudes studied. In general, there was cyclic hardening during the initial cycles followed by continuous softening till failure at lower strain amplitude. Cyclic softening exhibited during cyclic straining has been attributed to change in dislocation substructure from the original structure to sub-grain and decrease in dislocation density. TEM study revealed that planar defects were present at all the strain amplitudes in the non-USSPed condition, however, these defects were not prominent in the USSPed condition at strain

amplitudes of $\pm 0.80\%$, $\pm 0.70\%$ and $\pm 0.65\%$ because of grain refinement. Arrays and splits of dislocations were found in the USSPed fatigue tested samples at higher strain amplitudes. Distinct dislocation network structure was observed at strain amplitude of 0.80% in the fatigued USSPed sample. Fracture behavior is also discussed in this chapter.

Chapter-7 presents the summary of the present investigation along with suggestions for future work.

LIST OF FIGURES

Figure No	Figure Captions	Page No
Fig. 1.1	Sectional view of one model of the Rolls Royce RB 211 gas turbine engine	2
Fig. 1.2	Specific strength vs temperature of selected structural materials compared with titanium alloys	3
Fig. 1.3	Crystal structure of α (HCP) and β (BCC) phase	4
Fig. 1.4	Schematic three-dimensional phase diagram to classify titanium alloys	6
Fig. 1.5	Forged compressor disc made of the near α alloy IMI 685	8
Fig. 1.6	Pseudo-binary β isomorphous phase diagram showing locations of metastable and stable β titanium alloys	9
Fig. 1.7	Schematic phase diagram of Ti–6Al with varying content of V	11
Fig. 1.8	Ti–6Al–4V alloy, held for 1h at 1065 °C, above the beta transus (a) furnace cooled, (b) air cooled	12
Fig. 1.9	Equiaxed microstructures of alloy Ti–6Al–4V via recrystallization: (a) fine equiaxed, (b) coarse equiaxed	13
Fig. 1.10	Ti–6Al–4V alloy solution treated for 1h at 955 °C: (a) air cooled, and annealed for 2h at 705 °C, (b) water quenched	14
Fig. 1.11	Process parameters for laser shock peening	16
Fig. 1.12	Schematic diagram of shot peening process	17
Fig. 1.13	Schematic illustration of the equipment of air blast shot peening	18
Fig. 1.14	Principle of ultrasonic shot peening	20
Fig. 1.15	Schematic representation of ultrasonic shot peening	20
Fig. 1.16	Cross-sectional optical micrographs of cp-Ti close to the SMAT-treated surfaces under different conditions: (a) 10 minute, (b) 16 minute, (c) 30 minute and (d) 60 minute	22
Fig. 1.17	Bright field TEM micrographs with corresponding SAD	23

	patterns at the depth of (a) 5 μm (b) 20 μm from the surface of alloy Ti-6Al-4V following USSP with 3 mm balls diameter	
Fig. 1.18	Cross-sectional morphology of cp-Ti oxidised layer on USSPed sample at (a) 500 $^{\circ}\text{C}$, (b) 600 $^{\circ}\text{C}$ and non-USSPed at (c) 500 $^{\circ}\text{C}$, (d) 600 $^{\circ}\text{C}$	30
Fig. 1.19	Weight gain versus number of cycles for the Ti-6Al-4V samples subjected to cyclic oxidation in air, Na_2SO_4 -60% V_2O_5 and Na_2SO_4 -50% NaCl at 750 $^{\circ}\text{C}$	32
Fig. 1.20	Comparison of low-cycle fatigue life of Ti-6Al-4V in mill-annealed and β -annealed condition	33
Fig. 1.21	Coffin-Manson plot for non-USSPed and 10 minute USSPed specimens condition	36
Fig. 2.1	The peening head (left) and the central unit (right) of the ultrasonic shot peening device	39
Fig. 2.2	(a) Air brush (Model-BD203) and (b) open furnace for salt coating	45
Fig. 2.3	Schematic diagram of thermal cycling during hot corrosion	46
Fig. 2.4	Servohydraulic MTS for fatigue testing	47
Fig. 2.5	Schematic diagram showing ultrasonic shot peening of the LCF specimen	48
Fig. 3.1	Microstructure of solution treated alloy Ti-6Al-4V (a) optical (b) SEM	51
Fig. 3.2	Optical micrographs of cross-sections of the specimens USSPed for different durations: (a) 1 minute, (b) 5 minute, (c) 15 minute and (d) 30 minute	52
Fig. 3.3	SEM micrographs of the alloy Ti-6Al-4V: (a) non-USSPed, (b) 1 minute, (c) 5 minute, (d) 10 minute, (e) 15 minute and (f) 30 minute USSPed	53
Fig. 3.4	SEM micrographs of the cross-sections of the specimens USSPed for (a) 5 minute, (b) 15 minute and (c) 30 minute	54
Fig. 3.5	Bright field TEM micrographs of the Ti-6Al-4V alloy in solution treated condition and the corresponding SAD	55

