

**DESIGN AND DEVELOPMENT OF NOVEL MEDIUM
ENTROPY ALLOY USING MACHINE LEARNING FOR
RAPID MANUFACTURING OF IMPLANTS**

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**DEPARTMENT OF MECHANICAL ENGINEERING
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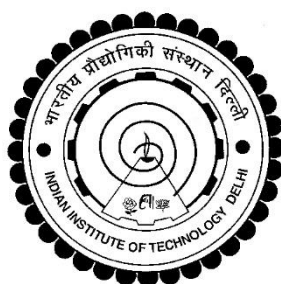
by

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Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy
to the



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DEDICATED TO
MY PARENTS AND THE ALMIGHTY

Certificate

This is to certify that the thesis entitled '**Design and development of novel medium entropy alloy using machine learning for rapid manufacturing of implants**' submitted by **Mr. Priyabrata Das** to the Indian Institute of Technology Delhi, for the award of the degree of *Doctor of Philosophy*, is a record of the original bonafide research work carried out by him under my guidance and supervision. The results contained in it have not been submitted in part or full to any other institute or university for the award of any degree/diploma.



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(Priyabrata Das)

Abstract

Medium entropy alloys (MEAs) are a subset of compositionally complex alloys (CCAs) whose mixing entropy lies between R and $1.5R$ where R is the universal gas constant. The properties of MEAs largely depend on the phases present in the alloy such as solid solution (SS), solid solution + intermetallic (SS+IM) and amorphous (AM). Hence, the correct prediction of phases can enable the efficient selection of material compositions with anticipated properties. Non equiatomic MEAs have gained significant attention due to their unique combinations of properties including high strength, good ductility, excellent thermal stability and corrosion resistance. The non equiatomic compositions provide flexibility in tailoring the mechanical, thermal, magnetic, biomedical and other functional properties to meet the specific application requirements. However, the literature survey reveals the scarcity of non-equiatomic MEA design strategy to explore the vast elemental search space.

To address the research gaps, an MEA specific dataset was constructed from the curation of available literature. Three machine learning (ML) algorithms viz. k-nearest neighbors (KNN), artificial neural network (ANN), and random forest (RF) were employed for the ternary phase classification problem. It was found that only three features were sufficient for the phase prediction in MEAs. Among the three ML algorithms, ANN had the highest macro averaged F1 score (86.7%) and accuracy (87.3%) in predicting the phases in MEAs, while RF has the lowest macro F1 score (84.67%) and accuracy (84.8%). However, for phase prediction between single phase SS and multi-phase SS, distance-based algorithm i.e. KNN was found to be suitable. After identifying the best performing algorithm and important features for phase prediction in MEA system, a novel design approach was proposed to identify quaternary non equiatomic MEA for biomedical application. The design methodology employs multi-objective optimization of empirical phase formation parameters and ML algorithm to design SS containing non equiatomic medium entropy alloy. The suggested

approach scans over a large composition space to find possible non-equiatomic MEAs with desired phases. This step significantly reduced the time and resources utilized in MEA design by decreasing the number of experimental runs. Based on the design strategy, $\text{Mg}_{60}\text{Ti}_{24.24}\text{Zn}_{9.66}\text{Nb}_{6.1}$ alloy was designed and selected for fabrication through powder metallurgy route by employing microwave sintering. The Mg rich alloy exhibited the presence of two SS phases viz HCP and BCC in both prealloyed powder and final sintered specimen. The developed alloy showed a high microhardness value of 153.9 ± 0.85 HV with a measured density of 2.82 ± 0.03 g/cm³. The mechanical properties such as yield strength (σ_{ys}), ultimate compressive strength (σ_{cs}), elastic modulus (E) and fracture strain of the developed alloy were found to be superior to that of pure Mg and AZ31 fabricated through the same manufacturing route. Mechanical properties of local phases present within the alloy were assessed through nanoindentation technique. Elastic modulus (E) and hardness (H) values for the Ti rich BCC phase were 118.9 ± 7.2 GPa and 4.65 ± 1.1 GPa, respectively, whereas the Mg rich HCP phase showed values of 65.2 ± 7 GPa and 1.6 ± 0.43 GPa, respectively.

