Development of Lightweight High Strength Ti-6Al-4V-xCr-yNi Alloys by μ-Plasma Powder Additive Manufacturing Process

Ph.D. Thesis

by

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Department of Mechanical Engineering Indian Institute of Technology Indore

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Development of Lightweight High Strength Ti-6Al-4V-xCr-yNi Alloys by μ-Plasma Powder Additive Manufacturing Process

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Submitted in partial fulfillment of the requirements for the award of the degree

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by

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Candidate's Declaration

l hereby certify that the work which is being presented in the thesis entitled as "Development of Lightweight High Strength Ti-6Al-4V-xCr-yNi Alloys by μ -Plasma Powder Additive Manufacturing Process" in the partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the Department of Mechanical Engineering, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from August 2020 to June 2024 under the supervision of Prof. Neelesh Kumar Jain and Dr. Dan Sathiaraj from the Department of Mechanical Engineering.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Pradyumn Kumar Arya

This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

18th June 2024

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Dedicated

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Abstract

This thesis reports on development of high-strength and lightweight Ti-6Al-4V-xCr-yNi alloys by μ -plasma powder additive manufacturing (μ -PPAM) process for aerospace, shipbuilding, and marine industries. Thermo-calc simulated phase diagram was used to design Ti-6Al-4V-xCr-yNi alloys. The experimental investigation was conducted in two stages. Thirty pilot and 27 main experiments were conducted making single-layer depositions of Ti-6Al-4V-xCr-yNi alloys to identify optimum values of μ -PPAM process parameters for manufacturing their multi-layer depositions. Microstructure, formation of phases, phase orientation maps, phase fraction, tensile properties, fracture toughness, and abrasion resistance were studied for multi-layer deposition samples of Ti-6Al-4V-xCr-yNi alloys. Corrosion behaviour Ti-6Al-4V-xCr-yNi alloys were studied in an aqueous solution of sodium chloride by evaluating potentiodynamic polarization, electrochemical impedance spectroscopy, morphology, and topography of their corroded surfaces and corrosion mechanisms. Tribological behaviour Ti-6Al-4V-xCr-yNi alloys was studied at different loads by evaluating the wear rate, morphology of wear track, and subsurface deformation. A thermo-calc simulated phase diagram revealed that 5 at.% of chromium and nickel are their upper limits that can be added to Ti-6Al-4V alloy without formation of any brittle phase and without increasing its β -transus temperature. Parametric combination of 319W as μ -plasma power, 2.9 g/min as mass flow rate of feedstock powder, and 47 mm/min as deposition head travel speed that yielded uniform and continuous deposition having combination of maximum deposition efficiency, minimum aspect ratio, and minimum dilution was identified as the optimum combination for manufacturing multi-layer deposition of Ti-6Al-4V-xCr-yNi alloys by the µ-PPAM process. Presence of chromium and nickel in Ti-6Al-4V-xCr-yNi alloys formed Cr₂Ti, and Ti₂Ni as the intermetallic phases whose melting point is higher than Ti-6Al-4V alloy. It led to accumulation of more gas bubbles thus imparting higher porosity. Results indicated that addition of chromium and/or nickel refined the grains of β -Ti and α -Ti phases of Ti-6Al-4V-xCr-yNi alloys. The α -Ti phase grains are refined due to formation of intermetallic phase Cr₂Ti in Ti6Al4V5Cr and Ti6Al4V2.5Cr2.5Ni alloys and Ti₂Ni in Ti6Al4V5Ni alloy. They act as nucleation sites for α -Ti phase, thus forming its finer grains. The β -Ti phase grains are refined due to generation of equiaxed grains enabled by the presence of chromium and nickel in the developed alloys as comparted to large columnar grains of Ti-6Al-4V alloy. It happens due to higher solidification temperature of the developed alloys than Ti6Al4V alloy. Elemental distribution in α -Ti and β -Ti phases of the developed alloys is not same because content of chromium, nickel, and vanadium in their β -Ti phase is more than their corresponding α -Ti phase. These observations are due to the eutectoid nature of chromium, nickel, and vanadium which enhances their solubility in β -Ti phase. It leads to the formation of their substitutional solid solutions within the β -Ti phase. Presence of more at.% of chromium and nickel in β-Ti phase of Ti-6Al-4V-5Cr, Ti-6Al-4V-5Ni, Ti-6Al-4V-2.5Cr-2.5Ni alloys help to improve their strength, fracture toughness, and abrasion resistance. Also, chromium in Ti-6Al-4V-5Cr alloy, chromium and nickel in Ti-6Al-4V-2.5Cr-2.5Ni alloy, and nickel in Ti-6Al-4V-5Ni alloy are uniformly distributed, which helps in improving their mechanical properties than Ti-6Al-4V alloy. Addition of chromium and nickel to Ti-6Al-4V alloy made most of the grains of the developed alloys to orient along different crystallographic planes of α -Ti phase thus reducing their anisotropy which will make their mechanical properties more uniform along a loading direction. Evolution of phases indicated formation of α/α' -Ti and β -Ti phases in Ti-6Al-4V-xCr-yNi alloys, an intermetallic phase Cr₂Ti in Ti-6Al-4V-5Cr and Ti-6Al-4V-2.5Cr-2.5Ni alloys, and an intermetallic phase Ti₂Ni in Ti-6Al-4V-5Ni alloy. Addition of chromium and/or nickel increased the yield and ultimate tensile strength of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni alloys but reduced their ductility due to grain refinement of their β -Ti and α -Ti phases, evolution of intermetallic phases Cr_2Ti and Ti_2Ni , and Dissolution of chromium and/or nickel in β -Ti phase to form solid solutions which act as barriers to movement of the dislocations, also improves strength of the developed

alloys. It changed their fracture mechanism to a combination of ductile and brittle mode possessing dimples, micropores, and cleavage facets. Average microhardness of Ti-6Al-4V-xCr-yNi alloys increases along their deposition height due to faster cooling of the top deposition layer, which forms a higher hardness phase such as martensitic α '-Ti phase. Repeated heating and cooling of the previously deposited layers allowed them to relieve stress, reducing their microhardness. Enhanced microhardness and presence of harder intermetallic phase Cr₂Ti, and Ti₂Ni phases improved abrasion resistance and fracture toughness of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni alloys thus imparting them higher resistance to crack propagation and abrasive wear. Addition of chromium and/or nickel to Ti-6Al-4V alloy increased the corrosion potential, reduced corrosion current density, and corrosion rate of the developed alloys due to formation of a protective layer of Cr_2O_3 and NiO, which acts as the barrier and prevents the direct contact of their surfaces with the corrosive environment. The EIS findings indicated that the values of polarization resistance and layer thickness of oxides increased with the addition of chromium and/or nickel to Ti-6Al-4V alloy. Pitting is suggested as the corrosion mechanism for Ti-6Al-4V-xCr-yNi which is confirmed by morphology and elemental composition of the corroded surfaces of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys. Several big size pits are observed on the corroded surface of Ti-6Al-4V alloy, whereas smaller size pits are seen on the corroded surfaces of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, and Ti-6Al-4V-5Ni alloys due to formation of relatively more stable layer of Cr₂O₃ and NiO. Addition of chromium and/or nickel to Ti-6Al-4V alloy reduced their coefficient of friction, wear volume, wear rate, worn scar depth, damage to worn surfaces, surface roughness of the worn surfaces, and thickness of plastically deformed layer due to higher microhardness value, formation of intermetallic Cr₂Ti, and Ti₂Ni phases. Morphology of wear track of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, and Ti-6Al-4V-5Ni alloys revealed formation of shallow grooves along the sliding direction, compacted debris, and delamination, whereas wear track of Ti-6Al-4V alloy showed deep grooves, micro-cracks and delamination. It can be summarized that µ-PPAM process is an energy, material-efficient, and environment-friendly process that contributed immensely to the development of Ti-6Al-4V-xCr-yNi alloys as the better high-strength and corrosion and wear resistant materials for aerospace, shipbuilding, and marine industries by minimizing the heat affect zone, thermal distortion, enhancing mechanical properties of their multi-layer depositions along with minimizing elemental segregation.

Keywords: Additive Manufacturing; Ti-6Al-4V; Microstructure; Texture analysis; Phase analysis; Mechanical properties; Corrosion resistance; Wear resistance; Thermo-calc simulation;

Publications of Pradyumn Kumar Arya

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- 4. Pradyumn Kumar Arya, Pankaj Kumar, Balbir Singh Negi, Neelesh Kumar Jain, Dan Sathiaraj (2024), "Tribological characteristics of additively manufactured Ti6Al4VxCryNi alloys", Materials Today Communications, 38, Article ID: 108113, https://doi.org/10.1016/j.mtcomm.2024.108113 (Impact factor 3.8)
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- 9. Pradyumn Kumar Arya, Dan Sathiaraj, Neelesh Kumar Jain, Jayaprakash Murugesan, Kuldeep K Saxena (2022), "Microstructure, mechanical and corrosion behaviour of friction stir welding of AA6061 Al alloy and AZ31B Mg alloy" Metallurgical Research & Technology, 119(4), 413, <u>https://doi.org/10.1051/metal/2022057</u> (Impact Factor: 1.1)

(A2) Journal Papers from Collaborative work

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- 13. Pradyumn Kumar Arya, Bhavesh Chaudhary, Neelesh Kumar Jain, Jayaprakash Murugesan (2022) "Effect of Tool Pin Profile on Mechanical and Wear Properties of Friction Stir Welding of Dissimilar AA6061 and AA5052 Aluminium Alloys" Chapter 18 in Modern Manufacturing Systems: Trends and Developments (Editors: Rajiv Kumar Garg, Ravi Pratap Singh, Rajeev Trehan, Ramesh Singh), Apple Academic Press, Florida (USA) pp 245-260, e-book ISBN: 9781003284024; Print ISBN: 9781774910443, DOI: <u>https://doi.org/10.1201/9781003284024</u>
- 14. Pradyumn Kumar Arya, Neelesh Kumar Jain, Jayaprakash Murugesan (2022) "Optimization of Process Parameters for Friction Stir Welding of Aluminium Alloy AA5052-H32 by Using Taguchi Method" Chapter 6 in Advancement in Materials Processing Technology (Editors: R. Prasad, R. Sahu, R. K.L. Sahoo, G.N. Jadhav), Springer Proceedings in Materials, Springer, Singapore, pp 71-81, DOI: https://doi.org/10.1007/978-981-16-3297-6_7
- 15. Pradyumn Kumar Arya, V. Kumar, D. Sathiaraj, I.A. Palani, Neelesh Kumar Jain (2022) "Microstructural and Mechanical Properties Analysis of Fibre Laser Welding of Dissimilar AA6061 and AA2024 Aluminium Alloy" Chapter 55 in Recent Advances in Manufacturing Processes and Systems (Editors: H.K. Dave, U.S. Dixit, D. Nedelcu) Springer, Singapore, pp 681-688, DOI: <u>https://doi.org/10.1007/978-981-16-7787-8_55</u>

(C) Conference Papers (1)

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NT. 1.4 ____

	Nomenclature
A_D	Deposition area
A_i	Atomic weight of the i^{th} constituent
A_P	Dilution area
at. %	Atomic percentage
A_w	Exposed area
B_o	Bond order
$(\boldsymbol{B_o})_i$	Covalent bond strength of the i th constituent
C_i	Atomic percentage of the i th constituents
C_j	Atomic percentage of the j th constituents
C_R	Corrosion rate
D	Dilution
d	Depth of a scratch track
d_i	Interplanar distance
d_o	Thickness of oxide layer
Ecorr	Corrosion potential
E_w	Electrochemical equivalent
F_{c}	Fracture toughness
Feq	Equivalent applied scratch load
F_{f}	Mass flow rate of feedstock powder
F_p	Applied load during the sliding wear test
F_t	Scratch load applied in horizontal directions
F_{v}	Scratch load applied in vertical directions
H	Deposition height
H_S	Scratch hardness number
h_t	Depth of a wear track
Icorr	Corrosion current
K	Constant having its value as 3,272 mm/A-cm-year
L	Length of a scratch track
L_t	Length of wear track
ma	Mass of an alloy in air
M_d	d-orbital energy level
$(M_d)_i$	d-orbital energy level of the i th constituent
m_f	Mass of an alloy in deionized (DI) water
n	Number of constituents in a multi-component alloy
P_p	Porosity
Q	High growth limitation parameter
R	Universal gas constant

A_R	Aspect ratio
$ar{r}$	Average atomic size of a multi-component alloy
r _i	Atomic radius of the i th constituent
r_L	Atomic radius of the largest atoms
r _s	Atomic radius of the smallest atoms
\boldsymbol{r}_t	Radius of the silicon nitride ball
S	Shape factor
S_d	Deposition head travel speed
S_t	Total sliding distance
S_{v}	Scratch track volume
T_d	Tip diameter
T_m	Theoretical melting temperature
T_{m_i}	Melting temperature of the i th constituent
T_P	Diluted depth
W	Deposition width
W	Width of a scratch track
Wt	Width of the wear track
wt.%	Weight percentage
x_i	Mass fraction
Zi	Valency of electrochemical dissolution
α	Angle between vertical direction and conical diamond
γ	Geometrical variable
δ	Atomic size difference
η	Powder deposition efficiency
θ	Diffraction angle
θ_t	Angle of the arc
Λ	Thermodynamic parameter
λ	Wavelength
$ ho_{e}$	Experimental density
$ ho_{f}$	Density of DI water
$ ho_i$	Density of the i^{th} constituent
ρ_P	Feedstock powder density
$ ho_r$	Relative density
ρ_t	Theoretical density
ρ_w	Experimental density
ΔH_{mix}	Mixing enthalpy
$\wedge H$ mix	Mixing enthalpy between the i^{th} and j^{th} constituents
ij ij	
ΔS_{mix}	Mixing entropy

- ΔT_{CS} Constitutional supercooling
 - χ_i Pauling electronegativity of the ith constituent
 - $\overline{\boldsymbol{\chi}}$ Average Pauling electronegativity
 - $\Delta \boldsymbol{\chi}$ Electronegativity
 - $\boldsymbol{\Omega}$ Variable parameter
 - $\boldsymbol{\Omega}_{ij}$ Standard interaction parameter
 - $\boldsymbol{\Phi}$ Half apex angle

Abbreviations

AM	Additive Manufacturing
ASTM	American Society for Testing and Materials
BCC	Body Centered Cubic
BL	Bottom Layer
CAD	Computer Aided Design
CALPHAD	Calculations of Phase Diagrams
CET	Columnar to Equiaxed Transition
CNC	Computer Numerical Control
COF	Coefficient of Friction
СР	Commercially Pure
CPE	Constant Phase Elements
CVD	Chemical Vapor Deposition
DC	Direct Current
DED	Directed Energy Deposition
DLF	Directed Light Fabrication
DLP	Digital Light Processing
DMD	Direct Metal Deposition
DMLS	Direct Metal Laser Sintering
EBFF	Electron Beam Freeform Fabrication
EBM	Electron Beam Melting
EBSD	Electron Back Scattered Diffraction
EDX	Energy Dispersive X-Ray Spectroscopy
EEC	Electrochemical Equivalent Circuit
EIS	Electrochemical Impedance Spectroscopy
FBAM	Fusion Based Additive Manufacturing
FCC	Face Centered Cubic
FDM	Fused Deposition Modelling
FGM	Functionally Graded Materials
FSP	Friction Stir Processing
GMA	Gas Metal Arc
GTA	Gas Tungsten Arc
НАр	Hydroxyapatite
HAZ	Heat Affected Zone
HCP	Hexagonal Close Packed
HSS	High-Speed Steel
IC	Intermetallic Compounds
JCPDS	Joint Committee on Powder Diffraction Standards

LBMD	Laser-Based Metal Deposition
LDC	Laser Direct Casting
LENS	Laser Engineering Net Shape
LFF	Laser Freeform Fabrication
LMD	Laser Metal Deposition
LOM	Laminated Object Manufacturing
MIG	Metal Inert Gas
MJF	Multi Jet Fusion
MJM	Multi-Jet Modelling
NCD	Nonuniform and Discontinuous Deposition
Nl/min	Normal liter per minute
OCP	Open Circuit Potential
PA	Plasma Arc
PBF	Powder Bed Fusion
PBIH	Powder Bed and Inkjet Head
PDL	Plastically Deformed Layer
PDP	Potentiodynamic Polarization
PP	Plaster-Based 3D Printing
PPAD	Pulsed Plasma Arc Deposition
PTA	Plasma Transferred Arc
PVD	Physical Vapor Deposition
SD	Standard Deviations
SEM	Scanning Electron Microscopic
SLM	Selective Laser Melting
SLS	Selective Laser Sintering
SMAT	Surface Mechanical Attrition Treatment
SOD	Stand-off Distance
SS	Solid Solution
SSAM	Solid-State Additive Manufacturing
STL	Stereolithography
TEM	Transmission Electron Microscopy
TIG	Tungsten Inert Gas
TL	Tribo-Layer
UAM	Ultrasonic Additive Manufacturing
UCD	Uniform and Continuous Deposition
VEC	Valence Electron Concentration
WAAM	Wire-Arc Additive Manufacturing
WSEM	Wire Spark Erosion Machining
XRD	X-Ray Diffractometer

μ-PMAM Micro-Plasma Metal Additive Manufacturing

µ-PPAM Micro-Plasma Powder Additive Manufacturing

Chapter 1

Introduction

This chapter provides a brief overview of Ti alloys, their classification, crystal structure, phase transformation, and phase stabilizing elements. It also discusses the need for enhancing properties of Ti alloys, different methods for it, and design methodology of multi-components alloys. It also provides brief introduction of additive manufacturing (AM), their classifications and applications, and AM of properties enhanced Ti alloys. It concludes with the organization of this PhD thesis.

1.1 Introduction of Ti Alloys

Continuous evolution of industrial technologies necessitates development of novel materials with tailored properties to meet application specific requirements for aerospace, automobile, marine, biomedical, energy, chemical, sports, and other industries (**Cann et al. 2021**). Researchers are actively engaged in developing lighter, stronger, novel, and biocompatible materials to meet the following requirements:

- Applications that seek better performance at an elevated temperature and harsh environment.
- Enabling production of next-generation high-strength lightweight aircraft and automotive parts that give better performance, safety, fuel efficiency, resistance to oxidation, corrosion and fire, and result in reduced harmful emissions.
- Seamless integration with the human body enabling improved orthopedic and dental implants and drug delivery systems thus significantly improving their surgical success rates.
- Meet demands of chemical and pharmaceutical industries such as superior corrosion and heat resistance, durability, cost-effectiveness, and eco-friendliness.
- Assist in absorption of a broader wavelength spectrum of sunlight thereby converting solar energy into electricity more efficiently resulting in cost reduction of the solar panels.
- Meet the critical challenges faced by shipbuilding and marine industries such as superior corrosion resistance, fuel efficiency, weight reduction, and safety of ships in extremely adverse working environment.
- Minimize adverse environmental impacts thus enhancing sustainability.

Advanced computational tools are enabling the researchers to model and simulate the behavior of the developed materials at the atomic level thus facilitating precise prediction and optimization of their properties. Traditional materials such as iron, nickel, copper, aluminum, magnesium, and their alloys have been extensively studied for their diverse properties and they continue to find numerous applications across the different industries (Ebrahimi et *al.* 2023; Mostafaei et *al.* 2023; Yang et *al.* 2023; Aboulkhair et *al.* 2019; Chen et *al.* 2017). Fig. 1.1 shows strength-to-weight ratio and fracture toughness for different materials. These properties play a vital role in selection of materials across diverse industries.



Fig. 1.1: Strength-to-weight ratio and fracture toughness for various metals and alloys.

It can be seen from Fig. 1.1 that steel and nickel alloys possess higher toughness but lower strength-to-weight ratio whereas aluminum alloys, magnesium alloys, and polymers have high strength-to-weight ratio but possess less toughness. In this context, Ti alloys offer a desirable balance between strength-to-weight ratio and fracture toughness. Low density of Ti alloys reduces weight of aerospace and automotive parts that translates to reduced fuel consumption and operational costs. They also have higher specific strength over a considerable range of service temperature and smaller corrosion rate which leads to extended service life and reduced maintenance cost (**Moridi et al. 2020**). Therefore, Ti alloys are highly sought-after for different applications across various industries despite being costly as compared to the traditional metals and alloys. Ti alloys containing α -Ti and β -Ti phases, and metastable β -Ti alloys are particularly attractive for both aerospace and automotive applications.

1.1.1 Classification of Ti Alloys

Ti alloys are categorized into the following five groups based on the phases present in them at room temperature as shown in Fig. 1.2.



Concentration of β stabilizers

Fig. 1.2: Classification of Ti alloys.

- α-Ti alloys contain maximum amount of commercially pure (CP) Ti, α-Ti phase stabilizers (i.e., aluminum, boron, rare earth elements, germanium, and gallium), neutral elements (i.e., tin and zirconium), minimal amounts of impurities such as carbon, oxygen, and nitrogen. They have hexagonal close packed (HCP) crystal structure at room temperature. They are commonly used in chemical and marine industries due to their superior corrosion and creep resistance. But their low strength limits their high-strength applications. Ti-5Al-2.5Sn alloy is the most commonly used α-Ti alloy for making honeycomb structures and turbomachinery pumps (Zhang et al. 2019).
- Near α-Ti alloys contain 5-10 vol.% of β-Ti phase which has body centered cubic (BCC) crystal structure, up to 2 wt.% of β-Ti phase stabilizers (i.e., vanadium, molybdenum, niobium, tantalum, rhenium, iron, copper, nickel, chromium, cobalt, manganese, and silicon), α-phase stabilizers, and the neutral elements. The presence of β-phase stabilizers in near α-Ti alloys modifies their microstructure, enhance their properties, and stabilizes β-Ti phase at room temperature. The Ti-3Al-2.5V is a near α-Ti alloy which is widely used in aircraft hydraulic tubing (Shabir and Sharma, 2024). Other near α-Ti alloys namely Ti-6Al-2Sn-4Zr-2Mo and Ti-5.8Al-4Sn-3.5Zr-0.5Mo-0.7Nb-0.35Si are commonly used in aerospace applications due to their high strength, toughness, and creep

resistance at elevated temperatures (up to 500°C). But they have lower resistance to corrosion, wear and oxidation which limit their use in other industrial applications (**Yazar et** *al.* **2020**; **Jia et** *al.* **2014**).

- α+β Ti alloys contain 5 to 40 vol.% of β-Ti phase, 4 to 10 wt.% of β-Ti phase stabilizers, α-Ti phase stabilizers, and the neutral elements. The β-Ti phase stabilizers modify their microstructure which contains α and β phases of Ti at room temperature, enhance their properties, and stabilizes β-Ti phase. These alloys are widely used in aerospace, automotive, shipbuilding, and chemical industries due to their lightweight, high strength, good corrosion and oxidation resistance, and excellent high-temperature strength (up to 600°C). The Ti-6Al-4V is the mostly used α+β Ti alloy. Other commonly used α+β Ti alloys are: Ti-6Al-6V-2Sn, Ti-4Al-4Mo-2Sn-0.5Si, Ti-4Al-4Mo-4Sn-0.5Si, and Ti-6Al-Mo-2Sn-4Zr (Zhang et al. 2024; Williams and Boyer, 2020; Barriobero et al. 2015).
- Metastable β-Ti alloys contain more than 50 vol.% of β-Ti phase, 10 to 20 wt.% of β-Ti phase stabilizers, α-Ti phase stabilizers, and the neutral elements. The β-Ti phase in these alloys is not thermodynamically stable state but it is kinetically trapped due to rapid cooling processes or due to addition of specific alloying elements. These alloys possess high strength, good formability, excellent corrosion resistance, lower young modulus, and higher capacity for mechanical damping as compared to α+β Ti alloys and near α-Ti alloys. These properties make them well-suited in biomedical and aerospace applications. The following are the most commonly used metastable β-Ti alloys: Ti-3Al-8V-4Mo-6Cr-4Zr, Ti-5Al-5V-5Mo-3Cr, and Ti-3Al-15V-3Cr-3Sn (Naseri et al. 2024; Arohi et al. 2024).
- β-Ti alloys primarily consist of β-Ti phase only, 30 wt.% of β-Ti phase stabilizers, α-Ti phase stabilizers, and the neutral elements. They possess high-temperature strength, high wear, corrosion, fatigue, and creep resistance, and higher thermal stability. But they have several drawbacks such as embrittlement, self-diffusion, creep failure at high temperatures, formation of brittle phases which restrict their applications.

1.1.2 Crystal Structure of Ti Alloys

Ti alloys are allotropic because they exist in two phases namely, α -Ti phase at room temperature having HCP crystal structure, and β -Ti phase which exists beyond 882°C temperature and has BCC crystal structure (**Guercio et al. 2020**). The α -Ti phase exhibits a desirable combination of high strength and corrosion resistance, whereas β -Ti phase has high strength at elevated temperature, and good formability which facilitates manufacturing of intricate shapes (**Weng et al. 2021**). Figs. 1.3a and 1.3b depict crystal structure and slip planes for α -Ti and β -Ti phases respectively.



Fig. 1.3: Crystal structure and slip planes for (a) α -Ti phase, and (b) β -Ti phase of Ti alloys.

It can be seen from Fig. 1.3a that α -Ti phase has the basal (0001), prismatic (10 $\overline{1}0$), and pyramidal (10 $\overline{1}1$) as its slip planes (**Cizek et al. 2024**). It has lattice parameter ratio (i.e., ratio of crystallographic axis 'c' to 'a') is 1.578 which is less than ideal value of ~1.633 for an HCP lattice. This deviation influences the predominant slip system of α -Ti phase thus making its slip to occur primarily along the prismatic plane (10 $\overline{1}0$) having [11 $\overline{2}0$] as its direction (**Krawczyk et al. 2023; Kim et al. 2015**). It can be observed from the crystal structure of β -Ti phase (Fig. 1.3b) that (110) plane is the most densely packed plane and slip occurs along this plane which has [111] as its direction (**Chandramohan, 2019**). It has lattice parameter value of 0.332 nm (**Amirnejad et al. 2020**). The other possible slip planes are (112) and (123) which generally become active at higher temperatures (**Dixit et al. 2023; Benmessaoud et al. 2020**).

1.1.3 Phase Transformations for Ti Alloys

Transformation from β -Ti to α -Ti phase is an important process in the Ti alloys because it significantly affects their microstructure and mechanical properties. The mechanism by which this transformation occurs depends on composition of a Ti alloy and its cooling rate (**Liu and Shin, 2019**). There are two mechanisms for this phase transformation: martensitic and diffusional. Martensitic transformation is a displacive and diffusion-less transformation where crystal structure changes abruptly thereby resulting in a distorted crystal lattice of a Ti alloy. In the diffusional transformation, the crystal structure changes through movement of the atoms within the lattice. It occurs at a relatively low temperature and is affected by the temperature value, type of alloying elements, and cooling duration. Cooling rate affects kinetics, nucleation, and grain growth of phase transformation from β -Ti to α -Ti phase (**Yi et al. 2020; Cottam et al. 2019**). The following five phases are formed from the β -Ti phase in
the Ti alloys depending upon the cooling rate. They are depicted in Fig. 1.4 for Ti alloys developed by additively manufacturing (AM).

- Martensitic phase α': It is formed at fast cooling rate via the displacive mechanism in which crystal structure changes without long range atomic diffusion (Wang et al. 2022). Its microstructure has acicular (or needle like) morphology inside the β-Ti phase (Zhao et al. 2022).
- Massive martensitic phase 'a_m': Its formation was observed by Ahmed and Rack (1998) in Ti-6Al-4V alloy at a moderate cooling rate. Its microstructure either has lamellar morphology inside the β-Ti phase or block-like morphology with significant presence of dislocations or non-uniformly shaped precipitate at the grain boundaries of β-Ti phase (Plichta et al. 1978).



Fig. 1.4: Phase transformations for Ti alloys developed by additive manufacturing.

- Grain boundary phase ' a_{gb} ': Its formation is a diffusion-controlled process which occurs at a slow cooling rate because it provides sufficient time for diffusion of atoms thus promoting its nucleation and growth (**Buhairi et al. 2023**). It is characterized by its continuous or discontinuous layer inside the β -Ti phase. **Banerjee et al. (2004)** reported that discontinuous layers are formed due to relatively faster cooling rate. **Sahoo and Roy** (**2023**) and **Huet et al. (2022**) observed that this phase has Burger orientation relationship with the β -Ti phase.
- Colony phase '*a_{col}*': Its formation occurs at fast cooling rate. Its plates nucleate and grow along the grain boundaries inside the β-Ti phase and these plates cluster together forming colonies with a distinct microstructure (Pathania et al. 2022). These plates preferentially

align parallel to one another thus minimizing interfacial energy inside the β -Ti phase (**Zhang et** *al.* **2022**).

Widmanstatten phase 'a_w': It occurs at fast cooling rate. It nucleates preferentially at grain boundaries inside the β-Ti phase due to its lower interfacial energy (Takajo et al. 2021). Its microstructure has basket weave morphology characterized by the presence of its lamellar plates embedded inside the β-Ti phase (Buffa et al. 2024).

It can be summarized from the phase transformations for Ti alloys that (Fig. 1.4) the formation of β -Ti phase starts with onset of the solidification process for the additively manufactured Ti alloys. Formation of ' α_{gb} ' phase inside the β -Ti phase starts as the cooling continues. Subsequently, nucleation of α -Ti and α' phases start inside the β -Ti phase. The final microstructure of the additively manufactured Ti alloys consists of α -Ti, α' , α_{gb} , and α_w phases inside the β -Ti phase and cooling rate (i.e., slow or fast) determines whether these phases will be coarse or fine.

1.1.4 Phase Stabilizing Elements for Ti Alloys

Phase stabilizing elements for Ti alloys are classified into the following three categories based on their effects on the microstructure, solubility, and phase stability: α -Ti phase stabilizing elements, β -Ti phase stabilizing elements, and neutral elements. They can either increase or decrease the β -transus temperature as depicted in Figs. 1.5a-1.5d. The addition of these phase stabilizing elements significantly affects the final microstructure of Ti alloys.





Fig. 1.5: Effect of different types of elements on β -transus temperature of Ti alloys: (a) α -Ti phase stabilizing elements, (b) β -isomorphous, (c) β -eutectoid, and (d) neutral elements.