	patterns	
Fig. 3.6	Bright field TEM micrograph and the corresponding SAD pattern from surface region of the sample USSPed for 5 minute	56
Fig. 3.7	Bright field TEM micrograph and the corresponding SAD pattern from surface region of the sample 5 minute USSPed+SR	57
Fig. 3.8	Bright field TEM micrograph and the corresponding SAD pattern from surface region of the sample USSPed for 10 minute	57
Fig. 3.9	Bright field TEM micrograph and the corresponding SAD pattern from surface region of the sample USSPed for 15 minute	58
Fig. 3.10	Bright field TEM micrograph and the corresponding SAD pattern from surface region of the sample USSPed for 30 minute	58
Fig. 3.11	X-ray diffraction of the alloy Ti-6Al-4V in the non-USSPed and USSPed for different durations	60
Fig. 3.12	X-ray diffraction of the material in USSPed and USSPed+SR conditions	60
Fig. 3.13	Surface roughness profiles with different durations of USSP	63
Fig. 3.14	Variation of microhardness of the non-USSPed, USSPed and USSPed+stress relieved specimens from surface towards interior	65
Fig. 3.15	Variation of residual stress from the treated surface towards interior of the USSPed and USSPed+SR sample	66
Fig. 4.1	Potentiodynamic polarization curves of the non-USSPed and USSPed 0.25, 1, 5, 15 and 30 minute in Ringer's solution	72
Fig. 4.2	Potentiodynamic polarization curves of the USSPed and USSPed+SR specimens in Ringer's solution	73
Fig. 4.3	Variation of corrosion rate with duration of USSP	75

Fig. 4.4	Surface micrograph and EDS analysis of the corroded non-USSPed sample	75
Fig. 4.5	Surface micrographs and EDS analysis of the corroded samples, USSPed for different durations: (a) 0.25 minute, (b) 1 minute, (c) 5 minute, (d) 10 minute, (e) 15 minute and (f) 30 minute	77
Fig. 4.6	Surface morphology of corroded specimens: (a) 1 minute USSPed+SR, and (b) 5 minute USSPed+SR	77
Fig. 5.1	Digital photographs of the non-sprayed and salt/mixed salts sprayed samples prior to exposure at elevated temperatures	85
Fig. 5.2	Digital photographs of the non-USSPed and USSPed samples exposed at 400 °C for 100h	86
Fig. 5.3	Digital photographs of the non-USSPed and USSPed samples exposed at 500 °C for 100h	86
Fig. 5.4	Digital photographs of the non-USSPed and USSPed samples exposed at 600 °C for 100h	87
Fig. 5.5	Weight gain plots of Type–1 salt sprayed samples for the non-USSPed and USSPed conditions, exposed at 400 °C up to 100h: (a) weight gain per unit area vs time of exposure, (b) square of weight gain per unit area vs time of exposure	88
Fig. 5.6	Weight gain plots of Type–2 mixed salts sprayed samples for non-USSPed and USSPed conditions, exposed at 400 °C up to 100h: (a) weight gain per unit area vs time of exposure, (b) square of weight gain per unit area vs time of exposure	89
Fig. 5.7	Weight gain plots of Type–3 mixed salts sprayed samples for non-USSPed and USSPed conditions, exposed at 400 °C up to 100h: (a) weight gain per unit area vs time of exposure, (b) square of weight gain per unit area vs time of exposure	89
Fig. 5.8	Weight gain plots of Type–1 salt sprayed samples for	90

