TRIBO-CORROSION OF HIGH ENTROPY ALLOYS

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In this dissertation, tribo-corrosion behavior of several single-phase and multi-phase high entropy alloys were investigated. Tribo-corrosion of body centered cubic MoNbTaTiZr high entropy alloy in simulated physiological environment showed very low friction coefficient (~0.04), low wear rate (~10-8 mm3/Nm), body-temperature assisted passivation, and excellent biocompatibility with respect to stem cells and bone forming osteoblast cells. Tribo-corrosion resistance was evaluated for additively manufactured face centered cubic CoCrFeMnNi high entropy alloy in simulated marine environment. The additively manufactured alloy was found to be significantly better than its as-cast counterpart which was attributed to the refined microstructure and homogeneous elemental distribution. Additively manufactured CoCrFeMnNi showed lower wear rate, regenerative passivation, less wear volume loss, and nobler corrosion potential during tribo-corrosion test compared to its as-cast equivalent. Furthermore, in the elevated temperature (100 °C) tribo-corrosion environment, AlCoCrFeNi2.1 eutectic high entropy alloy showed excellent microstructural stability and pitting resistance with an order of magnitude lower wear volume loss compared to duplex stainless steel. The knowledge gained from tribo-corrosion response and stress-corrosion susceptibility of high entropy alloys was used in the development of bio-electrochemical sensors to sense implant degradation. The results obtained herewith support the promise of high entropy alloys in outperforming currently used structural alloys in the harsh tribo-corrosion environment.
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By

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This dissertation is dedicated to my late brother Ismail Shittu.
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CHAPTER 1

INTRODUCTION

1.1 High Entropy Alloys (HEAs)

High entropy alloys have been the center of interest since it first debut in 2004 [1], showing superior mechanical, functional and corrosion properties that point towards solving critical material problems in major industries [2]. High entropy alloys (HEA) also known as multi-principal element alloys (MPEA) or complex concentrated alloys (CCA) are alloys having five or more principal elements with concentrations between 5 and 35 at.%. They have significantly higher mixing entropies from their random solid solution states when compared with conventional alloys and thus referred to as HEAs. Their corrosion behavior has been studied widely in different environments. Additionally, their wear or tribological behavior has been reported under widely varying conditions. However, the synergy between these two degradation mechanisms has not been investigated. Understanding of wear-corrosion synergy (tribo-corrosion) in high entropy alloys is of great importance in determining their application worthiness in wide ranging areas of interest including bio-implants, oil and gas, marine engineering and nuclear industry.

Contrary to knowledge from binary and ternary phase diagrams, HEAs have suppressed formation of intermetallic compounds which enhances formation of solid solution phases with simple structures. There are four core effects attributed to the enhanced property adjustments achieved by HEAs namely; high-entropy effect, sluggish diffusion effect, severe-lattice distortion effect, and cocktail effect.

1.1.1 High-Entropy Effect

Basically, achieving a lower free energy requires a higher configurational mixing entropy to facilitate formation of solid solution phases especially at higher temperatures [3]. Therefore,
considering the thermodynamic relationship:

\[ G = H - TS \]  

(Eq. 1-1)

where

- \( G \) denotes Gibbs free energy
- \( H \) denotes enthalpy
- \( T \) denotes temperature
- \( S \) denotes entropy

Figure 1-1: The XRD patterns of a series alloy designed by the sequential addition of one extra element to the previous one. All the alloys have one or two major phases that have simple structures.

[3]

Phases with higher entropy of alloying components will have a lower Gibbs free energy by supporting high mixing entropy in HEAs to form random solid solution phases over the formation of intermetallic phases [2]. Although high mixing entropy favors solid solution phases, the
guarantee of simple solid-solution phases in multi-component alloys are influenced by other factors such as mixing enthalpy ($\Delta H_{mix}$), atomic size difference ($\delta$) and valence electron configuration (VEC) [3–5]. Considering Eq.1, high entropy effect contribution to the stability of random solid-solution decreases with the decrease in temperature, thus giving rise to intermetallic phase transformation if HEAs are annealed at relatively low temperatures [6,7]. To demonstrates the evidence of high entropy effect using XRD patterns of a series of binary to septenary alloys, Figure 1-1 shows a trend in phase evolution going from binary CuNi at the bottom which is FCC till the septenary FCC+BCC at the top. A simple structure of BCC and FCC with the suppression of the minor intermetallic phases can be seen as the increase in entropy of the system with increasing the number of alloying elements. This trend is contrary to conventional alloying expectation of formation of various kinds of binary/ ternary compounds.

1.1.2 Sluggish Diffusion Effect

As a result of greater variety of surrounding atoms in each lattice site, the variety of scattering atoms directly influence diffusion to create a slower diffusion effect than conventional alloys. This sluggish diffusion effect has been used to explain the exceptional high-temperature strength, formation of nanostructures and impressive high-temperature structural stability [8]. Due to compositional complexity, sluggish diffusion effect is based on secondary observations of slow kinetics when compared to conventional alloys. Sluggish diffusion effect allows for better microstructure control, nucleation, and grain growth, because phase transformation resulting from coordinated diffusion of many elements requires redistribution to reach desired composition. Figure 1-2 shows Ni atom diffusing in pure metal, Fe-Cr-Ni and CoCrFeMn$_{0.5}$Ni single phase FCC HEA. Mean potential energy difference of 60.3 meV between lattice sites of the HEA accounts for 50% higher mean potential energy difference than that in Fe-Cr-Ni alloy. Thereby resulting in 1.73
longer occupation time at lower energy sites than at high energy sites as a direct result of higher activation energy of diffusion in the HEA than in the FCC ternary alloys and pure elements.

![Figure 1-2: Schematic diagram of the potential energy change during the migration of a Ni atom. The mean difference (MD) in potential energy after each migration for pure metals is zero, whereas that for HEA is the largest [9]](image)

**1.1.3 Severe Lattice Distortion Effect**

As a result of having multiple principal elements in a HEA, the HEA lattice is made up of varying atomic sizes which in turn creates a lattice with mismatched atoms to form a severely distorted lattice. The mismatch creates a strain energy associated with lattice distortion which increases the overall free energy of the HEA lattice. These distorted lattices benefit the HEA by impeding dislocation movement which leads to exceptional strength in the form of solid solution
strengthening. Increased scattering of propagating electrons and phonons relates to the lowered electrical and thermal conductivity of HEAs. Figure 1-3 shows the strain in the severe lattice distortion of the HEA by indicating how offset the atomic centers are relative to surrounding atoms and average lattice sites. The distorted lattice also points to the fact that coordination number which is typically 12 for FCC or HCP crystals and 14 for BCC crystals will differ for different HEA systems and different constituent atoms.

![Image](image_url)

**Figure 1-3:** Severe lattice distortion of a complex concentrated solution showing no dominant atom species with atom position deviating from mean lattice positions.

1.1.4 Cocktail Effect

The synergistic mixture of atom of different sizes, different bond lengths, chemistries, mechanical properties, diffusion constants, melting temperature and crystal structures creates multiple interactions which results in an unpredictable “cocktail effect”. The unexpected synergies between the atoms account for exceptional physical, structural, and functional properties such as near-zero coefficient of thermal expansion, catalytic response, photo-voltaic conversion, ultra-high strength, good fracture toughness, fatigue resistance, and ductility. Figure 1-4 shows how the...
addition of Al to the Al\textsubscript{x}CoCrCuFeNi HEA system indicates an increase in hardness as atomic percent of Al increases and the phase changes from FCC to BCC. The cocktail effect is the reason soft and low melting Al continues to increase the hardness of the Al\textsubscript{x}CoCrCuFeNi HEA system.

![Figure 1-4: Hardness of the Al\textsubscript{x}CoCrCuFeNi alloys as a function of Al content [3].](image)

1.2 Material Degradation

Material degradation is a global challenge that affects the useful life of components as a result of loss of design performance and functional efficiency occurring from fatigue, creep, corrosion, wear, stress, or defects acting externally or imminent in the material. Material degradation can be synergistic from a combination of these mechanisms (at imperceptible levels) or they may occur separately [10]. Material degradation imposes cost penalty on all engineering systems in the form of maintenance, over-designing safety factor, additional design weight, expensive regular inspection, mitigation research and development, and monitoring instrumentation cost. Material degradation can directly influence health as possible toxicants when
material degradation occurs in implants, food processing, water processing or even drug processing industries. A critical minimum level of the loss of performance forms the base between cost penalty and catastrophic damage. Avoiding excessive cost penalty and catastrophic failure is the foundation of the scientific study of material degradation to predict declining performance. Material degradation life cycle can be summarized graphically as shown in Figure 1-5.

![Graphical representation of material degradation as a loss of performance.][10]

1.2.1 Classification of Material Degradation

Irrespective of the aggressiveness of environment, material degradation can occur via different mechanisms. Material degradation can be classified based on the external stimulus that initiates and propagates time-dependent damage into three main groups namely: physical, chemical, and biological stimulus. A chart of this material degradation stimulus is represented in Figure 1-6. Failure mechanism depends largely on material type and applications; therefore, all material classes can experience different types of failures. Thus, a combination of physical failure in a chemical application leads to accelerated failure due to synergistic effects. Synergistic material degradation is the primary failure mechanism for most metallic applications. To establish measures
for reducing metallic material degradation requires understanding the synergistic degradation mechanism.

Figure 1-6: Graphical representation of material degradation as a loss of performance.[11]

1.3 Tribology

Tribology is the science and technology of interacting surfaces in relative motion. It encompasses friction, lubrication, wear and contact mechanics of these contacting surfaces [12]. It accounts for in-service failure of simple and complex individual components, assemblies, manufacturing processes and natural phenomena ranging from atomic scale to tectonic plates and beyond. It cuts across several engineering fields and industries such as aerospace, agriculture, automotive, cosmetology, dental/bioimplants, energy, transportation etc. Tribological surfaces are influenced by physical and chemical properties of the surfaces that invariably dictates the severity and modes of interaction. Owning to the fact that tribological surfaces are atomically corrugated,
formation of asperities from the undulating nature of the surfaces leads to frictional resistance during interaction. Surpassing the static frictional resistance leads to deformation of the asperities in the form of wear. The chemistry of the interacting surfaces typically forms a tribological layer with lubricating properties at the interface to reduce the wear degradation process.