- α -Ti phase stabilizing elements: They are soluble in α -Ti phase and increase the β -transus temperature as shown in Fig. 1.5a. They are further classified as substitutional and interstitial elements (Bettles et *al.* 2011). Aluminium is the most widely used substitutional type stabilizer for the α -Ti phase due to its atomic size and crystal structure being similar to that of Ti imparting it higher solid solubility. Boron, gallium, germanium, and rare earth elements other substitutional type stabilizers for the α -Ti phase but they have limited solubility in it. Oxygen, nitrogen, and carbon are interstitial type stabilizers for the α -Ti phase. Addition of α -Ti phase stabilizers improve corrosion resistance, flow stress, thermal stability, thermal and electrical conductivity, and weldability of Ti alloys (Kolli and Devaraj, 2018).
- β-Ti phase stabilizing elements: They readily dissolve in β-Ti phase and decrease the β-transus temperature as depicted in Figs. 1.5b and 1.5c. They are further categorized as β-isomorphous and β-eutectoid (Pesode and Barve, 2023; Carman et al. 2011). Vanadium, molybdenum, niobium, tantalum, and rhenium are the important β-isomorphous elements for stabilizing the β-Ti phase due to their high solubility in it (Kaouka et al. 2017). Iron, copper, nickel, chromium, cobalt, manganese, and silicon are the important β-eutectoid elements for stabilizing the β-Ti phase due to their limited solubility in it (Sui et al. 2021; Chen et al. 2020). The addition of higher amounts of β-eutectoid elements can promote formation of intermetallic phases. These intermetallic phases can degrade the mechanical properties of Ti alloys therefore proper selection of β-eutectoid elements is necessary to achieve the desired outcome. Addition of β-Ti phase stabilizers improve the high

temperature strength, creep resistance, toughness, strain rate sensitivity, heat treatment capacity, hardness, fatigue strength, and dimensional stability.

Neutral elements: They are soluble in both α-Ti and β-Ti phases with minimal influence on the β-transus temperature as shown in Fig. 1.5d. Tin and zirconium are important neutral elements due to their high solubility in Ti (Zhuo et al. 2021; Xia et al. 2016). These neutral elements can act as strengthening agents and slow down kinetic reactions.

1.2 Need for Enhancing Properties of Ti Alloys

Manufacturing useful engineering components from the newly developed novel materials presents major challenges, such as their unavailability in the raw form for manufacturing useful components and limited understanding of their structure-property relationships. Moreover, these materials may experience degradation of their useful properties during manufacturing of components from them and often incur higher manufacturing costs (**Xu et al. 2022; Zhang et al. 2020**). Ti alloys suffer from certain limitations such as strength reduction at temperatures exceeding 600°C, and low values of fatigue strength, fracture toughness, modulus of elasticity, wear resistance, abrasion resistance, corrosion resistance, oxidation resistance particularly at elevated temperature, and surface hardness (**Liu et al. 2022a; Meng et al. 2021; Zhao et al. 2021; Li et al. 2019; Dong et al. 2017**). Fig. 1.6 presents the causes of failures of the Ti alloy components in aerospace, biomedical, marine and shipbuilding, automotive, and other industries. Table 1.1 presents a summary of typical applications of Ti alloys in these industries and the corresponding properties required for these applications.

Industry type	Typical applications	Required properties	
Aerospace	Propeller, stator and rotor blade,	High strength, hardness, fatigue strength,	
	engine valve, casing, and disk	corrosion resistance and oxidation resistance	
Biomedical	Knee and hip joint, dental implant,	Low elastic modulus	
	stent, bone and carnival plate,	High corrosion and wear resistance, good	
	cardiac intima	biocompatibility	
Marine and	Pressure vessels, pump, fire	High corrosion resistance and strength	
shipbuilding	extinguisher, riser, pipe		
Chemical	Heat exchanger, reactor, piping,	High corrosion resistance and oxidation	
industries	pump, reaction tower, and	resistance	
	autoclave	Low density	
Automotive	Connecting rods, exhaust pipes,	High specific strength, wear resistance toughness	
	valve and valve springs, and	and fatigue resistance	
	mufflers	Low density	
Defense	Wheel, tank, cannon barrel,	High strength and corrosion resistance	
	tailstock, shaft	Low density	

Table 1.1: Summary of typical applications of Ti alloys and their required properties.



Fig. 1.6: Causes of failure of components of Ti alloys in different industries.

Reduced values of wear resistance, fatigue strength, fracture toughness, and creep strength of Ti alloys at elevated temperature restrict their aerospace applications. Whereas reduced values of their corrosion resistance, abrasion resistance, fatigue strength, fracture toughness, and increased stress corrosion cracking of Ti alloys in the harsh marine and saline environment restrict their marine applications. Biomedical applications of some Ti alloys (such as Ti-6Al-4V) are restricted due to their relatively higher modulus of elasticity which can lead to stress shielding effect. Moreover, they have relatively less fatigue strength, corrosion resistance, and wear resistance in the human body environment which can cause failure of knee, hip, and dental implants (**Zhang and Chen, 2019**). The aforementioned limitations of Ti alloys and failures of their components in different industries necessitate enhancement of their properties. Literature review of different techniques used for it is mentioned in Chapter 2.

1.3 Design of Multi-Component Alloys

Design of a multi-component alloy is very challenging due to mixing of different constituents having significant difference in their melting point, thermal properties, and atomic size. These differences lead to formation of diverse microstructures during the solidification including single-phase solid solution, multi-phase structure, and intermetallic compounds (IC). Researchers have used the following three approaches to design a multi-component alloy: (i) design employing thermodynamic and Hume-Rothery parameters, (ii) design using CALPHAD modelling, and (iii) Design utilizing the bond order and d-orbital energy diagram. They are described in the following three subsections:

1.3.1 Design using Thermodynamic and Hume-Rothery Parameters

Following are thermodynamic and Hume-Rothery parameters that are used to design a multi-component alloy: mixing enthalpy ' ΔH_{mix} ' (kJ/mol); mixing entropy ' ΔS_{mix} ' (J/mol K); variable parameter ' Ω ' (dimensionless); theoretical melting temperature ' T_m ' (K); atomic size

difference ' δ ' (%); thermodynamic parameter ' Λ ' (dimensionless); electronegativity ' $\Delta \chi$ '; valence electron concentration (dimensionless); and geometrical variable ' γ ' (dimensionless) (**Cunliffe et** *al.* **2012; Yang and Zhang, 2012; Zhang et** *al.* **2008; Cantor et** *al.* **2004; Yeh et** *al.* **2004**). The enthalpy of mixing ' ΔH_{mix} ' for a multi-component alloy can be calculated by the Eq. 1.1.

$$\Delta H_{mix} = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \Omega_{ij} C_i C_j \qquad (1.1)$$
$$\Omega_{ij} = 4\Delta H \frac{mix}{ij} \qquad (1.1a)$$

where, 'n' is number of constituents in a multi-component alloy; ' C_i ' and ' C_j ' are at.% of the i^{th} and j^{th} constituents; and ' Ω_{ij} ' is the standard interaction parameter between the i^{th} and j^{th} constituents which is calculated from the Eq. 1.1a in which ΔH_{ij}^{mix} is the mixing enthalpy between the i^{th} and j^{th} constituents. Takeuchi and Inoue (2005) proposed a method for determining the ' ΔH_{mix} ' for a binary alloy system using the concept given by Miedema et al. (1980) in which they have considered ΔH_{mix} as a parameter to predict formation and stability of the solid solutions in an alloy. A negative value of ΔH_{mix} generally indicates that the attractive forces between the constituents are strong to promote formation of a solid solution. Whereas, a positive value of ΔH_{mix} ' suggests a preference for formation of separate phases. As value of ΔH_{mix} becomes more negative, the binding forces between the constituents become even stronger which leads to formation of more stable intermetallic phases thereby reducing the overall stability (Zhang et al. 2008). As the value of ΔH_{mix} approaches zero, the interatomic forces become weak, and the constituents may randomly distribute within the lattice thus potentially forming a solid solution during solidification. Calculated value of ΔH_{mix} for a multi-component alloy is observed to be in a specific range of $-22 \leq \Delta H_{mix} \leq 7$ for formation of a solid solution (Cunliffe et al. 2012; Zhang et al. 2008; Cantor et al. **2004**). Entropy of mixing ΔS_{mix} (kJ/K) for a multi-component alloy is specified by Boltzmann's hypothesis and is calculated from Eq. 1.2 (Zhang et al. 2008).

$$\Delta S_{mix} = -R \sum_{i=1}^{n} C_i \log_e C_i \qquad (1.2)$$

where, 'n' is number of constituents in a multi-component alloy; ' C_i ' is the at.% of the *i*th constituent; and 'R' is the universal gas constant (kJ/mol K). Value of ' ΔS_{mix} ' plays a crucial role in stabilizing a solid solution and generally it is a positive value. A higher value of ' ΔS_{mix} ' favours formation of disordered solid solutions which are often more stable than the ordered intermetallic phases or ordered other phases. Researcher suggests that the value of ' ΔS_{mix} ' for

formation of a solid solution generally lies within a range of $11 \le \Delta S_{mix} \le 19.5$ (**Zhang et al. 2008**). Subsequently, a dimensionless thermodynamic parameter ' Ω ' was introduced to provide a more comprehensive assessment of stability of a solid solution. It can be calculated using the Eq. 1.3.

$$\Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|} \tag{1.3}$$

where, T_m is theoretical melting temperature (K) of a multi-component alloy that can computed from the Eq. 1.4.

$$T_m = \sum_{i=1}^n C_i T_{m_i}$$
(1.4)

where, T_{m_i} is the melting temperature of the *i*th constituent of a multi-component alloy. Value of ' Ω ' less than 1 indicates a condition for formation of an intermetallic phase. Its value greater than 1 indicates favorable conditions for formation of a solid solution. **Cunliffe et al.** (2012), Yang and Zhang (2012), Zhang et al. (2008), and Yeh et al. (2004) have suggested that threshold value for ' Ω ' for formation of a solid solution in a multi-component alloy should be greater or equal to 1.1. Difference between atomic sizes of constituents of a multicomponent alloy ' δ ' is another critical factor influencing formation of solid solutions in it. It can be computed using the Eq. 1.5.

$$\delta = \sqrt{\sum_{i=1}^{n} C_i \left(1 - \frac{r_i}{\bar{r}}\right)^2}$$
(1.5)
$$\bar{r} = \sum_{i=1}^{n} C_i r_i$$
(1.5*a*)

where, ' C_i ' is atomic percentage of the *i*th constituent; ' r_i ' is atomic radius of the *i*th constituent; and ' \bar{r} ' is the average atomic size of a multi-component alloy which can be computed from the Eq. 1.5a. A very large value of ' δ ' can cause severe lattice distortions within a multi-component alloy which hinders stability of a solid solution. Whereas very small value of ' δ ' can slow down phase transformations and promote segregation, where all constituents separate rather than forming a uniform solution. **Zhang et al. (2008)** suggested that formation of a solid solution phase in a multi-component alloy occurs when value of ' δ ' is $\leq 6.6\%$. He also suggested that the following criteria can influence formation of a solid solution in a multi-component alloy: mixing enthalpy $-20 \leq \Delta H_{mix} \leq 5$ kJ/mol; mixing entropy $12 \leq \Delta S_{mix} \leq 17.45$ J/mol K, atomic size difference $\delta \leq 6.6\%$. Subsequently, **Zhang et al. (2012)** suggested that $\Omega \geq 1.1$; and $\delta \leq 6.6\%$ are the most important factors for achieving a solid solution. Two key factors that influence formation of a solid solution are entropy of

mixing ' ΔS_{mix} ' and atomic size difference ' δ '. Therefore, an additional dimensionless thermodynamic parameter ' Λ ' was introduced to represent relationship between them. It can be computed using Eq. 1.6.

$$\Lambda = \frac{\Delta S_{mix}}{\delta^2} \tag{1.6}$$

Zhang et al. (2012) suggested the following criteria based on values of ' Λ ' for formation of a solid solution or multiple phases in a multi-component alloy: (i) formation of singlephase solid solution if $\Lambda > 0.960$; (ii) formation of mix of two-phases if $0.240 < \Lambda < 0.960$; and (iii) formation of a compound when $\Lambda < 0.240$. **Dong et al. (2014)** mentioned that electronegativity difference ' $\Delta \chi$ ' for a multi-component alloy defines its stability and it can be calculated by the Eq. 1.7.

$$\Delta \chi = \sqrt{\sum_{i=1}^{n} C_i (\chi_i - \overline{\chi})^2}$$
(1.7)
$$\overline{\chi} = \sum_{i=1}^{n} C_i \chi_i$$
(1.7*a*)

where, ' χ_i ' is the Pauling electronegativity of the *i*th constituent; and $\overline{\chi}$ is the average Pauling electronegativity for a multi-component alloy that can be calculated by the Eq. 1.7a. **Dong et al. (2014)** suggested that if $\Delta \chi > 0.133$ then formulation of stable phase occurs and if $\Delta \chi < 0.117$ then an unstable phase is formed. **Guo et al. (2011)** suggested another dimensionless parameter and named the valence electron concentration '*VEC*' for predicting the type of crystal structure formed in a multi-component alloy. It can be computed using Eq. 1.8.

$$VEC = \sum_{i=1}^{n} C_i (VEC)_i \tag{1.8}$$

where, $(VEC)_i$ is VEC for the *i*th constituent. **Guo et al.** (2011) suggested that if $VEC \ge 8$ then FCC crystal structure is formed for a multi-component alloy; if 6.87 < VEC < 8 then a mix of FCC and BCC crystal structure is formed; and if $VEC \le 6.87$ then BCC crystal structure is formed. **Singh et al.** (2014a) proposed a new dimensionless geometrical variable ' γ ' that can more effectively demonstrate the formation of solid solution or an intermetallic phase in a multi-component alloy. It can be computed using Eq. 1.9.

$$\gamma = \frac{\left(1 - \sqrt{\frac{r_s - \bar{r} - \bar{r}^2}{(r_s + \bar{r})^2}}\right)}{\left(1 - \sqrt{\frac{r_L + \bar{r} - \bar{r}^2}{(r_L + \bar{r})^2}}\right)}$$
(1.9)

where, ' r_L ' and ' r_s ' are atomic radius of the largest and smallest atoms of a multicomponent alloy; and \bar{r} is its average atomic size which is calculated using the Eq. 1.5a. The value of ' γ ' depends on the solid angles of the larger and smaller atoms within a multicomponent alloy. **Singh et al. (2014a)** suggested that when value of ' γ ' is less than 1.175 then formation of a solid solution phase takes place. If the value of ' γ ' is greater than 1.175 then an intermetallic phase is formed. The relationships between ' δ ' with ' ΔH_{mix} ' ' Ω ', ' $\Delta \chi$ ', and 'VEC' can be visualized as the phase prediction maps for predicting formation of phases in a multi-component alloy. Fig. 1.7 depicts phase prediction maps showing relations between ' δ ' and ' ΔH_{mix} ' (Fig. 1.7a), ' δ ' and ' Ω ' (Fig. 1.7b), ' δ ' and ' $\Delta \chi$ ' (Fig. 1.7c), and ' δ ' and 'VEC' (Fig. 1.7d). These relationships indicate solid solution (SS), intermetallic compound (IC), and their combination for a multi-component alloy.



Fig. 1.7: Phase prediction maps for a multi-component alloy showing relations between (a) ' δ ' and ' ΔH_{mix} '; (b), ' δ ' and ' Ω ', (c) ' δ ' and ' $\Delta \chi$ ', and (d) ' δ ' and 'VEC' (**Shao et al. 2018**).

Computation complexity, predictive power limited for the simple crystal structures, and neglect of entropy effects are the major limitations of thermodynamic and Hume-Rothery parameters approach in designing a multi-component alloy.

1.3.2 Design using CALPHAD Modelling

A simulation software known as CALPHAD (acronym of CALculations of PHAse Diagrams) is most commonly used for predicting and understanding the phase equilibria in a multi-component alloy. It leverages thermodynamic databases and computational algorithms to simulate the phase diagrams of a multi-component alloy thus enabling the researchers to predict the phases that will form under various combinations of temperature and composition. The CALPHAD software offers a more comprehensive and versatile approach as compared to the traditional design approach based on thermodynamic and Hume-Rothery parameters. This makes it a preferred choice for researchers to design and understand different phases of a multi-component alloy (Zhang and Gao, 2016; Miracle et *al.* 2014; Senkov et *al.* 2013 Zhang et *al.* 2012).



Fig. 1.8: Thermo-calc simulation results for: (a) Al-Cr-Nb-V-Mo alloy (Kang et al. 2021),
(b) Ti-6Al-4V-0.9Ni alloy (Sui et al. 2021), and (c) Ti-6Al-4V-3Cu alloy (Vilardell et al. 2020).

The CALPHAD has been used for Thermo-Calc simulations of the following Ti based multi-component alloys: Al-Cr-V-Nb-Mo (Kang et *al.* 2021), Ti-6Al-4V-0.9Ni (Sui et *al.* 2021), Ti-6Al-4V-3Cu (Vilardell et *al.* 2020) which are shown Figs. 1.8a to 1.8c respectively. Simulation results from the CALPHAD generally show good agreement with the experimental results for various multi-component alloys.

1.3.3 Design using Bond Order and d-Orbital Energy Level Diagram

Abdel et *al.* (2006) and Kuroda et *al.* (1998) used *DV-Xa* method to design a multicomponent alloy and to predict physical phenomena related to phase transformation, amount of phases present, and the stability of phases. This method relies on two key parameters namely d-orbital energy level ' M_d ' and bond order ' B_o ' of a multi-component alloy. The ' M_d ' parameter is related to electronegativity and atomic radius of the multi-component alloy constituents. It essentially reflects the energy level of d-electrons in their atoms. The ' B_o ' parameter indicates strength of chemical bonding between different constituents of a multicomponent alloy. Higher values of these parameters indicate stronger bonding between its constituents. Values of ' M_d ' and ' B_o ' parameters can be calculated by the Eqs. 1.10, and 1.11.

$$M_{d} = \sum_{i=1}^{n} C_{i}(M_{d})_{i}$$
(1.10)
$$B_{o} = \sum_{i=1}^{n} C_{i}(B_{o})_{i}$$
(1.11)

where, $(M_d)_i$ is d-orbital energy level of the *i*th constituent of a multi-component alloy; and $(B_o)_i$ is its covalent bond strength. Relations between (B_o) and (M_d) influence different deformation mechanisms (such as dislocation slip, twinning, and stress-induced martensite formation) by which a designed multi-component alloy deforms under a stress condition (**Li** et *al.* 2023; Abdel et *al.* 2006; Kuroda et *al.* 1998). Fig. 1.9a depicts the (B_o) and (M_d) diagram for a multi-component alloy which can be used to predict the dominant deformation mechanism. Fig. 1.9b illustrates the influence of various alloying elements on the values of (B_o) and (M_d) in a multi-component alloy. It can be observed from Fig. 1.9b that addition of different elements can either increase, decrease, or cause a combined increase and decrease in both (B_o) and (M_d) values (**Li et al. 2023; Sadeghpour et al. 2015**). This highlights the ability of this design approach to tailor the properties of a multi-component alloy by carefully selecting its alloying constituents.



Fig. 1.9: (a) Bo-Md diagram, and (b) effects of constituents of a multi-component alloy on the values of ' B_o ' and ' M_d ' (Li et al. 2023; Sadeghpour et al. 2015).

1.4 Applications of Properties Enhanced Ti Alloys

Properties enhanced Ti alloys find many applications in aircraft, spacecraft, biomedical, automotive, marine, and chemical industries which are described in the following paragraphs. Properties enhanced Ti alloys are being used in aerospace applications due to their enhanced corrosion resistance, fatigue, and fracture toughness and their inherent high strength-to-weight ratio. They are used for fabrication of lightweight, durable, and fuel-efficient aircraft components such as airframes, wing box, skin panel, landing gear, and cockpit window frame (**Liu et al. 2021a; Fereiduni et al. 2020**) as shown in Fig. 1.10a. They are also used in the components of a jet engine such as fan blades and casing, compressor blades and casing,

rotors disc and blade, and stator blade due to their enhanced creep resistance, and corrosion resistance, and high-temperature strength (Liu et al. 2021a) as depicted in Fig. 1.10b. They are used for the landing gear components due to their high strength, fatigue resistance, and impact toughness. This provides a reliable performance during landing and take-off of an aircraft, and absorb shocks under dynamic loading conditions (Sarraf et al. 2022). Properties enhanced Ti alloys are used in manufacturing of spacecraft components such as satellite frames, payload housings, and propulsion systems. In these applications, weight saving is critical for achieving the mission objectives and reducing launch costs (Cheng et al. 2009). They are used to manufacture missile components namely airframes, fuel tanks, and guidance systems due to their high creep and corrosion resistance, high-temperature strength, and low density (Herzig et al. 2002; Rugg et al. 2016).



Fig. 1.10: Some aerospace applications of Ti alloys with enhanced properties: (a) aircraft components, and (b) components of jet engine (Fereiduni et *al.* 2020).

Properties enhanced Ti alloys are being used in different biomedical and dental applications as shown in Fig. 1.11. It is due to their very good biocompatibility, osseointegration, enhanced corrosion and wear resistance inside the human body, and lower modulus of elasticity. They are widely used to manufacture the (i) orthopedic implants for the replacement of knee joints, elbow joints, hip joints, and shoulder joints, and for fabrication of bone plates, screws, and spinal implants (**Rugg et al. 2016; Li et al. 2014**], (ii) patient-specific mandibular prosthetic implants in maxillofacial clinical applications, and to manufacture cranial plates and mesh in conjunction with acrylic materials for cranioplasty applications, and (iii) dental implants which serve as artificial tooth roots to support dental prostheses such as crowns, bridges, and dentures (**Gou et al. 2020; Sui et al. 2020; Wang et al. 2020a**). They are used to make surgical and dental instruments such as scalpels, forceps, probes, scissors, and retractors (**Kaur and Singh, 2019**).



Fig. 1.11: Some biomedical applications of Ti alloys with enhanced properties (Li et *al.* 2014).

Properties enhanced Ti alloys are used in manufacturing chemical plant items such as tanks, vessels, reactors, heat exchangers, pumps, valves, and piping systems. It is due to their high corrosion and oxidation resistance in alkaline and acidic environments (**Sui et al. 2021; Sasikumar et al. 2019**). They are used in marine applications to manufacture to ship hull, propeller, heat exchanger, engine valve, and piping systems as shown in Fig. 1.12. It is due to their high corrosion resistance in saline and reactive environment and wear resistance under extreme sea weather (**Li et al. 2019; Oryshchenko et al. 2015**). Properties enhanced Ti alloys

are used in racing cars for manufacturing exhaust system, suspension components (such as coil springs, shock absorbers). It also manufactured engine components (such as connecting rods, intake valves), and turbocharger components due to their high-strength, fatigue and toughness, and corrosion resistance (**Chen et al. 2020; Mereddy et al. 2017**). Their higher cost and manufacturing challenges restrict their large-scale applications in the automotive industry.



Fig. 1.12: Some marine applications of properties enhanced Ti alloys (**Oryshchenko et** *al.* **2015**).

1.5 Introduction to Additive Manufacturing

American Society for Testing and Materials (ASTM) standard ISO/ASTM 52900/2021 defines additive manufacturing (AM) as "a process of joining materials to make objects from the data of 3D computer aided design (CAD) model, usually layer upon layer, as opposed to subtractive manufacturing processes". AM process is also referred to as 3D printing, freeform manufacturing, additive fabrication, or toolless manufacturing process. A CAD model is created using the appropriate design software and its data is exported to stereolithography (STL) file format which can be read by an AM machine. Some AM machines use computer numerical control (CNC) part program written in G and M codes.

1.5.1 Classification of Additive Manufacturing Processes

According to the ASTM F-42 standard, different AM processes are classified into following seven major categories: (i) Powder Bed Fusion (PBF), (ii) Directed Energy Deposition (DED), (iii) Sheet Lamination, (iv) Binder Jetting, (v) Material jetting, (vi) Material Extrusion, and (vii) Vat Photo Polymerization. Table 1.2 presents their working principle, some examples, and applicable material i.e., the material type that can be used for the making the components from a particular category of AM processes.

Category Working principle		Some examples	Applicable material	
Powder Bed Fusion (PBF)	Thermal energy selectively fuses regions of a powder bed	Electron Beam Melting (EBM), Selective Laser Sintering (SLS), Selective Laser Melting (SLM), Multi Jet Fusion (MJF), and Direct Metal Laser Sintering (DMLS)	Metallic materials, Polymers	
Directed Energy Deposition (DED)	Focused thermal energy is used to fuse materials by melting as the material is being deposited	Laser Engineering Net Shaping (LENS) Laser Metal Deposition (LMD) Wire-Arc Additive Manufacturing (WAAM) µ-Plasma Metal Additive Manufacturing (µ-PMAM)	Metallic materials	
Sheet Lamination	Sheets of material are bonded to form an object	Laminated Object Manufacturing (LOM) Ultrasonic Additive Manufacturing (UAM)	Metallic materials, Fabric, Paper	
Binder Jetting	A liquid bonding agent is selectively deposited to join powder materials	Powder Bed and Inkjet Head (PBIH), Plaster-based 3D Printing (PP)	Metallic materials, Polymers	
Material Jetting	Droplets of build material is selectively deposited	Multi-Jet Modelling (MJM)	Polymers, Waxes	
Material Extrusion	Material is selectively dispensed through a through Nozzle or orifice	Fused Deposition Modelling (FDM)	Polymers	
Vat Photo Polymerization	Liquid photopolymer in a vat is selectively cured by light activated polymerization	Stereo Lithography (SLA), Digital Light Processing (DLP)	Photopolym ers	

 Table 1.2: Classification of AM processes according to the ASTM F-42 standard (Pei and Kabir, 2022).

The AM processes can also be classified according to the requirement of melting of the deposition or feedstock material and type of heat source as shown in Fig. 1.13. Accordingly, the AM processes are divided into following two major categories: (i) fusion based additive manufacturing (FBAM) processes which require melting of the feedstock material and are referred to as the directed energy deposition (DED) process, and (ii) solid-state additive manufacturing (SSAM) processes which do not require melting of the feedstock material.



Fig. 1.13: Classification of metal additive manufacturing processes according to melting requirement of the feedstock material.

The FBAM type processes have unique multi-functional capabilities of freeform manufacturing of complicated parts, coating, cladding, surface texturing, surface alloying, repairing, remanufacturing, rapid prototyping, and rapid tooling. They are used for various applications in the fields of biomedical, post-injury rehabilitation, aerospace, automobile, marine, power generation, gas turbines, oil, and gas extraction, and sports equipment. The FBAM processes can be further classified into the following two subcategories based on the type of heat source used for melting of the feedstock material: (a) Beam based AM processes using either (a-i) electron beam as the heat source such as electron beam melting (EBM, Galati and Iuliano, 2018), or (a-ii) using laser beam as the heat source such as selective laser melting (SLM, Hu et al. 2022), selective laser sintering (SLS, Lupone et al. 2021), direct metal laser sintering (DMLS, Ishfaq et al. 2021), laser engineered net shaping (LENS, Zhang et al. 2023), Laser Metal Deposition (LMD), and (b) Arc-based AM processes which use (b-i) arc for melting the feedstock material in wire form and are referred to as wire arc additive manufacturing (WAAM) using gas metal arc (GMA), gas tungsten arc (GTA), or plasma arc (PA) (Ren et al. 2020), and (b-ii) AM processes which use the arc for forming a plasma or micro-plasma arc inside the nozzle and then the formed plasma or micro-plasma arc is used as the heat source i.e., plasma transferred arc (PTA) AM process, and micro-plasma arc AM process (Sawant and Jain 2018a; Sawant and Jain 2017).

Laser beam is the most commonly used heat source in the commercially available machines for FBAM processes. It started with the development of LENS process by Sandia National Laboratories in 1995 and its commercialization by Optomec in 1998 (**Banerjee et** *al.* **2005**). It is also referred to as Directed Light Fabrication (DLF), Direct Metal Deposition

(DMD), Laser-Based Metal Deposition (LBMD), Laser Freeform Fabrication (LFF), Laser Direct Casting (LDC), 3D Laser Cladding, Laser Cast, and Laser Consolidation (Calignano et al. 2017). Different types of lasers used in the commercial machine for FBAM processes include CO₂ laser, Nd:YAG laser, Yb-fiber laser, and Excimer laser. Laser based FBAM processes are generally applicable to powder form of the feedstock material. High-intensity laser irradiation is focused to fuse the feedstock material particles which solidify to form a deposition layer on the substrate or previously deposited layer. Significant process parameters are spot size, beam power and beam focal offset of the laser, flow rate, morphology and moisture content of feedstock material powder, travel speed of deposition head, and inert gas flow (DebRoy et al. 2018). The deposition process is carried out with a coaxially flowing shielding gas to protect the melt pool or in a hermetically sealed chamber filled with argon gas to regulate the oxygen and moisture level. Electron beam based FBAM is another category of FBAM process which was developed by NASA Langley research center and named as Electron Beam Freeform Fabrication (EBFF) process. It uses a high-power electron beam in a highly vacuum environment (10^{-4} torr or below) to melt the feedstock material thus eliminating the need of a shielding gas as used in laser based FBAM processes. The EBFF process can be used to build very complicated components using wire form of the feedstock material and found to have almost 100% deposition efficiency and 95% efficiency in power utilization. It can be for the materials having high reflectivity such as aluminum, copper and their alloys for which laser-based FBAM processes cannot be used.

Arc-based FBAM processes have low machine cost, less built time, and better deposition efficiency (Geng et al. 2017). Spencer and Dickens from University of Nottingham (Spencer et al. 1998) made feasibility study in 1998 to use GMA or metal inert gas (MIG) in a FBAM process by generating arc between the consumable wire electrode and substrate to fuse the wire to make its deposition. Deposition melt pool was protected by a shielding gas flowing through the GMA torch and it does not require any customized working environment for the deposition. This process has low buy-to-fly ratios, higher deposition rates and unlimited built volume potential but it is limited for wire form of the feedstock only. However, heat accumulation, accuracy and surface roughness are major drawbacks associated with multi-layer depositions made by GMA using FBAM process. With the increase in number of the deposited layers, shape of each layer cannot be controlled easily because of more heat accumulation, especially melt pool located at the boundaries of components. Moreover, bubbles and cavities may generate in the melt pool at high temperature due to an intense metallurgical reaction (Zhang et al. 2003). GTA or tungsten inert gas (TIG) based FBAM is another arc-based deposition process where arc generated is between the non-consumable

tungsten electrode and metallic substrate to fuse the feedstock material. The melt pool is protected by a shielding gas flowing through the GTA torch. It also does not require any customized working environment for deposition as required in case of laser or electron beam based FBAM processes. The tungsten electrode projects out of the torch and the formed arc is coned shaped and has an aperture angle of 45° resulting in lower energy density, lower deposition rate, higher heat affected zone (HAZ) and distortion. This process is also limited to wire form of the feedstock material because powder particles adhere to the projected tungsten electrode and interrupt the deposition process. Terakubo et al. (2005) developed µ-GTA based FBAM process to overcome the overheating problem and successfully used this process by depositing µ-bead of titanium using low amperage to reduce heat input and found that deposition width increases from 1.1 to 3.3 mm with an increase in peak current from 5A to 30A. Plasma arc based FBAM process is another arc-based FBAM process where plasma arc generated from a tungsten electrode within the nozzle is forced through a hole in it which constricts the arc resulting in arc stability even at low current, higher energy density, smaller HAZ, and less thermal distortion as compared to GTA and GMA based FBAM processes. Since the electrode is inside the nozzle, deposition material refrains from encountering the feedstock material enabling this process to use both its powder and wire form. Moreover, plasma deposition is adaptable to automatic operations because of more reliable arc for high production requirements. Higher heat input is a consistent problem incurred in arc-based FBAM processes and to curb this problem attempts were made by different researchers to lower it. Xu et al. (2013) used pulsed plasma arc deposition (PPAD) and noted that it has benefits of high production efficiency, low cost, fine microstructure, excellent mechanical properties, and high density. Jhavar et al. (2014a) developed a new process named as microplasma powder additive manufacturing (µ-PPAM) at IIT Indore (India) to reduce heat input during deposition. It has been successfully used for deposition of wire of AISI P20 tool steel on substrate of the same material (Jhavar et al. 2014b), repairing of dies and molds (Jhavar et al. 2016), deposition of powder of Ti-6Al-4V on a substrate of the same material (Sawant et al. 2018a), coating of Stellite 6 powder on AISI 4130 steel substrate (Sawant et al. 2018b), and dimple and spot texturing on high-speed steel (HSS) cutting tool (Sawant et al. 2018c). These investigations have confirmed that µ-PPAM process is a material and energy-efficient process.