	non-USSPed and USSPed conditions, exposed at 500 °C up to 100h: (a) weight gain per unit area vs time of exposure, (b) square of weight gain per unit area vs time of exposure	
Fig. 5.9	Weight gain plots of Type–2 mixed salts sprayed samples for non-USSPed and USSPed conditions, exposed at 500 °C up to 100h: (a) weight gain per unit area vs time of exposure, (b) square of weight gain per unit area vs time of exposure	91
Fig. 5.10	Weight gain plots of Type–3 mixed salts sprayed samples for non-USSPed and USSPed conditions, exposed at 500 °C up to 100h: (a) weight gain per unit area vs time of exposure, (b) square of weight gain per unit area vs time of exposure	91
Fig. 5.11	Weight gain plots of non-sprayed samples for the non-USSPed and USSPed conditions, exposed at 600 °C up to 100h: (a) weight gain per unit area vs time of exposure, (b) square of weight gain per unit area vs time of exposure	93
Fig. 5.12	Weight gain plots of Type–1 salt sprayed samples for the non-USSPed and USSPed conditions, exposed at 600 °C up to 100h: (a) weight gain per unit area vs time of exposure, (b) square of weight gain per unit area vs time of exposure	93
Fig. 5.13	Weight gain plots of Type–2 mixed salts sprayed samples for the non-USSPed and USSPed conditions, exposed at 600 °C up to 100h: (a) weight gain per unit area vs time of exposure, (b) square of weight gain per unit area vs time of exposure	94
Fig. 5.14	Weight gain plots of Type–3 mixed salts sprayed samples for the non-USSPed and USSPed conditions, exposed at 600°C up to 100h: (a) weight gain per unit area vs time of exposure, (b) square of weight gain per unit area vs time	94

	of exposure	
Fig. 5.15	XRD analysis of the non-sprayed and different salt/mixed salts sprayed samples, exposed at 500 °C for 100h; (a) non-USSPed (b) USSPed	95
Fig. 5.16	XRD analysis of the non-sprayed and different salt/mixed salts sprayed samples, exposed at 600 °C for 100h; (a) non-USSPed (b) USSPed	96
Fig. 5.17	SEM/EDS analysis of Type-1 salt (100% NaCl) sprayed samples exposed at 400 °C for 100h: (a) non-USSPed, (b) USSPed	99
Fig. 5.18	SEM/EDS analysis of Type-2 mixed salts (75%Na ₂ SO ₄ +25% NaCl) sprayed samples exposed at 400 °C for 100h: (a) non-USSPed, (b) USSPed	99
Fig. 5.19	SEM/EDS analysis of Type-3 mixed salts (90%Na ₂ SO ₄ +5%NaCl+5%V ₂ O ₅) sprayed samples exposed at 400 °C for 100h: (a) non- USSPed, (b) USSPed	100
Fig. 5.20	SEM/EDS analysis of Type-1 salt (100% NaCl) sprayed samples exposed at 500 °C for 100h: (a) non-USSPed, (b) USSPed	100
Fig. 5.21	SEM/EDS analysis of Type-2 mixed salts (75%Na ₂ SO ₄ +25% NaCl) sprayed samples, exposed at 500 °C for 100h: (a) non-USSPed, (b) USSPed	101
Fig. 5.22	SEM/EDS analysis of Type-3 mixed salts (90%Na ₂ SO ₄ +5%NaCl+5%V ₂ O ₅) sprayed samples, exposed at 500 °C for 100h: (a) non-USSPed, (b) USSPed	101
Fig. 5.23	SEM/EDS analysis of non-sprayed samples, exposed at 600 °C for100h: (a) non-USSPed, (b) USSPed	102
Fig. 5.24	SEM/EDS analysis of Type-1 salt (100% NaCl) sprayed samples, exposed at 600 °C for 100h: (a) non-USSPed, (b) USSPed	102
Fig. 5.25	SEM/EDS analysis of Type-2 mixed salts	102