1.3.1 Friction

This is defined as the resistance to movement of one body in contact with another body. This could occur between gas-solid interface as aerodynamic friction, or liquid-solid interface as viscous flow friction or solid-solid interface as sliding friction [13,14]. Interaction between surfaces creates a resistance which can be attributed to either forces of molecular adhesion (such as electrostatic or weak Van der Waals forces) or mechanical abrasion (such as elastic-plastic deformation) or contaminants. Amontons-Coulomb (AC) friction law states that “no sliding occurs as long as the ratio of the shear force Q to the normal load P remains below a certain threshold that is defined as the static friction coefficient $\mu_s$” [15]. To overcome the tangential force to initiate sliding requires the application of equal opposite kinetic force $F$ given as:

$$F = \mu P$$  \hspace{1cm} (Eq. 1-2)

where

$F$ denotes friction force

$\mu$ denotes friction coefficient

$P$ denotes normal load

The coefficient of friction is simply a proportionality constant that portrays the relationship between the normal and tangential frictional force, which is greater for static conditions than kinetic conditions of friction. The coefficient of friction is affected by surface roughness, lubricant, surface chemistry, environment, temperature, sliding speed, contact stress and contact geometry.
1.3.2 Wear

Wear is a tribological process in which solid surfaces in contact and relative motion suffer progressive damage with severity ranging from the interface to the bulk of the material [16]. This damage process is typically accompanied by continuous loss or displacement of mass from the contacting area at a rate known as the material wear rate. Resistance of a body to removal of material by the wear process is known as the wear resistance expressed mathematically as the reciprocal of wear rate [12]. Wear is accompanied by the evolution of energy dissipation as heat from frictional heating.

The two-body abrasion process postulated by Archard is given by:

\[ V = K \frac{P}{H_s} L \]  

(Eq. 1-3)

where

- \( K \) denotes wear coefficient
- \( P \) denotes normal load
- \( H_s \) denotes hardness
- \( L \) denotes total sliding distance

Volume of material removed per unit load and sliding distance \( K \) is usually measure in units of \( \text{mm}^3/\text{N.m} \) to maintain physical meaning of \( K \).

Fundamentally, wear can be divided into six primary modes

- Abrasive wear (scratching)
- Adhesive wear (galling, scuffing)
- Fretting wear (vibration)
- Erosive wear (cavitation, impact, electro-arcing)
- Rolling contact fatigue (spalling, delamination)
For the scope of this dissertation, we shall introduce abrasive, adhesive, and fretting wear. Then we shall elaborate on tribo-corrosion in detail in section 1.6.

Abrasive wear is associated with damage having hard protuberances forced against the solid sliding surfaces. Surfaces are characterized by scratches, micro-cutting, ridges, and valleys aligned parallel to the direction of motion with depth varying depending on application, initial roughness and severity of deformation. This mode of wear is typical in systems experiencing high friction, low wear rate and high noise level.

Adhesive wear is associated with damage having a plastic shear deformation fracture with a scale-like topography on the surface. Surfaces are characterized by smearing, galling, scuffing, scoring or seizures depending on the application and severity of deformation. This mode of wear is typical in systems experiencing high friction, high wear rate and high noise level.

Fretting wear is associated with damage having a vanishingly small angle of attack between the contacting surfaces. Surfaces are characterized with virtually no loss of material. This form of wear creates a driving force for phase transformations from the steep elastic stress gradients. This mode of wear is typical of systems experiencing low friction, low wear rate and vibrational noise.

1.3.3 Lubrication

With the aim of reducing friction and wear at the sliding interface, lubrication is typically designed in the form of gases, liquid, or solids to carry away heat and wear debris generated during interface interaction. Lubricants act as shearing surfaces introduced deliberately to separate the asperity junction totally or partially to reduce tangential force required to initiate sliding [13]. Liquid and gaseous lubricants form thick-film or thin-film lubrication or a mixture as mixed lubrication on the surfaces of interaction. Based on the loading, speed, lubricant viscosity, contact
geometry and surface roughness of the system, lubrication can transition from thick to thin or
remain at the boundary of lubricated or unlubricated sliding. Corrosive fluids can form
hydrodynamic lubricating films which can provide load bearing effect to reduce the actual load
transmitted through the contacting asperities and thus limit wear [17].

1.4 Corrosion

The electrochemical process resulting in destruction and deterioration of a material as a
consequence of reaction with its environment is known as corrosion [18]. Corrosion of metals and
alloys can be distinguished into two major mechanisms namely aqueous corrosion and gaseous
corrosion [19]. Aqueous corrosion sometimes referred to as wet corrosion is concerned with the
metallic degradation when exposed to a liquid electrolyte such as water, alkali, or acid. Gaseous
corrosion sometimes referred to as dry corrosion is concerned with metallic degradation when
there is a limited supply of electrolyte but a significant presence of gaseous components. Gaseous
corrosion can be viewed as surface oxidation forming oxide layers in an oxidizing atmosphere.
Both mechanisms share similarities such as the lowering of the Gibbs free energy of the system,
and presence of the anodic and cathodic reaction taking place [19]. Each reaction involves
chemical species that make up the oxidation-reaction system, and the fluctuations in species ratio
makes corrosion potential a non-equilibrium potential. This is the reason why corrosion potential
is probabilistic within a range rather than a fixed value. The electrochemical process of aqueous
corrosion occurring at the interface are commonly characterized by oxidation reaction resulting in
metal dissolution and metal oxide formation simultaneously with reduction reaction resulting in
proton or water or dissolved oxygen reduction. This Red-Ox reaction can be broken down into
equations as:

- Anodic (Oxidation)
\[ M \rightarrow M^{n+} + ne^- \]  \hspace{1cm} (Eq. 1-4)

- Cathodic (Reduction)

\[ Ox + ne^- \rightarrow Red \]  \hspace{1cm} (Eq. 1-5)

where

- M denotes metal
- \( M^{n+} \) denotes dissolved metal cation
- Ox denotes soluble oxidant
- Red denotes the reduced form of the oxidant

1.4.1 Types of Corrosion in Metals

The most common categorization of the forms of corrosion proposed by Fontana and Green [18] can be divided into eight forms:

1. **Uniform corrosion**: occurs evenly over the exposed electrolyte-metal surface because of the uniformly distributed anodic-cathodic reaction. This is the most common and predictable form of corrosion, typically abated with the corrosion allowance in design.

2. **Galvanic corrosion**: occurs as a result of coupling of two metals with different potentials in a conductive electrolyte. Accelerated attack of the anodic metal at the expense of protecting the cathodic metal may occur near contact surface depending on geometry and conductivity of electrolyte.

3. **Pitting corrosion**: occurs as a result of localized concentration of halides or oxygen anodic-cathodic reaction capable of forming pits of small diameters at the electrolyte-metal surface. These pits are extended into the bulk of the material and are often covered by the corrosion products on the surface.
4. **Crevice corrosion**: occurs as a result of small standing electrolyte gathering around fasteners or coupling to form a narrow-dissolved region. Halides create a conducive environment for this autocatalytic process.

5. **Intergranular corrosion**: occurs as a result of grain boundary attack due to higher anodic reactivity of the grain boundaries compared to the bulk of the grains. This form of corrosion commonly occurs at weld decay in the heat affected zone (HAZ).

6. **Selective leaching or dealloying**: occurs as a result of a selective removal of a particular element from an alloy in the electrolyte. This form of corrosion is usually invisible to the naked eye but leads to porosity that reduces alloy strength.

7. **Impact corrosion (erosion corrosion)**: occurs as a result of corrosive fluid moving with a turbulent velocity (erosion) or particles abrading the immersed metal surface (impingement) or gas bubbles imploding near the metal surface (cavitation). The metal surface is removed gradually as dissolved ions or corrosion product into the electrolyte.

8. **Stress corrosion cracking**: occurs as a result of interaction between the metal, environment and mechanical load usually in the form of tensile strain. This form of corrosion is characterized by its distinct intergranular or transgranular branched cracking pattern.

1.4.2 Passivity

According to Uhlig, “a metal is passive if it substantially resists corrosion in a given environment despite a marked thermodynamic tendency to react” [20]. First studied by Kier of England in 1790, he uncovered that the prompt dissolution of silver (Ag) on iron immersed in concentrated HNO₃ was followed by resistance of the underlying iron to further attack. But this chemical resistance of the underlying iron can be disrupted by scratching or touching the iron with *fresh* iron [21]. Schonbein and Faraday furthered this experiment by comparing iron immunity in
concentrated and dilute HNO₃ in the 1830s, until Pourbaix developed electrochemical thermodynamic diagrams in 1960 [22]. Passivity of metallic materials appear at a critical composition usually associated with the tendency to fill the d-band electronic energy states with electrons [23]. Passive films forms as a bilayer structure comprising of defective oxide layer as the primary passive film directly on the metal, and a precipitated outer layer that forms by hydrolysis of cations above the primary passive film as the secondary passive film. These passive films are weakly doped semiconductor in nature, and Mott-Schottky analyses reveal dopant levels of about 10²⁰-10²¹ cm⁻³ which are generally unattainable in bulk oxides [22].

It should be noted that, although passive oxide films greatly reduce the dissolution rates of metals, they are incapable of completely protecting the surfaces from corrosion. Thereby making these passive surfaces susceptible to various forms of localized corrosion which ranges from corrosion fatigue, pitting corrosion, stress corrosion cracking, and crevice corrosion. The breakdown of passivity initiates these corrosion susceptibility that exposes the underlying metal to the environment, and corrosion is propagated as separation of regions into anode and cathode occur [22,24,25].