1.5.2 Advantages of Additive Manufacturing Processes

Following are some unique advantages offered by the AM processes:

• Free-form fabrication: The AM processes have potential to manufacture components having intricate geometry which are impractical to produce using any other manufacturing

process. They surpass the limitations of conventional manufacturing processes such as casting, forming, powder metallurgy, and machining.

- **Digital-driven fabrication is highly controllable and repeatable:** Optimized complicated geometries of products generated by a computer program can be manufactured repeatedly by AM processes with same accuracy.
- **Development of different materials:** Functionally graded materials, shape memory materials, biomaterials, and smart materials can be developed by AM processes using their constituents in the desired proportion.
- **Personalized manufacturing at low cost:** Traditional large-scale production usually needs an expensive prefabricated mold, which is a time-consuming process. In comparison, AM processes allow solid realization directly from a CAD model without a mold, which is much more efficient and cheaper. This is favored by applications such as multi-functional surgical tools, customized bone replacement, and heritage replication and repair.
- Automatic manufacturing process: Computer designed part geometries and multimaterial manufacturability of AM processes allow unmanned manufacturing of a complicated product and material-diverse object through a single machine.
- **Reduction of material waste:** In conventional manufacturing processes, material is typically removed from a larger size piece; think timber milling or cutting shapes from sheets of steel. In contrast AM starts from scratch, adding material to create a component or part. By using the substance only to create a part, the AM ensures minimal waste. The AM also reduces the need for tooling, therefore limiting the amount of material needed to produce different components.
- Environment friendliness: The environmental benefits of additive manufacturing are an advantage to businesses seeking to improve manufacturing sustainability. They yield significantly saving of material, energy, and time as compared to the traditional manufacturing processes such as casting, machining, and forming. AM processes do need any synthetic lubricants, coolants, or fluid used in the conventional manufacturing processes. Most of the processes do not emit harmful gases. All these benefits make AM processes very environmentally friendly.

1.5.3 Limitations of Additive Manufacturing Processes

Although AM processes offer many significant advantages, they still suffer from the following limitations.

• Material limitation: Machine for an AM process is usually designed for a limited range of materials that have similar properties. This restricts processing of entirely different

materials on a particular AM machine. Developments in materials science can considerably contribute in realization of AM technology.

- Large manufacturing time for large-scale production: Even though AM is good at making customized products, the technology is positioned in the small-scale production. There are constraints on the size of AM machine and additively manufactured components Preferably, AM processes are frequently used to manufacture complex geometries that are usually unmanageable in traditional ways.
- **Poor manufacturing accuracy:** The layered manufacturing strategy of AM processes ignores the edge shape in a single layer in the spatial direction to fit the real surface curvature. The layered structure on the surface is not ignorable.
- **Post-processing requirements:** Generally, AM processes are not net-shape manufacturing processes but only a core step of the process. The AM manufactured component requires further processing to be a functional product.
- Large cost for metallic materials: Though production costs of additively manufactured components are quite favorable and economically attractive for polymers, wax, fabric materials. But production costs of additively manufactured metallic components are high due to complexity of obtaining the required metallic material in the desired form and complexity of AM of metallic materials.

1.6 Additive Manufacturing of Ti Alloys

Abilities to manufacture complex geometry of a product and to customize material properties makes the AM processes very attractive for a wide range of applications in aerospace, automotive, marine, shipbuilding, space, biomedical, and electrical industries. Fig. 1.14 shows schematic diagrams of PBF and DED type processes used for AM of Ti alloys and Table 1.3 presents their advantages and disadvantages.

The PBF processes use high-energy heat sources such as laser (CO₂ or Nd:YAG laser) and electron beam, which is directed onto the powder bed of the feedstock material. The highenergy heat source melts the powder particles of the feedstock to fuse them together to form a solid layer corresponding to the sliced model of the required product. After deposition of each layer, the build platform is lowered, and a new layer of feedstock powder is spread over the previous layer. This process continues till the desired product is fabricated. The PBF processes are preferred for high-precision applications requiring fine and complicated geometries. They have been used for AM of the following Ti alloys by adding different elements: Ti-6A-l4V-0.9Ni (**Sui et al. 2021**), Ti-6Al-4V-xB (**Prasad et al. 2011**), Ti-xNb (**Wang et al. 2017a**), Ti-6Al-xNb (**Ismaeel and Wang, 2019**), Ti-6Al-4V-5Nb (**Sui et al. 2020**), Ti-6Al-4V-7.5Cr (**Chen et al. 2022**), Ti-6Al-4V-Cu (**Ma et al. 2015**), Ti-6Al-4V-6Cu (**Krakhmalev et** *al.* **2017**), Ti-6Al-4V-3Cu (**Vilardell et** *al.* **2020**), functionally graded Ti-6Al-4V-xHAp (**Miranda et** *al.* **2016**), Ti-6Al-4V-5HAp (**Terrazas et** *al.* **2019**), and Ti-6Al-4V-2HAp (**Jaber et** *al.* **2021**).

AM process	Advantages	Disadvantages
EBM	 Fast scan speed Produces fully dense parts Minimal support structures Reduced material contamination 	 High energy consumption Thermal distortion in produced parts High equipment and operating costs Difficulty in removal of un-melted powder particles
SLM	 Produces dense parts Reduced post-processing Applicable for wide range of materials Reduced lead times 	 Small scan speed High residual stresses High energy consumption High equipment and operating costs
SLS	 Can quickly build large parts Reduced post-processing No support structures Produced parts have high precision Applicable for wide range of materials 	Rough surface and porosityHigh shrink rateHigher wastage of materials
LENS	 Higher deposition efficiency Fine grain size Ability to fabricate fully dense parts Applicable for wide range of materials Reduced lead time 	 Slow process Limited build volumes Poor surface finish High equipment and operating costs Limited materials properties
Arc based additive manufacturing	 High deposition efficiency High deposition rate Cost effectiveness Can manufacture large parts Produced parts have good precision Applicable for wide range of materials 	 Higher warping, thermal distortion, and porosity in the produced parts Poor surface finish Need for post-processing

Table 1.3: Advantages and disadvantages of different powder-based additive manufacturing processes used in development of properties enhanced Ti alloys.

The directed energy deposition (DED) processes use different heat sources to melt the powder or wire of the feedstock material and create a molten pool for manufacturing the desired product. The DED processes use an appropriate powder or wire feeding mechanism to deliver the feedstock material to the molten pool. The heat source melts the feedstock material forming a molten pool that solidifies to create the required geometry of the desired product. The DED processes are suitable for deposition of larger parts and repairing of the defective yet useful parts. They have used for the AM of the following Ti alloys by adding different elements: TC17-Sn-Cr (**Zhuo et al. 2021**), Ti-6Al-4V-LaB₆-B (**Bermingham et al. 2018**); Ti-6Al-4V-Nb (**Gou et al. 2020**), Ti-6Al-4V-Mo (**Arthur et al. 2021**), Ti-6Al-4V-

2.5Ni (Sui et *al.* 2022), Ti-6Al-4V-7.5Ni (Han et *al.* 2022), and Ti-6Al-4V-Si (Mereddy et *al.* 2017).



Fig. 1.14: Schematic diagrams of PBF and DED type AM processes used for Ti alloys.

1.7 Organization of the thesis

This thesis is organized into eight chapters explaining all the aspects of present work:

- **Chapter 2** describes review of the relevant past research work on enhancing properties of Ti alloys through different surface modification techniques, by adding α -phase stabilizing elements, β -phase stabilizing elements, neutral elements, and hydroxyapatite, summary of the past works, identified research gaps, research objectives of the present work and the methodology used to meet them.
- **Chapter 3** presents details of design of Ti-6Al-4V-xCr-yNi alloys, preparation of the powders, machine for μ-PPAM process, design and planning of experiments, evaluation of different responses such as density and porosity, microstructure, evolution of phases, mechanical properties, corrosion behaviour, and tribological behaviour of μ-PPAM manufactured Ti-6Al-4V-xCr-yNi alloys along with details of sample preparation for them.
- **Chapter 4** describes results for single-layer deposition of Ti-6Al-4V-5Cr and Ti-6Al-4V-5Ni alloys in terms of deposition width and height, aspect ratio, diluted depth, aspect ratio, dilution, and deposition efficiency and their analysis. It also results of multi-layer depositions of Ti-6Al-4V-xCr-yNi alloys along with evaluation of their theoretical and experimental density and porosity.
- Chapter 5 presents analysis of microstructure, grain size, elemental analysis, phase fraction, phase orientation maps, evolution of phases, tensile properties, fractography of tensile test samples, microhardness, fracture toughness, and abrasion resistance of µ-PPAM manufactured Ti-6Al-4V-xCr-yNi alloys.
- **Chapter 6** describes study of corrosion behaviour of µ-PPAM manufactured Ti-6Al-4V-xCryNi alloys in terms of open circuit potential, potentiodynamic polarization or Tafel curve, electrochemical impedance spectroscopy, mechanism of corrosion, and morphology and topography of the corroded surface.
- **Chapter 7** presents study of tribological behaviour of μ-PPAM manufactured Ti-6Al-4VxCr-yNi alloys using coefficient of friction, sliding wear rate, morphology of worn surfaces, and analysis of worn subsurface.
- **Chapter 8** summarizes significant achievements of the present work, comparison of all the results for Ti-6Al-4V-xCr-yNi alloys, conclusions, some identified directions for the future research.

Chapter 2

Review of Past Work and Research Objectives

This chapter describes review of the relevant past research work on enhancing properties of Ti alloys through different surface modification techniques, by adding α -phase stabilizing elements, β -phase stabilizing elements, neutral elements, and hydroxyapatite. It also presents summary of the past works, identified research gaps, research objectives of the present work and the methodology used to meet them.

2.1 Enhancing Properties of Ti Alloys by Surface Modifications

Researchers have used different surface modification techniques to enhance the properties of Ti alloys. All these techniques are categorized as mechanical, physical, and chemical as shown in Fig. 2.1.

- Mechanical type conventional surface modification techniques commonly used to enhance properties of Ti alloys include sand blasting (Wang et al. 2020a) and shot peening (Kumar et al. 2021). Though they improve properties of Ti alloys, they have limitations such as surface contamination, undesired residual stresses, minor dimensional changes, and high surface roughness values. Use of advanced mechanical surface modification techniques such as surface mechanical attrition treatment (SMAT) by Alikhani et al. (2018) and friction stir processing (FSP) by Ding et al. (2019), provided more precise control over surface modification than conventional techniques. However, these techniques have their own limitations such as limited depth of modification, damage to the subsurface, high surface roughness, and high processing time and cost.
- Physical type conventional surface modification techniques used for Ti alloys are thermal spraying (Baltatu et al. 2020) and glow discharge plasma treatment Januszewicz and Siniarski, 2006). These methods offer some advantages, but they suffer from limitations such as non-uniform coating thickness, limited depth of modification, formation of porosity, oxidation, and high processing time. Advanced physical surface modification techniques such as ion implantation by Rautray et al. (2010), physical vapor deposition (PVD) by Jeong et al. (2011), and laser surface modification techniques (i.e., laser cladding, laser surface alloying, laser surface remelting) offer more precise control and better results than the conventional techniques (Tian et al. 2005). But these techniques also have their own limitations such as damage and distortion of Ti alloy surface, limited depth of modification, limited range of applicable materials, and high cost of equipment.
- **Chemical** type conventional surface modification techniques use chemical reactions to modify the surface of Ti alloys. They can be further classified as chemical treatment

processes (i.e., passivation, pickling, alkali), and electrochemical treatment processes (i.e., electroplating and electropolishing) (Escobar et *al.* 2021). While these methods offer a way to enhance certain properties of Ti alloys, they also have limitations such as electrolyte contamination, surface damage, limited depth of modification, high processing time, and high surface roughness (Mohammed et *al.* 2014). Use of advanced chemical type surface modification techniques namely chemical vapor deposition (CVD) by Sitek et *al.* (2013), sol-gel deposition (i.e., spin coating, dip coating, and spraying) by Gurrappa and Gogia (2001), and plasma electrolyte oxidation by Kostelac et *al.* (2022), provide better control over surface properties than the traditional techniques. However, they also have their own limitations such as non-uniform coating, porosity, slow process, high surface roughness, and equipment complexity.





2.2 Enhancing Properties of Ti Alloys by Adding Different Elements

To overcome above-mentioned limitations of conventional and advanced type thermal, physical and chemical surface modification techniques in enhancing properties of Ti alloys, researchers started exploring addition of appropriate elements to Ti alloys for this purpose. Addition of appropriate elements to Ti alloys is more fundamental, simple, and efficient approach than the surface modification techniques to enhance properties of Ti alloys. Table 2.1 summarizes influence of different elements adding to Ti alloys on mechanical properties, wear resistance, and corrosion resistance of the resultant alloy along with their typical applications.

propertie	s along with som	ie typical applications	of the resultant alloys	
Element	Phases formed	Effect on mechanical properties	Effect on wear, corrosion, and oxidation resistance	Typical applications of properties enhanced Ti alloys
Boron	α-Ti; β-Ti; TiB intermetallic	Tensile and creep strength increased but ductility decreased	Oxidation resistance increased	Orthopedic and dental implants, and surgical instruments
Rare earth elements: Er, Y, La, Nd, Gd	$\begin{array}{l} \alpha \text{-Ti; } \beta \text{-Ti} \\ Er_2O_3; Al_2Er \\ Y_2O_3; \\ (TiAlNb)_2Er_3 \end{array}$	Creep strength increased, Y addition increased microhardness and compressive strength	-	Fiber optic communications and laser technology
Niobium	α-Ti; β-Ti α'-Ti; β-Ti-Nb solid solution	Tensile strength increased but ductility decreased	Corrosion resistance increased	Knee and hip implants
Molybdenum	ια-Τi; β-Ti; α'-Ti	Tensile strength increased but ductility and hardness decreased	-	Nuclear reactor vessels, fuel cladding, and control rods Defense and military equipment: armor plates, ballistic penetrators, and missile parts
Iron	α-Ti; β-Ti; α'-Ti	Tensile strength increased but ductility decreased	wear resistance increased	Automotive and outdoor equipment, engine brackets, chassis parts, exhaust systems, camping gear, bicycles, and sporting goods
Nickel	α-Ti; β-Ti; Ti ₂ Ni; Ni ₂ Ti	Tensile strength increased but ductility decreased	Corrosion and wear resistance increased	Aerospace and automobile engine valves, blade, and exhaust pipes
Chromium	α-Ti; β-Ti Cr ₂ Ti; CrTi ₄	Tensile strength increased but ductility decreased	Corrosion, wear, and oxidation resistance increased	Chemical and marine: Heat exchanger, pump, pipe, and riser Gas turbines and jet engines: turbine blades, vanes, and casings
Copper	α-Ti; β-Ti Ti ₂ Cu	Increase tensile strength	Corrosion and wear resistance increased	Knee implant, alveolar bone regeneration, cardiovascular devices, and surgical instruments
Silicon	α-Ti; β-Ti Ti ₅ Si ₃	-	Wear and oxidation resistance increased	Electronics and semiconductor components, electrical contacts, heat sinks, electrical contacts, and vacuum furnace parts
Scandium	α-Ti; β-Ti; α'-Ti Sc ₂ O ₃ ; Al ₃ Sc	Tensile and creep strength increased but ductility decreased	-	Smartphones, laptops, wearable devices, and other electronic gadgets
Zirconium	α-Ti; β-Ti; α'-Ti	Tensile strength, ductility, and toughness increased	Corrosion resistance increased	Automotive engine parts, exhaust systems, and suspension components
Hydroxy apatite		Tensile strength, toughness and ductility decreased but hardness increased	Corrosion resistance decreased	Orthopaedic and dental implants, surgical instruments, and cardiovascular devices

Table 2.1: Influence of adding different elements to Ti alloys on phase formation and properties along with some typical applications of the resultant alloys.

Fig. 2.2 presents classification of the different elements that have been added to Ti alloys to the following three categories: α -Ti phase stabilizing elements, β -Ti phase stabilizing elements, and neutral elements. The α -Ti phase stabilizing elements are further divided into interstitial and substitutional elements. Interstitial elements include C, N, and O, while substitutional elements include Ga, Ge, B, and rare earth elements. The β -Ti phase stabilizing elements are further divided into β -isomorphous and β -eutectoid elements. β -isomorphous elements include Mo, Nb, Ta, and V, whereas β -eutectoid elements include Co, Cr, Cu, Fe, Mn, Ni, and Si. Lastly, neutral elements consist of Sn and Zr.



Fig. 2.2: Different types of elements added to enhance properties of Ti alloys.

Following paragraphs present review of the past research done on addition of different elements to enhance the properties of Ti alloys.

2.2.1 Addition of Elements Stabilizing α-Ti Phase

Aluminium is the most widely used substitutional type stabilizer for α -Ti phase due to its atomic size and crystal structure similar to Ti like resulting its higher solubility. Boron, gallium, germanium, and rare earth elements other substitutional type stabilizers for α -Ti phase but they have limited solubility in α -Ti phase. Oxygen, nitrogen, and carbon are the interstitial type stabilizers for α -Ti phase.

Addition of **boron** to Ti alloys refines their grains due to its limited solid solubility (less than 0.02 at.%) in both α -Ti and β -Ti phases. This encourages boron to reside at grain boundaries, hindering grain growth during solidification thus promoting finer grains of Ti

alloys (Feng et *al.* 2006a). Boron reacts with titanium to form a stiff needle-like intermetallic titanium boride (TiB) phase which is often observed at the prior β -Ti phase grain boundaries throughout the microstructure of Ti alloys as illustrated in Fig. 2.3 (Xue et *al.* 2019; Singh et *al.* 2014b; Sen and Ramamurty, 2010; Panda and Chandran, 2006; Feng et *al.* 2006a). Grain growth inhibiting nature of boron induces significant constitutional supercooling (ΔT_{CS}) which encourages columnar to equiaxed transition (CET) for Ti alloys during their solidification. It implies a shift from the microstructure having elongated columnar grains to a microstructure having more equiaxed spherical grains leading to a finer and more desirable microstructure of Ti alloys. Ability of boron to induce the CET is likely due to its high growth limitation parameter 'Q' (Sola and Trinchi, 2023)



Fig. 2.3: Microstructure of boron added Ti alloy (Singh et al. 2014b)

Addition of boron to Ti alloys enhances their strength, elastic modulus, high-temperature stiffness, hardness, and corrosion resistance. Its addition up to 0.1 wt.% can enhance ductility of Ti alloys. However, addition beyond this limit decreases ductility due to increased volume fraction of the brittle TiB intermetallic phase. This phase acts as the sites for crack initiation and hinders movement of dislocations thereby reducing ability of Ti alloys to deform plastically (Sen et al. 2010). Following are mechanisms of strength enhancement through boron addition to Ti alloys: (i) Hall-Petch strengthening: strength increases due to grain refinement, (ii) Orowan strengthening: strength increases due to bowing of dislocations between matrix of a Ti alloy and TiB intermetallic phase, (iii) Load sharing mechanism: interfacial stress transfer between the TiB intermetallic phase and matrix of a Ti alloy enhances its strength, and (iv) Increase in dislocation density between Ti alloy matrix and TiB intermetallic phase increases strength. Boron addition increases fatigue strength of Ti alloys due to combined effects of grain refinement and load sharing mechanism (Chandravanshi et al. 2011). It improves creep resistance of Ti alloys due to finer grains, strengthening due to load sharing mechanism, weak texture of α -Ti phase, and increase in modulus of elasticity (Boehlert, 2009). It also improves oxidation resistance of Ti alloys due

to formation of a dense and stable TiB intermetallic phase at the grain boundaries which acts as preferential nucleation sites for the growth of a protective oxide layer at an elevated temperature. This oxide layer consists of titanium dioxide (TiO₂) and boron oxide (B₂O₃) (**Brice et al. 2016; Zhang et al. 2002; Koh et al. 2001**). Figs. 2.4a and 2.4b illustrate the effect of boron content on the tensile properties of Ti alloys along the build direction and the normal direction (**Prasad et al. 2011**). Yield and ultimate tensile strength in both directions increase with increase in boron content whereas % elongation decreases with it. Fig. 2.4c shows that β -transus temperature increases with increasing boron content (**Niu et al. 2021; Xue et al. 2019**). Morphology of tensile fractured surface of boron added Ti alloy typically has dimple features for small amount of boron, but it changes to a quasi-cleavage mode with increase in boron content (**Tamirisakandala et al. 2005**). This change suggests a transition from a more ductile to a more brittle behaviour with increasing boron content.



Fig. 2.4: Effect of boron content in Ti alloys on their: (a) strength along the build direction, (b) strength along the normal direction, and (c) β -transus temperature (**Xue et** *al.* **2019**).

Addition of precious **rare earth metals** such as erbium (Er) yttrium (Y), lanthanum (La), neodymium (Nd), gadolinium (Gd), and cerium (Ce) to Ti alloys enhance their grain morphology, thermal properties, creep resistance. It also increases nucleation rate and crystal

nucleus kinetic energy, and reduce their surface tension (**Wu et al. 2019; Wang et al. 2017b; Yan et al. 2015; Ueda et al. 2013**). It is advantageous in manufacturing components from Ti alloys because they minimize the absorption of oxygen in them (**Yan et al. 2015**). They act as surface active ingredients and modify coefficient of friction and structure of subsurface. **Wu et al. (2019**) reported that addition of erbium to Ti alloys refined grains of α-Ti and β-Ti phases and formed Er_2O_3 and Al_2Er phases inside the β-Ti phase as shown in Fig. 2.5 through transmission electron microscopy (TEM) images.



Fig. 2.5: TEM images of erbium added Ti alloy showing formation of (a) Er₂O₃ phase, and (b) Al₂Er phase (Wu et *al.* 2019).

Bermingham et *al.* (2018) reported that addition of lanthanum hexaboride (LaB₆) and boron to Ti alloys improved their tensile strength. Liu et *al.* (2010) observed that addition of yttrium to Ti alloys enhanced their microhardness and compressive strength due to formation of Y₂O₃ phase and refined their microstructure during solidification. Ke et *al.* (2010) observed that addition of erbium to Ti alloys improved their compression properties due to presence of fine precipitates of (TiAlNb)₂Er₃ phase inside the β -Ti phase.

2.2.2 Addition of Elements Stabilizing β-Ti Phase

The elements stabilizing β -Ti phase readily dissolve in it and decrease its β -transus temperature. They are further categorized as β -Ti phase isomorphous and β -Ti phase eutectoid elements. Niobium, molybdenum, vanadium, tantalum, and rhenium are the important β -Ti phase isomorphous elements due to their high solubility in it. Whereas iron, nickel, chromium, copper, silicon, scandium, cobalt, and manganese are the important β -Ti phase eutectoid elements due to their limited solubility in it.

Addition of **niobium** to Ti alloys refine grains of β -Ti and α -Ti phases and increases volume fraction of β -Ti phase (**Wang et al. 2020b**). It promotes stability of β -Ti phase at lower temperature and has a substantial influence on transition from α -Ti to β -Ti phase due to its complete dissolution in the β -Ti phase or formation of solid solution of β -Ti-Nb (**Wang et al. 2017a**). Niobium plays a crucial role in stabilizing the microstructure of Ti alloys at

high temperature by impeding recovery, recrystallization, and movement of dislocations. Recovery involves rearrangement of atoms within the crystal lattice to relieve internal stresses, recrystallization implies formation of entirely new, strain-free grains, and movement of dislocations contribute to plastic deformation of Ti alloys (Sun et al. 2019). Gou et al. (2020) observed that addition of niobium to Ti alloys increases the inter-planar spacing of β -Ti phase and shifts the solidification pattern from planar to cellular. It enhances their compressive strength, yield strength, toughness, and corrosion resistance (Ismaeel and Wang, 2019; Fu et al. 2015). Sui et al. (2020) investigated the impact of niobium addition on microstructure and properties of Ti-6Al-4V alloy fabricated by the SLM process. They found that it refined the grains of β -Ti phase, formed columnar and cellular microstructure, and increased volume fraction of β -Ti phase. It enhanced the ductility and corrosion resistance due to increase in volume fraction of β -Ti phase and reduction in volume fraction of α ' phase. Fig. 2.6 illustrates the effect of niobium addition on tensile strength of Ti alloys in horizontal and vertical directions. Yield and ultimate tensile strength in both directions increase, while % elongation decreases, and higher yield and ultimate tensile strength are observed in horizontal specimens due to higher vol. % of β -Ti phase (**Guo et al. 2020**). The morphology of tensile fractured surface of niobium added Ti alloy changed to combination of dimples, cleavage facets (brittle features), and voids, suggesting a shift towards a brittle fracture mode (Zhang et al. 2015).



Fig. 2.6: Effect of niobium addition to Ti alloys on their strength in horizontal and vertical directions (Guo et al. 2020).

Molybdenum is a popular choice for adding to Ti alloys as a β -Ti phase isomorphous element due to its low elastic modulus and high strength. It is biocompatible, also implying

that it does not trigger allergic reactions or cause harm to the human body, but excessive molybdenum concentration can be detrimental. It exhibits greater solubility in the β -Ti phase as compared to α -Ti phase. Lu et al. (2013) investigated the effects of adding molybdenum to Ti alloys and identified Ti-6Al-3Mo and Ti-6Al-5Mo as particularly promising alloys due to their enhanced strength, ductility, and corrosion resistance. This improvement is attributed to the presence of a metastable β -Ti phase in their microstructure. Kaouka et al. (2017) reported that molybdenum addition to Ti alloys leads to increase vol% of β-Ti phase, grain refinement of α -Ti phase, reduction in the elastic modulus, and improvement in fracture toughness of the developed Ti alloys. Yamanoglu et al. (2021) observed that molybdenum addition refines the grains of β -Ti phase within the undissolved molybdenum zones, which contributes to a reduction in the coefficient of friction and wear rate. Arthur et al. (2021) reported that molybdenum addition shifted microstructure from planar to cellular in Ti alloys. It lowered the β -transus temperature, promoting the stability of the β -Ti phase. Presence of higher molybdenum contents in Ti alloys showed the insoluble molybdenum-rich zone within both α -Ti and β -Ti phases as illustrated in Fig. 2.7. Fan et al. (2013) reported that molybdenum addition improved wear resistance and decreased coefficient of friction in Ti alloys, which enhanced their tribological performance. Xu et al. (2020) observed an interesting trend in tribo-corrosion resistance of molybdenum added Ti alloys in which it increased with increasing molybdenum content up to a certain point and started decreasing with further addition of molybdenum.





Iron emerged as an attractive β -Ti phase eutectoid element for adding to Ti alloys due to its potential for significant cost-effective development of Ti alloys. Addition of iron to Ti alloys enhances their strength and wear resistance but exceeding a critical iron content can lead to embrittlement (**El Kadiri et al. 2009; Esteban et al. 2008**). **Kanou et al. (2016**) reported that iron addition can enhance tensile and yield strength of Ti alloys by 5-25% but reduces % elongation due to presence of α ' phase and β -Ti phase. Iron exhibits a higher inter-

diffusion coefficient than Ti promoting preservation of β -Ti phase during cooling which contributes to enhanced ultimate and yield strength but reduced cryogenic toughness of Ti alloys (Chandrasekaran and Xia, 2005). Ehtemam et al. (2017) observed that iron addition to Ti alloys improves wear resistance, increases stability and fraction of β -Ti phase, and decreases elastic modulus making them more attractive for biomedical applications. Chen et al. (2020) investigated the effects of iron addition on microstructure and mechanical properties of Ti-6Al-4V alloy and revealed that V and Fe at.% is more in the β-Ti phase which increased lattice displacement thus contributing to a higher elastic modulus and fracture toughness. Morphology of tensile fractured surface of iron added Ti alloy shows a combination of dimples, cleavage facets, micropores, and river markings indicating inducement of some brittleness. Wu et al. (2018a) investigated the combined effects of iron addition and heat treatment on the microstructure of Ti-6Al-4V alloy. Their study found that quenching of iron added Ti-6Al-4V alloy resulted in formation of a metastable phase called α " lamellae inside the microstructure. Subsequent isothermal aging led to the coarsening of these a" lamellae and final microstructure after heat treatment and aging exhibited a highvolume fraction (50-60%) of fine α -Ti phase which is likely more stable than metastable α " phase and influences mechanical properties of the developed alloy.

Addition of **nickel** to Ti alloys stabilize β -Ti phase at room temperature. The maximum solubility of nickel in α -Ti phase is limited to 0.5wt.% and exceeding this limit leads to formation of undesirable Ti₂Ni intermetallic phase. But nickel exhibits significantly higher solubility of around 8 wt.% in β-Ti phase and exceeding this solubility limit causes swelling of the developed alloy (Rominivi et al. 2019; Robertson and Schaffer, 2009). Nickel addition reduces activation energy for self-diffusion of Ti in Ti alloys because it has higher mass diffusivity than Ti (Herzig et al. 2002). It significantly refines the grains of α -Ti and β -Ti phases due to presence of intermetallic Ti₂Ni phase which act as nucleation sites making it an effective grain refinement agent for Ti alloys (Sui et al. 2021). It significantly influences phase transformation behaviour in Ti alloys from β -Ti to α -Ti phase and β -Ti to α' phase (Xiong et al. 2021). Limited at.% of nickel dissolves within the α -Ti phase and remaining nickel is segregated at the boundaries between the α -Ti phase laths (Tan et al. 2018). Nickel addition promotes transformation in microstructure of Ti alloys such as equiaxed a-Ti phase grains can be replaced by α_w phase morphology and β -Ti phase can transformed into a lamellar microstructure with well-defined grain boundaries (Muthuchamy et al. 2019). It leads to the formation of intermetallic phases Ti₂Ni and TiNi₂ having face centered cubic (FCC) and HCP crystal structure respectively with needle-like morphology. These phases are generally much harder than the surrounding Ti alloy matrix and they act as effective obstacles

to the movement of dislocations during plastic deformation (**Rominiyi et al. 2020**). The presence of hard Ti₂Ni and TiNi₂ intermetallic phases contribute to enhanced wear resistance of Ti alloys (**Verma and Kumar, 2017**). Nickel addition to Ti alloys increases tensile strength and decreases ductility due to: (a) grain refinement of β -Ti and α -Ti phases, (b) higher phase fraction of β -Ti phase, and (c) presence of hard intermetallic phases (**Sui et al. 2022; Han et al. 2022**). Addition of nickel to Ti alloys can form some ductile intermetallic compounds with Ti thus imparting high impact resistance and good damping properties to them (**Kundu and Chatterjee, 2006; He et al. 1999**). It can also be employed for diffusionbased surface modification of Ti alloys, known as diffusion modification, which can lead to a significant increase in surface hardness of Ti alloys (**Xu et al. 2007**). It also promotes better sinterability implying that the Ti alloys will bond together better during the sintering process which will lead to formation of higher density products from them (**Panigrahi, 2007**). It can also significantly enhance adhesion strength between each layer in multi-layer depositions of Ti alloys because it promotes better interdiffusion between the deposited layers which will give improved bonding between them (**Fedorova et al. 2010**).