	(75%Na ₂ SO ₄ +25% NaCl) sprayed samples, exposed at 600 °C for 100h: (a) non-USSPed, (b) USSPed	
Fig. 5.26	SEM/EDS analysis of Type–3 mixed salts (90%Na ₂ SO ₄ +5%NaCl+5%V ₂ O ₅) sprayed samples, exposed at 600 °C for 100h: (a) non-USSPed, (b) USSPed	103
Fig. 5.27	Oxide scale morphology from surface towards interior across the thickness of the non-sprayed samples, subjected to hot corrosion for 100h at 500 °C: (a) non-USSPed (b) USSPed	104
Fig. 5.28	Oxide scale morphology from surface towards interior across the thickness of the Type–1 salt sprayed (a, b), Type–2 mixed salts (c, d) and Type–3 (e, f) mixed salts sprayed samples, subjected to hot corrosion for 100h at 500 °C: non-USSPed (a, c, e) and USSPed (b, d, f)	105
Fig. 5.29	Oxide scale morphology from surface towards interior across the thickness of the non-sprayed sample, subjected to hot corrosion for 100h at 600 °C: (a) non-USSPed (b) USSPed	106
Fig. 5.30	Oxide scale morphology from surface towards interior across the thickness of the Type–1 salt sprayed, subjected to hot corrosion for 100h at 600 °C: (a) non-USSPed (b) USSPed	107
Fig. 5.31	Oxide scale morphology from surface towards interior across the thickness of the Type–2 mixed salts sprayed, subjected to hot corrosion for 100h at 600 °C: (a) non-USSPed (b) USSPed	107
Fig. 5.32	Oxide scale morphology from surface towards interior across the thickness of the Type–3 mixed salts sprayed, subjected to hot corrosion for 100h at 600 °C: (a) non-USSPed (b) USSPed	108
Fig. 5.33	X-ray mapping and variation of elemental concentration from surface towards interior across the thickness of the non-sprayed sample, subjected to hot corrosion for 100h	110

	at 600 °C for the non-USSPed sample	
Fig. 5.34	X-ray mapping and variation of elemental concentration from surface towards interior across the thickness of the non-sprayed sample, subjected to hot corrosion for 100h at 600 °C for the USSPed sample	111
Fig. 5.35	X-ray mapping and variation of elemental concentration from surface towards interior across the thickness of the sample sprayed with Type-1 salt, subjected to hot corrosion for 100h at 600 °C for the non-USSPed sample	112
Fig. 5.36	X-ray mapping and variation of elemental concentration from surface towards interior across the thickness of the sample sprayed with Type-1 salt, subjected to hot corrosion for 100h at 600 °C for the USSPed sample	113
Fig. 5.37	X-ray mapping and variation of elemental concentration from surface towards interior across the thickness of the sample sprayed with Type-2 mixed salts, subjected to hot corrosion for 100h at 600 °C for the non-USSPed sample	114
Fig. 5.38	X-ray mapping and variation of elemental concentration from surface towards interior across the thickness of the sample sprayed with Type-2 mixed salts, subjected to hot corrosion for 100h at 600 °C for the USSPed sample	115
Fig. 5.39	X-ray mapping and variation of elemental concentration from surface towards interior across the thickness of the sample sprayed with Type-3 mixed salts, subjected to hot corrosion for 100h at 600 °C for the non-USSPed sample	116
Fig. 5.40	X-ray mapping and variation of elemental concentration from surface towards interior across the thickness of the sample sprayed with Type-3 mixed salts, subjected to hot corrosion for 100h at 600 °C for the USSPed sample	117
Fig. 6.1	Tensile engineering stress-strain curves of the non-USSPed and USSPed samples	126
Fig. 6.2	Variation of yield strength, tensile strength and elongation with the duration of USSP	127
Fig. 6.3	The true stress (σ) vs true plastic strain (ϵ_p) plot on log	127