1.5 Tribo-Corrosion

A combination of two detrimental degradation interaction between tribology and corrosion [26,27] synergistically results in an elevated detrimental process termed “tribo-corrosion” [28]. Tribo-corrosion processes largely accounts for loss of material design capability, significant decrease in performance, efficiency, increase in energy consumption, decrease in safety factor, and decreased lifetime of equipment and components [29]. Passive metals have always been the materials of choice when constructing metallic components that interface with any electrolyte [30]. Passive metal tribo-corrosion is complex because of the interaction of the base metal degradation
and the oxidation of the metal [31]. Metallurgical transformations and work-hardening near the contact surface coupled with surface chemical reactions ultimately influence the tribological phenomena and consequently the wear [26,31,32]. ASTM standard G119 [33] guide for determining the synergism between wear and corrosion can be summarized as:

\[ T = W_0 + C_0 + S \quad \text{(Eq. 1-6)} \]
\[ S = \Delta C_w + \Delta W_c \quad \text{(Eq.1-7)} \]

where

- \( W_0 \) denotes wear rate in the absence of corrosion
- \( C_0 \) denotes corrosion rate in the absence of wear
- \( S \) denotes synergistic component of both corrosion and wear
- \( \Delta C_w \) denotes change in corrosion rate due to wear
- \( \Delta W_c \) denotes change in wear rate due to corrosion

1.5.1 Tribo-Corrosion Environment

Tribo-corrosion is a leading cause of failure and loss in industrial sectors such as mining and mineral processing, marine and offshore, food processing and biomaterials, petroleum and aerospace, nuclear and chemical industries as shown in Figure 1-3. Structural materials that experience tribo-corrosion are passivating alloys such as stainless steel, stellite, inconel, zirconium alloys, P92 steel, refractory metal alloys, graphite, ceramic composite and coatings, ferritic and martensitic alloys, and nickel superalloys [34]. In a tribo-corrosion environment, contact could be two or three body contact with relative sliding either unidirectional or reciprocating motion [35]. Parameters that affect tribo-corrosion can be categorized in 4 categories:

- Material parameters: microstructure, hardness, plasticity, surface roughness, oxide film, and wear debris.
• Electrochemical parameters: active dissolution, applied potential, repassivation kinetics, ohmic resistance, oxide film growth, and valence of electrode-electrolyte couple.

• Mechanical parameters: characteristic motion, normal load, contact geometry, sliding velocity, vibrations, and alignment.

• Electrolyte parameters: (viscosity, pH, temperature, conductivity, and oxygen content.

Figure 1-7: Schematic showing the most common tribo-corrosion environments.

1.6 Thesis Overview

High entropy alloys (HEAs) representing a new paradigm of metal alloying technique with multi-principal element alloys gives better property control over conventional alloying techniques. This advantageous property control allows for alloy systems with exceptional corrosion resistance, wear resistance, predictable phase stability, suppressed intermetallic, and hopefully better tribo-corrosion. These attractive properties make HEAs potential candidates to study, address, and tailor tribo-corrosion resistance of other alloys. Study of HEAs in this dissertation was organized into chapters as follows:
Chapter 1 is centered around providing the necessary background in the key topics that aids understanding of this multidisciplinary study of tribo-corrosion. The background addresses problem, motivation, scope, high entropy alloys, material degradation, tribology, corrosion, and tribo-corrosion.

Chapter 2 is mainly focused on addressing the materials and methods used in the tribo-corrosion study of this research. It also addresses surveying designs and shortcomings of state-of-the-art tribo-corrosion testing setup that aided design of the tribo-corrosion setup used in this research.

Chapter 3 is focused on tribo-corrosion resistance of BCC MoNbTaTiZr biocompatible high entropy alloy. This study compares the tribo-corrosion degradation of BCC MoNbTaTiZr to SS304 at body temperature in simulated body fluid. This chapter explores the corrosion resistance, effect of reciprocating frequency, effect of normal load, and biocompatibility study of BCC MoNbTaTiZr biocompatible high entropy alloy and SS304.

Chapter 4 is centered around tribo-corrosion resistance of FCC CoCrFeMnNi high entropy alloy in the marine environment. This study compares the tribo-corrosion degradation of both additively manufactured and as-cast FCC CoCrFeMnNi in 3.5 wt.% NaCl at room temperature. This chapter explores the effect of build orientation, effect of reciprocating frequency, effect of applied load and effect of countersurface on the tribo-corrosion resistance of both additively manufactured and as-cast CoCrFeMnNi high entropy alloy.

Chapter 5 is focused on the tribo-corrosion resistance of dual phase (L12 and B2) eutectic AlCoCrFeNi2.1 high entropy alloy at elevated temperature. This study compares the tribo-corrosion of dual-phase AlCoCrFeNi2.1 HEA and duplex steel 2205 at room temperature, 50°C and 100°C. This chapter reports the microstructural stability, corrosion resistance, effect of temperature,
dynamic frequency and load, and wear mechanism on the tribo-corrosion resistance of AlCoCrFeNi$_{2.1}$ HEA and duplex steel 2205.

Chapter 6 focuses on the stress-corrosion susceptibility of Al$_{0.1}$CoCrFeNi high entropy alloy. This study looks at the corrosion behavior under uniaxial tensile stress of Al$_{0.1}$CoCrFeNi in 3.5 wt.% NaCl environment. This chapter reports on the stress-corrosion degradation mechanism and stress-accelerated electrochemical measurement of Al$_{0.1}$CoCrFeNi high entropy alloy.

Chapter 7 is the summary chapter, and it covers the tribo-corrosion degradation findings of chapters 3 through 6 with pertinent conclusions to shape future investigations and suggested research pathways.

1.7 References


CHAPTER 2
EXPERIMENTAL AND METHODS

2.1 Introduction

Establishing the crystal structure conformity, phases, and absence of intermetallic in the high entropy alloys and stainless steel studied within the scope of this research required exploiting X-ray diffraction (XRD) characterization techniques. Characterizing the surface morphology, microstructure, elemental distribution, and phase fractions involved the use of advanced microscopy such as scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS). Both destructive and non-destructive electrochemical characterizations such as electrochemical impedance spectroscopy (EIS), Potentiodynamic polarization, Potentiostatic polarization, chronoamperometry and open circuit potential were used to establish the chemical stability of the studied alloys in various electrolytes. Hardness and modulus characterization were also carried out using nano-indentation techniques. Cylindrical tribo-corrosion samples were cut into specification size using wire electric discharge machining (EDM) and computerized numerical cutting machining (CNC). Tribo-corrosion testing was performed with the aid of the tribo-corrosion testing rig (design and setup explained in Chapter 3) mounted atop the universal tribometer coupled with a potentiostat. Post tribo-corrosion analysis required characterizing volume loss for both worn sample surface and the worn counter surface which was achieved with the aid of white light interferometry (WLI). Surface oxides after exposure to tribo-corrosion environment were characterized with X-ray photoelectron spectroscopy (XPS). This chapter addresses HEA fabrication processes in section 2.2, sample preparation 2.3, and pre/post characterization in section 2.4.
2.2 High Entropy Alloy Fabrication

All the as-cast high entropy alloys studied in this research work were fabricated using vacuum arc melting, while the additively manufactured high entropy alloy was fabricated using the laser engineered net shaping (LENS) process.

2.2.1 Vacuum Arc Melting

Melting reactive metals such as titanium and zirconium, and high melting point refractories such as tungsten and molybdenum effectively without contamination requires vacuum technology. Vacuum arc melting of the high entropy alloy system was achieved in the vacuum arc furnace which comprises of a cooper cooled mound at the bottom for faster solidification and a cooled vacuum chamber atop. A consumable tungsten electrode was mounted on an adjustable-fixed electrode holder that is cooled. The multi-principal alloy feedstock charged into the system can be powdered or pelletized, but typically pellet sized to resist compositional change from plasma-arc dispersal during melting. Vacuum was achieved with the aid of a turbo-molecular pump down to \(~10^{-6}\) atm to sustain the plasma formation used to melt the pellets. The melted cast was flipped multiple times to achieve homogeneous melt composition (typically five re-melt flips).

2.2.2 Laser Engineered Net Shaping (LENS)

Direct energy deposition (DED) using the laser engineered net shaping (LENS) additive manufacturing technique was achieved with a 400W Nd:YAG fiber laser melting pre-alloyed powders of 36.8 \(\mu\)m average particle size. This deposition happens in a high purity argon environment (oxygen below \(~10\) ppm) with pre-alloyed powders been fed into the system by four coaxial nozzles while the laser moves in a predefined path according to the stereo-lithography (.STL) file input. Standard low carbon steel plate of 6.35 mm thickness was used as the printing substrate. Standoff between the nozzle and deposition level was kept at 8.89 mm to maintain melt
pool homogeneity. Bi-directional scan strategy was used with a scan direction rotation of 90° for consecutive layers.

2.3 Sample Preparation

After sample fabrication, the as-cast and as-printed high entropy alloys were further processed into cylindrical shapes with 6.35 mm diameter to facilitate mounting into the sample holder of the tribo-corrosion test rig. For high dimensional consistency wire electric discharge machining (EDM) and computerized numerical cutting (CNC) techniques were used to prepare samples to specification shown in Figure 2-1.

![Figure 2-1: Tribo-corrosion sample specification.](image)

2.3.1 Electric discharge machining (EDM)

Kent USA electrical discharge machine (EDM) is a programable CNC machine that uses AC power supply to power its wire-cut technology. Electrical discharge from a brass (Zn-Cu) wire electrode continually erodes the contact surface of the electrically conductive high entropy alloy. The as-cast high entropy alloy is placed in the dielectric tank and affixed to the clamps before backfilling with deionized water. The predesigned g-code from MasterCAM software was loaded into the EDM machine to cut a 6.35 mm diameter cylindrical samples (as shown in Figure 2-1).
Due to the impact of severe lattice distortion on the resistivity and hardness of high entropy alloys, difficulty in cutting the BCC high entropy alloy (MoNbTaTiZr) resulted in using CNC machining.

2.4 Pre/Post Characterization

Most of the equipment and methods used to characterize the samples and surfaces before and after tribo-corrosion are addressed in the subsection

2.4.1 X-Ray Diffraction (XRD)

To quantitatively determine the crystallographic preferred orientations in the polycrystalline high entropy alloys and stainless steels studied, X-ray diffraction (XRD) techniques were used on the Rigaku Ultima III in this study. Based on a working principle of Bragg’s law of diffraction, constructive and destructive interference were used for phase identification and lattice parameter measurements of the alloys studied. Flat buttonlike samples taken from the cylindrical samples were polished down to 0.5 µm to avoid X-ray scattering at the roughly milled surface. Monochromatic incident beam of Cu-Kα with a characteristic radiation of 1.5418 Å was the source of radiation in the Rigaku Ultima III diffractometer. Operating at with a 40kV and 44mA current, the diffractometer has a focus size of 0.4 × 12 mm which acquires data at an angle of 2θ within a range of 20° to 90° at a step size of 0.01°. The diffracted beam intensities are measured using a computer-controlled scintillation counter. This intensities are recorded on the computer software during the scan, peak intensities are observed at the characteristic (h,k,l) depending on the crystal structure of the alloy measured. Characteristic miller indices (h,k,l) peak intensity for body centered cubic occurs at an even sum of h+k+l, while for face centered cubic (h+k+l) results in an all odd or all even miller indices.
2.4.2 Scanning Electron Microscopy (SEM)

For greater depth of field, qualitative elemental analysis and better resolution, the Quanta 200 Field Emission Gun (FEG) environmental scanning electron microscopy (ESEM) achieves magnifications of over 100,000x. The Quanta 200 is capable of operating at 3 vacuum modes of high vacuum, low vacuum and ESEM mode with an accelerating voltage of 200V to 20kV at a vacuum chamber ranging from ~ 6e-4 Pa for high vacuum to 2600 Pa for ESEM. With a tungsten filament that allows for up to 3 nm resolution, the equipped detectors such as Everhardt-Thornley secondary detector (ETD), back scatter electron detector (BSED), SiLi energy dispersive spectrometer detector (EDS), and charge couple detectors (CCD) were used for surface analysis of the alloys pre/post tribo-corrosion to assess grain size distribution, grain orientation, surface defects, microstructural characterization, compositional analysis, wear track characterization, and phase identification and fractions.