Addition of **chromium** to Ti alloys stabilize β -Ti phase at room temperature (**Sawada et** al. 2020) and forms its several equiaxed grains by inhibiting formation of large grains of β -Ti phase. It leads to the formation of intermetallic phases Cr_2Ti and $CrTi_4$ in addition to α -Ti and β -Ti phases (Wei et al. 2012). It prevented oxygen embrittlement of Ti alloys at temperatures exceeding 400°C at which their surface properties generally degrade, thus making them suitable for high-strength and high-temperature applications. Chen et al. (2022) investigated the effects of chromium addition on microstructure, mechanical properties, and corrosion behaviour of Ti-6Al-4V-xCr alloy fabricated by SLM process. Their study revealed that chromium addition increased volume fraction of β-Ti phase and improved compressive strength and corrosion resistance. Chromium addition to Ti alloys enhanced their wear, oxidation, and corrosion resistance due to formation of chromium oxide layers which reduce surface damage caused by wear, oxidation and corrosion (Takemoto et al. 2009; Brady et al. 1997a, 1997b). It reduced width and depth of wear tracks and reduced coefficient of friction Ti alloys, which is attributed to the formation of Cr₂O₃ oxide layer, thereby making them suitable as antifriction agents (Wei et al. 2018a; Cheng et al. 2009). Surface chromizing of Ti alloys refined grains of α -Ti and β -Ti phases, formed intermetallic phases Cr₂Ti, CrTi₄, formed Cr-Ti solid solution, and improved their mechanical properties (Wei et al. 2018b; Yu et al. 2015).

Addition of **copper** to Ti alloys as the β -Ti phase eutectoid element is a lucrative option due to its higher biocompatibility. **Vilardell et** *al.* (2020) studied characterization of Ti-6Al-
4V-3Cu alloy fabricated by laser PBF process and found that the developed alloy consisted of α' and β -Ti phases, and CuTi₂ intermetallic phase which are shown in Fig. 2.8a through their TEM images. Addition of copper in Ti alloys enhanced mechanical properties, corrosion resistance, and biocompatibility. It modified surface properties, enhanced their resistance to bacterial colonization, and exhibited negligible cytotoxic effects (Liu et al. 2014; Song et al. 2014). It inhibits growth of various bacteria such as Escherichia coli (E. coli) and Staphylococcus aureus due to release of cupric ions thus making them suitable as an antibacterial reagent which is very useful in biomedical implants (Krakhmalev et al. 2017; Ma et al. 2015). Higher copper content in Ti alloys show stronger anti-bacterial activity which is highly desirable for combating bacterial infections associated with the implants. Whereas lower content of copper in Ti allovs is preferable for improving its tribo-corrosion resistance (Alshammari et al. 2019; Fowler et al. 2019; Wang et al. 2019). Xu et al. (2018) added copper to Ti-6Al-4V alloy by the SLM process and studied the biological responses of the developed alloy. They found that copper addition increased release rate of metallic ions without reducing viability of gingival fibroblasts and osteoblast cells. It is confirmed by Fig. 2.8b which shows that when copper added Ti-6Al-4V alloy was placed between gingival tissue and bone tissue then the copper ions released from the developed alloy did not reduce viability of the gingival fibroblasts and osteoblasts cells.



Fig. 2.8: (a) TEM image of copper added Ti alloys (Vilardell et *al.* 2020), and (b) in vitro cellular response model (Xu et *al.* 2018).

It resulted in enhanced angiogenic characteristics and reduced local inflammatory reactions. **Peng et al. (2019)** studied wear, corrosion, antibacterial analysis, and cytotoxicity of copper added Ti-6Al-4V alloy and found improvement in antibacterial properties due to growth of Ti₂Cu phase inside the microstructure. They also observed that cytotoxicity improved when copper content increased to 7.5wt.%. **Ren et al. (2014)** developed Ti-6Al-4V-xCu alloys and studied improvement in their antibacterial activity, corrosion resistance, and biocompatibility. Their study observed that antibacterial activity and biocompatibility improved with increase in copper content in Ti alloys. **Wang et al. (2015)** observed that copper addition to Ti alloys improved wear resistance due to formation of harder Ti₂Cu intermetallic phases inside the microstructure.

Addition of **silicon** to Ti alloys act as an effective grain refiner by restricting grain growth during the solidification (**Bermingham et al. 2008**). It is found to have refined grains of α -Ti phase by restricting the grain growth (**Mereddy et al. 2017**). Liu et al. (2021b) reported that it increased wear and oxidation resistance of Ti alloys due to presence of intermetallic Ti₅Si₃ phase inside the α -Ti and β -Ti phases. Silicon in Ti alloys is present in two forms namely substitutional solid solutions and precipitates. They inhibit movement of dislocations and enhances creep resistance of the developed Ti alloys (**Wang et al. 2018; Jia et al. 2011**). **Maeda et al. (2019**) observed that silicon addition to Ti alloys improved their oxidation resistance due to presence of Si⁴⁺ at interstitial sites which suppressed migration of oxygen through the oxide scale and led to formation of stable oxide layers of SiO₂.

Addition of **scandium** to Ti alloys act as grain refiner and solid solution strengthening agent. **Deng et** *al.* (2020) observed that scandium in Ti alloys exists in the following three primary forms: solid dissolved form, Sc_2O_3 precipitates, and Al_3Sc phase. Scandium addition to Ti alloys increased their tensile strength but reduced ductility after deformation at 850°C and 1000°C. It is due to formation of Sc_2O_3 oxides, grain refinement of α -Ti and β -Ti phases, and precipitation strengthening by scandium particles (Xiao et *al.* 2012; Liu et *al.* 2007). It increased creep resistance at high temperature due to formation of Sc_2O_3 and Al_3Sc oxides which inhibit movement of dislocations. It also hindered formation of silicide and encouraged development of α ' phase which also increases its creep resistance (Li et *al.* 2009).

2.2.3 Addition of Neutral Elements

Zirconium and titanium belong to the same group in the periodic table and have similarities in their chemical properties and same crystal structures (i.e., HCP). Similar crystal structure contributes to their solid solution behaviour. Binary phase diagram of Ti-Zr demonstrates a smooth solid solution area between Zr and Ti indicating that they are mutually soluble in each other over a certain range of composition and temperature (**Martins et al.** **2008**). Zirconium is a neutral alloying element that stabilizes α -Ti and β -Ti phases which enhances their stability and performance across a range of operating conditions. It increases chemical homogeneity of Ti alloys by promoting more uniform distribution of alloying elements within its α -Ti and β -Ti phases. This is beneficial for achieving consistent properties throughout the material and reducing the segregation and the defects related to inhomogeneity. This leads to improved mechanical properties such as strength, ductility, and toughness as well as enhanced thermal stability. Zirconium addition to Ti alloys increase their corrosion resistance because it refines their microstructure and forms homogeneous oxide layer of ZrO₂ (**Han et al. 2014; Martins et al. 2008**). Both Zr and Ti have a relatively high affinity towards oxygen forming stable oxides (ZrO₂ and TiO₂) that enhance corrosion resistance and passivation of Ti alloys in various environments. **Xia et al. (2016)** reported that Zr addition to Ti alloys reduced the width of α -Ti phase and increased the phase fraction of β -Ti phase which improved their passivation performance.

2.2.4 Addition of Hydroxyapatite (HAp)

Hydroxyapatite (HAp) is an excellent biocompatible material because it naturally occurs in mineral form of calcium apatite which is the main inorganic component of bone and teeth in mammals. It is biodegradable also because it can gradually dissolve and can be replaced by new bone tissues during the healing process. This property is particularly beneficial for orthopedic implants and bone substitutes because it allows for osseointegration with the surrounding bones promoting natural healing (Tampieri et al. 2000). Therefore, it is a favoured choice for biomedical implants. Decomposition of HAp occurs at a temperature of 900°C transforming it into dihydroxylation which further produces tri-calcium phosphate (TCP) and tetra calcium phosphate (TTCP). The TCP generally comprises of an α -TCP phase above 1200°C and β-TCP phase below 1200°C (Arifin et al. 2014). Ruys et al. (1995) reported that tensile strength of HAp significantly decreases beyond the temperature of 1350°C. Ye et al. (2009) found that HAp present in Ti alloys decomposes into CaO and TTCP, TTCP further decomposes into CaO and an amorphous phase. Balbinotti et al. (2011) observed that calcium titanate (i.e., $Ti_x P_y$) and TCP phases are present in HAp added Ti alloys at a temperature of 1026°C. Salman et al. (2009) added HAp to Ti alloys and collected HAp powder from bovine bones (BHA) and human enamel (EHA). Their results show that mechanical properties of the developed alloys can be improved after sintering. Pylypchuk et al. (2015) reported that HAp added Ti alloys show excellent biocompatibility provided that optimal proportion of calcium and phosphate is used. HAp and TCP are widely used bioactive ceramic materials for coating the implants due to their excellent biocompatibility, osteoconductivity, and ability to promote bone growth and osseointegration with the surrounding

tissues (**Saji et** *al.* **2023**). **Arifin et** *al.* (**2015**) reported that HAp addition to Ti alloys decreased density due to dihydroxylation and decomposition of HAp. **Dudek and Klimas** (**2013**) produced Ti6Al4V-20wt.% HAp alloy by the SPS process and observed higher microhardness value as compared to Ti-6Al-4V alloy. Fig. 2.9b shows the effect of variation in wt.% of HAp on compressive strength and elastic modulus on the developed Ti-13Nb-13Zr-xHAp alloys (**He et** *al.* **2016**). **Miranda et** *al.* (**2016**) manufactured Ti-6Al-4V-5/10Vol.% HAp alloys by hot pressing process and demonstrated concept of FGM for a hip implant part (shown in Fig. 2.9c). They observed that this approach enhanced bioactivity for promoting osteointegration and overcame the detachment problems of HAp coatings.



Fig. 2.9: Effect of adding HAp to Ti alloys on their: (a) Tensile properties (Jaber et al. 2021), (b) tensile and compressive strength and elastic modulus (He et al. 2016), and (c) concept of FGM for hip implant part (Miranda et al. 2016).

Bovand et *al.* (2015) studied effects of varying HAp content (from 10 to 30 wt.%) in the Ti alloy fabricated by mechanical alloying and observed that density of the developed alloy

decreased while hardness improved. **Han et** *al.* (2018) produced Ti-based functionally graded materials having different wt.% of HAp and observed that hardness of developed alloys increased while fracture toughness decreased. **Terrazas et** *al.* (2019) developed Ti-6Al-4V-5%HAp composite by electron beam powder bed fusion AM process for bone replacement scaffolds and implants applications. **Jaber et** *al.* (2021) added 2 wt.% HAp to Ti-6Al-4V alloy by the SLM process for osseointegration enhancement and biological fixation between implants and bone tissue. Fig. 2.9a shows the tensile properties of HAp added Ti alloys decreased due to formation of Ti₃P, CaTiO₃ intermetallic phases and precipitation of HAp along the grain boundary **Jaber et** *al.* (2021).

2.3 Summary of the Past Works

Following conclusions can be drawn from the review of the relevant past work described in the previous sections:

- Alloying elements stabilizing α -Ti and β -Ti phases, and neutral elements have been added to Ti and Ti-6Al-4V alloy by the conventional processes such as casting, double glow plasma, vacuum arc melting, and SPS to enhance microstructure and mechanical characteristic of the developed alloys. But these processes cause formation of some undesirable phases, elemental segregation, thermal distortion, and cracks.
- Some AM processes namely SLM, EBM, SLS, and LENS have been used to add different elements to Ti-alloys to enhance their properties. However, they suffer from higher thermal distortion, heat affected zone, higher dilution, low deposition efficiency, poor energy conversion efficiency, and higher energy consumption, higher costs of equipment, operation and maintenance.
- The μ-PPAM process is a cost-effective, energy-efficient, material efficient, and environment-friendly process because it uses maximum value of DC current up to 20 A (as against plasma-based AM process which use current ~ 250-300 A), maximum DC power up to 440 W, gives 10-50 g/min deposition rate, and fills the wide existing gaps between capabilities of beam-based and arc-based AM processes making it suitable for meso-scale AM applications (Jhavar et al. 2014; Sawant and Jain, 2018a, 2018b, 2017).

2.4 Identified Research Gaps

Following research gaps are identified based upon review of the relevant past work on development of Ti-6Al-4V-xCr-yNi alloys:

• Limited work has been done on adding boron, niobium, iron, copper, silicon, zirconium, tin, and hydroxyapatite to Ti-6Al-4V alloy using PBF type AM processes (such as SLM,

EBM, SLS, and LENS) to enhance microstructure and mechanical characteristic of the resultant alloys.

- Limited work has been done on addition of nickel and chromium to Ti-6Al-4V alloy using conventional processes such as double glow plasma and SPS processes, and PBF type AM processes such as SLM.
- No work is available on adding chromium and/or nickel powder to Ti-6Al-4V alloy by a DED type AM process.
- No work is available on study of microstructure, crystallographic texture, mechanical properties, corrosion behaviour, and tribological behaviour of the chromium and/or nickel added Ti-6Al-4V alloy

2.5 Research Objectives

Following research objectives were identified based on the existing research gaps:

- RO-1: Design Ti-6Al-4V-xCr-yNi alloys to determine addition amount of chromium and nickel. Depositions of the designed alloys (i.e., Ti-6Al-4V-5Cr; Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni and Ti-6Al-4V alloy by an in-house developed machine for micro-plasma powder additive manufacturing (μ-PPAM) process.
- **RO-2:** Study of microstructure, grain size, and mechanical properties of the developed Ti-6Al-4V-xCr-yNi alloys.
- **RO-3:** Study of corrosion behaviour of the developed Ti-6Al-4V-xCr-yNi alloys.
- **RO-4:** Study of tribological behaviour of the developed Ti-6Al-4V-xCr-yNi alloys.

2.6 Research Methodology

Table 2.2 presents the research methodology used in the present work to achieve the identified research objectives giving details of different stages of experimentation, constant and variable parameters used in them, and different characterization methods used to study the different responses.

Table 2.2: Identified research objectives (RO) for the present work and the methodology used to meet them.

RO-1: Design Ti-6Al-4V-xCr-yNi Alloys and their Depositions: Design of Ti-6Al-4V-xCr-yNi alloys to determine addition amount of chromium and nickel using Thermo-calc simulated phase diagram, Scheil solidification, and Equilibrium solidification diagrams. Pilot and main experiments for single-layer depositions of Ti-6Al-4V-5Cr and Ti-6Al-4V-5Ni alloys by micro-plasma powder additive manufacturing (μ-PPAM) process to identify its optimum parameters for their multi-layer depositions and that of Ti-6Al-4V-2.5Cr-2.5Ni and Ti-6Al-4V alloys. Evaluation of their theoretical and experimental density, and porosity.

	- P							
Type of	Pilot expe	riments: 30 pilot	Main experiments: 27 main experiments each for Ti-					
experiment experiment		ts for Ti-6Al-4V-5Cr and Ti-	6Al-4V-5Cr and Ti-6Al-4V-5Ni alloy using full					
6Al-4V-51		Ni alloy each using one-	factorial design of experiments to identify optimum					
factor-at-a		-time approach to identify	values of μ -plasma power, mass flow rate of					
optimum v		values/ranges of µ-PPAM	feedstock powder, and deposition head travel speed					
	process pa	rameters using good and	using uniform and continuous deposition, minimum					
	continuous	s deposition as the evaluation	aspect ratio (i.e., ratio of deposition width to					
	criteria.		deposition height), minimum dilution, and maximum					
Substrate		: Ti-6Al-4V alloy	deposition efficiency as the evaluation criteria.					
			Substrate: Ti-6Al-4V alloy					
Input	Used rang	ges of µ-PPAM parameters:	Identified values of <i>variable</i> parameters of µ-					
parameters	µ-plasma j	ower: 200-440 W; Mass	PPAM process: Pilot experiments identified 308;					
-	flow rate of	of deposition material	319; 330 W for μ-plasma power. 2.3: 2.9: 3.5 g/min					
	powder: 1	2-4.0 (g/min); Deposition	for mass flow rate of feedstock powder, and 43; 47;					
	head trave	l speed: 30-100 (mm/min);	51 mm/min for deposition head travel speed					
	u-plasma f	orming gas flow rate: 0.2-0.5 Identified values of <i>constant</i> parameters of u -						
	Normal lit	re per minute (Nl/min);	PPAM process: Pilot experiments identified 0.3					
	shielding g	gas flow rate: 2-7 (Nl/min);	Nl/min as µ-plasma forming gas flow rate, 5.0 Nl/min					
	Stand-off	distance (SOD): 5-11 mm.	as shielding gas flow rate, and 8 mm as the SOD.					
Response(s)	Visual exa	mination of depositions	Visual examination of depositions. Aspect ratio.					
	, 100001 0110		Dilution, and Deposition efficiency					
Multi-laver		The main experiments identi	fied 319 W: 2.9 g/min: and 47 mm/min as the optimum					
depositions	of Ti-6Al-	values of u-plasma power, m	ass flow rate of feedstock powder, and deposition head					
4V-xCr-vNi	allovs	travel speed respectively. It was used to manufacture multi-layer denositions of Ti-						
using the id	entified	6Al-4V-5Cr Ti-6Al-4V-5Ni Ti-6Al-4V-2 5Cr-2 5Ni and Ti-6Al-4V allove on						
ontimum narameters		substrate of Ti-6Al-4V alloy. Each multi-layer deposition has 8 layers resulting in a						
optimum parameters		total deposition height of 24 mm. Evaluation of their theoretical and experimental						
		density, and porosity.						
RO-2: Micr	ostructure	Microstructure analysis: St	tudy of microstructure and grain size of β -Ti and α -Ti					
and mechan	nical	phases of Ti-6Al-4V-xCr-vNi allovs. Analysis of evolution of phases phase						
properties o	of	orientation map, phase fraction, colour mapping and distribution of different						
Ti-6Al-4V-vCr-vNi constituents for Ti-6Al-4V-v		constituents for Ti-6Al-4V-x	Cr-vNi allovs.					
allovs Mechanical Properties: Stu		Mechanical Properties: Stu	idy of microhardness tensile properties fracture					
unojs		morphology, fracture toughn	ess, and abrasion resistance.					
RO-3: Corr	osion	Study of open circuit potential potentiodynamic polarization curves						
behaviour o	viour of Ti-6Al- electrochemical impedance spectroscopy (FIS) corrosion mechanism and							
4V-xCr-vNi allovs morphology and topography			of the corroded surfaces of Ti-6Al-4V-xCr-vNi allovs					
RO-4: Trib	ological	Evaluation and analysis of co	pefficient of friction, sliding wear rate, and morphology					
hehaviour of Ti-6AL		of worn surfaces and analysis of subsurface of Ti-6Al-4V-xCr-vNi allovs						
4V-xCr-vNi	allovs	==						
•								

This *chapter* described review of the relevant past research work on enhancing properties of Ti alloys through different surface modification techniques, by adding elements stabilizing the α -Ti phase and β -phase, neutral elements, and hydroxyapatite, summary of the past works, identified research gaps, research objectives of the present work and the methodology used to meet them.

The **next chapter** provides details of design of Ti-6Al-4V-xCr-yNi alloys, preparation of the powders, machine for μ -PPAM process, design and planning of experiments, evaluation of different responses such as density and porosity, microstructure, evolution of phases, mechanical properties, corrosion behaviour, and tribological behaviour of μ -PPAM manufactured Ti-6Al-4V-xCr-yNi alloys along with details of sample preparation for them.

Chapter 3

Details of Experimentation

This chapter presents details of design of Ti-6Al-4V-xCr-yNi alloys, preparation of the powders, machine for μ -PPAM process, design and planning of experiments, evaluation of different responses such as density and porosity, microstructure, evolution of phases, mechanical properties, corrosion behaviour, and tribological behaviour of μ -PPAM manufactured Ti-6Al-4V-xCr-yNi alloys along with details of sample preparation for them.

3.1 Design of Ti-6Al-4V-xCr-yNi Alloys

Fig. 3.1a presents the thermo-calc simulated phase diagram for Ti-6Al-4V-xCr alloy depicting the occurrence of different phases for variation in at.% of chromium and temperature. It shows that β -Ti phase formation temperature for Ti-6Al-4V alloy (i.e., minimum temperature required for the occurrence of 100% β-Ti phase) decreases with increase in at.% of chromium. It decreases to approximately 1150 K for 5 at.% of chromium. Generation of the C14 Laves phase starts approximately at 1025 K because of limited solubility of chromium in α -Ti phase and increases with at.% of chromium. Therefore, 5 at.% chromium was chosen as an upper limit for addition to Ti-6Al-4V alloy to enhance its microstructure and mechanical characteristics without formation of any brittle phase. It is supported by the finding of Chen et al. (2022) that adding more than 5% chromium to Ti can form brittle phases that reduce the strength and ductility of the developed alloy rather than improving them. Fig. 3.1b presents Scheil solidification showing variation in mole fraction of the solidified Ti-6Al-4V-5Cr alloy with decrease in temperature. It can be observed from Fig. 3.1b that entire liquid phase solidifies into the β -Ti phase at 1210°C, implying that the solidified Ti-6Al-4V-5Cr alloy has β-Ti phase only. Fig. 3.1c depicts equilibrium solidification diagram for Ti-6Al-4V-5Cr alloy showing mole fraction of the different phases formed in Ti-6Al-4V-5Cr alloy as a function of temperature. It can be observed from Fig. 3.1c that α -Ti phase begins to form at approximately 1145K and continues to form till 500 K attaining 0.88 mole fraction. The β -Ti phase begins to form at approximately 1875K and continue to form till 500K with 0.04 mole fraction, and evolution of the C14 Laves phase starts at approximately 1040 K and continues until 500 K attaining 0.07 mole fraction. It can be seen from Fig. 3.1c that solidus temperature of Ti-6Al-4V-5Cr alloy is approximately 1790 K.



Fig. 3.1: (a) Thermo-calc simulated phase diagram for Ti-6Al-4V-xCr alloy, (b) Scheil solidification diagram for Ti-6Al-4V-5Cr alloy, and (c) Equilibrium solidification diagram for Ti-6Al-4V-5Cr alloy.

Fig. 3.2a presents the thermo-calc simulated phase diagram for Ti-6Al-4V-yNi alloy depicting the occurrence of different phases change in at.% of nickel and temperature. It can be observed from Fig. 3.2a that β -transus temperature of Ti-6Al-4V alloy is approximately 1220 K, it reduces with increase in at.% of nickel and attains 1110 K for 5 at.% of nickel. The Ti₂Ni (shown as NiTi₂ phase) C14 Laves phases are formed at approximately 1025 K due to poor solubility of nickel in α -Ti phase of Ti-6Al-4V alloy. Formation of these phases and β -transus temperature increase gradually with an increase in nickel content beyond 5 at.%. It implies that addition of 5 at.% nickel content to Ti-6Al-4V alloy improves the grain refinement without increasing the β -transus temperature and without forming C14 Laves phase. Therefore, it was chosen to develop Ti-6Al-4V-5Ni alloy. It can be observed from Scheil solidification graph of Ti-6Al-4V-5Ni alloy (Fig. 3.2b) that approx. 85% of liquid is

solidified into β -Ti phase at approximately 1120°C i.e., 15% is liquidus. Further cooling of the liquidus and solidus phases up to 980°C forms C14 Laves phase. Completely solidified designed alloy contains β -Ti phase, C14 Laves phase, and intermetallic Ti₂Ni phase (shown as NiTi₂ phase). It can be observed from the equilibrium solidification diagram of Ti-6Al-4V-5Ni alloy (Fig. 3.2c) that formation of α -Ti phase having HCP crystal structure begins at approximately 1070 K and continues until 500 K attaining 0.68 as the mole fraction. Formation of β -Ti phase having BCC crystal structure begins at approximately 1800 K and completed at approximately 1000 K. Formation of C14 Laves phase starts at approximately 1100 K temperature and continues till 1000 K attaining 0.1 as the mole fraction. It can be seen from Fig. 3.2c that solidus temperature of Ti-6Al-4V-5Ni alloy is approx. 1590 K.



Fig. 3.2: (a) Thermo-calc simulated phase diagram for Ti-6Al-4V-yNi alloy, (b) Scheil solidification for Ti-6Al-4V-5Ni alloy, and (c) Equilibrium solidification for Ti-6Al-4V-5Ni alloy.

3.2 Preparation of Powders for Ti-6Al-4V-xCr-yNi Alloys

Powders of chromium and nickel were acquired from Loba Chemie Pvt Ltd Mumbai and powder of Ti-6Al-4V alloy was acquired from Tekna Inc. Canada. Powders of Ti-6Al-4V-5Cr alloy, Ti-6Al-4V-2.5Cr-2.5Ni alloy, and Ti-6Al-4V-5Ni alloy were prepared by respectively adding 5 at.% of chromium powder, 5 at.% of nickel powder, and 2.5 at.% of chromium and 2.5 at.% of nickel powder with 95 at.% of Ti-6Al-4V alloy powder. These powders were mixed in a planetary ball milling machine using 200 rpm as its speed and 2:1 as the ratio of tungsten carbide ball to the corresponding powder. The moisture content of the prepared powder for each alloy was removed by heating it in a furnace at 80°C for 25 minutes. Fig. 3.3 shows scanning electron microscopic (SEM) images depicting morphology of the prepared powder of Ti-6Al-4V-5Cr alloy (Fig. 3.3a), Ti-6Al-4V-2.5Cr-2.5Ni alloy (Fig. 3.3b), Ti-6Al-4V-5Ni alloy (Fig. 3.3c), and powder of Ti-6Al-4V alloy (Fig. 3.3d). These figures also depict elemental composition (in wt.%) obtained by energy dispersive x-ray spectroscopy (EDX) and distribution of powder particle size for these alloys. It can be observed from Fig. 3.3 that prepared powders consist of nearly spherical shaped particles having average size of 63±5.6 µm for Ti-6Al-4V-5Cr alloy, 66.3±6.1 µm for Ti-6Al-4V-2.5Cr-2.5Ni alloy, 65.4±4.8 µm for Ti-6Al-4V-5Ni alloy, and 66.5±5.2 µm for Ti-6Al-4V alloy.



(b)



Fig. 3.3: Morphology, elemental composition, and distribution of particle size of prepared powders for (a) Ti-6Al-4V-5Cr alloy, (b) Ti-6Al-4V-2.5Cr-2.5Ni alloy, (c), Ti-6Al-4V-5Ni alloy and (d) Ti-6Al-4V alloy.

3.3 Apparatus for µ-PPAM Process

Fig. 3.4 presents the working principle of micro-plasma powder additive manufacturing $(\mu$ -PPAM) process.



Fig. 3.4: Working principle of µ-PPAM process.

It uses direct current (DC) power supply to ionize the plasma forming gas to generate μ plasma arc inside the nozzle and between non-consumable tungsten electrode and the substrate. The generated μ -plasma arc is used as a heat source to melt the feedstock material and to fuse it with the substrate or previously deposited layer. It is forced through a fine hole in the nozzle which constricts it resulting in its stability even at low current, higher energy density, less HAZ, thermal distortion, and dilution. The μ -PPAM process uses a coaxially fed inert gas (i.e., argon) to shield the molten deposition from contamination by the surrounding environment. Since the electrode is inside the nozzle, feedstock material refrains from encountering it enabling this process to use deposition or feedstock material in powder, wire and combined powder-wire form. Fig. 3.5 shows photograph of in-house developed 5-axis computer numerical controlled (CNC) machine for μ -PPAM process.



Fig. 3.5: Photograph of 5-axis CNC machine developed in-house for μ-plasma powder additive manufacturing process.

It was developed by integrating the following five units: (i) 5-axis CNC worktable for mounting the substrate plate. Its controller is programmed in G and M codes through a dedicated computer, (ii) Power supply unit (*Dual Arc 82* from *Elderfield & Hall Inc. USA*) with option of operating either in continuous or pulsed mode and with capacity of supplying DC power up to 440 W and current up to 20 A with an increment of 0.1 A for formation of μ -plasma arc. It also has a cooling unit, (iii) Feeding system to supply powder of feedstock material to the deposition head at the required flow rate. It has hopper, powder feeder, and DC power unit to supply power to the powder feeding system, (iv) System to supply plasma forming gas and melt pool shielding gas (both argon) to the deposition head, and (v) In-house developed deposition head consisting of μ -plasma torch at its centre, and 4 nozzles inclined

at 60° to the vertical axis and placed circumferentially at equal intervals (enlarged view shown in Fig. 3.5) to supply feedstock material powder to the substrate.

3.4 Design and Planning of Experiments

Experiments were planned, designed and conducted in different stages namely pilot experiments, main experiments, and manufacturing of multi-layer depositions.

3.4.1 Single-layer Depositions of Ti-6Al-4V-xCr-yNi Alloys

Experimental investigation of single-layer deposition was performed in the following two stages: pilot experiment and main experiments for Ti-6Al-4V-5Cr and Ti-6Al-4V-5Ni alloy each by manufacturing their single-layer depositions by μ -PPAM process on the substrate of Ti6Al4V alloy. Table 3.1 presents range of μ -PPAM process parameters available on the μ -PPAM machine, used in the pilot experiments, and values identified for the main experiments along with design of experiments approach used in them. The substrate was of 200 mm length, 200 mm width, and 25 mm thickness. The substrate plate was cleaned with abrasive paper and scrubbed with acetone to remove contaminants from it before conducting the experiments.

Table 3.1: Range of μ -PPAM process parameters available on the μ -PPAM machine, used in the pilot experiments, and values identified for the main experiments along with design of experiments approach used in them.