	scale showing work hardening behavior of the non-USSPed and USSPed specimens	
Fig. 6.4	Fracture surface of the tensile tested specimens: (a, b) non-USSPed and (c, d) USSPed for 7.5 minutes	129
Fig. 6.5	Variation of LCF life with duration of USSP at constant strain amplitude of $\pm 0.75\%$	130
Fig. 6.6	Variation of cyclic stress amplitude with number of cycles at different total strain amplitudes at strain rate of $5 \times 10^{-3} \text{ s}^{-1}$: (a) non-USSPed, (b) USSPed for 5 minute and (c) USSPed+SR	132
Fig. 6.7	Coffin-Manson plot showing variation of fatigue life as number of reversals to failure ($2N_f$) with plastic strain amplitude, at strain rate of $5 \times 10^{-3} \text{ s}^{-1}$	133
Fig. 6.8	Fractographs showing fracture surfaces of the specimens tested in LCF at $\pm 0.60\%$ strain amplitude: (a, b) non-USSPed, (c, d) USSPed and (e, f) USSPed+SR	135
Fig. 6.9	Fractographs showing fracture surface of the LCF specimens tested at $\pm 0.65\%$ strain amplitude: (a, b) non-USSPed, (c, d) USSPed and (e, f) USSPed+SR	136
Fig. 6.10	Fractographs showing fracture surfaces of the specimens tested at $\pm 0.75\%$ strain amplitude: (a) non-USSPed, (b) 5 minute USSPed, (c) 7.5 minute USSPed and (d) 5 minute USSPed+SR	137
Fig. 6.11	Fractographs showing fracture surfaces of the specimens tested in LCF at $\pm 0.80\%$ strain amplitude: (a, b) non-USSPed, (c, d) USSPed and (e, f) USSPed+SR	138
Fig. 6.12	Fractographs showing fracture surfaces of the specimens tested at $\pm 1.0\%$ strain amplitude: (a, b) non-USSPed and (c, d) USSPed	139
Fig. 6.13	Variation of number of cycles for crack initiation (N_i) and crack propagation (N_p) of the non-USSPed, 5 minute USSPed and USSPed+SR samples, fractured in LCF at strain rate of $5 \times 10^{-3} \text{ s}^{-1}$	140

Fig. 6.14	Bright Field TEM micrographs and the corresponding SAD patterns of the specimens tested in LCF at strain amplitude of $\pm 0.60\%$: (a, b) non-USSPed, (c, d) USSPed and (e, f) USSPed+SR	142
Fig. 6.15	Bright Field TEM micrographs and the corresponding SAD patterns of the specimens tested in LCF at strain amplitude of $\pm 0.65\%$: (a, b) non-USSPed, (c, d) USSPed and (e, f) USSPed+SR	143
Fig. 6.16	Bright Field TEM micrographs and the corresponding SAD patterns of the specimens tested in LCF at strain amplitude of $\pm 0.70\%$: (a, b) non-USSPed and (c, d) USSPed samples	144
Fig. 6.17	Bright Field TEM micrographs and the corresponding SAD patterns of the specimens tested in LCF at strain amplitude of $\pm 0.80\%$: (a, b) non-USSPed, (c, d) USSPed and (e, f) USSPed+SR	145