2.4.3 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical experiments in a polarized electrochemical cell at fixed voltage whereby a small magnitude perturbation of alternating current (AC) oscillates harmonically in time to create an oscillating current in the system before it dissipates is known as electrochemical impedance spectroscopy (EIS). At a certain amplitude and frequency of applied voltage, the electrochemical cell responds with a particular amplitude of AC at same frequency. Frequency of the applied perturbation ranges across the mHz and kHz scale which produces a relative amplitude having a response and time shift (phase shift) between the input and out signals. The sinusoidal oscillation of the quantities can only be understood by comparing the complex quantities rather than the time-domain quantities. The real and imaginary parts of a complex number are used to represent the relationship between both amplitude and phase shift between the input and output response.
Impedance like resistance in a static system is the ratio of the voltage to current having both magnitude and phase representing resistive and capacitive effects of system. Impedance spectrum as a Nyquist plot simply plots the imaginary component of Impedance against the real component with one data point for every frequency measured. The semi-circular region shows coupling between double-layer capacitance and electrode kinetic effects at frequencies faster than the physical process of diffusion which is observed at lower frequencies. Equivalent circuit are typically used to interpret Nyquist plots by representing the system with resistors and capacitors which yield similar frequency-dependent impedance. EIS was used to determine the effect of temperature, electrolyte and exposed area before and after tribo-corrosion on the alloys studied. EIS was used because of its high precision, simplified current-potential characteristics and measurement over a wide frequency range (10⁻⁴ to 10⁶ Hz). This was achieved using a Gamry Reference-3000 potentiostat with a standard three electrode system having counter electrode as platinum wire, reference electrode as Ag/AgCl and the respective alloys as the working electrode.

2.4.4 Potentiodynamic Polarization

This electrochemical method involves the measurement of the potential evolving from the working electrode (HEA or stainless steel) with respect to a reference electrode (nonpolarizable platinum) at small applied anodic and cathodic current. With reference from ASTM G59 (Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurement), a standard three electrode cell was setup and connected to the Gamry Ref-3000 potentiostat which is capable of varying potential at constant scan rate of 0.1667 mV/s. Accelerated corrosion test from scanning the potential from cathodic to anodic region yields a potential versus current plot. The Tafel slopes of both the anodic and cathodic regions can be evaluated to determine the corrosion rate (CR), while the polarization resistance (R_p) can be identified from the slope of the potential vs current
curve. The corrosion current density \( \text{i}_{\text{corr}} \text{A/cm}^2 \) and corrosion potential \( \text{E}_{\text{corr}} \text{mV} \) are gotten from the intersection of the anodic and cathodic Tafel slopes.

2.4.5 Chronoamperometry

Electrochemical experiments carried out while recording current as a function of time are termed chronoamperometry. By imposing single forward scan potential sweep, the electrode is driven to a condition far from equilibrium to observe the response of the transient signal. If the reaction at the working electrode was assumed to be a faradaic process, the approximate metal loss can be estimated.

2.4.6 Nano-Indentation

In order to characterize the mechanical properties of the alloys studied, depth-sensing Ti-Premier nano-indenter measure the penetration depth as a function of applied load. The resulting load-displacement curve and data is processed using mechanical models such as the Oliver-Pharr method to obtain the hardness and modulus of the alloy been considered.

2.4.7 White Light Interferometry (WLI)

White light interferometry is an optical measurement technique used to acquire surface topography down to the nanometer scale. Surface topography is observed by sequencing images of deformed fringe (interference) patterns resulting from the coherence peak sensing of superposition wave principle. Waves in phase result in constructive interference while waves in out of phase result in destructive interference. Bruker-Alicona Infinite focus WLI was used to characterize the wear track surface after tribo-corrosion to measure the volume of material removed.
2.5 Tribo-Corrosion Experimental

Testing the tribo-corrosion resistance of the various high entropy alloys in this study required designing a reciprocating tribo-corrosion setup that closely duplicates the operating conditions associated with some of the most harsh and critical tribo-corrosion environments. Survey of the prevalent tribo-corrosion environments indicated that reciprocating tribo-corrosion conditions are more ubiquitous than unidirectional tribo-corrosion. Also, more information can be deduced from reciprocating tribo-corrosion when the rate of metal exposure, repassivation, area of metal exposed, and contact stresses which directly influence the tribo-corrosion resistance are considered. These fundamental differences for both techniques dictate the relevance of information obtained when immersed in an electrolyte. These differences account for the motivation of selecting reciprocating tribo-corrosion over unidirectional tribo-corrosion for this study. Investigating the design and weaknesses of the most recently developed reciprocating tribo-corrosion test setups identified critical design parameters and modifications which culminated in the design of the tribo-corrosion test set used in this study. Tribo-corrosion experiments carried out in this study were meticulously designed to closely mimic operating conditions and extreme conditions that exhibit how these high entropy alloys would perform in actual conditions and worse case scenarios.

2.6 Existing Tribo-Corrosion System Drawbacks

Reviewing the 4 tribo-corrosion testing system schematics in Figure 2-2 reveals the following drawbacks. Benea et al. (2015) [1] retrofitted a high frequency reciprocating rig (HFRR) in Figure 2-2(a) with the capabilities to simultaneously measure the electrochemical and tribological properties of the tribo-corrosion process. This retrofitted system was restrained to significantly minimal normal loads and shorter stroke lengths because of the original design of the
HFRR system. Also, the distal arrangement of the electrodes will increase ohmic drop and electrochemical noise which was easily seen on the data presented.

Figure 2-2: State-of-the-art tribo-corrosion testing setup; (a) Retrofitted High Frequency Reciprocating Rig (HFRR) by Benea et al. (2015); (b) Reciprocating tribo-corrosion setup by Pejaković et al. (2018) (c) Tribo-corrosion setup used by Liang et al. (2019); (d) Reciprocating tribo-corrosion set up by Rodrigues et al. (2020)

Figure 2-2(b) shows the schematic of the tribo-corrosion setup used by Pejaković et al. (2018) [2]. The normal load limits were 1 µN-1 N with a stroke length of 1 mm which cannot effectively model actual operating conditions of tribo-corrosion systems. Also, the ceramic ball holder constructed from metallic substrate limits full immersion to avoid galvanic coupling, which was remedied by partial immersion which runs the risk of electrochemical noise as short circuiting develops during the tribo-corrosion test. Figure 2-2(c) shows the schematic of the tribo-corrosion setup used by Liang et al. (2019) [3]. This system builds on the drawbacks from previous design by having improved normal load capabilities and increased stroke length. But electrode proximity and complete immersion still remain active areas of concern. Also, the increased risk of wire
leakage from connectivity of the immersed working electrode to the potentiostat through the electrolyte. More recently, Rodrigues et al. (2020) [4] fixed the normal load, stroke length, and complete immersion drawbacks as seen in Figure 2-2(d). But the electrode proximity and working electrode connectivity to the potentiostat remained active drawbacks. All the tribo-corrosion systems had no temperature control capabilities, which limited simulating elevated temperature tribo-corrosion. The body temperature (37 °C) tribo-corrosion test had a recirculating stream of simulated physiological fluid, which would typically alter electrochemical measurements.

2.7 Design of Tribo-Corrosion Test Setup

An aggregate of the key design rudiment determined from the state-of-the-art tribo-corrosion system drawbacks guided the design of a more suited tribo-corrosion system shown in Figure 2-3. Using an RTEC Instrument Tribometer coupled with a Gamry Ref-3000 potentiostat, the designed tribo-corrosion module was mounted as pictured in Figure 2-3(a). The tribometer uses a load cell capable of imposing normal loads from 1 N - 250 N on the setup. The stroke length can be varied from 500 µm to 7 mm depending on the system been simulated. The tribometer was equipped with a reciprocating stage capable of variable oscillation frequency from 1 Hz to 80 Hz. The tribo-corrosion module can be enclosed in a heating module capable of maintaining the testing environment temperature from room temperature to 500 °C as seen in Figure 2-3(b). But the tribo-corrosion testing temperature was restricted to 120 °C because the inert tribo-corrosion immersion container was constructed from PEEK polymer which has a melting temperature of 250 °C. The PEEK immersion container has a capacity of 115 ml. Figure 2-3(c) shows the electrode orientation at an angle of 30° enabling achieving the proximity of all three electrodes within 10 mm of each other. This reduces the ohmic drop between the electrodes as they are immersed in same electrolyte, and reduces concentration variation for distal electrode. This also increases the
sensitivity and selectivity of measurements recorded within this system, thereby boosting meaningful analysis and reliability of data obtained.

Figure 2-3: Tribo-corrosion setup showing; (a) Entire experimental setup with potentiostat and tribometer coupled; (b) Tribo-corrosion module coupled in the heating module; (c) Tribo-corrosion setup without the heating module; (d) Schematic of the tribo-corrosion setup.
Figure 2-3(d) showing the schematic of the tribo-corrosion module depicts an inverted ball-on-flat configuration. This configuration was chosen firstly to reduce the complexity of wear mechanism from three-body wear to two-body wear by eliminating the bulk of the wear particles dislodged during the tribo-corrosion with the aid of gravity. Secondly, this inverted ball-on-flat configuration remedies the need to use immersed wiring to connect the working electrode to the potentiostat through the electrolyte. This tribo-corrosion setup uses cylindrical 6.35 mm diameter samples as previously prepared, and a button shaped 1 mm by 6.35 mm button was cut out from same cylindrical cross-section successively after every tribo-corrosion test. This prevents large compositional changes between each tribo-corrosion surface exposed in the electrolyte. This tribo-corrosion testing setup solving most of the drawbacks from previous state-of-the-art experiments paves the way to having a unified reciprocating tribo-corrosion testing setup for the tribo-corrosion research community.

