Microstructural, Mechanical and Biocompatibility Evaluation of High Entropy Alloys for Hard Tissue Implants

Thesis submitted in partial fulfillment

for the award of degree

of

Doctor of Philosophy

by

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CERTIFICATE

It is certified that the work contained in the thesis titled **"Microstructural, Mechanical and Biocompatibility Evaluation of High Entropy Alloys for Hard Tissue Implants''** by **"Chitrance Kumar Srivastav"** has been carried out under our supervision and this work has not been submitted elsewhere for a degree.

It is further certified that the student has fulfilled all the requirements of Comprehensive Examination, Candidacy, and SOTA for the award of Ph.D. Degree.

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DECLARATION BY THE CANDIDATE

I, **"Chitrance Kumar Srivastav",** certify that the work embodied in this thesis is my own bonafide work and was carried out by me under the supervision of **"Dr. Debashis Khan** and **Prof. Nand Kishore Prasad",** from **July 2019** to **June 2024,** at the **"DEPARTMENT OF MECHANICAL ENGINEERING",** Indian Institute of Technology (BHU) Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work of this thesis. I further declare that I have not wilfully copied any other's work, paragraphs, text, data, results, *etc.*, reported in journals, books, magazines, reports dissertations, theses, *etc.*, or available on websites and have not included them in this thesis and have not cited as my work.

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(**CHITRANCE KUMAR SRIVASTAV**)

This Doctoral Thesis is dedicated to my family members, Mahamana Pt. Madan Mohan Malviya Ji, Maa Ganga, Baba Vishwanath, and Lord Sri Krishna

LIST OF FIGURES

LIST OF NOTATIONS/SYMBOLS

Å	Angstrom
nm	Nanometer
μm	Micrometer
mm	Millimeter
cm	Centimeter
mL	Millilitre
mV	Millivolt
s	Second
min	Minute
h	Hour
N	Newton
Hz	Hertz
Ω	Ohm
g	Gram
gf	Gram force
MPa	Mega Pascal
GPa	Giga Pascal
°C	Degree Celsius

%	Percentage
rpm	Revolution per minute
HV	Vickers hardness
E	Young's modulus
T_m	Melting temperature
δ	Atomic size difference
ΔH_{mix}	Mixing enthalpy
ΔS_{mix}	Mixing entropy
Ω	Dimensionless parameter
ρ	Density
β	FWHM in radians
θ	Peak position
ε	Lattice strain
λ	Wavelength
β	BCC
α	HCP
316LSS	Low-carbon stainless steel
cp-Ti	Commercially pure titanium
Al	Aluminium

B	Boron
Cr	Chromium
Co	Cobalt
Cu	Copper
Hf	Hafnium
Fe	Iron
Mn	Manganese
Mo	Molybdenum
Ni	Nickel
Nb	Niobium
Ag	Silver
Ta	Tantalum
Sn	Tin
Ti	Titanium
Zr	Zirconium
Al_2O_3	Aluminum oxide
CO_2	Carbon dioxide
Cr_2O_3	Chromium(III) oxide
Fe_2O_3	Iron(III) oxide

Nb_2O_5	Niobium pentoxide
Ta_2O_5	Tantalum pentoxide
TiO_2	Titanium dioxide
SiC	Silicon carbide
ZrO_2	Zirconium dioxide

LIST OF ABBREVIATIONS

HEAs	High entropy alloys
MA	Mechanical alloying
LS	Lattice strain
CS	Crystallite size
VEC	Valence electron concentration
wt. %	Weight percentage
at. %	atomic percentage
BCC	Body-centered cubic
FCC	Face-centered cubic
HCP	Hexagonal closed packed
DSC	Differential scanning calorimetry
EIS	Electrochemical impedance spectroscopy
EDM	Electric discharge machining
EDS	Energy dispersive spectroscopy
FFT	Fast Fourier transform
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
FE-SEM	Field emission scanning electron microscopy