LIST OF TABLES

Table No	Table Captions	Page No
Table 1.1	Typical applications and tensile strength of different grades of α alloys	7
Table 1.2	Typical applications and tensile strength of the near- α alloys	8
Table 1.3	Typical applications and tensile strength of the β alloys	10
Table 1.4	$\alpha+\beta$ titanium alloys and their applications	14
Table 1.5	The basic difference in between SP and USSP	19
Table 2.1	Chemical composition of the alloy Ti-6Al-4V	38
Table 2.2	Processing parameters for ultrasonic shot peening	40
Table 2.3	Test matrix of low cycle fatigue tests	49
Table 3.1	Average grain size in surface layer of the shot peened alloy Ti-6Al-4V measured from the TEM micrographs	59
Table 3.2	Average grain size and lattice strain in surface layer of the shot peened alloy Ti-6Al-4V	62
Table 3.3	Surface roughness of the non-USSPed and USSPed samples for different durations of USSP of the alloy Ti-6Al-4V	64
Table 4.1	Corrosion current density (i_{corr}) and corrosion potential (E_{corr}) of the specimens non-USSPed, USSPed and USSPed+SR	74
Table 5.1	Parabolic rate constant (k_p) of the samples hot corroded at 400 °C for 100h	90
Table 5.2	Parabolic rate constant (k_p) of the samples hot corroded at 500 °C for 100h	92
Table 5.3	Parabolic rate constant (k_p) of the samples hot corroded at 600 °C for 100h	94
Table 5.4a	Oxides formed from hot corrosion of non-USSPed	97

	material, characterized by XRD	
Table 5.4b	Oxides formed from hot corrosion of USSPed material, characterized by XRD	98
Table 5.5	Gibbs free energy (ΔG°) of formation of the main oxide products, per mole of oxygen, at 600 °C	98
Table 6.1	Effect of ultrasonic shot peening on tensile properties	128
Table 6.2	Effect of stress relieving treatment on LCF life of USSPed sample	130
Table 6.3	Numerical values of LCF parameters of non-USSPed and USSPed samples, tested at room temperature	134

PREFACE

Ti-6Al-4V alloy is used for wide applications such as chemical and aerospace industries due to its high specific strength. It is also used in orthopaedic and dental bio-implants because of its excellent biocompatibility and corrosion resistance in physiological environments due to formation of protective oxide layer of TiO_2 . It has dual phase microstructure with primary α and transformed β . Al is α stabilizer and V is β phase stabilizer.

Aerospace components mostly fail due to fatigue. Fatigue failures of the structural components arise from cyclic loading and initiation of cracks from the surface. Low cycle fatigue (LCF) results in the components like compressor disk and turbine blades due to start-up and shut-down operation.

Turbine engine components encounter hot corrosion, resulting from the combustion of oil fuel and ingressed air, particularly in marine environment. A low grade of fuel contains sulfur, sodium, potassium, vanadium, lead, and molybdenum as contaminants. These impurities in the fuel, following combustion in air, lead to deposition of alkali metal sulfates on blade surface and cause hot corrosion. Sodium sulfate is a well-known corrosive agent, formed in the flame from sodium chloride or other sodium compounds and sulphur containing organic compounds, which are present in the almost any fuel.

Surface of the metals/alloys are modified by various processes such as, laser shock peening, conventional shot peening and ultrasonic shot peening (USSP). These techniques are useful in enhancing mechanical properties and corrosion resistance of the structural components. Therefore, it is necessary to implement a process which is not only cost-effective but also produces a very high surface quality in successive process of manufacture. The grain refinement and compressive residual stress in the

surface region associated with USSP resist the process of crack initiation. Ultrasonic shot peening is an innovative method of producing nanostructure on the surface of metals/alloys.

The present study deals with characterization of surface nanostructure, electrochemical corrosion, hot corrosion, and LCF behavior of the alloy Ti-6Al-4V following ultrasonic shot peening. The thesis comprises of seven chapters. Chapter-1 presents a brief introduction along with literature review on properties and applications of the alloy Ti-6Al-4V. It also presents the details of grain refinement processes in metals/alloys. The objectives of present investigation are listed at the end of this chapter.