Parameter	Unit	Available on the μ-PPAM machine	Range used in the pilot experiments	Values identified for the main experiments				
Number of experiments	-		30	27				
Approach for design of experiments	-		One-factor-at-a-time	Full factorial				
μ-PPAM process parameters for Ti-6Al-4V-xCr-yNi alloys								
μ-plasma power	W	1-440	120-440	308; 319; 330				
Mass flow rate of feedstock powder	g/min	0.1-15	0.7-5.0	2.3; 2.9; 3.5				
Deposition head travel speed	mm/min	10-200	30-200	43; 47; 51				
Flow rate of µ-plasma forming gas	Nl/min	0.1-0.8	0.1-0.5	0.3				
Flow rate of shielding gas	Nl/min	1-12	2-9	5				
Stand-off distance	mm	1-20	3-15	8				

Pilot experiments for Ti-6Al-4V-5Cr and Ti-6Al-4V-5Ni Alloys: *Thirty* pilot experiments were conducted for Ti-6Al-4V-5Cr and Ti-6Al-4V-5Ni alloy each by manufacturing their single-layer depositions by µ-PPAM process on Ti-6Al-4V substrate. The one-factor-at-a-time experimental design approach was used in the pilot experiments in which one parameter was varied in its considered range and other parameters were kept constant at minimum values of their respective range. The objective of the pilot

experiments was to identify optimum values of six important parameters of μ -PPAM process for the main experiments using criterion of good and continuous deposition (through visual examination) by varying them in their following range: (a) μ -plasma power: 120-440 W; (b) mass flow rate of feedstock powder: 0.7-5.0 (g/min); (c) deposition head travel speed: 30-200 (mm/min); (d) µ-plasma forming gas flow rate: 0.1-0.5 Normal liter per minute (Nl/min); (e) shielding gas flow rate: 2-9 (Nl/min); and (f) stand-off distance (SOD): 3-15 mm. It was found that 0.3 Nl/min is the minimum required flow rate of μ -plasma forming gas to produce μ -plasma arc and transmit it to the substrate. Its higher values caused melt pool to expand leaving a dimple-like imprint on top surface of a deposition. Shielding gas flow rate 5 Nl/min was found to protect molten pool from contamination from the surrounding environment. Its greater value caused the melt pool to expand leaving a dimple-like imprint on top surface of deposition. It was observed that 8 mm of SOD was adequate to assure supply of feedstock powder to center of the melt pool. Its value of less than or more than 8 mm resulted in wastage of the feedstock powder. It was found that minimum µ-plasma power of 308 W was required to melt the powders of Ti-6Al-4V-5Cr and Ti-6Al-4V-5Ni alloys hence 308; 319; and 330 W were chosen as values for the main experiments. Mass flow rate of feedstock powder more than 2.3 g/min allowed smooth powder feeding and continuous deposition of powder of Ti-6Al-4V-5Cr and Ti-6Al-4V-5Ni alloys. Its value greater than 3.5 g/min resulted in their non-uniform and partially melted deposition. Therefore, values of 2.3; 2.9; and 3.5 g/min were selected for the main experiments. Discontinuous depositions were formed when deposition head travel speed exceeded 51 mm/min whereas its value less than 43 mm/min resulted in a larger HAZ. Consequently, 43; 47; and 51 mm/min were chosen for the main experiments. Summarily, the pilot experiments identified 0.3 Nl/min as µ-plasma forming gas flow rate; 5.0 Nl/min as shielding gas flow rate; and 8 mm as SOD as their best values. The optimum values for conducting the main experiments were 308; 319; and 330 W for μ plasma power, 2.3; 2.9; and 3.5 g/min for mass flow rate of feedstock powder, and 43; 47; and 51 mm/min for deposition head travel speed.

Main experiments for Ti-6Al-4V-xCr-yNi alloys: *Twenty-seven* full factorial main experiments were conducted for Ti-6Al-4V-5Cr and Ti-6Al-4V-5Ni alloy each by manufacturing their single-layer depositions by μ-PPAM process on Ti-6Al-4V substrate. The objective of the main experiments was to identify optimum parametric combination of μ-plasma power, mass flow rate of feedstock powder, and deposition head travel speed for manufacturing multi-layer depositions of Ti-6Al-4V-5Cr; Ti-6Al-4V-2.5Cr-2.5Ni; Ti-6Al-4V-5Ni; and Ti-6Al-4V alloy. This was done by μ-PPAM on Ti-6Al-4V substrate,

using criteria of combination of maximum deposition efficiency, and minimum aspect ratio and dilution among the uniform and continuous single-layer depositions obtained in the main experiments.

3.4.2 Multi-layer Depositions of Ti-6Al-4V-xCr-yNi Alloys

The identified optimum parametric combination of μ -plasma power, mass flow rate of feedstock powder, and deposition head travel speed from the main experiments were used to manufacture multi-layer depositions of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloy by μ -PPAM on Ti-6Al-4V substrate. In the deposition process, single tracks were combined to form multi-layer deposits using specific deposition patterns, such as uniform and continuous deposition (UCD) achieved through the μ -PPAM technique. A raster-like sequence of tracks was employed, optimizing deposition efficiency and minimizing dilution.

3.5 Evaluation of Responses and Characterization

Following sections describe preparation of samples and the procedure used to evaluate the considered responses for single-layer depositions of Ti-6Al-4V-5Cr and Ti-6Al-4V-5Ni alloys and multi-layer depositions Ti-6Al-4V-xCr-yNi alloys. These responses included (i) deposition width, deposition height, diluted depth, aspect ratio, dilution, and deposition efficiency for the single-layer depositions, and (ii) density, porosity, microstructure, grain size, elemental analysis, phase orientation maps, phase fraction, evolution of phases, microhardness, tensile properties, fractography of tensile test sample, fracture toughness, abrasion resistance, corrosion characteristics, and tribological characteristics for the multilayer depositions.

3.5.1 Evaluation of Responses for Single-Layer Depositions

One sample of 3 mm length was cut transversely (i.e., along the deposition width) by wire spark erosion machining (WSEM) process (model: *Ecocut;* Make: *Electronica India Ltd.* Pune, India) from each single-layer deposition of Ti-6Al-4V-5Cr alloy and Ti-6Al-4V-5Ni alloy obtained in their main experiments (i.e., total 27 samples were cut for each alloy). Each cut sample was polished with silicon carbide emery paper of 2500 grit size, then velvet finished with 1.0-1.5 μ m fine by alumina liquid. Figs. 3.6a and 3.6b depict cross-section and side-view of one such prepared sample.



Fig. 3.6: Sample cut from a single-layer deposition of Ti-6Al-4V-5Cr alloy: (a) cross-sectional view, and (b) side view.

Deposition width 'W'(mm), deposition height 'H' (mm), and diluted depth ' T_P ' (mm) of each prepared sample were measured by the stereo-zoom microscope (Model: *Leica EZ4 HD*; Make: *Leica*, Germany). Deposition area ' A_D ' (mm²) and dilution area ' A_P ' (mm²) of a sample were calculated by importing its stereo-zoom microscopic image in the AutoCAD software (from AutoDesk Inc.). Aspect ratio ' A_R ' of a single-layer deposition was computed by dividing its deposition width by its deposition height (Eq. 3.1). Dilution 'D' is the ratio of dilution area ' A_P ' to the summation of dilution area ' A_P ' and deposition area ' A_D ' and can be computing by Eq. 3.2. It indicates the amount of fusion of a deposition layer with the previously deposited layer or with the substrate. Its greater value is not desirable as it degrades the quality of a deposition and increases thermal distortion. Powder deposition efficiency ' η ' was computed by Eq. 3.3 using deposition area ' A_D ' (mm²), deposition head travel speed ' S_d ' (mm/min), mass flow rate of feedstock powder ' F_f ' (g/min), and feedstock powder density ' ρ_P ' (g/mm³) in it.

$$A_{R} = \frac{W}{H}$$
(3.1)

$$D = \frac{A_{P}}{A_{D} + A_{P}}$$
(3.2)

$$\eta = \frac{A_{D}S_{d} \rho_{P}}{F_{f}}$$
(3.3)

3.5.2 Evaluation of Responses for Multi-Layer Depositions

Standard samples were prepared from each multi-layer deposition of Ti-6Al-4V-xCr-yNi; Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloy to evaluate and study their density, porosity, microstructure, grain size, elemental analysis, phase orientation maps, evolution of phases, microhardness, tensile properties, fractography of tensile test samples, fracture toughness, abrasion resistance, corrosion characteristics, and tribological characteristics.

3.5.2.1 Preparation of Samples

Fig. 3.7 depict the photographs showing location of different samples cut from multi-layer depositions of Ti-6Al-4V-xCr-yNi alloys to study their considered responses. It includes sample to study microstructure, phase analysis and phase maps (shown in pink color in Fig. 3.7), sample for tensile testing (shown in yellow color in Fig. 3.7), sample to evaluate microhardness (shown in red color in Fig. 3.7), sample to study fracture toughness and abrasion resistance sample (shown in green color in Fig. 3.7), sample to study corrosion characteristics (shown in blue color in Fig. 3.7), and sample to study tribological characteristics (shown in orange color in Fig. 3.7). Three samples were cut by the WSEM process from each multi-layer deposition for its tensile testing, fracture toughness, abrasion resistance, corrosion characteristics, and tribological characteristics and average value of the three samples was used to analyses these responses for each alloy.



Fig. 3.7: Photographs showing location of different samples cut from multi-layer depositions of Ti-6Al-4V-xCr-yNi alloys to study their considered responses.

3.5.2.2 Evaluation of Density and Porosity

One square sample of 10 mm size and 3 mm thickness was cut by WSEM process from the multi-layer deposition of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloy along their deposition length (as shown in Fig. 3.7) for measurement of their density and porosity. The cut samples were ultrasonically cleaned and dried to remove loose powder particles and foreign matter from them. Experimental density ' ρ_e ' of an alloy sample was computed using Eq. 3.4 which is based on Archimedes principle. Theoretical density ' ρ_r ' (%) of an alloy is expressed as ratio of its experimental density to theoretical density (Eq. 3.6). Porosity ' P_p ' (%) was computed by subtracting its computed relative density ' ρ_r ' from 100 (Eq. 3.7).

$$\rho_e = \left(\frac{m_a}{m_a - m_f}\right)\rho_f \qquad (3.4)$$

$$\rho_t = \frac{\sum C_i A_i}{\sum \frac{C_i A_i}{\rho_i}} \qquad (3.5)$$

$$\rho_e = \frac{\rho_e}{\rho_t} 100\%$$
(3.6)

 $P_p = 100 - \rho_e$
(3.7)

where, ' m_a ' and ' m_f ' are respectively mass of a multi-layer deposition of an alloy in air and deionized (DI) water (g); ' ρ_f ' is density of DI water (g/cm³); ' A_i ', ' ρ_i ' and ' C_i ' are respectively atomic weight (g); density (g/cm³); and atomic % of the *i*th constituent of an alloy. Mass of each sample in DI water and air was measured using a weighing scale having ±1 mg least count (model: *SE-391*; make: *ScienTech*). Measurement was recorded in the DI water when no bubbles were visible on the surface of a multi-layer deposition sample. Each measurement was repeated thrice, and their average value was used for analysis. Each sample was preheated up to 80°C for 10 minutes before conducting the next measurement of density to eliminate any moisture content.

3.5.2.3 Microstructure and Grain Size

One square sample of 10 mm size and 3 mm thickness was cut by WSEM process from the multi-layer deposition of Ti-6Al-4V-xCr-yNi; Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloy along their deposition length (as shown in Fig. 3.7). These samples were used to study their microstructure, grain size, elemental analysis, phase orientation maps, and evolution of phases. Each cut sample was polished by SiC abrasive papers of 2500 grit size followed by velvet polishing with 1-1.5 μ m fine alumina solution. Kroll's etchant (containing 6 ml HNO₃, 2 ml HF acid, and 92 ml DI water) was used to etch the polished samples. Optical microscope (model: *DM 2500 M*; make: *Leica*, Germany) and SEM (model: *JSM-7610FPlus*; make: *JEOL*, Japan) were used to reveal microstructure of β -Ti and α -Ti phases of an alloy sample respectively. The SEM and optical microscopic images of each sample were imported to the *ImageJ* software to compute average particle size of its β -Ti and α -Ti phases.

3.5.2.4 Elemental Analysis

Elemental analysis of each alloy sample was done by the EDX facility available with the SEM equipment. Elemental mapping of a point on an alloy sample by EDX gives wt.% of its major constituents. Whereas elemental mapping of a specific area on an alloy sample by the EDX gives colored images in which each color belongs to its major constituent. It can further be used to analyze distribution of its major constituents i.e., chemical composition.

3.5.2.5 Phase Orientation Maps

Thickness of each alloy sample which was used to study its microstructure, grain size, and elemental analysis, was reduced from 3 mm to 1 mm to study its phase maps and phase fraction. Then the resized samples were polished with SiC emery papers up to 2500 grit size, electropolished in an electrolyte containing 80% methanol and 20% perchloric acid and using

15 V power supply. Electron Back Scattered Diffraction (EBSD) data of each alloy sample were processed in the *ATEX* software to obtain information about its phase maps and phase fractions.

3.5.2.6 Evolution of Phases

Formation of different phases in each alloy sample was analyzed using an X-ray diffractometer (XRD) (model: *PANalytical*; make: *Empyrean*, Netherlands) at room temperature. The XRD equipment works on Bragg's law of diffraction described by Eq. 3.8.

$$\lambda = 2d_i \,\sin\theta \tag{3.8}$$

where, ' θ ' is diffraction angle; ' d_i ' is interplanar distance (also called d-spacing); and ' λ ' is the wavelength of the used x-rays. The XRD equipment records intensity of peaks at different values of 2 θ angle. The value of ' λ ' as 1.54 Å, value of '2 θ ' from 20° to 90°, and a dwell period of 1-2 seconds were used in the present work to obtain XRD data of each alloy sample. The obtained XRD data were processed using the *X'Pert HighScore Plus* analysis tool for plotting the XRD graph. The peaks corresponding to various phases and their crystallographic planes of an alloy sample were identified using the Joint Committee on Powder Diffraction Standards (JCPDS) database.

3.5.2.7 Evaluation of Tensile Properties and Fractography

Three samples from the multi-layer deposition of each alloy were cut by the WSEM process along its deposition direction (as shown in Fig. 3.7) for its tensile testing. Each cut sample had its dimensions as per ASTM E8M standard as shown in Fig. 3.8a. Fig. 3.8b shows photographs of the cut sample multi-layer deposition of each alloy. The tensile test was conducted on the three prepared samples of each alloy on the universal tensile testing machine (model: *H50KL*; make: *Tinius Olsen*, USA) using 1 mm/min as the tensile head speed to evaluate their yield strength, ultimate strength, and % elongation. Average value of 3 samples of an alloy was used to analyses its tensile properties. The SEM image of the fractured surface of a tensile test sample of an alloy was used to study its fracture morphology.



Fig. 3.8: Tensile test samples cut from multi-layer depositions of Ti-6Al-4V-xCr-yNi alloys: (a) dimensions as per standard ASTM E8M, and (b) photographs.

3.5.2.8 Microhardness Evaluation

One sample having 24 mm height along the deposition height or build direction, 10 mm width (of the substrate) along the deposition width, and 3 mm thickness along the deposition direction was cut by the WSEM process. One such sample was cut from the multi-layer deposition of each alloy to study variation in their microhardness. Vicker's microhardness of a cut sample was measured following the ASTM E384 standard by applying it a load of 200 g for a dwell period of 15 seconds on the Vicker's microhardness equipment (model: *VMH-002*; make: *Walter UHL*, Germany). Twenty indentations at an interval of 1 mm were made along the height of a cut sample with three indentations being made at each location (i.e., along the thickness of the cut sample). The arithmetic average of the three microhardness values measured at a particular location was used to get microhardness profile of an alloy.

3.5.2.9 Assessment of Fracture Toughness and Abrasion Resistance

One square sample of 10 mm size and 3 mm thickness was cut by the WSEM process from the multi-layer deposition of each alloy along its deposition length (as shown in Fig. 3.7) to determine its fracture toughness and abrasion resistance. The cut sample was polished with SiC emery papers up to 2500 grit size. The scratch test was conducted on the scratch tester (model: *TR-101*; make: *Ducom Instruments*, India) having a conical shaped diamond stylus possessing 120° half apex angle and 200 μ m tip radius as depicted in Fig. 3.9. The test was conducted following the ASTM G171-03 standard by applying a scratch load of 10 N, sliding the stylus for a distance of 3 mm (i.e., length of a scratch track) at 0.5 mm/min sliding speed.





Width 'w' and depth 'd' of a scratch track were measured by the optical microscope (model: *DM 2500 M*; make: *Leica*, Germany) and optical profilometer (model: *NT9080*; make: *Veeco*, USA) respectively. Scratch hardness number ' H_s ' (MPa), scratch track volume ' S_v ' (mm³), and fracture toughness ' F_c ' were calculated from the Eqs. 3.9, 3.10, and 3.11 respectively as mentioned by **Akono et al. (2012)** and **Akono and Ulm (2014)**.

$$H_S = \frac{8F_v}{\pi w^2} \tag{3.9}$$

$$S_{v} = \frac{T_{d}^{2}L}{8} \left[2\sin^{-1}\left(\frac{w}{T_{d}}\right) - \sin\left\{2\sin^{-1}\left(\frac{w}{T_{d}}\right)\right\} \right]$$
(3.10)
$$F_{c} = \frac{F_{eq}}{S}$$
(3.11)

where, $F_{eq} = F_t$ if $\alpha = 0$; and $F_{eq} = \sqrt{(F_t^2 + 0.6 F_v^2)}$ if $\alpha > 0$ (3.11a) $S = \sqrt{4d^3 \left(\frac{\sin \emptyset}{\cos^2 \emptyset}\right)}$ (3.11b)

where, F_v and F_t are the scratch load applied in vertical and horizontal directions respectively (N); F_{eq} is equivalent applied scratch load (N) which is given by Eq. (3.11a); 'w' 'd', and 'L' are respectively width, depth, and length of a scratch track (mm); 'S', 'T_d', and ' Φ ' are respectively shape factor, tip diameter, and half apex angle of the conical diamond stylus with values of with 'T_d' and ' Φ ' being equal to 0.4 mm and 120° respectively for the present study; and ' α ' is the angle between vertical direction and actual position of the conical diamond stylus during the scratch test. Its value is equal to zero if axis of the stylus coincides with the vertical direction otherwise its value is non-zero.

3.5.2.10 Corrosion Behaviour

One square sample of 10 mm size and 3 mm thickness was cut by the WSEM process from the multi-layer deposition of each alloy along its deposition length (as shown in Fig. 3.7). These samples were used to study their corrosion behaviour in terms of open circuit potential (OCP), potentiodynamic polarization (PDP) or Tafel curve, electrochemical impedance spectroscopy (EIS), mechanism of corrosion, and morphology and topography of the corroded surface. Each cut sample was polished with SiC emery papers up to 2500 grit size and washed in the deionized water and ultrasonically cleaned in acetone for 10 minutes. These samples were used to study its corrosion behaviour in the aqueous solution of sodium chloride having 3.5 wt.% concentration via *Autolab PGSTAT 302N* electrochemical workstation. It consists of a platinum rod as the counter electrode, Ag/AgCl as the reference electrode, and 100 mm² exposed area of the prepared sample as the working electrode as shown in Fig. 3.10.

The electrochemical workstation was used to obtain OCP, PDP or Tafel curve, and EIS of the prepared sample of each alloy. The OCP represents the condition of equilibrium at the surface of working electrode where oxidation and reduction reactions occur at same rate with the net current being zero. Each prepared sample was immersed in the chosen electrolyte for 24 hours to assess its stability. Data for the OCP curve for each sample were recorded for the duration of 1 hour with an interval of 1 seconds to stabilize the surface/solution interface. Data for the PDP or Tafel curve for each sample were recorded using a scan rate of 1

mV/second and varying the potential of the working electrode from -1.2V to +1.8V as per the ASTM G5 standard.





The EIS test was performed after the PDP test, and the EIS observations were recorded using an AC potential of 10 mV and varying the frequency in a range from 0.01 Hz to 100 KHz. The *EC Labview* software was used to analyze the recorded EIS data corresponding to each sample. It used the non-linear least square curve fitting technique to get the best fit curve for the recorded EIS data using the electrochemical equivalent circuit (EEC) model. The average values of OCP, PDP data, and EIS data were used for further analysis. The corrosion potential '*E_{corr}*' (volts) of each alloy was obtained from its Tafel curve, corrosion current '*I_{corr}*' (μ A) of each alloy was calculated by Tafel slopes of anodic and cathodic reactions and polarization resistance. The corrosion rate '*C_R*' (mm/year) of each alloy was computed using the Eq. 3.12 (**O'Brien et al. 2023; Ji et al. 2023**).

$$C_R = \frac{K I_{corr} E_W}{\rho_W A_W}$$
(3.12)
$$E_W = \frac{1}{\sum_{i=1}^{x_i Z_i} A_i}$$
(3.13)

where, 'K' is a constant having its value as 3,272 mm/A-cm-year; ' I_{corr} ', ' E_w ', ' A_w ', and ' ρ_w ', are respectively corrosion current (μ A), electrochemical equivalent (g) computed using Eq. 3.13; exposed area (cm²); and experimental density (g/cm³) of an alloy i.e., working electrode; and ' x_i ', ' z_i ', and ' A_i ' respectively are mass fraction, valency of electrochemical dissolution, and atomic weight (g) of the *i*th constituent of that alloy. The corroded samples of each alloy after its PDP test, were washed using deionized water followed by ultrasonically cleaning with acetone for 10 minutes. Morphology of a corroded surface of each alloy was obtained through its SEM image, and its topography in terms of average surface roughness

value was obtained by the optical profilometer (model: *NT9080*; make: *Veeco*). The elemental analysis of a corroded surface was performed through EDX facility of the SEM equipment.

3.5.2.11 Tribological Behaviour

One square sample of 10 mm size and 3 mm thickness was cut by the WSEM process from the multi-layer deposition of each alloy along its deposition length (as shown in Fig. 3.7). These samples were used to study their tribological behaviour in terms of coefficient of friction, sliding wear rate, morphology of worn surfaces, and analysis of worn subsurface. The sliding wear test was carried out on a reciprocating tribometer (model: *CM-9104*; Make: *Ducom Instruments Ltd.* India) at 25-30°C ambient temperature and 40% mean relative humidity. It involved sliding the 6 mm diameter ball of silicon nitride (having Vickers hardness in a range from 1600 to 1800 HV) over a length of 3 mm at 10 Hz frequency for a time duration of 30 min under three values of applied load of 10, 15, and 20 N. It resulted in a total sliding distance of 54 m for each applied load. Fig. 3.11 depicts the schematic diagrams of the sliding wear test (Fig. 3.11a), geometry of the silicon nitride ball, (Fig. 3.11b), three-dimensional view of geometry of the wear track (Fig. 3.11c), and top view of the wear track geometry (Fig. 3.11d).



Fig. 3.11: Schematic representation of (a) sliding wear test, (b) geometry of silicon nitride ball, (c) three-dimensional view of wear track geometry, and (d) top view of the wear track geometry.

The silicon nitride ball was chosen due to its higher Vickers hardness value than the balls made of Al₂O₃, ZrO₂, and stainless steel. It results in less damage to the silicon nitride ball.

The width of a sliding wear track was measured by the optical microscope and its depth was evaluated by the optical profilometer. Sliding wear test of each sample at a particular load was repeated thrice and arithmetic average value of the obtained values was used for the analysis purpose. The wear track can be divided into following two regions (Fig. 3.11d) to calculate the wear volume: (i) region '*A*' having geometry of a truncated cylinder traced by the arc '*BDC*' (shown in Fig. 3.11b) having its length as the wear track length '*L*_t', its width as wear track width '*w*_t' and (ii) region '*B*' at both the end of the wear track with each end having geometry of a truncated sphere traced by the silicon nitride ball. Volume of region A i.e., '*V*_A' (mm³) can be calculated by the Eq. 3.14.

$$V_A = L_t \times A_{BDC} \tag{3.14}$$

where, ${}^{\prime}L_{t}$ ' is the length of wear track (mm), and ${}^{\prime}A_{BDC}$ ' is the area of region ${}^{\prime}A'$ (mm²) which can is computed by subtracting the area of triangle *ABC* i.e., ${}^{\prime}A_{ABC}$ ' (mm²) from the area of the arc *ABDC* i.e., ${}^{\prime}A_{ABDC}$ ' (as shown in Fig. 3.12b) which are expressed by the Eq. 3.15 and Eq. 3.16.

$$A_{BDC} = A_{ABDC} - A_{ABC}$$
(3.15)
$$A_{BDC} = \frac{1}{2}\theta_t r_t^2 - \frac{1}{2}w_t(r_t - h_t)$$
(3.16)

where, ' h_t ' is the depth of a wear track (mm); ' w_t ' is width of the wear track (mm); ' r_t ' is radius of the silicon nitride ball (mm); and ' θ_t ' is angle of the arc 'ABDC' (radians) which is given by $\theta_t = 2 \sin^{-1} \left(\frac{w_t}{2r_t}\right)$. Volume of the region 'B' (mm³) at both end of a wear track is computed by summation of volumes of both ends of a wear track assuming it to be a spherical cap whose expression is given by the Eq. 3.17.

$$V_B = \frac{\pi h_t^2}{3} (3r_t - h_t)$$
(3.17)

Total volume of sliding wear and sliding wear rate are computed by Eq. 3.18 and Eq. 3.19 respectively.

$$V_{total} = V_A + V_B$$
(3.18)

$$Wear \, rate = \frac{V_{total}}{F_p \, S_t}$$
(3.19)

where, F_p is the applied load during the sliding wear test (N); and S_t is the total sliding distance (= 54 m). Morphology of a wear track of an alloy was obtained through its SEM image, changes in its chemical composition were found through the EDX facility of the SEM equipment. Its 3D surface roughness profile was acquired by the optical profilometer. Wear track of each alloy sample was cut at the middle of its length and was hot mounted. Then it was polished by the SiC emery papers up to grit size of 2,500 followed by 1 to 1.5 µm fineness alumina liquid spread over a velvet cloth and etched in the Kroll's reagent to reveal its

subsurface region through the SEM. The acquired SEM images were used to study microstructure of its subsurface and to understand its deformation mechanism.

This *chapter* provided details of design of Ti-6Al-4V-xCr-yNi alloys, preparation of the powders, machine for µ-PPAM process, design and planning of experiments, evaluation of different responses such as density and porosity, microstructure, evolution of phases, mechanical properties, corrosion characteristics, and tribological behaviour of µ-PPAM manufactured Ti-6Al-4V-xCr-yNi alloys.

The *next chapter* presents results for single-layer deposition of Ti-6Al-4V-5Ni and Ti-6Al-4V-5Cr alloys in terms of deposition width, deposition height, diluted depth, aspect ratio, dilution, and deposition efficiency along with their analysis, results of multi-layer depositions of Ti-6Al-4V-xCr-yNi alloys along with evaluation of their theoretical and experimental density and porosity.

Chapter 4

Deposition Results and Analysis

This chapter presents results for single-layer deposition of Ti-6Al-4V-5Ni and Ti-6Al-4V-5Cr alloys in terms of deposition width, deposition height, diluted depth, aspect ratio, dilution, and deposition efficiency and their analysis. It also results of multi-layer depositions of Ti-6Al-4V-xCr-yNi alloys along with evaluation of their theoretical and experimental density and porosity.

4.1 Results for Single-Layer Depositions and their Analysis

Twenty-seven full factorial main experiments were conducted for Ti-6Al-4V-5Cr and Ti-6Al-4V-5Ni alloy each by manufacturing their 27 single-layer depositions by μ -PPAM process on Ti-6Al-4V substrate. Objective of the main experiments was to identify optimum parametric combination of μ -plasma power, mass flow rate of feedstock powder, and deposition head travel speed. This was achieved using criteria of combination of maximum deposition efficiency, and minimum aspect ratio and dilution among the uniform and continuous single-layer depositions obtained in these experiments. The identified optimum parametric combination was used to manufacture multi-layer depositions of Ti-6Al-4V-xCryNi alloys by μ -PPAM on Ti-6Al-4V substrate.

4.1.1 Single-Layer Depositions of Ti-6Al-4V-5Cr Alloy

Table 4.1 presents the measured values of width of deposition 'W', height of deposition 'H', and diluted depth ' T_P ' and computed values of aspect ratio ' A_R ', dilution 'D', and efficiency of deposition ' η ' for the 27 combinations of power for μ -plasma power, mass flow rate of feedstock powder, and deposition head travel speed used in the main experiments for **Ti-6Al-4V-5Cr alloy**. Among the 27 manufactured single-layer depositions of Ti-6Al-4V-5Cr alloy, 15 depositions were found to be nonuniform and discontinuous deposition (NCD) due to their uneven deposition width, defective deposition layer, and some of them are even in the form of droplets. They are shown in Fig. 4.1a. Whereas, 12 depositions were identified as uniform and continuous deposition (UCD) owing to possessing continuity and uniformity in their deposition width along their entire length of deposition and they are depicted in Fig. 4.1b.

Exp.	Variable input parameters			Measured responses			Computed responses		
No.	µ-plasma	deposition head	l Mass flow rate	Deposition	Deposition	Diluted	Aspect	Dilution	Deposition
	power (W)	travel speed	of feedstock	width 'W'	height 'H'	depth	ratio	'D'	efficiency
		(mm/min)	powder (g/min)	(mm)	(mm)	T_p	'A _R '	(%)	'η'
						(mm)			(%)
	Uniform and continuous depositions (UCD)								
1	308	43	2.3	4.08	3.13	0.853	1.30	10.27	69.4
10	319	43	2.3	4.23	2.89	0.876	1.46	10.76	73.5
11	319	43	2.9	4.38	3.19	0.759	1.37	8.23	68.8
12	319	43	3.5	4.45	3.31	0.748	1.34	7.78	60.4
14	319	47	2.9	4.29	2.93	0.647	1.46	7.46	71.0
15	319	47	3.5	4.37	3.14	0.568	1.39	6.33	65.4
17	319	51	2.9	4.01	2.63	0.513	1.52	7.25	66.8
18	319	51	3.5	4.11	2.87	0.467	1.43	5.69	67.7
23	330	47	2.9	4.57	2.74	0.693	1.67	8.12	71.0
24	330	47	3.5	4.61	2.97	0.627	1.55	6.96	66.6
26	330	51	2.9	4.37	2.45	0.569	1.78	7.53	71.5
27	330	51	3.5	4.49	2.64	0.497	1.70	6.12	71.0
		Nonun	iform and disc	continuou	s depositio	on (NCE))		
2	308	43	2.9	4.11	3.37	0.741	1.22	8.03	61.8
3	308	43	3.5	4.23	3.44	0.726	1.23	7.32	56.0
4	308	47	2.3	3.94	2.97	0.689	1.33	8.77	69.4
5	308	47	2.9	4.01	3.11	0.604	1.29	7.28	60.9
6	308	47	3.5	4.12	3.27	0.518	1.26	5.90	61.2
7	308	51	2.3	3.79	2.66	0.527	1.42	8.28	66.4
8	308	51	2.9	3.91	2.74	0.465	1.43	6.90	61.3
9	308	51	3.5	3.98	3.01	0.438	1.32	5.49	62.5
13	319	47	2.3	4.09	2.81	0.726	1.46	9.21	75.8
16	319	51	2.3	3.95	2.57	0.579	1.54	8.96	72.4
19	330	43	2.3	4.56	2.76	0.903	1.65	10.99	77.7
20	330	43	2.9	4.76	3.01	0.791	1.58	8.58	72.9
21	330	43	3.5	4.83	3.17	0.779	1.52	8.14	63.7
22	330	47	2.3	4.41	2.63	0.754	1.68	10.58	74.0
25	330	51	2.3	4.16	2.49	0.593	1.67	9.43	73.3

Table 4.1: Measured and computed responses of Ti-6Al-4V-5Cr alloy for variouscombinations of variable input parameters of μ -PPAM process.





discontinuous deposition (NCD), and (b) uniform and continuous deposition (UCD).