Further, volumetric shrinkage (V_s) and σ_{cs} of MEA were statistically modeled by using three microwave sintering process factors viz sintering temperature (ST), heating rate (HR) and dwell time (DT). Two evolutionary optimization algorithms viz multi objective genetic algorithm (NSGA II) and multi objective particle swarm optimization (MOPSO) were incorporated to identify optimum process parameters. The samples fabricated at optimized parameters (ST=867°C, HR=30°C/min, DT=34 min) exhibited a V_s of and σ_{cs} of $20.82 \pm 0.4\%$ and 347.1 ± 6.8 MPa which were in close agreement with the predicted values.

The corrosion behavior of $\text{Mg}_{60}\text{Ti}_{24.24}\text{Zn}_{9.66}\text{Nb}_{6.1}$ MEA in physiological environment was evaluated by four different tests i.e., hydrogen evolution reaction, static immersion test, potentiodynamic polarization and electrochemical impedance spectroscopy. The corrosion

rate of the $\text{Mg}_{60}\text{Ti}_{24.24}\text{Zn}_{9.66}\text{Nb}_{6.1}$ MEA was compared against the corrosion rates of pure Mg and AZ31. The developed alloy exhibited a corrosion rate of 0.46 ± 0.09 mmpy which is significantly lesser than the corrosion rate of AZ31 and pure Mg (4.19 ± 0.62 mmpy and 3.92 ± 0.45 mmpy respectively). The corrosion layer formed on the MEA showed the presence of multiple oxides and hydroxides. Further, the formation of hydroxyapatite and $\text{Ca}_3(\text{PO}_4)_2$ over the surface was confirmed from both EDX and XPS which is beneficial for tissue regeneration. The MEA sample at all concentrations (100%, 75%, 50%, 25% and 10%) exhibited no toxicity (cell viability > 80%) which led to minimal cell death and can be visualized from live-dead staining images. Further, the hemocompatibility analysis performed on the MEA sample demonstrated a low hemolysis ratio of $1.3 \pm 0.6\%$, indicating minimal hemolysis. The absence of fibrin network/pseudopods on the platelets confirmed the antiplatelet adhesion characteristic of MEA.

Thereafter, the prealloyed $\text{Mg}_{60}\text{Ti}_{24.24}\text{Zn}_{9.66}\text{Nb}_{6.1}$ MEA powders were blended with spherical carbonyl iron powder (CIP) and specimens were fabricated by a rapid manufacturing approach which combined additive manufacturing and pressureless microwave sintering. The volume percent of MEA was varied and multiple properties such as mechanical, corrosion and biological properties were studied. The Fe-10MEA exhibited a σ_{ys} of 67.9 ± 2.87 MPa, corrosion rate of 0.384 ± 0.03 mmpy and cell viability of $105.9 \pm 6.26\%$ and further utilized for bone scaffold fabrication. A computational scheme for designing graded scaffolds was proposed, which employed the normal distribution function to determine feature position and size. The graded design demonstrated a higher energy absorption per unit volume as compared to the uniform design. The permeability of the uniform and graded scaffolds was confirmed to meet the requirement of trabecular bone. The wall shear stress (WSS) value obtained from the CFD analysis of uniform and graded scaffold are consistent with the requirement for cell differentiation.

सार

मध्यम एन्ट्रॉपी मिश्र धातु (MEAs) संरचनागत रूप से जटिल मिश्र धातुओं (CCAs) का एक उपसमूह हैं जिनकी मिश्रण एन्ट्रॉपी R और $1.5R$ के बीच होती है जहाँ R सार्वभौमिक गैस स्थिरांक है। MEAs के गुण काफी हद तक मिश्र धातु में मौजूद चरणों पर निर्भर करते हैं जैसे ठोस घोल (SS), ठोस घोल + इंटरमेटेलिक (SS+IM) और अनाकार (AM)। इसलिए, चरणों का सही पूर्वानुमान प्रत्याशित गुणों के साथ सामग्री रचनाओं के कुशल चयन को सक्षम कर सकता है। गैर समपरमाण्विक MEAs ने उच्च शक्ति, अच्छा लचीलापन, उत्कृष्ट तापीय स्थिरता और संक्षारण प्रतिरोध सहित गुणों के अपने अनूठे संयोजनों के कारण महत्वपूर्ण ध्यान आकर्षित किया है। गैर-समपरमाण्विक रचनाएँ विशिष्ट अनुप्रयोग आवश्यकताओं को पूरा करने के लिए यांत्रिक, थर्मल, चुंबकीय, बायोमेडिकल और अन्य कार्यात्मक गुणों को तैयार करने में लचीलापन प्रदान करती हैं। हालाँकि, साहित्य सर्वेक्षण से विशाल मौलिक खोज स्थान का पता लगाने के लिए गैर-सम-परमाणु एमईए डिजाइन रणनीति की कमी का पता चलता है।