Chapter-2 deals with details of the experimental procedure of USSP and characterization of the nanostructure in surface region of the alloy Ti-6Al-4V. This chapter also presents, the details of experimental methods used for electrochemical corrosion, hot corrosion, tensile test, low cycle fatigue test and study of deformation and fracture behavior.

Chapter-3 describes the effect of USSP on microstructure modification, surface roughness and microhardness. Solution treated samples of the alloy Ti-6Al-4V USSPed for different durations from 0.25 to 30 minute were examined for microstructural changes, and phase transformation. There was refinement of initial grains of $\sim 12 \mu\text{m}$ size into nano scale from USSP. It may be understood in terms of severe plastic deformation, twinning, intersection of twin systems, and further breakdown of submicron grains into nano grains.

The average grain size of the samples USSPed for 5, 10, 15, and 30 minute was found to be 25 ± 3 , 20 ± 4 , 18 ± 4 and 16 ± 3 nm, respectively. The average grain size was

found to decrease and Bragg peaks to broaden with increase in USSP duration. Microhardness and surface roughness increased with increase in peening duration.

Chapter-4 presents systematic study of electrochemical corrosion in Ringer's solution. Polarization study was carried out for the samples USSPed for different durations from 0.25, to 30 minute in the Ringer's solution to examine the effect of USSP on corrosion resistance of this alloy. Surface morphology of the corroded samples was examined by SEM. The passive layer was analyzed by EDS. In general, corrosion resistance was improved by USSP up to the duration of 15 minute and there was maximum improvement in the specimen USSPed for 1 minute. However, corrosion resistance was drastically reduced due to USSP for long duration of 30 minute. Thus, corrosion behavior of the surface nanocrystallized specimen cannot be explained only in terms of the grain refinement; it is also affected by other factors like dislocation density, deformation, micro twinning, compressive residual stress, surface roughness and cracking.

Chapter-5 presents hot corrosion behavior of the alloy Ti-6Al-4V under salt covering of Type-1 (100%NaCl) salt and mixed salts of Type-2 (75%Na₂SO₄+25%NaCl) and Type-3 (90%Na₂SO₄+5%NaCl+ 5%V₂O₅), at elevated temperatures of 400, 500 and 600 °C. Specimens were subjected to cyclic heating and cooling for 100h. Surface morphology of the corroded non-USSPed and USSPed samples was characterized by SEM. Formation of the various oxides resulting from hot corrosion was characterized by EDS and XRD analysis.

The elemental maps revealed variation of titanium, aluminium, vanadium, and oxygen in the hot corroded samples of the both non-USSPed and USSPed specimens.

Corrosion resistance was enhanced due to surface nanostructure both in air as well as in salt and salt mixtures at elevated temperatures of 400, 500 and 600 °C. Corrosion rate was found to be lower for the ultrasonic shot peened specimens as compared to those of the non-shot peened ones. Corrosion resistance of the sample exposed in Type-1 salt was found to be lowest among the three salt/mixed salts. Corrosion resistance was observed to be higher in the Type-2 mixed salts than that in the Type-3 mixed salts. It was improved in USSPed samples due to formation of double oxide layer. In general, corrosion kinetics was lower of the specimens subjected to USSP. The main corrosion products were characterized as TiO_2 , Ti_2O_3 , V_2O_3 , V_2O_5 and Al_2O_3 oxides on the corroded samples.

Chapter-6 brings out the effect of USSP on tensile and low cycle fatigue (LCF) behavior of the alloy Ti-6Al-4V. Tensile results showed that yield and ultimate tensile strength increased with increase in peening duration whereas ductility decreased with increase in of USSP. Strain controlled LCF tests were conducted for the non-USSPed and 5 minute USSPed samples, at different total strain amplitudes ($\Delta\epsilon_t/2$) of $\pm 0.60\%$, $\pm 0.65\%$, $\pm 0.70\%$, $\pm 0.75\%$, $\pm 0.80\%$, $\pm 0.90\%$, and $\pm 1.0\%$. In general, fatigue life was increased with decrease in strain amplitude, as expected, for the both, non-USSPed as well as USSPed samples. However, the improvement in fatigue life of the USSPed samples was more prominent at lower strain amplitudes. Fatigue life was observed to increase nearly by four times at the lowest strain amplitude. The increase in fatigue life observed in the present investigation may be attributed to delay in the process of crack initiation due to high surface compressive residual stresses and refinement of the surface grains to nanostructure by USSP.