It can be seen from Table 4.1 that among the UCD of Ti-6Al-4V-5Cr alloy, the Exp. No. 14 gave the combination of maximum deposition efficiency, minimum aspect ratio, and minimum dilution. Such a parametric combination generally promotes strong bonding between the deposition layers and homogeneity in an additively manufactured component. It is confirmed by photograph of the single-layer deposition of Ti-6Al-4V-5Cr alloy shown in Fig. 4.1b. Therefore, this combination (i.e., μ-plasma power as 319 W, mass flow rate of feedstock powder as 2.9 g/min, and deposition head travel speed as 47 mm/min) was identified as the optimum parametric combination to manufacture multi-layer deposition of Ti-6Al-4V-xCr-yNi alloys by the μ-PPAM process.

4.1.2 Single-Layer Depositions of Ti-6Al-4V-5Ni Alloy

Table 4.2 presents the measured values of width of deposition 'W', height of deposition 'H', and diluted depth ' T_P ' and computed values of aspect ratio ' A_R ', dilution 'D', and

efficiency of deposition ' η ' for the 27 combinations of power for μ -plasma power, mass flow rate of feedstock powder, and deposition head travel speed used in the main experiments for *Ti-6Al-4V-5Ni alloy*. Among the 27 manufactured single-layer depositions of Ti-6Al-4V-5Ni alloy, 15 depositions were found to be nonuniform and discontinuous deposition (NCD) due to their uneven deposition width, defective deposition layer, and some of them are even in the form of droplets. They are shown in Fig. 4.2a. Whereas, 12 depositions were identified as uniform and continuous deposition (UCD) owing to possessing continuity and uniformity in their deposition width along their entire length of deposition and they are depicted in Fig. 4.2b.

Table 4.2: Measured and computed responses of **Ti-6Al-4V-5Ni** alloy for various combinations of variable parameters of μ -PPAM process.

Exn	Variable input parameters			Measured responses			Computed responses			
No.	u-nlasma denosition head Mass flow rate			Deposition	Deposition Deposition Diluted			Aspect Dilution Deposition		
	power (W)	travel speed	of feedstock	width 'W'	height 'H'	depth	ratio	'D'	efficiency	
	•	(mm/min)	powder (g/min)	(mm)	(mm)	T_p	'A _R '	(%)	' η'	
						(mm)			(%)	
	Uniform and continuous depositions (UCD)									
1	308	43	2.3	4.11	3.17	0.857	1.31	10.31	69.2	
10	319	43	2.3	4.19	2.93	0.879	1.43	10.80	73.1	
11	319	43	2.9	4.35	3.17	0.762	1.37	8.32	68.9	
12	319	43	3.5	4.49	3.28	0.753	1.37	7.81	60.6	
14	319	47	2.9	4.23	2.94	0.641	1.43	7.41	71.6	
15	319	47	3.5	4.31	3.09	0.573	1.39	6.39	65.1	
17	319	51	2.9	4.06	2.61	0.523	1.55	7.28	66.3	
18	319	51	3.5	4.13	2.91	0.479	1.43	5.75	67.1	
23	330	47	2.9	4.52	2.76	0.698	1.64	8.17	71.0	
24	330	47	3.5	4.59	2.99	0.630	1.54	7.03	66.1	
26	330	51	2.9	4.41	2.48	0.572	1.78	7.59	71.1	
27	330	51	3.5	4.47	2.67	0.503	1.67	6.18	69.9	
		Nonu	niform and dis	continuous	s deposition	(NCD)				
2	308	43	2.9	4.19	3.31	0.741	1.27	8.03	61.8	
3	308	43	3.5	4.27	3.39	0.726	1.26	7.32	56.0	
4	308	47	2.3	4.01	3.01	0.689	1.33	8.77	69.4	
5	308	47	2.9	4.07	3.19	0.609	1.28	7.31	61.3	
6	308	47	3.5	4.19	3.31	0.523	1.27	5.93	61.7	
7	308	51	2.3	3.84	2.73	0.529	1.41	8.33	66.9	
8	308	51	2.9	3.97	2.78	0.469	1.43	6.93	61.6	
9	308	51	3.5	3.99	2.97	0.441	1.34	5.53	62.1	
13	319	47	2.3	4.13	2.77	0.730	1.49	9.32	75.2	
16	319	51	2.3	3.91	2.61	0.583	1.52	9.01	72.9	
19	330	43	2.3	4.51	2.72	0.909	1.66	10.97	77.3	
20	330	43	2.9	4.79	3.08	0.789	1.56	8.63	73.1	
21	330	43	3.5	4.87	3.19	0.781	1.53	8.19	63.2	
22	330	47	2.3	4.43	2.68	0.759	1.65	10.61	73.9	
25	330	51	2.3	4.21	2.50	0.596	1.68	9.47	73.6	



Fig. 4.2: Quality of single-layer depositions of **Ti-6Al-4V-5Ni** alloy: (a) nonuniform and discontinuous deposition (NCD), and (b) uniform and continuous deposition (UCD).

It can be seen from Table 4.2 that among the UCD of Ti-6Al-4V-5Ni alloy, Exp. No. 14 gave the combination of maximum deposition efficiency, minimum aspect ratio, and minimum dilution. Such a parametric combination generally promotes strong bonding between the deposition layers and homogeneity in an additively manufactured component. It is confirmed by photograph of the single-layer deposition of Ti-6Al-4V-5Ni alloy shown in Fig. 4.2b. Therefore, this combination (i.e., μ-plasma power as 319 W, mass flow rate of feedstock powder as 2.9 g/min, and deposition head travel speed as 47 mm/min) was identified as the optimum parametric combination to manufacture multi-layer deposition of Ti-6Al-4V-xCr-yNi alloys by the μ-PPAM process.

4.2 Results for Multi-Layer Depositions and their Analysis

The parametric combination of μ -plasma power as 319 W, mass flow rate of feedstock powder as 2.9 g/min, and deposition head travel speed as 47 mm/min identified from the main experiments for Ti-6Al-4V-5Cr and Ti-6Al-4V-5Ni alloys was used to manufacture multilayer depositions of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloy. Their photographs are shown in Figs. 4.3a, 4.3b, 4.3c, and 4.3d respectively along with their side views. Each deposition comprised of 8 layers resulting in a total deposition height of 24 mm.



(a)



(c)



Fig. 4.3: Photographs of multi-layer depositions of: (a) Ti-6Al-4V-5Cr alloy, (b) Ti-6Al-4V-2.5Cr-2.5Ni alloy, (c), Ti-6Al-4V-5Ni alloy, and (d) Ti-6Al-4V alloy, along with their side views.

It can be observed from Fig. 4.3 that the multi-layer depositions exhibit some surface waviness implying the need of some post-processing to achieve the desired dimensional and shape accuracy and surface finish. It can also be seen from the side views that the manufactured multi-layer depositions have good bonding between their deposition layers indicating complete melting of the feedstock material during their manufacturing by the μ -PPAM process.

4.3 Density and Porosity of Ti-6Al-4V-xCr-yNi Alloys

Table 4.3 presents values of experimental density (computed using Eq. 3.4), theoretical density (computed using Eq. 3.5), relative density computed using Eq. 3.6), and % porosity (computed using Eq. 3.7) of the manufactured multi-layer depositions of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloy. It can be observed from Table 4.3 that the values of both experimental and theoretical density of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni alloys are more than Ti-6Al-4V alloy thus resulting in smaller relative density and higher porosity than Ti-6Al-4V alloy. It can be explained by the following facts: (i) Density and atomic mass of chromium (7.19 g/cm³ and 51.99 amu) and nickel (8.9 g/cm³ and 58.69 amu) are higher than the constituents of Ti-6Al-4V alloy therefore their addition increases respectively theoretical and experimental density of the developed alloys than Ti-6Al-4V alloy, and (ii) presence of chromium and nickel in Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, and Ti-6Al-4V-5Ni alloys result in formation of intermetallic phases Cr₂Ti, and Ti₂Ni whose melting point is higher than Ti-6Al-4V alloy which lead to accumulation of more gas bubbles thus imparting them higher porosity. It can also be observed from Table 4.3 that among Ti-6Al-4V-5Ni has maximum values of theoretical and experimental density and porosity followed by that of Ti-6Al-4V-2.5Cr-2.5Ni and Ti-6Al-
4V-5Cr alloys. It is due to higher density and atomic mass of nickel (8.9 g/cm³ and 58.69 amu) more than that of chromium (7.19 g/cm³ and 51.99 amu).

Table 4.3: Density and porosity of multi-layer depositions of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloy.

Alloy	Theoretical density	Experimental density	Relative density	Porosity (%)
	(g/cm ³)	(g/cm ³)	(%)	
Ti-6Al-4V-5Ni	4.52	4.39	97.12	2.88
Ti-6Al-4V-2.5Cr-2.5Ni	4.49	4.37	97.33	2.67
Ti-6Al-4V-5Cr	4.47	4.36	97.54	2.46
Ti-6Al-4V	4.37	4.32	98.85	1.15

4.4 Concluding Remarks

This chapter presented deposition width, deposition height, diluted depth, aspect ratio, dilution, and deposition efficiency for single-layer deposition of Ti-6Al-4V-5Ni and Ti-6Al-4V-5Cr alloys and their analysis. The combination of 319W as μ -plasma power, 2.9 g/min as mass flow rate of feedstock powder, and 47 mm/min as deposition head travel speed yielded uniform and continuous single-layer depositions of Ti-6Al-4V-5Ni and Ti-6Al-4V-5Cr alloys and had combination of maximum deposition efficiency, minimum aspect ratio, and minimum dilution was identified as the optimum parametric combination for manufacturing multi-layer deposition of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloy by the μ -PPAM process. It also provided theoretical and experimental density, and porosity of these multi-layer depositions. Addition of chromium and nickel to Ti-6Al-4V alloy formed Cr₂Ti, and Ti₂Ni as the intermetallic phases (confirmed by the XRD plots of Fig. 5.6) whose melting point is higher than Ti-6Al-4V alloy. It led to accumulation of more gas bubbles thus imparting higher porosity.

The *next chapter* describes analysis of microstructure, elemental analysis, phase fraction, phase orientation maps, evolution of phases, tensile properties, fractography of tensile test samples, microhardness, fracture toughness, and abrasion resistance of μ -PPAM manufactured Ti-6Al-4V-xCr-yNi alloys.

Chapter 5

Microstructure and Mechanical Properties

This chapter presents analysis of microstructure, grain size, elemental analysis, phase fraction, phase orientation maps, evolution of phases, tensile properties, fractography of tensile test samples, microhardness, fracture toughness, and abrasion resistance of μ -PPAM manufactured multi-layer depositions of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni Ti-6Al-4V alloys.

5.1 Analysis of Microstructure

This section describes results and analysis of microstructure and grain size of β -Ti and α -Ti phases, elemental analysis, phase orientation maps, phase fraction, evolution of phases of μ -PPAM manufactured multi-layer depositions of Ti-6Al-4V-xCr-yNi alloys. It also presents results of their mechanical properties in terms of tensile properties, fractography of tensile test samples, microhardness, fracture toughness, and abrasion resistance.

5.1.1 Microstructure of Ti-6Al-4V-xCr-yNi Alloys

Fig. 5.1 presents the optical micrographs showing grain boundaries of β -Ti phase of Ti-6Al-4V-5Cr alloy (Fig. 5.1a), Ti-6Al-4V-2.5Cr-2.5Ni alloy (Fig. 5.1b), Ti-6Al-4V-5Ni alloy (Fig. 5.1c), and Ti-6Al-4V alloy (Fig. 5.1d). The computed average grain sizes of their β -Ti phase are 208.6 µm, 229.3 µm, 261.7, and 559.8 µm (Fig. 5.1e), respectively implying grain refinement of their β -Ti phase as compared to that of Ti-6Al-4V alloy. It is due to (i) generation of equiaxed grains which is enabled by the presence of chromium and/or nickel in the Ti-6Al-4V-5Cr (Fig. 5.1a), Ti-6Al-4V-2.5Cr-2.5Ni (Fig. 5.1b), Ti-6Al-4V-5Ni (Fig. 5.1c) alloys as compared to large columnar grains of Ti-6Al-4V alloy (Fig. 5.1d), and (ii) higher solidification temperature of these alloys than Ti-6Al-4V alloy. It can also be observed that grains of β -Ti phase of Ti-6Al-4V-5Cr are finer than that of Ti-6Al-4V-5Ni alloy which help it have better mechanical properties.



(a)





Fig. 5.1: Microstructure of β-Ti phase of: (a) Ti-6Al-4V-5Cr, (b) Ti-6Al-4V-2.5Cr-2.5Ni, (c) Ti-6Al-4V-5Ni, and Ti-6Al-4V, and (e) average grain size of their β-Ti phase.

Fig. 5.2 depicts the SEM micrographs showing that α -Ti phase of Ti-6Al-4V-5Cr alloy (Fig. 5.2a), alloy Ti-6Al-4V-2.5Cr-2.5Ni (Fig. 5.2b), Ti-6Al-4V-5Ni alloy (Fig. 5.2c), and Ti-6Al-4V (Fig. 5.2d) alloy has laminar structure and it is inside the grain boundaries of their β -Ti phase. The computed average grain sizes of α -Ti phase of these alloys are 2.01 µm, 2.46 µm, 2.97 µm, and 4.89 µm respectively (Fig. 5.2e). It implies that addition of chromium and/or nickel has refined the grains of α -Ti phase of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, and Ti-6Al-4V-5Ni alloys as compared to that of Ti-6Al-4V-3Cr, Ti-6Al-4V-2.5Cr-2.5Ni, and Ti-6Al-4V-5Ni alloys as Cr₂Ti and Ti₂Ni in these alloys which hinders grain growth of α -Ti phase and role of these intermetallic phases as nucleation sites for α -Ti phase. It can also be observed that grains of α -Ti phase of Ti-6Al-4V-5Cr are finer than that of Ti-6Al-4V-5Ni alloy which help it have better mechanical properties.



Fig. 5.2: Microstructure of α -Ti phase of: (a) Ti-6Al-4V-5Cr, (b) Ti-6Al-4V-2.5Cr-2.5Ni,

(c) Ti-6Al-4V-5Ni, and Ti-6Al-4V, and (e) average grain size of their α -Ti phase.

5.1.2 Elemental Analysis of Ti-6Al-4V-xCr-yNi Alloys

Fig. 5.3 presents EDX obtained color mapping of major constituents (i.e., titanium, aluminum, vanadium, chromium, and nickel) of Ti-6Al-4V-5Cr (Fig. 5.2a), Ti-6Al-4V-2.5Cr-2.5Ni (Fig. 5.2b), Ti-6Al-4V-5Ni (Fig. 5.2c), and Ti-6Al-4V (Fig. 5.2d) alloy. Table 5.1 presents summary of the elemental distribution in their α -Ti and β -Ti phases. It can be seen from Fig. 5.3 that there is uniform distribution of chromium in Ti-6Al-4V-5Cr alloy, chromium and nickel in Ti-6Al-4V-2.5Cr-2.5Ni alloy, and nickel in Ti-6Al-4V-5Ni alloy.

Such a uniform distribution will help in improving mechanical properties of these alloys as compared to Ti-6Al-4V alloy.



Fig. 5.3: Color mapping of major constituents of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloy.

Alloy	Phase	Ti	Al	V	Ni	Cr
Ti-6Al-4V-5Cr	α-Ti	86.2	10.8	1.8	-	1.2
	β-Ti	79.1	8.8	3.9	-	8.2
Ti-6Al-4V-2.5Cr-2.5Ni	α-Ti	85.3	11.6	2.0	0.6	0.5
	β-Ti	79.1	9.1	3.7	4.2	3.9
Ti-6Al-4V-5Ni	α-Ti	85.4	11.4	2.1	1.1	-
	β-Ti	77.3	10.0	3.5	9.2	-
Ti-6Al-4V	α-Ti	86.1	11.5	2.4	-	-
	β-Τί	84.9	9.2	5.9	-	-

Table 5.1: Elemental distribution by at.% of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys.

Following are the observations from Table 5.1: (i) distribution of constituents is not same in α -Ti and β -Ti phases for all the four alloys, (ii) the at.% of vanadium and chromium in β -Ti phase of Ti-6Al-4V-5Cr alloy is respectively 2.16 and 6.83 times more than its α -Ti phase; (iii) the at.% of vanadium, nickel, and chromium, in β -Ti phase of Ti-6Al-4V-2.5Cr-2.5Ni alloy is respectively 1.85, 7, and 7.8 times more than its α -Ti phase, and (iv) the at.% of vanadium and nickel in β -Ti phase of Ti-6Al-4V-5Ni alloy is respectively 1.67 and 8.36 times more than its α -Ti phase. These observations are due to the eutectoid nature of chromium, nickel, and vanadium which enhances their solubility in β -Ti phase. It leads to formation of their substitutional solid solutions within the β -Ti phase. Presence of more at.% of chromium and nickel in β -Ti phase of Ti-6Al-4V-5Cr, Ti-6Al-4V-5Ni, Ti-6Al-4V-2.5Cr-2.5Ni alloys will help to improve their strength, fracture toughness, and abrasion resistance. It can also be seen from Table 5.1 that at.% of aluminium is higher in α -Ti phase for all the four alloys as compared to their β -Ti phase.

5.1.3 Phase Orientation Maps of Ti-6Al-4V-xCr-yNi Alloys

Fig. 5.4 presents EBSD obtained phase orientation maps for α -Ti phase of Ti-6Al-4V-5Cr alloy (Fig. 5.4a), Ti-6Al-4V-2.5Cr-2.5Ni alloy (Fig. 5.4b), Ti-6Al-4V-5Ni alloy (Fig. 5.4c), and Ti-6Al-4V alloy (Fig. 5.4d). These maps show orientation of their α -Ti phase grains along different crystallographic planes which are shown in different colors using the legends shown Fig. 5.4e.





Fig. 5.4: Phase orientation maps for α-Ti phase of: (a) Ti-6Al-4V-5Cr alloy, (b) Ti-6Al-4V-2.5Cr-2.5Ni alloy, (c) Ti-6Al-4V-5Ni alloy, (d) Ti-6Al-4V alloy, and (e) legends for different crystallographic planes.

Majority grains of α -Ti phase of Ti-6Al-4V-5Cr alloy (Fig. 5.4a) are oriented along the 0001 and $10\overline{1}0$ crystallographic planes and between these planes while, some grains are oriented between the 0001 and $2\overline{1}\overline{1}0$ crystallographic planes. Most of the grains of α -Ti phase of Ti-6Al-4V-2.5Cr-2.5Ni alloy (Fig. 5.4b) are oriented along the 0001 and $10\overline{10}$ crystallographic planes and between these planes while, few grains are oriented along the $2\overline{1}\overline{1}0$ crystallographic plane. Majority grains of α -Ti phase of Ti-6Al-4V-5Ni alloy (Fig. 5.4c) are oriented along the 0001 and $2\overline{1}\overline{1}0$ crystallographic planes, and between the 0001 and $10\overline{1}0$ crystallographic planes while some grains are oriented between 0001 and $2\overline{1}\overline{1}0$ crystallographic planes. Most of the grains of α -Ti phase of Ti-6Al-4V alloy (Fig. 5.4d) are oriented along the $2\overline{1}\overline{1}0$ crystallographic plane, and between the 0001 and $10\overline{1}0$ crystallographic planes. It can be inferred from these observations that addition of chromium and/or nickel to Ti-6Al-4V alloy made most of the grains of α -Ti phase of the resultant alloys to orient along different crystallographic planes thus reducing their anisotropy which will make their mechanical properties more uniform in different directions. This will be beneficial for the components subjected to multi-directional loads in aerospace and automobile applications.

5.1.3 Phase Fraction of Ti-6Al-4V-xCr-yNi Alloys

Fig. 5.5 presents EBSD obtained phase fraction maps for Ti-6Al-4V-5Cr (Fig. 5.5a), Ti-6Al-4V-2.5Cr-2.5Ni (Fig. 5.5b), Ti-6Al-4V-5Ni (Fig. 5.5c), and Ti-6Al-4V (Fig. 5.5d) alloys. These maps show fraction of their α -Ti and β -Ti phases in red and green colors respectively along with their values written on the bottom of each figure. It can be observed from these figures that fraction of β -Ti phase in Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, and Ti-6Al-4V-5Ni alloys are 19.2, 18.4%, 17.3% respectively which are much higher than that of 5.9% in Ti-6Al-4V alloy. It implies that addition of chromium and/or nickel to Ti-6Al-4V alloy increased fraction of β -Ti phase in these alloys. It is because these elements act as stabilizers to the β -Ti phase due to their eutectoid nature which increases their solubility in β -Ti phase thus forming their substitutional solid solutions inside it. Such a higher fraction of β -Ti phase in these alloys will also help in improving their mechanical properties as compared to Ti-6Al-4V alloy.



Fig. 5.5: Fraction of α -Ti and β -Ti phases (%) for the: (a) Ti-6Al-4V-5Cr alloy, (b) Ti-6Al-4V-2.5Cr-2.5Ni alloy, (c) Ti-6Al-4V-5Ni alloy, and (d) Ti-6Al-4V alloy.

5.1.3 Evolution of Phases of Ti-6Al-4V-xCr-yNi Alloys

Fig. 5.6 shows the XRD plots for multi-layer deposition samples of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys indicating presence of the peaks corresponding to α/α' -Ti and β -Ti phases in them. Additionally, evolution of one intermetallic phase Cr₂Ti is indicated in Ti-6Al-4V-5Cr and Ti-6Al-4V-2.5Cr-2.5Ni alloys, and evolution of an intermetallic phase Ti₂Ni is indicated in Ti-6Al-4V-5Ni alloy. Since, both α -Ti and α' -Ti have HCP crystal structure and same crystallographic planes thus making it difficult to distinguish between them. Slight movements of peaks in the XRD plots of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, and Ti-6Al-4V-5Ni alloys is also indicated implying occurrence of some lattice distortions. Evolution of the intermetallic phases Cr₂Ti and Ti₂Ni occur due to strong atomic interactions between atoms of Ti and Cr, and between the atoms of Ti and Ni, respectively.



Fig. 5.6: Evolution of phases in multi-layer deposition samples of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys.

5.2 Mechanical Properties

This section describes evaluation of tensile properties, fracture morphology of tensile samples, microhardness, fracture toughness, and abrasion resistance of multi-deposition samples of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys in terms of and their analysis.

5.2.1 Analysis of Tensile Properties and Fracture Morphology

Fig. 5.7 shows stress-strain curves for multi-layer deposition samples of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys along with photographs of their fractured samples. Table 5.2 summarizes their average values of yield and ultimate tensile strengths and % elongation along with their associated standard deviations (SD).



Fig. 5.7: Stress-strain graph for multi-layer deposition samples of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys.

Table	5.2:	Average	and SI) values	of yield	and	ultimate	tensile	strength	s and	% (elongat	ion
for Ti-	-6Al-4	V-5Cr,	Ti-6Al-	4V-2.50	Cr-2.5Ni	, Ti-6	5Al-4V-5	5Ni, and	l Ti-6Al-	4V al	loys	s.	

Alloy	Avg. yield	Avg. ultimate	Avg. elongation
	strength and its	tensile strength	and its SD (%)
	SD (MPa)	and its SD (MPa)	
Ti-6Al-4V-5Cr	1178.4 ± 6.4	1368.4 ± 9.1	5.8 ± 0.7
Ti-6Al-4V-2.5Cr-2.5Ni	$1149.4{\pm}6.8$	1311.9± 8.7	5.9 ± 0.8
Ti-6Al-4V-5Ni	1121.6 ± 7.4	1248.4 ± 7.9	6.2 ± 0.9
Ti-6Al-4V	989.2 ± 7.7	1059.4 ± 8.9	9.9 ± 0.8

It is evident from Fig. 5.7 and Table 5.2 that multi-layer deposition sample of Ti-6Al-4V-5Cr alloy has maximum avg. values of yield and ultimate tensile strengths (1178.4 and 1368.4 MPa) but minimum avg. value of elongation (5.8%), followed by that of Ti-6Al-4V-2.5Cr-2.5Ni alloy (1149.4 MPa; 1311.9 MPa; 5.9%) and Ti-6Al-4V-5Ni alloy (1121.6 MPa; 1248.4 MPa; 6.2%). Whereas Ti-6Al-4V alloy has minimum avg. values of yield and ultimate tensile strengths (989.2 and 1059.4 MPa) but maximum avg. value of elongation (9.9%). It implies that tensile fracture of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, and Ti-6Al-4V-5Ni alloys occurred earlier than Ti-6Al-4V alloy as shown in Fig. 5.7. Increase in yield and ultimate tensile strengths and reduction in elongation of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, and Ti-6Al-4V-5Ni alloys as compared to Ti-6Al-4V alloy can be explained by the following reasons: (i) Formation of finer grains of α -Ti and β -Ti phases (Figs. 5.1 and 5.2) caused by presence of chromium and/or nickel. The finer grains result in a higher volume fraction of grain boundaries, which obstructs movement of the dislocations thus increasing strength. It also causes crack deflection at grain boundaries, which reduces crack propagation and improves fracture resistance. Value of increase in strength of Ti-6Al-4V-xCr-yNi alloys due to: (i) grain refinement of their α -Ti and β -Ti phases can be found using the Hall-Petch relation as mentioned by Luo et al. (2016) and Bhattacharjee et al. (2006), (ii) uniform distribution of chromium in Ti-6Al-4V-5Cr alloy, chromium and nickel in Ti-6Al-4V-2.5Cr-2.5Ni alloy, and nickel in Ti-6Al-4V-5Ni alloy (Fig. 5.3) also help in improving their mechanical properties as compared to Ti-6Al-4V alloy, (iii) Evolution of an intermetallic phase Cr₂Ti in Ti-6Al-4V-5Cr and Ti-6Al-4V-2.5Cr-2.5Ni alloys, and Ti₂Ni in Ti-6Al-4V-5Ni alloy (Fig. 5.6) which improve their strength but reduces their ductility, and (iv) Dissolution of chromium and/or nickel in β -Ti phase to form solid solutions which act as barriers to movement of the dislocations, also improves strength of these alloys. Solid solution strengthening mechanism for a two-phase alloy can be understood using the relationship mentioned by Zhao et al. (2019).

Fig. 5.8 shows the fracture morphology of tensile test samples of all the four alloys revealing presence of fine dimples, cleavage facets, and micropores in Ti-6Al-4V-5Cr alloy (Fig. 5.8a) and Ti-6Al-4V-2.5Cr-2.5Ni alloy (Fig. 5.8b), presence of dimples and cleavage facets in Ti-6Al-4V-5Ni alloy (Fig. 5.8c), and presence of dimples only in Ti-6Al-4V alloy (Fig. 5.8d). It implies that fracture mechanism of Ti-6Al-4V-5Cr alloy, Ti-6Al-4V-2.5Cr-2.5Ni alloy, and Ti-6Al-4V-5Ni alloy is a combination of ductile and brittle fracture. Formation of cleavage facets in Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni alloys is due to intermetallic phases Cr₂Ti and Ti₂Ni in them. These intermetallic phases act as stress concentration sites leading to initiation and propagation of cracks during deformation thus leading to the cleavage facets in the fractured surface. Formation of the micropores in Ti-6Al-4V-2.5Cr-2.5Ni alloys is due to presence of intermetallic phase Cr₂Ti in them. Presence of micropores and cleavage facets reduce ductility of these alloy which is confirmed by smaller values of their % elongation (Table 5.2). Presence of only dimples in the fractured surface of Ti-6Al-4V alloy indicate its ductile mode of fracture.



Fig. 5.8: Fracture morphology of tensile test sample of: (a) Ti-6Al-4V-5Cr alloy, (b) Ti-6Al-4V-2.5Cr-2.5Ni alloy, (c) Ti-6Al-4V-5Ni, and (d) Ti-6Al-4V alloy.

5.2.3 Analysis of Microhardness

Fig. 5.9 depicts microhardness profile for multi-layer deposition of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys along their deposition height or build direction. It can be observed from Fig. 5.9 that (i) Average values of microhardness of multi-layer deposition samples of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys increase along their deposition height. It is due to faster cooling of the top deposition layer which results in the formation of higher hardness phases such as martensitic α '-Ti phase. Additionally, the previously deposited layers undergo repeated cycles of heating and cooling during the deposition process. Similar observations have been reported by Han et al. (2022); Chen et al. (2020); and Sawant and Jain, (2018a). Such a cyclic heating and cooling allows the previously deposited layers for stress relieving which reduces their microhardness, and (ii) The multi-layer deposition sample of Ti-6Al-4V-5Cr alloy is found to have maximum avg. values of microhardness (i.e., 571.5 HV) and Ti-6Al-4V alloy possess minimum avg. values of microhardness (i.e., 452.3 HV) throughout their deposition height. It is due to the smallest and largest grain size of α -Ti and β -Ti phases in Ti-6Al-4V-5Cr alloy and Ti6Al4V alloy respectively. Smaller grains hinder movement of the dislocations thus enabling to offer more resistance to indentation. Microhardness values of multi-layer deposition samples Ti-6Al-4V-2.5Cr-2.5Ni alloy (i.e., 565.4 HV) and Ti-6Al-4V-

5Ni alloy (i.e., 512.6 HV) lie in between them. Evolution of harder intermetallic Cr_2Ti phase in Ti-6Al-4V-2.5Cr-2.5Ni and Ti-6Al-4V-5Cr alloys and formation of the intermetallic phase Ti₂Ni in Ti-6Al-4V-5Ni alloy also impart higher microhardness than Ti-6Al-4V alloy.



Fig. 5.9: Microhardness profile of multi-layer deposition samples of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloy along their deposition height.

5.2.4 Study of Fracture Toughness and Abrasion Resistance

Fig. 5.10 depicts the graphs showing variation in scratch coefficient of friction (COF) along the scratch track length at 10 N applied load for multi-layer deposition samples of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys.



Fig. 5.10: Variation in scratch coefficient of friction along scratch track length at 10 N load for Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloy.

The graphs of Fig. 5.10 can be divided into two zones namely (i) running-in zone in which COF rises quickly up to 0.5 mm scratch length because these alloys offer more resistance when the initial contact between scratch indenter and an alloy surface take place, and (ii) steady-state zone in which scratch COF attains a steady state value with relatively minor fluctuations because the scratch track is formed thus allowing smooth travel of the scratch indenter. Fig. 5.11 shows photograph of scratch track width and profile of scratch track depth at 10 N applied load for multi-layer deposition sample of Ti-6Al-4V-5Cr alloy (Fig. 5.11a), Ti-6Al-4V-2.5Cr-2.5Ni alloy (Fig. 5.11b), Ti-6Al-4V-5Ni alloy (Fig. 5.11c), and Ti-6Al-4V alloy (Fig. 5.11d). Table 5.3 presents the computed averages values of scratch COF (computed from the graphs of Fig. 5.10), measured values of scratch track width and depth (computed from Fig. 5.11), and computed values of scratch hardness number (using Eq. 3.9) and fracture toughness (using Eq. 3.11) of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloy at 10N applied load. Fig. 5.12 shows the average value of scratch COF, computed value of scratch volume, abrasion resistance, and fracture toughness for Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys at 10 N applied scratch load.