2.8 Tribo-Corrosion Experiment

Tribo-corrosion experiments in this study were mostly performed at open circuit potential, potentiodynamic, and chronoamperometric conditions were performed with the tribo-corrosion experimental setup shown in Figure 3-3. A summary of the testing parameters is tabulated in Table 2-2 for all the test conditions simulated in this study. A step-by-step approach to setting up and running the tribo-corrosion experiment is itemized as follow:

- Mount the polished 6.35 mm cylindrical sample into the pin sample holder rigidly and coat the exposed walls of the sample with acrylic to avoid galvanic coupling.
- Mount the ball counter-body in a cold epoxy cast
- Place both ball and sample in their respective holders on the tribometer.
- Fill the PEEK electrolyte container with 100 ml of electrolyte
• Apply desired temperature (if needed) to environment while allowing acclimation time, and measure temperature of the electrolyte to determine stabilization.

• Immerse both ball and sample completely in the corrosive environment.

• Attach the reference and counter electrode and make all connections to the potentiostat and computer.

• Initiate the Gamry software for data acquisition of the open circuit potential with a time set at 5800 s for the total tribo-corrosion test.

• After open circuit potential stabilization of 3600 s, apply appropriate normal load with the tribometer software and initiate active tribo-corrosion testing.

• After 1800 s of active tribo-corrosion, the equipment stops the tribo-corrosion test and separates the contact interface to begin the re-passivation of the worn surface.

• After 300 s of re-passivation, the Gamry data acquisition software stops collecting data.

• Unmount the sample to inspect the tribo-corrosion surface.

• Repeat testing thrice to establish statistical reproducibility and confidence level of data collected.

Table 2-1: Tribo-corrosion experimental test parameters.

<table>
<thead>
<tr>
<th>Test Parameters</th>
<th>Test Variables</th>
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</thead>
<tbody>
<tr>
<td>Normal load (n)</td>
<td>5, 10, 15</td>
</tr>
<tr>
<td>Reciprocating frequency (Hz)</td>
<td>3, 5, 9</td>
</tr>
<tr>
<td>Stroke length (mm)</td>
<td>3.5</td>
</tr>
<tr>
<td>Counter-body (ball)</td>
<td>Al₂O₃, Si₃N₄</td>
</tr>
<tr>
<td>Ball diameter (mm)</td>
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</tr>
<tr>
<td>Electrolyte</td>
<td>3.5 wt.% NaCl, SBF, Deionized water</td>
</tr>
<tr>
<td>Open circuit stabilization time (s)</td>
<td>3600</td>
</tr>
<tr>
<td>Active tribo-corrosion time (s)</td>
<td>1800</td>
</tr>
<tr>
<td>Re-passivation time (s)</td>
<td>300</td>
</tr>
<tr>
<td>Working electrode</td>
<td>High Entropy Alloy/ Stainless steel</td>
</tr>
<tr>
<td>Reference electrode</td>
<td>Ag/AgCl</td>
</tr>
<tr>
<td>Counter electrode</td>
<td>Platinum wire</td>
</tr>
<tr>
<td>Relative humidity</td>
<td>10 - 35%</td>
</tr>
<tr>
<td>Temperature</td>
<td>RT' (22 °C), BT' 37 °C, 50 °C, 100 °C</td>
</tr>
</tbody>
</table>

RT’ = room temperature BT’ = body temperature
2.9 Reference


CHAPTER 3

BIOCOMPATIBLE BCC HIGH ENTROPY ALLOY TRIBO-CORROSION IN SIMULATED PHYSIOLOGICAL ENVIRONMENT*

3.1 Abstract

Bioimplants are susceptible to simultaneous wear and corrosion degradation in an aggressive physiological environment. High entropy alloys with equimolar proportion of constituent elements represent a unique alloy design strategy for developing bioimplants due to their attractive mechanical properties, superior wear, and corrosion resistance. In this study, the tribo-corrosion behavior of an equiatomic MoNbTaTiZr high entropy alloy consisting of all biocompatible elements was evaluated and compared with 304 stainless steel as a benchmark. The high entropy alloy showed low wear rate and friction coefficient as well as quick and stable passivation in simulated body fluid. Increase from room temperature to body temperature showed excellent temperature assisted passivity and nobler surface layer of the high entropy alloy resulting in four times better wear resistance compared to stainless steel. Polygonal proliferating epithelium sheets of stem and osteoblast cells displayed migratory behavior while several filopodia extensions on the cell indicated early osteogenic commitment and cell adhesion on the high entropy alloy. These results pave the way for utilizing the unique combination of tribo-corrosion resistance, excellent mechanical properties, and biocompatibility of MoNbTaTiZr high entropy alloy to develop bioimplants with improved service life and low risk of implant induced cytotoxicity in the host body.

3.2 Introduction

Bioimplant degradation in the physiological environment is exacerbated by synergistic corrosion and wear known as tribo-corrosion, which results in irreversible deterioration over time and ultimate failure of the implant [1–3]. Furthermore, increasing from room temperature to body temperature (37 °C) further accelerates the degradation process after surgical implantation [4]. Tribo-corrosion in bioimplants commonly leads to material debris which may cause severe pain [5], inflammatory response [6], and locking of joints among other complications. Thus, the guide to selection of appropriate implant material is governed by its biocompatibility, mechanical and chemical stability [7]. Metals possess excellent mechanical properties such as high strength and toughness, making them suitable for load-bearing orthopedic applications such as hip, knee or shoulder prosthesis [8]. This makes metals the majority of currently used bioimplant materials, each alloy with their own functionality, unique benefits, and limitations. Passivity of the adherent oxide that forms on the surface of metallic bioimplants is critical in maintaining its chemical stability and consequently its biocompatibility [9]. The breakdown of this passive layer and the ability to re-passivate rapidly usually determines the susceptibility to failure in an aggressive physiological environment.

Ti alloys, Co-Cr alloys, and stainless steels are the most used metals for orthopedic applications because they satisfy these prerequisites in the short term [10]. However, steels and Ti-alloys are prone to localized corrosion in the physiological environment after prolonged exposure. Abrasion of these metals due to movement and contact stresses also leads to accumulation of metal debris in soft tissues of the body. In contrast, refractory metals and alloys show excellent wear resistance, osseointegration, biocompatibility and significantly reduced metal release rates compared to the conventional biomedical alloys [10–13]. Even though the density of
refractory metals is high, the faster wound healing characteristics and use in small dimensions for surgical implantation has attracted recent interest in these alloy systems [14,15]. High entropy alloys (HEAs), with multiple elements in (near) equimolar proportions, offer a new alloy design strategy in structural applications because of excellent corrosion resistance, high strength and hardness, outstanding wear resistance, and good structural stability [16–20]. HEAs are very attractive in the context of bioimplants due to their biocompatibility and superior surface properties attributed to the four core effects of solid solution strengthening, sluggish diffusion, severe-lattice distortion and cocktail effects [17,21]. Development of high entropy alloys with desirable surface properties to resist degradation in the physiological environment will open up a new paradigm of specifically tailored metallic implants with significantly longer service life to overcome the limitations of presently used Ti-alloys and stainless steels.

Here, the tribo-corrosion behavior of a MoNbTaTiZr high entropy alloy was evaluated at room and body temperature. The alloy was chosen because of the biocompatibility of constituent elements and its good wear and corrosion resistance [22,23]. While wear and corrosion behavior of several high entropy alloys have been reported, their synergistic effect is not well understood particularly in the physiological environment. Tribo-corrosion response of coatings and bulk materials have been evaluated [24–27], but there are no reports for high entropy alloys. The tribo-corrosion response of MoNbTaTiZr in simulated body fluid showed excellent passivity and wear response compared with 304 stainless steel. Viability, adhesion, and morphology studies using stem cells and osteoblast cell cultures showed desirable biocompatibility for the MoNbTaTiZr high entropy alloy.

3.3 Materials and Methods

3.3.1 Alloy Synthesis
Five-component equiatomic MoNbTaTiZr alloy ingot was synthesized by vacuum/argon arc melting using high purity elements (>99.9%). Both MoNbTaTiZr and 304 stainless steel (SS304) as-cast samples were cut into cylinders of diameter 6.34 mm with a length of 35 mm using wire electrical discharge machine (EDM) from Kent (USA). The cylinder flat bottom was polished up to 1200-grit abrasive paper and then polished on 1 µm diamond suspension to reveal a mirror surface finish before cleaning in acetone. The cylindrical length of the samples (cylinder walls) was sealed using acrylic nail polish to prevent exposure to simulated body fluid electrolyte. Al₂O₃ ball with 6.35 mm diameter was selected as the counter-body for testing after identifying relevant Hertzian contact stresses. Nano-indentation hardness and modulus of the samples were obtained using TI-Premier Tribo-indenter (Bruker, Minneapolis, MN, USA). The sample was loaded to 1 N in 5 s and held for 2 s, followed by unloading in 5 s. The hardness was obtained from the load-displacement plot using the Oliver and Pharr method [28].

3.3.2 Tribo-Corrosion Test

Tribo-corrosion experiments were performed using a linear reciprocating inverted ball-on-flat setup as shown schematically in Figure 1. The reciprocating tribo-corrosion setup was mounted on a RTEC Instruments tribometer (RTEC San Jose, CA, USA) coupled with a Gamry potentiostat (Gamry Warminster, PA, USA). 6.35 mm diameter alumina ball was held in a resin cast at the bottom with the top of the ball aligned with the center of the polished alloy cylinder. Both sample and counter-body were held for 3600 s in simulated body fluid (SBF) to achieve open circuit potential (OCP) stability. The red terminal in Figure 3-1 indicates the working electrode (cylindrical MoNbTaTiZr/SS304 sample), the blue terminal indicates the counter electrode (platinum wire), and the green terminal indicates the reference electrode (Ag/AgCl electrode). All the electrodes were within 10 mm of each other as stipulated by ASTM standard for correction of
electrolyte resistance in electrochemical tests (STP 1056) to reduce ohmic overpotential [29]. 1000 ml batch of SBF was prepared at 37 °C to mimic the human physiological environment [30]. 100 ml of SBF was measured out of the batch for each tribo-corrosion experiment to immerse the contacting surface, Al2O3 counter-body and all electrodes in SBF and prevent electrolyte contamination. Remaining batch was continually mixed at 25 Hz frequency and 37 °C temperature throughout the period of the experiment. The effect of load on alloy tribo-corrosion performance was measured at body temperature with 5 Hz frequency at 3.5 mm stroke length while varying the load to 5 N, 10 N and 15 N for 1800 s of wear after 3600 s of open circuit potential stability. The effect of frequency on alloy tribo-corrosion performance was studied by varying the reciprocation frequency from 3 Hz to 9 Hz while keeping the temperature and load fixed at 37 °C and 5 N, respectively. After the wear test, the sample was left in the SBF solution to measure the open circuit potential for another 300 s for surface re-passivation. Three tribo-corrosion tests were performed for each condition to obtain the average and standard deviation in wear volume loss and wear rate.