USSP produces compressive residual stress which reduces the effective tensile stress at the surface which is important for crack initiation and propagation of small

cracks. Fatigue life was reduced after stress relieving. However, the LCF life was still higher than that of the non-USSPed one. The variation of cyclic stress with number of cycles, i.e. cyclic stress response, showed pronounced cyclic softening at all the strain amplitudes studied. In general, there was cyclic hardening during the initial cycles followed by continuous softening till failure at lower strain amplitudes. Cyclic softening exhibited during cyclic straining has been attributed to change in dislocation substructure from the original structure to sub-grain and decrease in dislocation density. TEM study revealed dislocation pile-ups in the non-USSPed samples at lower strain amplitudes; however, these dislocations were not prominent in the USSPed condition at strain amplitudes of $\pm 0.80\%$, $\pm 0.70\%$, $\pm 0.65\%$ and $\pm 0.60\%$. Individual dislocations were observed in the USSPed sample tested at $\pm 0.65\%$ strain amplitude. Planar slip and intersections of planar slip were observed at higher strain amplitude (± 0.80) in the both, non-USSPed and USSPed samples. Fracture behavior is also discussed in this chapter.

Chapter-7 presents the summary of the present investigation along with suggestions for future work.

LIST OF SYMBOLS

1. Abbreviations

α	Alpha phase
β	Beta phase
cp-Ti	Commercially pure titanium
Al	Aluminium
Sn	Tin
O	Oxygen
N	Nitrogen
Mo	Molybdenum
Nb	Niobium
Cr	Chromium
Fe	Iron
Si	Silicon
Ni	Nickel
Cu	Copper
Mn	Manganese
W	Tungsten
Bi	Bismuth
Zr	Zirconium
Hf	Hafnium
H	Hydrogen
C	Carbon
HNO ₃	Nitric acid

Na	Sodium
S	sulphur
Cl	Chlorine
Na ₂ SO ₄	Sodium sulphate
NaCl	Sodium chloride
V ₂ O ₅	Vanadium pentoxide
wt. %	Weight percentage
HV	Vickers hardness
i_{corr}	Corrosion current density
E_{corr}	Corrosion potential
k_p	Parabolic rate constant
$\Delta W/A$	Weight gain per unit surface area (mg/cm ²)
ΔG°	Gibbs free energy
σ	True stress
ε_p	Plastic true strain
n	Strain hardening exponent
K	Strength coefficient
$\Delta\varepsilon_t/2$	Total strain amplitudes
$\Delta\sigma/2$	Average cyclic stress
N_f	Number of cycles to failure
$\Delta\varepsilon_p/2$	Plastic strain amplitude
ε'_f	Fatigue ductility coefficient
c	Fatigue ductility exponent
N_i	Number of cycles spent in the process of crack initiation

N_f	Number of cycles to failure
N_p	Number of cycles for crack propagation

2. Acronyms

ST	Solution treated
SP	Conventional Shot Peening
ABSP	Air Blast Shot Peening
USSP	Ultrasonic Shot Peening
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
XRD	X-ray diffractometer
SCE	Saturated calomel electrode
Type-1	100%NaCl
Type-2	75%Na ₂ SO ₄ +25%NaCl
Type-3	90%Na ₂ SO ₄ +5%NaCl+5%V ₂ O ₅
h	Hour
SR	Stress relieving
EDS	Energy dispersive spectroscopy
EPMA	Electron probe micro analyzer
WDS	Wavelength dispersive spectroscopy
EDS	Energy dispersive spectroscopy
YS	Yield strength
UTS	Tensile strength
LCF	Low cycle fatigue