(**d**)

Fig. 5.11: Photographs of scratch track width and profile of scratch track depth at 10N applied load for (a) Ti-6Al-4V-5Cr, (b) Ti-6Al-4V-2.5Cr-2.5Ni, (c) Ti-6Al-4V-5Ni, and (d)





Fig. 5.12: Average value of scratch COF, scratch volume, abrasion resistance and fracture toughness for multi-layer deposition samples of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloy.

Alloy	Avg.	Avg. depth of	Avg. width of	Scratch	Fracture	Scratch
	scratch	scratch track	scratch track	volume	toughness	hardness
	COF	(µm)	(µm)	(μm ³)	(x10 ^{1.5} MPa-mm ^{0.5}	⁵) (x10 ³ MPa)
Ti-6Al-4V-5Cr	0.21	2.73	50.1	1.58	123.8	10.1
Ti-6Al-4V-2.5Cr-2.5Ni	0.21	2.86	52.9	1.86	119.9	9.1
Ti-6Al-4V-5Ni	0.22	2.98	54.9	2.08	116.8	8.4
Ti-6Al-4V	0.23	3.23	59.0	2.58	106.9	7.3

Table 5.3: Computed values of average scratch COF, average width and depth of scratch track, fracture toughness, and scratch hardness number at 10N applied load for Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys.

It can be seen from the Fig. 5.12 and the Table 5.3 that multi-layer deposition sample of Ti-6Al-4V-5Cr alloy has minimum avg. values of depth and width of the scratch track (i.e., 2.73 and 50.1 μ m), scratch volume (i.e., 1.58 μ m³) and average scratch COF (i.e., 0.21). Whereas, Ti-6Al-4V alloy sample has maximum avg. values of depth and width of the scratch track (3.23 and 59 μ m), scratch volume (i.e., 2.58 μ m³), and average scratch COF (i.e., 0.23). Their values for multi-layer deposition samples Ti-6Al-4V-2.5Cr-2.5Ni and Ti-6Al-4V-5Ni alloys lie in between them. These observations are due to maximum microhardness of Ti-6Al-4V-5Cr alloy (i.e., 571.5 HV) and minimum microhardness of Ti-6Al-4V alloy (i.e., 546.3 HV), and evolution of harder intermetallic Cr₂Ti phase in Ti-6Al-4V-5Ni alloy. All these factors result in more resistance to the movement of the scratch indenter which decreases its contact area thus resulting in smaller values of width, depth, and volume of scratch track. It is also noticeable that the average value of scratch COF for all the four alloys lies in a very narrow range from 0.21 to 0.23.

It can be observed from Fig. 5.12 and Table 5.3 that the multi-layer deposition sample of Ti-6Al-4V-5Cr alloy has maximum values of fracture toughness (i.e., $123.8 \times 10^{1.5}$ MPa-mm^{0.5}) and scratch hardness (i.e., 10.1×10^3 MPa) followed by that of Ti-6Al-4V-2.5Cr-2.5Ni alloy (i.e., $119.9 \times 10^{1.5}$ MPa-mm^{0.5}; and 9.1×10^3 MPa) and Ti-6Al-4V-5Ni alloy (116.8 \times 10^{1.5} MPa-mm^{0.5}; and 8.4×10^3 MPa). Whereas, Ti-6Al-4V alloy has minimum values of its fracture toughness (i.e., $106.9 \times 10^{1.5}$ MPa-mm^{0.5}) and scratch hardness (7.3×10^3 MPa). It is due to formation of finer grain of α -Ti and β -Ti phases of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, and Ti-6Al-4V-5Ni alloy. These finer grains enhance the resistance of these alloys to crack propagation thus improving their fracture toughness. Another reason is the presence of harder intermetallic phases Cr₂Ti and Ti₂Ni which induce a strengthening effect by causing lattice distortion and cause formation of dislocations that impede crack movement and effectively prevent further crack propagation. They also increase microhardness of these alloys as

explained earlier. Both these factors enhance the abrasion resistance and fracture toughness of these alloys.

5.3 Concluding Remarks

This chapter presented study of microstructure, grain size, elemental analysis, phase fraction, phase orientation maps, evolution of phases, tensile properties, fractography of tensile test samples, microhardness, fracture toughness, and abrasion resistance of µ-PPAM manufactured Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys. Addition of chromium and/or nickel to Ti-6Al-4V refined the grains of β -Ti and α -Ti phases of the resultant Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni alloys. The α-Ti phase grains are refined due to formation of intermetallic phase Cr₂Ti in Ti-6Al-4V-5Cr and Ti-6Al-4V-2.5Cr-2.5Ni alloys and Ti₂Ni in Ti-6Al-4V-5Ni alloy which hinders grain growth of α -Ti phase and act of these intermetallic phases as nucleation sites for α -Ti phase. The β -Ti phase grains of these alloys are refined due to generation of equiaxed grains by chromium and/or nickel as compared to the large columnar grains in Ti-6Al-4V alloy. Elemental distribution in α -Ti and β -Ti phases of the developed alloys is not same because content of chromium, nickel, and vanadium in their β -Ti phase is more than their corresponding α -Ti phase. Evolution of phases indicated formation of α/α' -Ti and β -Ti phases in Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys, an intermetallic phase Cr₂Ti in Ti-6Al-4V-5Cr and Ti-6Al-4V-2.5Cr-2.5Ni alloys, and an intermetallic phase Ti₂Ni in Ti-6Al-4V-5Ni alloy. Addition of chromium and/or nickel increased the yield and ultimate tensile strength, and microhardness of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni alloys but reduced their ductility due to grain refinement of their β -Ti and α -Ti phases and evolution of intermetallic phases Cr₂Ti and Ti₂Ni. It also changed their fracture mechanism to a combination of ductile and brittle mode possessing dimples, micropores, and cleavage facets. Average microhardness of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys is found to increase along their deposition height due to faster cooling of the top deposition layer which formed higher hardness phase such as martensitic α '-Ti phase. Enhanced microhardness and presence of harder intermetallic phase Cr₂Ti, and Ti₂Ni phases improved abrasion resistance and fracture toughness of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni alloys thus imparting them higher resistance to crack propagation and abrasive wear.

The *next chapter* presents results and their analyses on corrosion behaviour of μ -PPAM manufactured Ti-6Al-4V-xCr-yNi alloys in terms of open circuit potential, potentiodynamic polarization or Tafel curve, electrochemical impedance spectroscopy, mechanism of corrosion, and morphology and topography of the corroded surface.

Chapter 6

Corrosion Behaviour of Ti-6Al-4V-xCr-yNi Alloys

This chapter describes study of corrosion behaviour of μ -PPAM manufactured multi-layer deposition samples of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys using open circuit potential, potentiodynamic polarization or Tafel curve, electrochemical impedance spectroscopy, mechanism of corrosion, and morphology and topography of the corroded surface.

6.1 Open Circuit Potential

Fig. 6.1 presents curves showing variation of OCP value (i.e., ' E_{OCP} ') with the immersion time in the aqueous solution of sodium chloride for multi-layer deposition samples of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloy.



Fig. 6.1: Variation of open circuit potential with immersion time in aqueous solution of sodium chloride for the alloys Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V.

The OCP curves can be divided into two zones: (i) In the 1st zone, the ' E_{OCP} ' value increases rapidly due to dissolution of the layer of oxides that might have been formed initially on an alloy surface. This dissolution is caused by the attack of Cl⁻ ions on the alloy surface, thus releasing the metallic ions from it, and (ii) In the 2nd zone, the ' E_{OCP} ' value varies in a narrow range with the immersion time and gradually attains a steady state value due to formation of the passive layers. It is due to the reaction of the dissolved oxygen in the NaCl

solution with the released metallic ions to form various oxides. Layer thickness of these oxides increases, and they grow over the entire surface of an alloy sample which stabilizes its ${}^{E_{OCP}}$ value. These layers of oxides act as a barrier, reducing the rate of the electrochemical reaction of an alloy and thus providing protection against its further corrosion (**Zhang et al. 2021**). A stable and relatively positive value of OCP indicates lower corrosion rate of an alloy, while a fluctuating or more negative value of OCP suggests its higher corrosion rate. More positive value of OCP indicates formation of more stable layer of oxides on an alloy surface which enhances its corrosion resistance (**Resendiz et al. 2022**). It can be concluded from Fig. 6.1 that the Ti-6Al-4V-5Cr alloy has more positive OCP value followed by that of Ti-6Al-4V-2.5Cr-2.5Ni alloy, and Ti-6Al-4V-5Ni alloy, whereas Ti-6Al-4V alloy has minimum positive OCP value indicating their higher resistance to corrosion than Ti-6Al-4V alloy. It implies that addition of chromium and/or nickel to Ti-6Al-4V alloy makes OCP of the resultant alloys more positive due to the formation of oxides such as TiO₂, Cr₂O₃, and NiO thus enhancing corrosion resistance of the resultant alloys.

6.2 Potentiodynamic Polarization Curves

Fig. 6.2 depicts the potentiodynamic polarization curve (or Tafel curve) for multi-layer deposition samples of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloy showing variation of their ' E_{OCP} ' with the current density which is represented on a logarithmic scale.



Fig. 6.2: Potentiodynamic polarization or Tafel curve for Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloy.

It can be seen from Fig. 6.2 that all the four alloy samples have passivation potential in a range from 0.25 to 1.2 V in the aqueous solution of sodium chloride. Passivation range refers to a region where the current density does not increase significantly with an increase in the potential. More passivation range in a Tafel curve is beneficial because it shows better corrosion resistance, good material stability, and better performance in different corrosive environments (**Deng et al. 2023**). During the passivation process, a stable layer of oxides is formed on a working electrode of a developed alloy, which acts as an inhibitor and prevents corrosive attacks by the aqueous solution of sodium chloride. It can be seen from Fig. 6.2 that Ti-6Al-4V-5Cr alloy has a longer passivation range, followed by Ti-6Al-4V-2.5Cr-2.5Ni and Ti-6Al-4V-5Ni alloy, whereas Ti-6Al-4V alloy has the smallest passivation range.

Table 6.1 summarizes the values of corrosion potential E_{corr} (volts) identified from the Tafel curve of Fig. 6.2, corrosion current density i_{corr} (μ A/cm²) calculated from the slopes of anodic and cathodic reactions in the Tafel curve (**Xiao et al. 2023**), and the computed values of corrosion rate (using Eq. 3.12) for the Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys.

Table 6.1: Corrosion parameters for Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys obtained from their Tafel curves.

Alloy	Corrosion potential	Corrosion current density	Corrosion rate
	<i>'E_{corr}'</i> (volts)	<i>'icorr'</i> (µA/cm ²)	(µm/year)
Ti-6Al-4V-5Cr	-0.302	0.195	1.55
Ti-6Al-4V-2.5Cr-2.5Ni	-0.348	0.237	1.92
Ti-6Al-4V-5Ni	-0.412	0.294	2.43
Ti-6Al-4V	-0.473	0.349	3.11

Larger value of corrosion potential and smaller value of corrosion current density indicate higher stability for a material generally caused by the formation of a protective layer of oxides, which inhibits its further corrosion, thus giving it smaller value of corrosion rate (**Resendiz et al. 2022**). It can be observed from Table 6.1 that the Ti-6Al-4V-5Cr alloy has maximum value of corrosion potential (i.e., -0.302 volts) and minimum value of corrosion current density (i.e., $0.195 \ \mu A/cm^2$), followed by Ti-6Al-4V-2.5Cr-2.5Ni alloy (i.e., $-0.348 \ volts$ and $0.237 \ \mu A/cm^2$) and Ti-6Al-4V-5Ni alloy (i.e., $-0.412 \ volts$ and $0.294 \ \mu A/cm^2$) whereas, Ti-6Al-4V alloy has minimum value of corrosion potential (i.e., $0.349 \ \mu A/cm^2$). It is because of formation of layer of oxides namely Cr₂O₃ and NiO caused by addition of chromium and/or nickel to Ti-6Al-4V alloy. These layers of oxides act as the barrier, thus preventing direct contact of an alloy surface with the corrosive environments, thereby giving a smaller corrosion rate. It is confirmed by their corrosion rate values listed in Table 6.1. Overall, it can be summarized

that adding chromium and/or nickel to Ti-6Al-4V alloy modified the microstructure of the developed alloys and created the galvanic effect, thus reducing their corrosion rate.

6.3 Electrochemical Impedance Spectroscopy

Study of electrochemical impedance spectroscopy (EIS) of material involves study of the following: (i) Nyquist plot representing the relation between the real impedance and the imaginary impedance, (ii) Bode Plot 1, which depicts variation of absolute value of impedance with the frequency with both being represented on the logarithmic scales, (iii) Bode plot 2 which shows variation of the phase angle with the frequency being represented on the logarithmic scale, and (iv) Modified Randle model to fit the EIS data for Nyquist plot, Bode Plot 1, and Bode Plot 2 to get deeper insights into corrosion behaviour of a material in a corrosive environment. Randle model is described by resistance of the aqueous solution of the electrolyte ' R_s ' (ohm), polarization resistance ' R_f ' (ohm), and capacitance 'Q' of the layer of oxides (Farad). Constant phase elements (CPE) are used to replace the ideal capacitor in the modified Randle model because it accounts for the non-ideal behaviour of the layer of oxides (**Qiao et al. 2022**). This modification allows more accurate representation of the EIS data and the corrosion behaviour of the working electrode in an aqueous solution of an electrolyte. Impedance of CPE ' Z_{CPE} ' (ohm) can be computed by the Eq. 6.1 (**Wu et al. 2018b**):

$$Z_{CPE} = \frac{1}{Q \ (j \ \omega)^{n_d}} \tag{6.1}$$

where, 'j' is an imaginary number $(=\sqrt{-1})$, ' ω ' is the angular frequency (radians per second), and ' n_d ' is a deviation parameter related to the phase angle. The CPE represents the behaviour of the layer of oxides. It becomes an ideal capacitance for the value of ' n_d ' equal to one and behaves as an ideal resistance when value of ' n_d ' is equal to zero (**Deng et al. 2023; Liu et al. 2022b**). Impedance of the working electrode ' Z_{ω} ' (ohm) and polarization resistance of the layer of oxides ' R_f ' (ohm) are computed using the Eq. 6.2 and Eq. 6.3 respectively (**Lu et al. 2018**).

$$Z_{\omega} = \frac{1}{\frac{1}{R_s} + Q (j \omega)^{n_d}}$$
(6.2)
$$R_f = \lim_{\omega \to 0} (Z_{\omega})$$
(6.3)

Thickness of the layer of oxides ' d_o ' (cm) is computed treating it as a parallel plate capacitor from the Eq. 6.4 (Qiao et al. 2022; Liu et al. 2022b; Wu et al. 2018b):

$$d_o = \frac{\varepsilon_0 \varepsilon A_w}{C_{eff}} \tag{6.4}$$

where, ' A_w ' is exposed area of the working electrode; ' ε_0 ' is permittivity of vacuum (= 8.85x10⁻¹⁴ Farad/cm); ' ε ' is dielectric constant of layer of oxides and its value is 60 for TiO₂; 10 for Cr₂O₃; 11.9 for NiO; and 9 for Al₂O₃ (**Lu et al. 2018; Fan et al. 2016**); and ' C_{eff} ' is the effective capacitance of the working electrode which can be computed from Eq. 6.5.

$$C_{eff} = (CPE)^{\frac{1}{n_d}} (R_f)^{\frac{1-n_d}{n_d}}$$
 (6.5)

Fig. 6.3 presents the results of EIS for the multi-layer deposition samples of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys in the aqueous solution of sodium chloride showing their Nyquist plots (Fig. 6.3a), Bode Plot 1 (Fig. 6.3b), and Bode plot 2 (Fig. 6.3c) and the modified Randle model (Fig. 6.3d). The graphs presented in Figs. 6.3a-6.3c depict the experimental values (represented by different colored legends) along with the fitted curves (shown as solid line curves).





Fig. 6.3: Results electrochemical impedance spectroscopy for the Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys: (a) Nyquist plot, (b) Bode plot 1, (c) Bode plot 2, and (d) equivalent electrochemical circuit model.

Nyquist plots (Fig. 6.3a) for Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys reveal different capacitive semi-circular arcs for them, indicating a particular type of charge transfer process occurring at the interface between the working electrode and aqueous solution of sodium chloride (**Weicheng et al. 2021**). The polarization resistance of the layer of oxides ' R_f ' is represented by the diameter of a semi-circular arc, and it increases with its diameter. It can be observed from Fig. 6.3a that Ti-6Al-4V-5Cr alloy has the largest diameter of its capacitive semi-circular arc, followed by Ti-6Al-4V-2.5Cr-2.5Ni alloy and Ti-6Al-4V-5Ni alloy, whereas Ti-6Al-4V alloy has the smallest diameter of its capacitive semi-circular arc. Such variation is due to composition modification of the layer of oxides and altered kinetics of charge transfer which are enabled by the addition of chromium and/or nickel to Ti-6Al-4V alloy. It implies that Ti-6Al-4V-5Cr alloy has maximum value of polarization resistance of its protective layer of oxides and Ti-6Al-4V alloy possesses its minimum value, and its values for Ti-6Al-4V-2.5Cr-2.5Ni alloy and Ti-6Al-4V-5Ni alloy lie in between them. It is also confirmed by the values of their ' R_f ' listed in Table 6.2. The Bode plots 1 (Fig. 6.3b) for Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys can be divided into two zones i.e., low-frequency zone (up to 1,000 Hz) and the high-frequency zone beyond 1,000 Hz. The impedance in the lowfrequency zone is mainly influenced by the resistance of the working electrode and provides important insights into its corrosion behaviour in terms of the electrochemical reactions occurring at it. Whereas impedance in the high-frequency zone is primarily influenced by the resistance of aqueous solution of the electrolyte ' R_s '. Higher impedance value in the lowfrequency zone means higher resistance of the working electrode, implying development of more stable layer of oxides (Bahrami et al. 2019), and higher impedance value in the highfrequency zone indicates its higher resistance in the electrolyte solution (Zhou et al. 2020). It can be seen from Fig. 6.3b that Ti-6Al-4V-5Cr alloy has maximum value of impedance in the low-frequency zone, suggesting higher resistance of its working electrode, and Ti-6Al-4V alloy possesses its minimum value, indicating lower resistance of its working electrode. Impedance values of Ti-6Al-4V-2.5Cr-2.5Ni and Ti-6Al-4V-5Ni alloys in the low-frequency zone lie in between them. It can be observed from Fig. 6.3b that Ti-6Al-4V-2.5Cr-2.5Ni alloy has maximum impedance in the high-frequency zone, suggesting its higher resistance in the electrolyte solution ' R_s ' and Ti-6Al-4V alloy possesses minimum impedance in the highfrequency zone, indicating its minimum resistance in the electrolyte solution. These observations are confirmed by the values of ' R_s ' listed in Table 6.2. It is evident from Fig. 6.3c that Ti-6Al-4V-5Cr alloy has more value of phase angle over a wide frequency range than the other three alloys. It has peak value of its phase angle approximately equal to 80° , which implies development of a more stable layer of oxides than the other three alloys (Gai et al. 2022). It can be observed from Table 6.2 that Ti-6Al-4V-5Cr alloy has maximum thickness of layer of oxides followed by Ti-6Al-4V-2.5Cr-2.5Ni and Ti-6Al-4V-5Ni alloys whereas, Ti-6Al-4V alloy has minimum thickness of layer of oxides. The formation of thicker layers of oxides on the alloy surface will provide better protection against corrosion, thus improving its corrosion resistance. Therefore, Ti-6Al-4V-5Cr alloy has maximum resistance to corrosion, followed by Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys. It again proves that addition of chromium and/or nickel to Ti-6Al-4V alloys improves the corrosion resistance of the resultant alloys.

Table 6.2 presents the values of ' R_s ', ' R_f ', 'CPE', 'n', and ' χ^2 ' obtained from the modified Randle model by fitting the EIS data for Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys and computed values of their layer thickness of oxides from Eq. 6.4. It can be seen from Table 6.2 that values of χ^2 for the four alloys range from 1.09×10^{-3} to 2.87×10^{-3} , implying that the fitted curves are the best-fit curves. The value of '*n_d*' for all four alloys is in a range from 0.697 to 0.75, indicating that the layer of oxides formed on them does not behave as a perfect capacitor.

Table 6.2: Parameters obtained from fitting the EIS data of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys by the modified Randle model and computed thickness values of formed layer of oxides.

Alloy	Resistance of	Polarization	Constant	Deviation	χ^2	Thickness of
	electrolyte	resistance of layer	phase	parameter	(x10 ⁻³)	layer of
	solution ' <i>R</i> _s '	of oxides ' <i>R_f</i> '	element	'n _d '		oxides 'd _o '
	(Ω)	$(\mathbf{k}\Omega)$	(CPE)			(nm)
Ti-6Al-4V-5Cr	31.8	516.6	24.9	0.719	2.43	96.4
Ti-6Al-4V-2.5Cr-2.5Ni	32.8	461.7	33.7	0.697	2.87	84.8
Ti-6Al-4V-5Ni	29.9	374.7	39.9	0.729	1.77	66.1
Ti-6Al-4V	25.6	197.8	45.3	0.750	1.09	64.8

6.4 Mechanism of Corrosion and Morphology of Corroded Surface

Fig. 6.4 explains the suggested corrosion mechanism for the Ti-6Al-4V-xCr-yNi alloys, which is confirmed by the SEM images of their corroded surfaces and elemental compositions obtained by EDX for Ti-6Al-4V-5Cr alloy (Fig. 6.5a), Ti-6Al-4V-2.5Cr-2.5Ni alloy (Fig. 6.5b), Ti-6Al-4V-5Ni alloy (Fig. 6.5c), and Ti-6Al-4V alloy (Fig. 6.5d), and summary of their elemental composition presented in Table 6.3. It can be seen in Fig. 6.4a that a very thin inherent oxide layer is present on the surface of the Ti-6Al-4V-xCr-yNi alloys due to their exposure to the atmosphere. This layer acts as a barrier to prevent their corrosion and protect them from the surrounding environment. When these alloys are exposed to the aqueous solution of sodium chloride, then the chlorine ions present in it breach this layer. Movement speed of chlorine ions increases with application of an external voltage during the corrosion behaviour study of Ti-6Al-4V-xCr-yNi alloys in the aqueous solution of sodium chloride (Hu et al. 2022). It makes chlorine ions quickly diffuse through this layer and reach the underlying material, thus leading to early pitting corrosion, as shown in Fig. 6.4b. This reaction releases Ti^{4+} , Al^{3+} , V^{5+} , Cr^{3+} , and Ni^{2+} ions which react with the chlorine ions to form the coordination compounds $[TiCl_6]^2$, $[AlCl_4]^2$, $[VCl_6]^2$, $[CrCl_3]^2$, and $[NiCl_2]^2$ as mentioned in Eq. 6.6 to 6.10. Reactions of these coordination compounds with water results in the formation of metallic oxides such as TiO₂, Al₂O₃, V₂O₅, Cr₂O₃, and NiO as shown in Fig. 6.4c and as described by Eqs. 6.6 to 6.10. As the corrosion of Ti-6Al-4V-xCr-yNi alloys continues, the layer of oxides grows over the entire surface of the alloys as shown in Fig. 6.4d.

$[TiCl_6]^{2-} + 2H_2O \rightarrow TiO_2 + 4H^+ + 6Cl^-$	(6.6)
$2[\text{AlCl}_4]^- + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{H}^+ + 8\text{Cl}^-$	(6.7)
$2[VCl_6]^- + 5H_2O \rightarrow \mathbf{V_2O5} + 10H^+ + 12Cl^-$	(6.8)
$2[CrCl_3]^- + 3H_2O \rightarrow Cr_2O_3 + 6H^+ + 6Cl^-$	(6.9)





Fig. 6.4: Suggested corrosion mechanism for Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-





(a)



(**d**)

Fig. 6.5: Morphology of the corroded surfaces and elemental composition for: (a) Ti-6Al-

4V-5Cr, (b) Ti-6Al-4V-2.5Cr-2.5Ni, (c) Ti-6Al-4V-5Ni, and (d) Ti-6Al-4V.

Table 6.3: Elemental composition (by wt.%) of the corroded surfaces of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloy.

Alloy	0	Ti	Al	V	Cr	Ni
Ti-6Al-4V-5Cr	11.9	73.1	6.0	3.4	5.6	-
Ti-6Al-4V-2.5Cr-2.5Ni	13.5	71.4	5.8	3.3	2.9	3.1
Ti-6Al-4V-5Ni	10.7	73.9	5.7	3.6	-	6.1
Ti-6Al-4V	9.6	76.6	10.7	3.1	-	-

The above-mentioned pitting corrosion mechanism is confirmed by the presence of the peak corresponding to oxygen in EDX images of the corroded surfaces of Ti-6Al-4V-5Cr (Fig. 6.5a), Ti-6Al-4V-2.5Cr-2.5Ni (Fig. 6.5b), Ti-6Al-4V-5Ni (Fig. 6.5c), and Ti-6Al-4V (Fig. 6.5d) alloys and their elemental composition presented in Table 6.3. It confirms that the corrosion products are primarily composed of oxides due to the reaction of their constituents with oxygen during their corrosion process. The developed oxides consist of TiO₂, Al₂O₃, and V₂O₅ in all four alloys, Cr₂O₃ in Ti-6Al-4V-5Cr alloy, NiO in Ti-6Al-4V-5Ni alloy, and both Cr₂O₃ and NiO in Ti-6Al-4V-2.5Cr-2.5Ni alloy. The suggested pitting corrosion mechanism is confirmed by the SEM images of the corroded surface of Ti-6Al-4V-5Cr (Fig. 6.5a), Ti-6Al-4V-2.5Cr-2.5Ni (Fig. 6.5b), Ti-6Al-4V-5Ni (Fig. 6.5c), and Ti-6Al-4V (Fig. 6.5d) alloys which show pits and deterioration of the inherent oxide layer caused by chemical reactions by Cl⁻ ions present in aqueous solution of NaCl (Parangusan et al. 2021). Several big size pits can be seen on the corroded surface of Ti-6Al-4V alloy (Fig. 6.5d) due to more penetration of TiO₂ layer by Cl⁻ ions, which disrupts its stability and breaks it down. Whereas smaller size pits can be observed on the corroded surfaces of Ti-6Al-4V-5Cr (Fig. 6.5a), Ti-6Al-4V-2.5Cr-2.5Ni (Fig. 6.5b), and Ti-6Al-4V-5Ni (Fig. 6.5c) alloys. It is due to formation of relatively more stable layer of Cr₂O₃ and NiO enabled by the addition of chromium and/or nickel to Ti-6Al-4V alloy. These oxides act as more effective barriers to penetration by chlorine ions thus protecting them from the formation of larger size pits and minimize their corrosion.

6.5 Topography of the Corroded Surfaces

Fig. 6.6 shows topography of the corroded surfaces and average surface roughness values for Ti-6Al-4V-5Cr alloy (Fig. 6.6a), Ti-6Al-4V-2.5Cr-2.5Ni alloy (Fig. 6.6b), Ti-6Al-4V-5Ni alloy (Fig. 6.6c), and Ti-6Al-4V alloy (Fig. 6.6d). It can be observed from Fig. 6.6 that Ti-6Al-4V-5Cr alloy has minimum value of avg. surface roughness (i.e., 1.49 μ m) followed by Ti-6Al-4V-2.5Cr-2.5Ni alloy (i.e., 2.18 μ m) and Ti-6Al-4V-5Ni alloy (i.e., 2.3 μ m), whereas Ti6Al4V alloy has maximum value of avg. surface roughness (i.e., 4.58 μ m). It is due to formation of layers of Cr₂O₃ and NiO on their surface which is enabled by addition of chromium and/or nickel to Ti-6Al-4V alloy. These oxides play a crucial role in reducing the damage to the corroded surface of the developed alloys which decreases their surface roughness values. It indicates that the surfaces of the developed three alloys become more uniform and exhibit less damage after undergoing corrosion. It can be concluded that Ti-6Al-4V-5Cr alloy provides the best protection to its surface against its corrosion, followed by Ti-6Al-4V-2.5Cr-2.5Ni alloy, and Ti-6Al-4V-5Ni alloy whereas, Ti-6Al-4V alloy provides the least protection to its surface against its corrosion.



Fig. 6.6: Topography of the corroded surfaces of: (a) Ti-6Al-4V-5Cr alloy, (b) Ti-6Al-4V-2.5Cr-2.5Ni alloy, (c) Ti-6Al-4V-5Ni alloy, and (d) Ti-6Al-4V alloy.

6.6 Concluding Remarks

This chapter described study of corrosion behaviour of μ -PPAM manufactured Ti-6Al-4V-xCr-yNi alloys in terms of open circuit potential, potentiodynamic polarization or Tafel curve, electrochemical impedance spectroscopy, mechanism of corrosion, and morphology and topography of the corroded surface. Addition of chromium and/or nickel to Ti-6Al-4V alloy increased the corrosion potential, reduced corrosion current density, and corrosion rate of the developed alloys due to formation of protective layer Cr₂O₃ and NiO, which acts as the barrier and prevents the direct contact of their surfaces with the corrosive environment. The EIS findings indicated that the values of polarization resistance and layer thickness of oxides increased with the addition of chromium and/or nickel to Ti-6Al-4V alloy. Pitting is suggested as the corrosion mechanism for Ti-6Al-4V-xCr-yNi which is confirmed by morphology and elemental composition of their corroded surfaces. Big size pits are observed on the corroded surface of Ti-6Al-4V alloy due to more penetration of TiO₂ layer by chlorine ions, whereas smaller size pits are seen on the corroded surfaces of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, and Ti-6Al-4V-5Ni alloys due to formation of relatively more stable layer of Cr₂O₃ and NiO which are enabled by the addition of chromium and/or nickel to Ti-6Al-4V alloy. The *next chapter* presents study of tribological behaviour of μ -PPAM manufactured Ti-6Al-4V-xCr-yNi alloys using coefficient of friction, sliding wear rate, morphology of worn surfaces, and analysis of worn subsurface.

Chapter 7

Tribological Behaviour of Ti-6Al-4V-xCr-yNi Alloys

This chapter describes study of tribological behaviour of μ -PPAM manufactured multilayer deposition samples of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys in terms of coefficient of friction, sliding wear rate, morphology of worn surfaces, and analysis of worn subsurface.

7.1 Coefficient of Friction

Fig. 7.1 shows variation in coefficient of friction (COF) with time for Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys at applied load of 10 N (Fig. 7.1a), 15 N (Fig. 7.1b), 20 N (Fig. 7.1c), and computed average values of their COF (Fig. 7.1d) from the graphs of Figs. 7.1a to 7.1c.



Fig. 7.1: Variation in coefficient of friction with time for Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys at the applied load of: (a) 10 N, (b) 15 N, (c) 20 N, and (d) computed average values of their coefficient of friction.