अनुसंधान अंतर को संबोधित करने के लिए, उपलब्ध साहित्य के संग्रह से एक एमईए विशिष्ट डेटासेट का निर्माण किया गया था। तीन मशीन लर्निंग (ML) एल्गोरिदम अर्थात् टर्नरी चरण वर्गीकरण समस्या के लिए के-निकटतम पड़ोसियों (KNN), कृत्रिम तंत्रिका नेटवर्क (ANN), और यादृच्छिक वन (RF) को नियोजित किया गया था। यह पाया गया कि MEAs में चरण भविष्यवाणी के लिए केवल तीन विशेषताएँ पर्याप्त थीं। तीन ML एल्गोरिदम में से, ANN का MEAs में चरणों की भविष्यवाणी करने में उच्चतम मैक्रो औसत F1 स्कोर (86.7%) और सटीकता (87.3%) थी, जबकि RF का सबसे कम मैक्रो F1 स्कोर (84.67%) और सटीकता (84.8%) थी। हालांकि, एकल चरण SS और बहु-चरण SS के बीच चरण भविष्यवाणी के लिए, दूरी-आधारित एल्गोरिदम यानी KNN उपयुक्त पाया गया। MEA प्रणाली में चरण भविष्यवाणी के लिए सर्वश्रेष्ठ प्रदर्शन करने वाले एल्गोरिदम और महत्वपूर्ण विशेषताओं की पहचान करने के बाद सुझाया गया तरीका वांछित चरणों के साथ संभावित गैर-समपरमाणुक एमईए को खोजने

के लिए एक बड़े संयोजन स्थान पर स्कैन करता है। इस कदम ने प्रयोगात्मक रन की संख्या को कम करके एमईए डिजाइन में उपयोग किए जाने वाले समय और संसाधनों को महत्वपूर्ण रूप से कम कर दिया। डिजाइन रणनीति के आधार पर, $Mg_{60}Ti_{24.24}Zn_{9.66}Nb_{6.1}$ मिश्र धातु को माइक्रोवेव सिंटरिंग का उपयोग करके पाउडर धातु विज्ञान मार्ग के माध्यम से निर्माण के लिए डिज़ाइन और चुना गया था। Mg समृद्ध मिश्र धातु ने प्रीअलॉयड पाउडर और अंतिम सिंटर्ड नमूने दोनों में दो SS चरणों अर्थात् HCP और BCC की उपस्थिति प्रदर्शित की। विकसित मिश्र धातु ने $2.82 \pm 0.03 \text{ g/cm}^3$ के मापा घनत्व के साथ $153.9 \pm 0.85 \text{ HV}$ का उच्च माइक्रोहार्डनेस मान दिखाया। विकसित मिश्र धातु के यांत्रिक गुण जैसे उपज शक्ति (σ_{ys}), अंतिम संपीड़न शक्ति (σ_{cs}), लोचदार मापांक (E) और फ्रैक्चर स्ट्रेन को उसी विनिर्माण मार्ग के माध्यम से निर्मित शुद्ध Mg और AZ31 से बेहतर पाया गया। मिश्रधातु में मौजूद स्थानीय चरणों के यांत्रिक गुणों का मूल्यांकन नैनोइंडेंटेशन तकनीक के माध्यम से किया गया। Ti समृद्ध BCC चरण के लिए लोचदार मापांक (E) और कठोरता (H) मान क्रमशः $118.9 \pm 7.2 \text{ GPa}$ और $4.65 \pm 1.1 \text{ GPa}$ थे, जबकि Mg समृद्ध HCP चरण ने क्रमशः $65.2 \pm 7 \text{ GPa}$ और $1.6 \pm 0.43 \text{ GPa}$ के मान दिखाए। इसके अलावा, MEA के वॉल्यूमेट्रिक सिकुड़न (V_s) और σ_{cs} को तीन माइक्रोवेव सिंटरिंग प्रक्रिया कारकों अर्थात् सिंटरिंग तापमान (ST), हीटिंग दर (HR) और डवेल टाइम (DT) का उपयोग करके सांख्यिकीय रूप से मॉडल किया गया। दो विकासवादी अनुकूलन एल्गोरिदम अर्थात् मल्टी ऑब्जेक्टिव जेनेटिक एल्गोरिदम (NSGA II) और मल्टी ऑब्जेक्टिव पार्टिकल स्वॉर्म ऑप्टिमाइज़ेशन (MOPSO) को इष्टतम प्रक्रिया मापदंडों की पहचान करने के लिए शामिल किया गया था। अनुकूलित मापदंडों (ST=867°C, HR=30°C/मिनट, DT=34 मिनट) पर निर्मित नमूनों ने $20.82 \pm 0.4\%$ और $347.1 \pm 6.8 \text{ MPa}$ के V_s और σ_{cs} प्रदर्शित किए जो पूर्वानुमानित मूल्यों के साथ काफी हद तक सहमत थे।