3.3.3 Microstructure Characterization and Surface Analysis

Microstructural characterization was performed using scanning electron microscopy (SEM) in FEI Quanta-ESEM 200™ (Thermo Fisher Scientific, Hillsboro, Oregon, USA). Chemical composition and structure of the alloys were determined using energy dispersive spectroscopy (EDS) and x-ray diffraction (XRD) analysis in Rigaku Ultima III (Rigaku, Tokyo, Japan), respectively. The surface topography of the wear scars was examined using white light interferometry. Wear volume loss was calculated from image analysis of 3D optical micrographs using Gwyddion software. The wear tracks were further analyzed in SEM to identify corrosion products, material removal mechanism, cell adhesion, and morphology.
3.3.4  Biocompatibility and Cell Proliferation Tests Using Human Stem Cells and Osteoblasts

Human Wharton's jelly derived mesenchymal stem cells (HW-MSCs) were purchased from HiMedia (India) and cultured in α-minimum essential medium (α-MEM) + 10% fetal bovine serum (FBS) and 1% penicillin/streptomycin (Complete medium) (Gibco/Life Technologies, USA). These cultures were maintained at 37 °C in 5% CO2 with 95% relative humidity. The media was changed every third day. The cells were grown up to 80%–90% confluence and trypsinized with 0.25% Trypsin/ Ethylene-diamine-tetra-acetic acid (EDTA) (1X) (Gibco/Life Technologies, USA) and used for cell studies. The experiments were carried out in between 2-5 passage numbers. Samples were sterilized by washing with 70% ethanol and kept under UV light overnight and rinsed three times with phosphate-buffered saline (PBS) (1X). Then, samples were placed in sterile 48 well plates, and complete media was added till immersion of samples. Later, samples were incubated in a cell culture incubator for 48 h and media was collected for MTT assay and Fluorescence imaging. Pre-osteoblasts (ATCC CRL-2593) were used for direct cell culture assays. The cells were maintained in Minimum Essential Medium Alpha (MEM-α) supplemented with 10% fetal bovine serum (FBS) and 1% penicillin and streptomycin at 37 °C and 5% carbon dioxide (CO2) in a cell incubator. The samples were sterilized by cleaning them with acetone, water, and ethanol, followed by sterilization in 70% isopropyl alcohol (IPA) for 1 hr and then under UV light for an additional 1 hr. A density of 25,000 cells/25 mm² was seeded onto sterilized samples and cultured for 2 days. After 2 days, the cell medium was removed and the cells were fixed in 4% paraformaldehyde and 2% glutaraldehyde solution in phosphate-buffered saline (PBS) for 1 hr. Following this, the cells were dehydrated in successive ethanol washes of 30%, 50%, 70%, 90%, and 100% for 10 mins each and then in hexamethyldisilazane (HDMS) for an additional 10 mins.
The cells were allowed to air dry for characterization using scanning electron microscopy and fluorescence microscopy.

![Schematic representation and image of the tribo-corrosion experimental setup.](image)

**Figure 3-1:** Schematic representation and image of the tribo-corrosion experimental setup. The electrochemical cell was setup with both reference and counter electrodes within 10 mm of the tribo-corrosion contact surface immersed in 100 ml simulated body fluid in an inert container. The working electrode was fixed while the Al2O3 counter surface was moved with a reciprocating stroke length of 3.5 mm.

3.4 Results and Discussion

3.4.1 Structural, Mechanical and Electrochemical Characterization

X-ray diffraction (XRD) analysis for the MoNbTaTiZr high entropy alloy is shown in Figure 3-2(a) indicating a body centered cubic (BCC) major solid-solution phase and small fraction of a BCC minor solid-solution phase with no intermetallic or secondary phase formation. Scanning electron microscope (SEM) image and corresponding elemental distribution obtained using energy dispersive spectroscopy (EDS) showed stabilization of the solid solution phases due to high configurational entropy of mixing of the constituent elements (Appendix Figure A1). Nanoindentation load-displacement curves at a peak load of 1000 mN in Figure 3-2(b) showed smaller indentation depth for MoNbTaTiZr (green curve) compared with SS304 (red curve), which is
attributed to the higher hardness or strength of the high entropy alloy. Measured modulus and hardness values for MoNbTaTiZr HEA were 164.06 ± 1.70 GPa and 6.45 ± 0.06 GPa, respectively. In comparison, SS304 modulus and hardness values were 233.05 ± 1.65 GPa and 2.36 ± 0.05 GPa, respectively. Thus, the HEA showed about three-fold higher hardness or strength and 30% lower modulus compared to SS304 stainless steel. Passivation characteristics of the two alloys were evaluated in terms of open circuit potential (OCP) prior to the tribo-corrosion test as shown in Figure 3-2(c) at room temperature and body temperature in simulated body fluid (SBF). MoNbTaTiZr reached faster stability at both temperatures compared to the stainless steel. For SS304, the room temperature open circuit potential was slightly nobler than body temperature while the reverse trend was observed in case of MoNbTaTiZr. This indicates that the slight temperature increase accelerated the passivation kinetics in MoNbTaTiZr and helped in the formation of a nobler surface layer. Potentiodynamic polarization characteristics of both the alloys at body temperature were evaluated after open circuit potential stabilization for 3600 s in SBF as shown in Figure 3-2(d). MoNbTaTiZr showed a corrosion current density of ~ 3.1 × 10^{-7} A/cm² while SS304 showed almost an order of magnitude higher corrosion current density of ~ 1.7 × 10^{-6} A/cm². This clearly demonstrates better corrosion resistance of the high entropy alloy compared to SS304 in simulated body fluid. Further, the HEA showed a wide passive region with no indication of pitting while stainless steel showed a low pitting potential and continuous increase in current density indicating poor surface stability. After 3600 s of OCP stabilization, impedance measurements were conducted at both room and body temperatures for fundamental understanding of the underlying passivation mechanisms. Figure 3-2(e) shows the Nyquist plots for MoNbTaTiZr and SS304 in SBF. The impedance spectra were analyzed in terms of an equivalent circuit shown in Figure 3-2(f) to best fit the experimental data.
Figure 3-2: (a) X-Ray diffraction pattern showing BCC major phase and BCC minor phase with no indication of intermetallic or secondary phase formation in MoNbTaTiZr high entropy alloy; (b) nano-indentation load-displacement curves for MoNbTaTiZr and SS304 measured using 1000 mN peak load with 5 s loading time, 2 s holding time and 5 s unloading; (c) open circuit potential for 3600 s prior to tribo-corrosion experiment at room temperature (RT) and body temperature (37 °C) in SBF indicating faster stability of HEA at both temperatures compared to SS304; (d) Potentiodynamic polarization curve for MoNbTaTiZr and SS304 in SBF at body temperature (37 °C); (e) Nyquist plot at room temperature (RT) and body temperature (37 °C) for MoNbTaTiZr HEA and SS304 in SBF showing larger semicircular radius and superior polarization resistance for the high entropy alloy at both temperatures; (f) equivalent circuit to model the Nyquist plot for the two alloys.
The equivalent circuit consisted of a reference electrode (R.E), solution resistance \((R_{\text{soln}})\), passive layer resistance \((R_{\text{pass}})\), passive layer capacitance \((C_{\text{pass}})\), pore resistance or passive layer stability \((R_{\text{pore}})\), passive layer constant phase element \((C_p)\), polarization resistance \((R_p)\), electrochemical reaction constant phase element \((C_p)\), and the working electrode (W.E). The Nyquist curves for MoNbTaTiZr at room temperature and body temperature showed a larger semicircular radius compared to SS304 indicating higher polarization resistance [31]. The values obtained for the different circuit elements for MoNbTaTiZr and SS304 at the two temperatures are summarized in Appendix Table A1. The polarization resistance \((R_p)\) for MoNbTaTiZr was about an order of magnitude larger than SS304 at both the temperatures indicating superior corrosion resistance for the high entropy alloy in simulated body fluid in agreement with the potentiodynamic polarization results (Figure 3-2(d)). The passive layer resistance \((R_{\text{pass}})\) for MoNbTaTiZr increased by a factor of four going from room temperature to body temperature indicating that the high entropy alloy undergoes temperature assisted passivation. In contrast, \(R_{\text{pass}}\) for SS304 decreased by a factor of ten going from room temperature to body temperature indicating deterioration of passivity with temperature increase for the stainless steel. The surface stability for MoNbTaTiZr and SS304 was quantified by \(C_{\text{pass}}\), with a higher value indicating better dielectric characteristics of the passive layer. The value of \(C_{\text{pass}}\) increased by three times for MoNbTaTiZr going from room temperature to body temperature while that for SS304 decreased with temperature increase. Overall, MoNbTaTiZr showed higher polarization resistance, increased passive layer resistance, temperature assisted passivation with greater stability compared to SS304 at room temperature as well as body temperature.

3.4.2 Tribo-Corrosion Behavior at Body Temperature

The wear rate, material removal, re-passivation mechanism, implant stability quotient
(ISQ), and extended exposure biocompatibility of an implant are dictated by a combination of load and host activity level which may be simulated by frequency of reciprocation. Therefore, tribo-corrosion resistance was evaluated as a function of variation in frequency and load for both MoNbTaTiZr HEA and SS304.