HR-SEM	High-resolution scanning electron microscopy
HR-TEM	High-resolution transmission electron microscopy
OCP	Open-circuit potential
PDP	Potentiodynamic polarization
SEM	Scanning electron microscope
SAD	Selected area diffraction
TEM	Transmission electron microscopy
XRF	X-ray fluorescence
XPS	X-ray photoelectron spectroscopy
AS	Artificial Saliva
FBS	Foetal bovine serum
PBS	Phosphate buffer saline
SBF	Simulated body fluid
pH	Potential of Hydrogen
DMEM	Dulbecco's modified eagle medium
DMSO	Dimethyl sulfoxide
OD	Optical density

LIST OF TABLES

PREFACE

Metallic biomaterials have garnered significant attention as prosthetics in repairing damaged hard tissues, such as dental roots, knee and hip joints, etc. Nevertheless, Young's modulus values of the commonly used conventional metallic implant materials, including 316L stainless steel, Co-Cr-Mo alloy, commercially pure titanium (cp-Ti), and Ti alloys exceed that of human bone. This discrepancy can lead to stress shielding, which may result in various complications like bone cell death, implant loosening, or even implant failure. Additionally, concerns regarding the cytotoxicity of elements, such as Al and V, further hinder its widespread acceptance. These toxic elements can impede bone growth and are associated with severe health issues like peripheral neuropathy and Alzheimer's disease. Therefore, exploring novel categories of Ti-alloys is essential to mitigate the adverse effects associated with existing Ti-based alloys. There are many existing proven bio-materials, such as Cr, Fe, Ta, Co, Mo, Hf, Nb, and Zr, that can be incorporated to replace V and Al. These materials offer potential pathways to develop safer and more effective metallic biomaterials for medical applications.

Recently, there has been a noticeable increase in interest in high entropy alloys (HEAs) as a promising solution to overcome the limitations inherent in conventional alloys. The concept of HEAs was initially introduced by Yeh and Cantor et al. in 2004. Over the past few years, extensive research efforts have been dedicated to a deeper understanding of the fundamental factors governing solid solution formation in HEAs systems. The distinctive characteristics exhibited by HEAs, such as high entropy mixing, lattice distortion, hysteresis diffusion, and cocktail effect, contribute to improved mechanical properties, superior wear, corrosion resistance, and adequate thermal stability.

Based on these research findings, it is being proposed here a novel class of HEAs, i.e., Ti-$Co_{0.35}$-$Cr_{0.35}$-Nb-Zr, Ti-Nb-Ta-Cr-$Co_{0.2}$, and Ti-Nb-Ta-$Fe_{0.35}$-$Co_{0.35}$ (at. %). This formulation can produce HEAs with better mechanical properties and improved biocompatibility at a lower cost. After reviewing the existing literature, it has been found that this particular combination of HEAs has yet to be explored as a potential implant material.

Thus, the present work aims to synthesize nanocrystalline Ti-$Co_{0.35}$-$Cr_{0.35}$-Nb-Zr, Ti-Nb-Ta-Cr-$Co_{0.2}$, and Ti-Nb-Ta-$Fe_{0.35}$-$Co_{0.35}$ (at. %) HEAs using ball milling followed by spark plasma/muffle furnace sintering. The phase, microstructure, and thermal stability of the milled powder and sintered sample were analyzed using X-ray diffraction, electron microscopy, and differential scanning calorimetry. Additionally, the mechanical and physical properties of the consolidated sample, including density, porosity, Young's modulus, hardness, and compressive strength, were also examined. Cell culture analysis was carried out to assess the biocompatibility of the sintered sample using human osteosarcoma (MG-63) cells.

The findings reveal that the newly developed HEAs have lower elastic modulus, higher compressive strength and hardness than those of conventional implant materials. The lower elastic modulus can further mitigate the effect of stress shielding. The HEAs show excellent corrosion and wear resistance in simulated body fluid. Cytocompatibility assessment of the developed HEAs shows non-toxic towards MG-63 cells. Consequently, the newly developed HEAs hold the potential to be explored as future implant materials.