शारीरिक वातावरण में $Mg_{60}Ti_{24.24}Zn_{9.66}Nb_{6.1}$ MEA के संक्षारण व्यवहार का मूल्यांकन चार अलग-अलग परीक्षणों द्वारा किया गया था, अर्थात् हाइड्रोजन विकास प्रतिक्रिया, स्थैतिक विसर्जन परीक्षण,

पोटेंशियोडायनामिक ध्रुवीकरण और इलेक्ट्रोकेमिकल प्रतिबाधा स्पेक्ट्रोस्कोपी।

Mg₆₀Ti_{24.24}Zn_{9.66}Nb_{6.1} MEA की संक्षारण दर की तुलना शुद्ध Mg और AZ31 की संक्षारण दरों से की गई। विकसित मिश्रधातु ने 0.46 ± 0.09 mmpy की संक्षारण दर प्रदर्शित की जो AZ31 और शुद्ध Mg (क्रमशः 4.19 ± 0.62 mmpy और 3.92 ± 0.45 mmpy) की संक्षारण दर से काफी कम है। MEA पर बनी संक्षारण परत ने कई ऑक्साइड और हाइड्रॉक्साइड की उपस्थिति दिखाई। इसके अलावा, सतह पर हाइड्रॉक्सीपैटाइट और Ca₃(PO₄)₂ के गठन की पुष्टि EDX और XPS दोनों से की गई जो ऊतक पुनर्जनन के लिए फायदेमंद है। सभी सांद्रताओं (100%, 75%, 50%, 25% और 10%) पर MEA नमूने ने कोई विषाक्तता (कोशिका व्यवहार्यता > 80%) नहीं दिखाई, जिसके कारण न्यूनतम कोशिका मृत्यु हुई और इसे जीवित-मृत धुंधला छवियों से देखा जा सकता है। इसके अलावा, हेमोकंपैटिबिलिटी विश्लेषण एमईए नमूने पर किए गए अध्ययन ने $1.3 \pm 0.6\%$ के कम हेमोलिसिस अनुपात को प्रदर्शित किया, जो न्यूनतम हेमोलिसिस को दर्शाता है। प्लेटलेट्स पर फाइब्रिन नेटवर्क/स्पूडोपोड्स की अनुपस्थिति ने एमईए की एंटीप्लेटलेट आसंजन विशेषता की पुष्टि की।