The COF variation curves shown in Figs. 7.1a to 7.1c can be divided into two zones namely (i) 1st zone is known as *initial wear zone* in which the COF increases rapidly for all

the four alloys because they offer more resistance when the initial contact between the silicon nitride ball and their surface takes place, (ii) 2nd zone is known as *stable wear zone* in which the COF varies in a relatively narrow range because as sliding wear starts, a wear track is formed which allows smooth travel of the silicon nitride ball. Following are observations from the Fig. 7.1d along with their explanations:

- Average value of COF for all the four alloys at the different values of the applied load lie in a range from 0.45 to 0.6.
- Avg. values of COF for all the four alloy samples are minimum at 10 N applied load, maximum at 15 N applied load, and lie in between them at 20 N applied load. It can be explained by inability of a smaller value of applied load to deform an alloy surface which can facilitate smooth sliding of the silicon nitride ball over its surface thus giving smaller avg. values of the COF. The contact pressure between the silicon nitride ball and an alloy surface increases with increase in the applied load up to 15 N causing increase in material removal, surface roughness, frictional forces, and consequently avg. values of the COF. However, avg. value of COF decreases for all the four alloys at an applied load of 20 N. It is due to generation of wear debris during the sliding wear. Some of the generated wear debris adheres to the sliding surfaces. As sliding action continues, the wear debris accumulates on the sliding surfaces and forms a protective layer which is referred to as a *tribo-layer* or *transfer film*. This layer acts as a solid lubricant between the sliding surfaces thus reducing direct contact between them which in turn reduces the COF (Liu and Sun. 2018; Yang et al. 2020).
- At all three values of applied load, Ti-6Al-4V-5Cr alloy and Ti-6Al-4V alloy have minimum and maximum avg. values of COF respectively, and avg. values of COF for Ti-6Al-4V-2.5Cr-2.5Ni and Ti-6Al-4V-5Ni alloys lie in between them. Coefficient of friction of an alloy depends on different factors such as grain size, microhardness, chemical composition, and presence of different phases in it. Ti-6Al-4V alloy has smaller microhardness value (i.e., 546.3 HV, Fig. 5.9), and minimum % of β-Ti phase (i.e., 5.9%, Fig. 5.5). Whereas Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, and Ti-6Al-4V-5Ni alloys have finer grains of their α-Ti phase (Fig. 5.2), higher microhardness than Ti-6Al-4V alloy (Fig. 5.9), and presence of harder intermetallic phase Cr₂Ti in Ti-6Al-4V-5Ni alloy (Fig. 5.6), which are enabled by the addition of chromium and/or nickel. Moreover, these alloys have more % of β-Ti phase (Fig. 5.5). Finer grains, higher microhardness, presence of harder intermetallic phases enhance resistance to movement of the silicon nitride ball

which decreases its contact area thus resulting in reduced avg. values of COF for Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, and Ti-6Al-4V-5Ni alloys than Ti-6Al-4V alloy.

7.2 Sliding Wear Rate

Figs. 7.2a and 7.2b present the computed values of sliding wear volume (using Eq. 3.18) and sliding wear rate (using Eq. 3.19) respectively for Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys at the different values of the applied load.





It can be observed from Figs. 7.2a 7.2b that for all the values of applied load, Ti-6Al-4V-5Cr alloy has minimum values of sliding wear volume, and sliding wear rate, Ti-6Al-4V alloy has their maximum values, whereas their values for Ti-6Al-4V-2.5Cr-2.5Ni alloy and Ti-6Al-4V-5Ni alloy lie in between them. These findings are due to (i) maximum microhardness of Ti-6Al-4V-5Cr alloy (i.e., 571.5 HV, Fig. 5.9) and minimum microhardness of Ti-6Al-4V alloy (546.3 HV, Fig. 5.9), (ii) evolution of harder intermetallic Cr₂Ti phase in Ti-6Al-4V-5Cr and Ti-6Al-4V-2.5Cr-2.5Ni alloys and intermetallic phase Ti₂Ni in Ti-6Al-4V-5Ni alloy (XRD plots of Fig. 5.6), and (iii) protection of the worn surfaces of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, and Ti-6Al-4V-5Ni alloys by the protective tribo-layer of the compacted debris from their further wear by the silicon nitride ball. All these factors result in a better wear resistance of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, and Ti-6Al-4V-5Ni alloys by providing greater resistance to their plastic deformation and minimizing surface damage during their sliding wear. It can also be seen from Figs. 7.2a and 7.2b that the sliding wear volume and sliding wear rate increase with increase in the applied load for all the four alloys. It is due to increase in contact area between the silicon nitride ball and an alloy surface leading to its more plastic deformation and subsequently removal of more material from it.

7.3 Morphology of Worn Surfaces

Fig. 7.3 presents SEM images showing morphology of sliding wear track for Ti-6Al-4V-5Cr (Fig. 7.3a), Ti-6Al-4V-2.5Cr-2.5Ni (Fig. 7.3b), Ti-6Al-4V-5Ni (Fig. 7.3c), and Ti-6Al-4V (Fig. 7.3d) alloys at 20 N applied load along with the presence of different elements in them (obtained by the EDX). Table 7.1 presents a summary of their elemental distribution.



Fig. 7.3: Morphology of wear track at 20N applied load for: (a) Ti-6Al-4V-5Cr, (b) Ti-6Al-4V-2.5Cr-2.5Ni, (c) Ti-6Al-4V-5Ni, and (d) Ti-6Al-4V alloys.

Alloy	0	Ti	Al	V	Cr	Ni
Ti-6Al-4V-5Cr	9.7	75.2	6.2	3.5	5.4	-
Ti-6Al-4V-2.5Cr-2.5Ni	9.2	75.4	5.9	3.4	3.1	3.0
Ti-6Al-4V-5Ni	8.9	75.5	5.8	3.7	-	6.1
Ti-6Al-4V	8.3	77.9	10.6	3.2	-	-

Table 7.1: Elemental distribution (by wt.%) in worn surface of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys.

Morphology of wear track of Ti-6Al-4V-5Cr alloy (Fig. 7.3a) and Ti-6Al-4V-2.5Cr-2.5Ni (Fig. 7.3b) alloy reveal shallow grooves and compacted debris along the sliding direction while, morphology of wear track of Ti-6Al-4V-5Ni alloy (Fig. 7.3c) shows some amount of delamination and wear debris in addition to the shallow grooves and compacted debris along the sliding direction. Whereas morphology of wear track of Ti-6Al-4V alloy (Fig. 7.3d) shows deep grooves, micro-cracks, and delamination along the sliding direction. These observations can be explained by the following facts: (i) Minimum microhardness of Ti-6Al-4V alloy (i.e. 546.3 HV) helps in easier removal of material from its surface during its sliding wear thus leading to the formation of deep grooves. It also experiences adhesive wear when it comes into contact with silicon nitride ball under higher applied load (Ju et al. 2021) which leads to formation of micro-cracks and delamination, (ii) Maximum microhardness of Ti-6Al-4V-5Cr alloy (i.e., 571.5 HV) followed by that of Ti-6Al-4V-2.5Cr-2.5Ni and Ti-6Al-4V-5Ni alloys and evolution of harder intermetallic Cr₂Ti phase in Ti-6Al-4V-5Cr and Ti-6Al-4V-2.5Cr-2.5Ni alloys and intermetallic phase Ti₂Ni in Ti-6Al-4V-5Ni alloy (Fig. 5.6) help these alloys to offer more resistance to their material removal by the silicon nitride ball resulting in formation of shallow grooves only. Material removal from their surfaces during their sliding wear results in debris formation and repeated sliding action causes this debris to convert into a compacted debris, (iii) Formation of grooves along the sliding direction in all the four alloys suggests that ploughing and micro-cutting actions remove material from their surfaces which indicates that abrasive wear is one of the mechanisms of their sliding wear, and (iv) Presence of oxygen peaks in elemental analysis of worn surfaces of all the four alloys (Figs. 7.3a-7.3d) and their elemental distribution (Table 7.1) suggest that they comprise different oxides formed due to reaction of their constituents with oxygen. It indicates oxidation wear as one of mechanisms of their sliding wear. Formation of oxides of chromium and nickel in Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni alloys act as better protective layer thus enhancing their wear resistance than Ti-6Al-4V alloy.

Fig. 7.4 shows depth profile of wear track (also referred to as worn scar depth) for Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys at the applied
loads of 10 N (Fig. 7.4a), 15 N (Fig. 7.4b), and 20 N (Fig. 7.4c). Fig. 7.4d shows the effect of applied load on their average value of worn scar depth.



Fig. 7.4: Worn scar depth profile for Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys at an applied load of: (a) 10 N, (b) 15 N, (c) 20 N, and (d) average values of their worn scar depth for different values of the applied loads.

It can be seen from Figs. 7.4a to 7.4d that worn scar depth (i.e., depth of wear track) increases with increase in the applied load for all the four alloys. It is due to an increase in contact area between the silicon nitride ball and an alloy surface leading to its more plastic deformation and subsequently removal of more material from it. It can be observed from Fig. 7.4d that Ti-6Al-4V-5Cr and Ti-6Al-4V alloys have respectively maximum and minimum average values worn scar depth for all the values of the applied load and the values for Ti-6Al-4V-2.5Cr-2.5Ni and Ti-6Al-4V-5Ni alloys lie in between them. It is due to (a) maximum microhardness of Ti-6Al-4V-5Cr alloy (i.e. 571.5 HV) followed by Ti-6Al-4V-2.5Cr-2.5Ni, and Ti-6Al-4V-5Cr alloy start intermetallic Cr₂Ti phase in Ti-6Al-4V-5Cr and Ti-6Al-4V-5Cr and Ti-6Al-4V-5Ni alloys for Ti-6Al-4V-5Ni alloys and intermetallic Cr₂Ti phase in Ti-6Al-4V-5Cr and Ti-6Al-4V-5Cr.

Fig. 7.5 shows the three-dimensional surface roughness profile of the wear track of Ti-6Al-4V-5Cr alloy (Fig. 7.5a), Ti-6Al-4V-2.5Cr-2.5Ni alloy (Fig. 7.5b), Ti-6Al-4V-5Ni alloy (Fig. 7.5c), and Ti-6Al-4V alloy (Fig. 7.5d) for 20 N applied load.



Fig. 7.5: Three-dimensional surface roughness profile of wear track at 20N applied load for: (a) Ti-6Al-4V-5Cr, (b) Ti-6Al-4V-2.5Cr-2.5Ni, (c) Ti-6Al-4V-5Ni, and (d) Ti-6Al-4V alloys.

It can be observed from Figs. 7.5a-7.5d that Ti-6Al-4V-5Cr alloy (Fig. 7.5a) has smoother surface having 13.5 μ m average surface ' R_a ' value, followed by Ti-6Al-4V-2.5Cr-2.5Ni alloy (14.2 μ m) and Ti-6Al-4V-5Ni alloy (14.9 μ m) whereas worn surface of Ti-6Al-4V alloy (Fig. 7.5d) has rough and irregular surface with ' R_a ' value as 16.1 μ m. It is due to formation of shallow grooves and compacted debris in Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni alloys as explained above with reference to their worn surface morphology. It is also noticeable from these ' R_a ' values that surface roughness is increasing with decrease in chromium content in Ti-6Al-4V-xCr-yNi alloys.

7.4 Analysis of Worn Subsurface

Fig. 7.6 presents SEM images showing subsurface microstructure and deformation regions for the worn surfaces of Ti-6Al-4V-5Cr (Fig. 7.6a), Ti-6Al-4V-2.5Cr-2.5Ni (Fig. 7.6b), Ti-6Al-4V-5Ni (Fig. 7.6c), and Ti-6Al-4V (Fig. 7.6d) alloys for an applied load of 20 N during their sliding wear test which can used to understand their deformation mechanism. The subsurface deformation regions for all four alloys can be divided into the following layers: (a) top layer known as *tribo-layer* (TL) formed due to chemical reaction between the

removed material from an alloy surface and the surrounding environment, (b) middle layer known as *plastically deformed layer* (PDL) formed due to changes in grain morphology of an alloy caused by the plastic deformation under the applied load, and (c) bottom layer known as the *base layer* (BL) which is the undeformed layer.





Fig. 7.6. Subsurface microstructure for the worn surfaces of: (a) Ti6Al4V5Cr, (b) Ti6Al4V2.5Cr2.5Ni, (c) Ti6Al4V5Ni, and (d) Ti6Al4V alloys. (BL: base layer; PDL: plastically deformed layer; and TL: tribo-layer)

The subsurface deformation regions such as TL and PDL are present in all the four alloys whereas kinking or bending of laths is observed for Ti-6Al-4V-5Ni alloy (Fig. 7.6c) and Ti-6Al-4V alloy (Fig. 7.6d) which occurred due to plastic deformation under the applied load, and due to their smaller microhardness values. Similar observations have been reported for subsurface microstructure for the cast Ti-6Al-4V alloy by **Mao et al. (2013)**. Fig. 7.6d also shows fragmented tribo-layer for Ti-6Al-4V alloy unlike Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, and Ti-6Al-4V-5Ni alloys. It may be due to presence of chromium and/or nickel in these alloys which influence formation of more stable and compact tribo-layer during their sliding wear. The reactive nature of chromium and nickel helps in their participation in tribo-chemical reactions which may lead to formation of stable oxides that contribute to the

development of a tribo-layer in the subsurface region. For all the four alloys, depth of the PDL layer varies with plastic flow characteristic, stability of TL, and microhardness. More the stability of TL, less is the plastic deformation and smaller is depth of the PDL. Ti-6Al-4V-5Cr alloy has minimum depth of PDL and Ti-6Al-4V alloy has its maximum value whereas its values for Ti-6Al-4V-2.5Cr-2.5Ni and Ti-6Al-4V-5Ni alloys lie in between them. It is due to maximum microhardness of Ti-6Al-4V-5Cr alloy (i.e., 571.5 HV) followed by Ti-6Al-4V-2.5Cr-2.5Ni, and Ti-6Al-4V-5Ni alloys and minimum microhardness Ti-6Al-4V alloy (i.e., 452.3 HV).

7.4 Concluding Remarks

This chapter studied of tribological behaviour of µ-PPAM manufactured Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys using coefficient of friction, sliding wear rate, morphology of worn surfaces, and analysis of worn subsurface. Developed Ti-6Al-4V-5Cr alloy has minimum values of its tribological characteristics namely coefficient of friction, wear volume, sliding wear rate, worn scar depth, surface roughness of the worn surface, thickness of plastically deformed layer due to maximum value of its microhardness. The Ti-6Al-4V alloy has maximum values of these tribological characteristics due to its minimum microhardness whereas, their values for Ti-6Al-4V-2.5Cr-2.5Ni and Ti-6Al-4V-5Ni alloys are found to lie in between them. Morphology of wear track of Ti-6Al-4V-5Cr and Ti-6Al-4V-2.5Cr-2.5Ni alloys revealed shallow grooves and compacted debris along the sliding direction while, morphology of wear track of Ti-6Al-4V-5Ni alloy showed some amount of delamination and wear debris in addition to the shallow grooves and compacted debris along the sliding direction. Whereas morphology of wear track of Ti-6Al-4V alloy found deep grooves, micro-cracks, and delamination along the sliding direction. Wear volume and wear rate increased with the applied load for all the four alloys. It is due to increase in contact area with the silicon nitride ball which led to more plastic deformation and subsequently removal of more material from the alloys.

The *last chapter* summarizes significant achievements of the present work, comparison of all the results for Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys, conclusions, some identified directions for the future research.

Chapter 8

Conclusions and Future Work

This chapter summarizes significant achievements of the present work, comparison of all the results for Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys, conclusions, some identified directions for the future research.

8.1 Significant Achievements

- Design and development of Ti-6Al-4V-5Cr, Ti-6Al-4V-5Ni, and Ti-6Al-4V-2.5Cr-2.5Ni alloys for high-strength and lightweight applications in view of obtained values of their density (< 5 g/cm³), higher yield and ultimate tensile strength, microhardness, fracture toughness, abrasion resistance, and absence of micro-cracks than Ti-6Al-4V alloy.
- The developed Ti-6Al-4V-xCr-yNi alloys are found to be corrosion resistant due to their lesser corrosion rate, higher polarization resistance, thicker oxide layers, and wear resistant due to their smaller wear rate. This makes the developed alloys to be very useful in marine, aerospace, and chemical applications.
- Use of energy efficient, material efficient, and environment friendly DED process namely μ-PPAM process to develop the Ti-6Al-4V-5Cr, Ti-6Al-4V-5Ni, and Ti-6Al-4V-2.5Cr-2.5Ni alloys. It made significant contribution in development of Ti-6Al-4V-xCr-yNi alloys as high-strength, high-corrosion resistant and high wear resistant material by minimizing their heat affect zone, thermal distortion, segregation of their constituents, enhancing mechanical properties, corrosion and wear resistance. It paves the way for its use in AM of aerospace components from the developed alloys in this work.

8.1.1 Comparison of Results for Ti-6Al-4V-xCr-yNi Alloys

Table 8.1 presents the comparison of all the quantitative results obtained in the present research work for μ -PPAM manufactured Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys. These results include evaluation and study of their (i) Density and porosity, (ii) Microstructure (i.e., grain size of α -Ti and β -Ti phases, fraction of β -Ti phase), (iii) Mechanical properties (i.e., yield tensile strength, ultimate tensile strength, elongation, microhardness, depth, width and volume of scratch track, fracture toughness, and scratch hardness number), (iv) Corrosion behaviour characteristics (i.e., open circuit or corrosion potential, corrosion current density, corrosion rate, resistance of electrolyte solution, polarization resistance of layer of oxides, constant phase element, deviation parameter, thickness of layer of oxides, surface roughness of corroded surface, and (v) Tribological behaviour characteristics (i.e., coefficient of friction, sliding wear rate, sliding volume, and worn scar depth).

Table 8.1: Comparison of all the quantitative results obtained in the present research work for μ -PPAM manufactured Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys.

Properties	Ti-6Al-4V-5Cr	Ti-6Al-4V-2.5Cr-2.5Ni	Ti-6Al-4V-5Ni	Ti-6Al-4V
Experimental density (g/cm ³)	4.36	4.37	4.39	4.32
Porosity (%)	2.46	2.67	2.88	1.15
Grain size of β -Ti phase (μ m)	208.6	229.3	261.7	559.8
Grain size of α -Ti phase (μ m)	2.01	2.46	2.97	4.89
Fraction of β -Ti phase (%)	19.2	18.4	17.3	5.9
Yield tensile strength (MPa)	1178.4	1149.4	1121.6	989.2
Ultimate tensile strength (MPa)	1368.4	1311.9	1248.4	1059.4
Elongation (%)	5.8	5.9	6.2	9.9
Vicker's microhardness (HV)	571.5	565.4	512.6	452.3
Depth of scratch track (μm)	2.73	2.86	2.98	3.23
Width of scratch track (μm)	50.1	52.9	54.9	59
Scratch volume (µm ³)	1.58	1.86	2.08	2.58
Fracture toughness	123.8	119.9	116.8	106.9
$(x10^{1.5}MPa-mm^{0.5})$				
Scratch hardness (x10 ³ MPa)	10.1	9.1	8.4	7.3
Corrosion potential 'Ecorr'	-0.302	-0.348	-0.412	-0.473
(volts)				
Corrosion current density ' i_{corr} '	0.195	0.237	0.294	0.349
$(\mu A/cm^2)$		1.00		
Corrosion rate (µm/year)	1.55	1.92	2.43	3.11
Resistance of electrolyte solution ' R_s '	31.8	32.8	29.9	25.6
Polarization resistance of layer	516.6	461.7	374.7	197.8
of oxides ' R_f ' (kilo ohm)				
Constant phase element (CPE)	24.9	33.7	39.9	45.3
Deviation parameter ' n_d '	0.719	0.697	0.729	0.75
Thickness of layer of oxides	96.4	84.8	66.1	64.8
<i>'d_o'</i> (nm)				
Surface roughness of corroded surface (µm)	1.49	2.18	2.3	4.58
Coefficient of friction (COF)	0.511	0.528	0.541	0.576
Sliding wear volume (µm ³)	0.987	1.087	1.316	1.524
Sliding wear rate	0.914	1.006	1.182	1.411
Worn scar depth (µm)	2.73	2.86	2.98	3.23

8.2 Conclusions

This PhD thesis described the design of Ti-6Al-4V-xCr-yNi alloys, their development by μ -PPAM process, study of microstructure, mechanical properties, corrosion behaviour, and tribological behaviour of the developed alloys. Following conclusions can be drawn from the presented research work:

8.2.1 Design and Depositions

- The thermo-calc simulated phase diagrams found that 5 at.% of chromium and nickel are their upper limits that can be added to Ti-6Al-4V alloy without forming any brittle phases and without increasing its β-transus temperature.
- Parametric combination of μ-plasma power as 319 W, mass flow rate of feedstock powder as 2.9 g/min, and deposition head travel speed as 47 mm/min was identified as the optimum parametric combination to manufacture multi-layer deposition of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, Ti-6Al-4V-5Ni, and Ti-6Al-4V alloys by the μ-PPAM process.
- Presence of Cr and/or Ni in Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, and Ti-6Al-4V-5Ni alloys formed intermetallic phases Cr₂Ti, and Ti₂Ni whose melting point is higher than Ti-6Al-4V alloy which led to accumulation of more gas bubbles thus imparting them higher porosity than Ti-6Al-4V alloy

8.2.2 Microstructure and Mechanical Properties

- Presence of Cr and/or Ni refined grains of β -Ti and α -Ti phases of the developed alloys. The β -Ti phase grains refined due to generation of equiaxed grains as compared to large columnar grains of Ti-6Al-4V alloy, and higher solidification temperature of the developed alloys than Ti-6Al-4V alloy. The α -Ti phase grains refined due to formation of intermetallic phases Cr₂Ti in Ti-6Al-4V-5Cr and Ti-6Al-4V-2.5Cr-2.5Ni alloys and Ti₂Ni in Ti-6Al-4V-5Ni alloy which hinder grain growth of α -Ti phase and role of these intermetallic phases as nucleation sites for α -Ti phase.
- Elemental distribution in α-Ti and β-Ti phases of the developed alloys is not same because content of Cr, Ni, and V in their β-Ti phase is more than their corresponding α-Ti phase. It is due to their eutectoid nature which enhances their solubility in β-Ti phase thus forming their substitutional solid solutions within β-Ti phase.
- Uniform distribution of Cr in Ti-6Al-4V-5Cr alloy, Cr and Ni in Ti-6Al-4V-2.5Cr-2.5Ni alloy, and Ni in Ti-6Al-4V-5Ni alloy helped in improving their mechanical properties as compared to Ti-6Al-4V alloy.

- Majority α-Ti phase grains of the developed alloys are found to be oriented along different crystallographic planes thus reducing their anisotropy. Presence of Cr and/or Ni in the developed alloys increased fraction of β-Ti phase.
- Formation of α/α '-Ti and β -Ti phases are found in the developed alloys along an intermetallic phase Cr₂Ti in Ti-6Al-4V-5Cr and Ti-6Al-4V-2.5Cr-2.5Ni alloys, and an intermetallic phase Ti₂Ni in Ti-6Al-4V-5Ni alloy.
- Presence of Cr and/or Ni increased the yield and ultimate tensile strength of the developed alloys but reduced their % elongation. It is due to grain refinement of their α-Ti and β-Ti phases, uniform distribution of Cr and Ni in the developed alloys, evolution of intermetallic phases Cr₂Ti and Ti₂Ni, and dissolution of Cr and/or Ni in β-Ti phase to form solid solutions. All these factors obstructed movement of the dislocations thus increasing strength of the developed alloys.
- Average microhardness of multi-layer depositions of the developed alloys is found to increase along their deposition height or build direction. It is due to faster cooling of the top deposition layer which formed higher hardness martensitic α'-Ti phase. Multi-layer deposition sample of Ti-6Al-4V-5Cr and Ti-6Al-4V alloys have maximum and minimum avg. microhardness.
- Developed alloys have increased fracture toughness and abrasion resistance due to grain refinement of β -Ti and α -Ti phases and strengthening effect induced by formation of harder intermetallic phases Cr₂Ti and Ti₂Ni through lattice distortion. Both these factors impede the crack propagation thus increasing abrasion resistance and fracture toughness of the developed alloys.

8.2.3 Corrosion Behaviour

- Presence of Cr and/or Ni increased corrosion potential, reduced corrosion current density, and corrosion rate of the developed alloys due to formation of protective layer Cr₂O₃ and NiO, which acts as the barrier and prevents the direct contact of their surfaces with the corrosive environment.
- The Ti-6Al-4V-5Cr alloy has maximum value of corrosion potential and minimum values of corrosion current density and corrosion rate, followed by Ti-6Al-4V-2.5Cr-2.5Ni and Ti-6Al-4V-5Ni alloy, whereas Ti-6Al-4V alloy has minimum value of corrosion potential and maximum values of corrosion current density and corrosion rate.
- The EIS found that polarization resistance and layer thickness of oxides is more for the developed alloys than Ti-6Al-4V alloy. The Ti-6Al-4V-5Cr alloy has maximum values of polarization resistance, layer thickness of oxides, and consequently maximum corrosion resistance followed by Ti-6Al-4V-2.5Cr-2.5Ni and Ti-6Al-4V-5Ni alloy

whereas, Ti-6Al-4V alloy has minimum value of polarization resistance, layer thickness of oxides and consequently minimum corrosion resistance.

- Pitting is suggested as the corrosion mechanism for the developed alloys which is confirmed by microstructure of the corroded surface and corrosion mechanism of these alloys.
- Several big size pits were seen on the corroded surface of Ti-6Al-4V alloy due to more penetration of TiO₂ layer by Cl⁻ ions. Whereas smaller size pits were observed on corroded surfaces of Ti-6Al-4V-5Cr, Ti-6Al-4V-2.5Cr-2.5Ni, and Ti-6Al-4V-5Ni alloys. It is due to the formation of relatively more stable layer of Cr₂O₃ and NiO enabled by presence of Cr and/or Ni.

8.2.4 Tribological Behaviour

- Developed Ti-6Al-4V-5Cr alloy is found to have minimum coefficient of friction, wear volume, sliding wear rate, worn scar depth, surface roughness of the worn surface, thickness of plastically deformed layer whereas Ti-6Al-4V alloy showed minimum values of these tribological characteristics and their values for Ti-6Al-4V-2.5Cr-2.5Ni and Ti-6Al-4V-5Ni alloys are found to lie in between them.
- The morphology of wear track of the developed alloys found formation of shallow grooves and compacted debris along the sliding direction whereas wear track of Ti-6Al-4V alloy showed deep grooves, micro-cracks and delamination.
- Worn surface of the developed alloy is found to have smoother, whereas worn surface of Ti-6Al-4V alloy showed rough and irregular.
- Wear volume and wear rate increased with the applied load for all the four alloys due to increase in contact area with the silicon nitride ball which caused more plastic deformation and subsequently removal of more material from all the four alloys.

8.3 Directions for Future Work

Following are some directions identified for future research work:

- Comparative study of metallurgical-mechanical performance of Ti-6Al-4V-xCr-yNi alloys developed by other processes such as GMAW, CMT or their hybrid processes.
- 3D-Finite element simulation of multi-layer deposition of Ti-6Al-4V-xCr-yNi alloys by μ-PPAM process and to predict the temperature distribution, thermal cycles, residual stresses, and thermal distortion.
- Study of high-temperature oxidation behaviour of Ti-6Al-4V-xCr-yNi alloys in air, through kinetic analysis and microstructural characterization
- Study of hot deformation behaviour of Ti-6Al-4V-xCr-yNi alloys by performing isothermal compression tests under a range of temperatures with strain rate.
- Improving surface finish and dimensional accuracy of μ-PPAM manufactured depositions of Ti-6Al-4V-xCr-yNi by some advanced finishing processes such as electrochemical finishing (ECF) or abrasive flow finishing (AFF) process.
- Development of AI based monitoring system for μ-PPAM process through detection and minimization of deposition defects.
- Development of vacuum assisted μ-PPAM process to enhance quality of manufactured parts.

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Appendix A: Details of the Equipment Used in Evaluation and Characterization of the Responses

A1: Leica Stereo Microscope (IIT Indore)



Make	Leica Microsystems, Germany	
Model	EZ4HD	
Full frame image acquisition	2048×1536 pixels, 3.1 megapixels	
Pixel size	3.2 μm × 3.2 μm	
A2: Scanning Electron Microscope (IIT Indore)



Make	JEOL Ltd., Japan
Model	JSM-7610F
Resolution	1.0 nm @ 15 kV
	1.5 nm @ 1 kV
	4.0 nm @ 15 kV
Acceleration Voltage	0.1 - 30 kV
Magnification	25x – 19,000 x (LM mode)
	130x – 1,000,000 (SEM mode)
Stages	Computer-controlled 5-axis (X, Y, R, T, Z)
	motor drive (with backlash connection)
	Stage X = 70 mm, Y = 50 mm and Z = 50 mm, T
	$= -5^{\circ}$ to $+ 70^{\circ}$, R $= 360^{\circ}$

A3: Microhardness Testing Machine (IIT Indore)



Make	Walter UHL Technische Mikroskopie GmbH,
	Germany.
Model	VMH002 V
Load Range	1 gram – 2000 gram
Type of intender	Diamond square base hexagonalPyramid

A4: Tensile Testing Machine (IIT Indore)



Make	Tinius Olsen USA	
Model	H50KL	
Load Range	1-50 kN	
Clearance Between Columns	405 mm	
Testing Speed Range	0.001 to 500 mm/min	

A5: 3D-Surface roughness-cum-contour tracing equipment (IIT Indore)



Make	Mahr GmbH, Germany
Model	MarSurf LD 130
Resolution	0.8 nm
Positioning speed	0.02 mm/s to 200 mm/s
Traversing lengths	0.1 mm - 130 mm

A6: X-ray Diffraction (XRD) (IIT Indore)



Make	Malvern Panalytical Empyrean, Netherland
Attachments	Capillary spinner, Micro-diffraction spinner, 3-axes (chi, phi, z) cradle with optional manual x, y platform, 5-axes (chi, phi, x, y, z) cradle, Programmable XYZ stage, High-throughput stage, Multipurpose sample stage
X-ray generator	A 4kW sealed tube x-ray generator Max. voltage 60kV, Max. current 100mA, with Cu target
High-accuracy theta-theta goniometer	Maximum usable range $-111 < 2$ theta $< 168^{\circ}$, Smallest addressable increment -0.0001° , Maximum angular speed -15 deg/s, Angular resolution (FWHM on LaB6) -0.026°
Detectors	0D Scintillation Counter (point detector), 1D Semiconductor Detector D/tex Ultra (linear detector)

A7: Reciprocating Tribometer (IIT Indore)



Make	Ducom Instruments Ltd. India.	
Model	СМ-9104	
Load range	5 N – 50 N	
Stroke range	1 mm – 20 mm	
Frequency	1 Hz – 50 Hz	
Type of intender	Ball on disc	

A8: Electrochemical Workstation (IIT Indore)



Make	Metrohm India.	
Model	Autolab PGSTAT 302N	
Frequency range	10 µHz - 32 MHz	
Potential range	+/- 10 V	
Current range	1 A to 10 nA	
Control software	NOVA	