3.4.2.1 Effect of Frequency

The open circuit potential (OCP) and coefficient of friction (COF) for the two alloys during tribo-corrosion test at different frequencies are shown in Figure 3-3. Figures 3-3(a) and 3-3(b) show the coefficient of friction and open circuit potential, respectively, for MoNbTaTiZr against alumina counter body at normal load of 5 N in SBF at body temperature and at frequencies of 3 Hz, 5 Hz, and 9 Hz. The COF depends on a combination of friction characteristics of the surface and counter body, contact mechanics, and surface changes as wear progresses. The COF measured in tribo-corrosion is typically lower than dry wear due to hydrodynamic lubrication in the liquid environment. The average COF at 3 Hz frequency for the HEA was $\sim 0.04 \pm 0.01$. Frequency of 3 Hz is close to the average active joint movement in normal human body and COF value as low as 0.04 would be ideal for joint prosthesis [32]. Increase in frequency to 5 Hz resulted in higher COF with an average value of $\sim 0.23 \pm 0.04$ (Figure 3-3(a)) which correlated with a sharp drop in OCP towards less-noble values (Figure 3-3(b)). This indicates rapid removal of the surface passivation layer and not enough time for re-passivation at 5 Hz frequency. Further increase in frequency to 9 Hz resulted in a drop in COF to relatively lower values with an average of $\sim 0.08 \pm 0.01$. This indicates that the increased reciprocating tangential force at 9 Hz may have altered the contact mechanics and shear force to create reduced contact pressure insufficient in wearing the surface between cycles. A small drop in OCP potential at the beginning of tribo-corrosion test was seen for 3 Hz and 9 Hz while a relatively large drop towards less noble values was seen for 5 Hz (Figure
The smaller change in OCP value for 3 Hz frequency may be attributed to the surface passivation layer regenerating at a rate faster than material removal while that at 9 Hz may be attributed to the reduced wear area with increased reciprocating tangential forces. In contrast, the high value of COF and sharp drop in OCP towards less noble values at 5 Hz indicates limited surface re-passivation for this intermediate frequency. The coefficient of friction and open circuit potential for SS304 as a function of frequency are shown in Figure 3-3(c) and 3-3(d), respectively. The average COF at 3 Hz frequency for SS304 was ~ 0.15 ± 0.03 (more than three times higher compared to MoNbTaTiZr at 3 Hz). At 5 Hz frequency, a higher average COF of ~ 0.27 ± 0.05, comparable to that for MoNbTaTiZr, indicates rapid removal of the surface passivation layer and not enough time for re-passivation. At 9 Hz frequency, average value of COF dropped to ~ 0.11 ± 0.03 demonstrating a trend similar to MoNbTaTiZr. The drop in OCP potential at the initiation of tribo-corrosion test was large for all three frequencies in the case of SS304 indicating that its surface oxide was less protective compared to MoNbTaTiZr. In addition, the OCP continually decreased towards less-noble values for SS304 with increasing time (Figure 3-3(d)) indicating inferior tribo-corrosion resistance as wear area continually increased compared to MoNbTaTiZr (Figure 3-3(b)). The variation in COF was significantly smaller while OCP fluctuations were larger for MoNbTaTiZr compared to SS304 at all three frequencies indicating continuous surface re-passivation in case of MoNbTaTiZr. Overall, the high entropy alloy showed nobler OCP and lower COF compared to the stainless steel in SBF at body temperature for the 3 Hz, 5 Hz, and 9 Hz frequencies studied. The wear volume loss and wear rate for the two alloys at 37 °C as a function of frequency are shown in Figure 3-3(e) and 3-3(f), respectively. MoNbTaTiZr showed about five times lower wear volume loss and wear rate compared with SS304 for the three frequencies studied, which is attributed to the higher hardness and better passivation characteristics of the high
entropy alloy. The wear rate for both MoNbTaTiZr and SS304 showed an increase going from 3 Hz to 5 Hz followed by a decrease going from 5 Hz to 9 Hz, which is consistent with the trend in COF and OCP.

Figure 3-3: (a) Coefficient of friction (COF) and (b) open circuit potential (E_{ocp}) as a function of frequency in SBF at 37 °C and 5 N load for MoNbTaTiZr; (c) COF and (d) OCP as a function of frequency in SBF at 37 °C and 5 N load for SS304; (e) wear volume loss for MoNbTaTiZr (solid black line) versus SS304 (dashed red line) as a function of frequency at a load of 5 N; (f) wear rate for MoNbTaTiZr (solid black line) versus SS304 (dashed red line) as a function of frequency at a load of 5 N showing increase of wear rate from 3 Hz to 5 Hz and a decrease from 5 Hz to 9 Hz for both alloys.
3.4.2.2 Effect of Applied Load

In a coupled tribological contact, wear increases with increase in applied load according to Archard’s relationship [33–35]. Joint prostheses and other body implants experience complex loading during service. Thus, studying the effect of applied load during tribo-corrosion is critical. Figures 3-4(a) and 3-4(b) show the coefficient of friction (COF) and open circuit potential (OCP) during tribo-corrosion of MoNbTaTiZr HEA and alumina counter body as a function of load (5 N, 10 N, and 15 N) at 5 Hz frequency and 37 °C in SBF. The COF versus time plot for MoNbTaTiZr in Figure 3-4(a) shows that the average COF value for 5 N, 10 N and 15 N was around 0.23, 0.14, and 0.13, respectively. Reduction in COF with increasing load has been reported in tribo-corrosion of stainless steel [36] and during chemical mechanical planarization (CMP) [37,38]. In this study, we attribute reduction in COF to flattening of contact asperity with increasing load. The corresponding open circuit potential for MoNbTaTiZr is shown in Figure 3-4(b) with an initial drop at the onset of wear followed by continuous passivation-depassivation spikes for 1800 s until the end of wear and final surface re-passivation for about 300 s. The open circuit potential showed a slight drop towards less-noble values with increase in load, which may be explained by the increasing contact area. The coefficient of friction and open circuit potential for SS304 are shown in Figure 3-4(c) and 3-4(d), respectively. The average COF at 5 N load for SS304 was 0.27 ± 0.04 (which is comparable to MoNbTaTiZr at 5 N). Lower average COF value of ~ 0.14 was measured for the higher loads of 10 N and 15 N, which is similar to the trend observed for MoNbTaTiZr. Decrease in OCP towards less noble values as wear progressed indicates wider area breakdown of the surface passive layer in the corrosive environment [39,40]. The fluctuation in OCP value for MoNbTaTiZr was greater than that observed for SS304 possibly due to the continuous re-passivation in case of the high entropy alloy. MoNbTaTiZr re-passivated in about 100 s, which
was three times faster compared to SS304 re-passivating over 300 s (Figure 3-4(b) and 3-4(d)). Overall, MoNbTaTiZr HEA showed nobler OCP and lower COF compared to SS304 for the 5 N, 10 N and 15 N loads studied.

Figure 3-4: (a) COF and (b) OCP as a function of load at a frequency of 5 Hz for MoNbTaTiZr; (c) COF and (d) OCP as a function of load for SS304; (e) wear volume loss for MoNbTaTiZr (solid black line) and SS304 (dashed red line) as a function of load; (f) wear rate for MoNbTaTiZr (solid black line) and SS304 (dashed red line) as a function of load at 5 Hz frequency indicating lower wear rate for HEA compared to SS304.
Wear volume loss for the two alloys is shown in Figure 3-4(e), with MoNbTaTiZr showing lower values compared to stainless steel for all three loads. The slope of volume loss versus load was steeper for MoNbTaTiZr (black solid line) with increase in load from 5 N to 10 N compared to that from 10 N to 15 N. This difference in slope may be attributed to reduced friction with increasing load [24,41,42]. For ductile SS304 (red dashed line in Figure 3-4(e)), there was no significant change in slope for the wear volume loss due to more plastic deformation compared to MoNbTaTiZr. Figure 3-4(f) shows that the wear rate for MoNbTaTiZr (solid black line) was lower compared to SS304 (dashed red line) at the three tested loads of 5 N, 10 N and 15 N. MoNbTaTiZr showed an initial increase in wear rate going from 5 N to 10 N from higher friction followed by a decrease in wear rate going from 10 N to 15 N due to reduced friction. SS304 showed a monotonic decrease in wear rate going from 5 N to 15 N due to work-hardening of the ductile alloy and reduced friction with increase in normal load.

3.4.2.3 Tribo-Corrosion Mechanism

Tribo-corrosion mechanism for the high entropy alloy and stainless steel showed a complex dependence on normal load, frequency of reciprocation, and temperature as established in the previous sections. This interplay of load and frequency creates a dynamic loading environment similar to the hip-joint prosthesis as shown schematically in Figure 3-5. Detailed SEM characterization of the wear tracks were done for fundamental understanding of the differences in tribo-corrosion mechanism for MoNbTaTiZr versus SS304 in SBF at body temperature as shown in Figure 3-5. Increasing load for the MoNbTaTiZr from 5 N to 15 N at 5 Hz frequency increased surface deformation area and abrasive ridges as shown in Figure 3-5 (a) and 3-5(b). This led to increase in the width of the wear track with increased load (shown schematically in Figure 3-5(c)) albeit with reduced coefficient of friction and open circuit potential discussed in section 3.2.2 for
MoNbTaTiZr. In contrast to the high entropy alloy, SS304 showed much more severe deformation as load was increased from 5 N to 15 N (Figures 3-5(d) and 3-5(e)) with increased surface deformation and surface micro-cracks at higher loads as schematically illustrated in Figure 3-5(f). This explains the trends observed in wear volume loss and wear rate for the two alloys. Increasing the frequency of reciprocation from 3 Hz to 9 Hz at 5 N load directly impacted the normal load distribution on the surface, the tangential shear force, and the re-passivation kinetics for MoNbTaTiZr alloy as shown in Figures 3-5(g) and 3-5(h). The effect of frequency on passivation layer removal and increase in wear track width is shown schematically in Figure 3-5(i). In contrast, SS304 showed relatively similar width of wear track going from 3 Hz to 9 Hz as shown in Figure 3-5(j) and 3-5(k) but some crack formation normal to the reciprocation direction as shown schematically in Figure 3-5(l). SS304 showed mild to severe ridges which developed into micro-cracks at high frequencies indicative of contact fatigue (Figures 3-5(j) and 3-5(k)).