इसके बाद, प्रीअलॉयड Mg₆₀Ti_{24.24}Zn_{9.66}Nb_{6.1} MEA पाउडर को गोलाकार कार्बोनिल आयरन पाउडर (CIP) के साथ मिश्रित किया गया और नमूनों को एक तेज़ विनिर्माण दृष्टिकोण द्वारा तैयार किया गया, जिसमें एडिटिव मैनुफैक्चरिंग और प्रेशरलेस माइक्रोवेव सintering को मिलाया गया। MEA का आयतन प्रतिशत भिन्न था और यांत्रिक, संक्षारण और जैविक गुणों जैसे कई गुणों का अध्ययन किया गया था। Fe-10MEA ने 67.9 ± 2.87 MPa का σ_{ys} , 0.384 ± 0.03 mmpy की संक्षारण दर और $105.9 \pm 6.26\%$ की सेल व्यवहार्यता प्रदर्शित की और आगे अस्थि मचान निर्माण के लिए उपयोग किया। ग्रेडेड मचानों को डिज़ाइन करने के लिए एक कम्प्यूटेशनल योजना प्रस्तावित की गई थी, जिसमें फीचर की स्थिति और आकार निर्धारित करने के लिए सामान्य वितरण फ़ंक्शन का उपयोग किया गया था। ग्रेडेड डिज़ाइन ने एक समान डिज़ाइन की तुलना में प्रति इकाई आयतन में उच्च ऊर्जा अवशोषण का प्रदर्शन किया। एक समान और ग्रेडेड मचानों की पारगम्यता की पुष्टि ट्रेबिकुलर हड्डी

की आवश्यकता को पूरा करने के लिए की गई थी। एक समान और ग्रेडेड मचानों के CFD विश्लेषण से प्राप्त दीवार कतरनी तनाव (WSS) मूल्य कोशिका विभेदन की आवश्यकता के अनुरूप हैं।

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Acronym

Adj. MS	Adjusted mean square
AM	Amorphous
ANOVA	Analysis of variance
CCA	Compositionally complex alloy
CCD	Central composite design
CE	Counter electrode
CIP	Carbonyl iron particle
CPE	Constant phase element
CRSS	Critical resolved shear stress
DF	Degree of freedom
DLS	Digital light scattering
DMEM	Dulbecco's Modified Eagle's Medium
DOE	Design of experiment
DSC	Differential scanning calorimetry
DT	Dwell time
EDS	Energy dispersive spectroscopy
EIS	Electrochemical impedance spectroscopy
EW	Equivalent weight
F	Fisher's value
FBS	Fetal bovine serum
FE-SEM	Field emission scanning electron microscopy
FFT	Fast Fourier transform
HEA	High entropy alloy
HER	Hydrogen evolution reaction

HR	Heating rate
HR	Hemolysis ratio
HRTEM	High resolution transmission electron microscopy
IM	Intermetallic
LEA	Low entropy alloy
MA	Mechanical alloying
MEA	Medium entropy alloy
MEM	Minimum essential medium
mmpy	mm per year
MOPSO	Multi-objective particle swarm optimization
MPEA	Multi principal element alloy
NSGA	Non dominated sorting genetic algorithm
OCP	Open circuit potential
PBS	Phosphate buffer saline
PI	Propidium iodide
PM	Powder metallurgy
PP	Potentiodynamic polarization
RDA	Recommended dietary allowance
RSM	Response surface methodology
SBF	Simulated body fluid
SCE	Saturated calomel electrode
SD	Standard deviation
Seq. SS	Sequential sum of square
SS	Solid solution
ST	Sintering temperature

WE	Working electrode
WSS	Wall shear stress
XPS	X-ray photo electron spectroscopy
XRD	X-ray diffraction

Nomenclature

ρ	Density
σ_{ys}	Compressive yield strength
σ_{cs}	Ultimate compressive strength
V_s	Volumetric shrinkage
E_{corr}	Corrosion potential
i_{corr}	Corrosion current density
n	Impedance parameter to the frequency
C	Impedance parameter to the frequency
EW	Equivalent weight
ΔW	Weight loss
$Re(Z)$	Real part of impedance
$Im(Z)$	Imaginary part of impedance
R^2	Coefficient of determination
$wt\%$	Weight percentage
$vol\%$	Volume percentage
r_{corr}	Corrosion rate
β_c	Cathodic slope
β_a	Anodic slope
R_s	Solution resistance
R_f	Film resistance
R_o	Pore resistance
R_t	Charge transfer resistance
L	Inductance

CPE_f	Capacitance of film
CPE_{dl}	Capacitance of the double layer