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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 shoch 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 ~12 μm 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 nanocrytallized 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%Na_2SO_4+25%NaCl) than that in the Type–3 mixed salt (90%Na_2SO_4+5%NaCl+ 5%V_2O_5). 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 ±0.60%, ±0.65%, ±0.70%, ±0.75%, ±0.80%, ±0.90%, and ±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 ±0.80%, ±0.70% and ±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.

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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 sock 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.

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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

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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%Na_2SO_4+25%NaCl) and Type–3 (90%Na_2SO_4+5%NaCl+ 5%V_2O_5), 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 ($\Delta\varepsilon_t/2$) of ±0.60%, ±0.65%, ±0.70%, ±0.75%, ±0.80%, ±0.90%, and ±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 ±0.80%, ±0.70%, ±0.65% and ±0.60%. Individual dislocations were observed in the USSPed sample tested at ±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_2SO_4	Sodium sulphate
NaCl	Sodium chloride
V_2O_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)
$\Delta G°$	Gibbs free energy
σ	True stress
ε_ρ	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_2SO_4+25%NaCl
Type–3	90%Na_2SO_4+5%NaCl+5%V_2O_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