The dominant material removal mechanism for both SS304 and MoNbTaTiZr was abrasive wear as seen in the SEM micrographs in Figure 3-5, characterized by parallel ridges in the sliding direction. Abrasive wear resulted in a smooth appearance for the wear scar with no delamination or debris pullout, particularly for higher frequencies due to a “polishing effect”. Apatite formation was seen on the surface of MoNbTaTiZr in the form of black spots as marked on Figures 5(a), 3-5(b), 3-5(g) and 3-5(h). This was confirmed by spot EDS as shown in Figure A2 with the composition summarized in Table A2 (see appendix). This indicates osteoinductivity in case of the high entropy alloy and supports its superiority and suitability as a bioimplant material compared to SS304 which showed corrosion products (rust) on the surface (Figures 3-5(d), 3-5(e), 3-5(j) and 3-5(k)). The edges of the wear tracks for MoNbTaTiZr did not show any pile up consistent with abrasive wear mechanism for alloys with low ductility [39].
Figure 3-5: SEM micrographs of wear tracks and schematics to illustrate the effect of load and frequency on wear behavior of MoNbTaTiZr and SS304 with alumina ball counter body in simulated body fluid at body temperature: (a) SEM micrograph of MoNbTaTiZr wear track at 15 N load and 5 Hz frequency; (b) SEM micrograph of MoNbTaTiZr wear track at 5 N load and 5 Hz frequency; (c) schematic showing the effect of load (5 N, 10 N and 15 N) for MoNbTaTiZr; (d) SEM micrograph of SS304 wear track at 5 N load and 5 Hz frequency; (e) SEM micrograph of SS304 wear track at 15 N load and 5 Hz frequency; (f) schematic showing the effect of load (5 N, 10 N and 15 N) for SS304; (g) SEM micrograph of MoNbTaTiZr wear track at 3 Hz frequency and 5 N load; (h) SEM micrograph of MoNbTaTiZr wear track at 9 Hz frequency and 5 N load; (i) schematic showing the effect of frequency (3 Hz, 5 Hz, and 9 Hz) for MoNbTaTiZr; (j) SEM micrograph of SS304 wear track at 9 Hz frequency and 5 N load; (k) SEM micrograph of SS304 wear track at 3 Hz frequency and 5 N load; (l) schematic showing the effect of frequency (3 Hz, 5 Hz, and 9 Hz) for SS304. The green double-sided arrow shows the direction of reciprocation during the tribo-corrosion test.
The edges of the wear tracks for SS304 showed pile up, which became larger with increased normal load. For SS304, micro-cracks perpendicular to the sliding direction were seen at increased loads and frequencies (Figures 3-5(e) and 3-5(j)) likely from the cyclic tensile and compressive forces of reciprocation causing contact fatigue as well as localized corrosion in SBF. The wear tracks for MoNbTaTiZr showed no detectable cracks, which may be attributed to its higher strength or hardness that retarded crack initiation and better surface passivation characteristics discussed in section 3.1. The average density of MoNbTaTiZr alloy at room temperature was measured to be 9.31 g/cm³, which is significantly higher than the human bone density of 3.88 g/cm³. However, the mechanical properties and superior tribo-corrosion resistance of MoNbTaTiZr makes it attractive for use as thin cranioplasty plates, compression hip screws, and pedicle screws which are small in size but subjected to simultaneous corrosion and wear in the physiological environment. Superior surface properties and potentially faster healing time has attracted recent interest in refractory alloys such as Molybdenum-Rhenium (MoRe) as bioimplants \[14,15,43\].

3.4.3 Biocompatibility Study of MoNbTaTiZr HEA using Human Stem Cells and Osteoblast Cells

Biocompatibility studies using stem cells and osteoblast cells for MoNbTaTiZr high entropy alloy and SS304 stainless steel are shown in Figure 3-6. Figures 3-6(a) and 3-6(b) show the reflected light and fluorescence microscopy images, respectively, of stem cells cultured on a control surface (tissue culture polystyrene (TCPS)). The corresponding images for MoNbTaTiZr HEA are shown in Figures 3-6(c) and 3-6(d). Average cell viability was determined by assessing attachment of cells to the alloy surface and quantification of attached cells using image analysis after fluorescence microscopy. Figure 3-6(b) shows stem cells on control TCPS surface using fluorescence microscopy in a 48-well cell culture plate and Figure 3-6(d) shows the corresponding
image for MoNbTaTiZr HEA. In the control stem cell study in Figure 3-6(b), cell coverage and spread over the surface was designated as 100% in the red control bar in Figure 3-6(e). In Figure 3-6(d), the coverage and spread of stem cells on the MoNbTaTiZr HEA surface was similar to the control sample with optical density of around 89% (green bar in Figure 3-6(e)). With average cell viability of ~89% compared to control TCPS, MoNbTaTiZr showed significant biocompatibility with respect to stem cells. These values are comparable to cytocompatibility tests for Ti-Nb [44] and TiNbTaZrO [45]. Extended polygon-like morphology of the cells seen for the high entropy alloy are indicative of good adhesion and spreading. The cells on the MoNbTaTiZr surface were larger in size compared to the cells on the control sample at same magnification (Figure 3-6(b) versus 3-6(d)). This may be a result of stable oxide passivation for the HEA supporting better cell adhesion and growth. Common sterilization techniques strip native oxide from the surface of metallic implants that may affect the level of protein secreted by osteoblast cells grown on these surfaces, notably osteocalcin and phosphatase [46]. Thus, MoNbTaTiZr showing more stable native oxide is expected to maintain its passivation layer after the pre-implantation sterilization of the surface and thereby support protein secretion for osteoblast growth and integration. To investigate osteoblast-compatibility, osteoblast cell culture study was carried out on the high entropy alloy and SS304 stainless steel. Figure 3-6(f) through 3-6(m) show the SEM micrographs and florescence micrographs of pre-osteoblast cells attached to the surface of SS304 and MoNbTaTiZr alloy. Osteoblasts cells on the surface and around the wear track were elongated with long finger-like projections emanating from the cell body as seen in Figure 3-6(f) and high magnification images in Figures 3-6(g) and 3-6(h). These cells also showed migratory behavior but relatively less filopodia extensions at the cell periphery and smaller cell sizes compared to the high entropy alloy at similar magnification.
Figure 3-6: Stem cells biocompatibility study on control sample with (a) reflected light microscopy and (b) fluorescence microscopy; stem cells biocompatibility study on MoNbTaTiZr HEA surface with (c) reflected light microscopy and (d) fluorescence microscopy; (e) average viability of stem cells measured from cell-culture study; (f), (g), (h), SEM micrographs of osteoblast cell culture on SS304 and (i) fluorescence microscopy of osteoblast cell culture on SS304; (j), (k), (l) SEM micrographs of osteoblast cell culture on MoNbTaTiZr HEA and (m) fluorescence microscopy of osteoblast cell culture on MoNbTaTiZr HEA.

Figure 3-6(i) shows the viable cell bloom on the stainless-steel surface. On the MoNbTaTiZr HEA, osteoblast cells formed a monolayer on the surface with elongated and spindle shaped morphologies as seen at higher magnification in Figures 3-6(j) and 3-6(k). Numerous long cytoplasmic extensions formed a network in contact with adjacent cells around the surface of the biocompatible HEA and within the wear track area as seen in Figure 3-6(j). At higher magnification in Figure 3-6(l), the cells displayed migratory behavior with leading and trailing
edges and several filopodia extensions as evident on the periphery of the cell. This indicates bundles of actin-binding proteins that promotes osteoblast cell adhesion typically seen for biocompatible materials [47]. Figure 3-6(m) shows the florescence microscopy image of the attached osteoblast cells and further confirms the biocompatible nature of MoNbTaTiZr. Overall, MoNbTaTiZr HEA surface supported cell attachment by filopodia extensions and the elongated cell morphologies are indicative of early osteogenic commitment [48].

3.5 Conclusion

In summary, the tribo-corrosion behavior of Mo-Nb-Ta-Ti-Zr high entropy alloy consisting of all biocompatible elements was studied in simulated body fluid at body temperature. Results were compared with 304 stainless steel under identical conditions. The following conclusions may be drawn from the obtained results:

- MoNbTaTiZr showed about three-fold higher hardness and strength and 30% lower modulus compared to SS304.
- MoNbTaTiZr achieved stability before and during wear test at a rate faster than observed in SS304, which was attributed to its excellent temperature assisted passivity at body temperature.
- Friction coefficient as low as 0.04 at 3Hz reciprocating frequency and wear rate of about $10^{-8}$ mm$^3$/Nm was achieved for MoNbTaTiZr, and this was attributed to surface passivation and contact mechanics.
- Wear mechanism for MoNbTaTiZr was primarily abrasive in nature, while extensive abrasion and micro-cracking resulted in a wear rate that was three times higher for SS304 compared to the MoNbTaTiZr high entropy alloy.
- MoNbTaTiZr HEA showed good cell viability in biocompatibility tests using stem cells. Several filopodia extensions with polygon-like morphology indicated excellent cell adhesion, growth, and biocompatibility for tests using osteoblast cells.

3.6 References


CHAPTER 4
ADDITIVELY MANUFACTURED FCC HIGH ENTROPY ALLOY TRIBOCORROSION IN MARINE ENVIRONMENT

4.1 Abstract

Additively manufactured parts for specialty applications in marine environment and dimension critical bioimplants are susceptible to simultaneous wear and corrosion. High entropy alloys with multiple principal elements have attracted widespread interest in a range of structural applications because of their excellent surface degradation resistance. Here, the tribo-corrosion response of laser engineered net shaped CoCrFeMnNi high entropy alloy was evaluated in 3.5 wt.% NaCl solution at room temperature. The tribo-corrosion resistance for the additively manufactured alloy was found to be significantly better than its as-cast counterpart which was attributed to the refined microstructure and homogeneous elemental distribution. Additively manufactured CoCrFeMnNi showed lower wear rate, regenerative passivation, less wear volume loss, and nobler corrosion potential during tribo-corrosion test compared to its as-cast equivalent. These results highlight the potential of utilizing additive manufacturing of high entropy alloys for use in extreme environments that require a combination of tribo-corrosion resistance, mechanical durability, extended service life, and low dimensional tolerance.

4.2 Introduction

Directed energy deposition (DED) has proven to be a versatile additive manufacturing approach, especially for complex geometries, with enhanced microstructural features that are difficult to obtain by conventional casting techniques [1,2]. This advantage provides alternatives to traditional subtractive manufacturing which are subject to property variations, processing defects, residual stresses and undesirable phase transformation. The desirable attributes of DED
over other additive manufacturing techniques include rapid deposition time, microstructural refinement, and ability for multi-component alloying to obtain functionally graded and layered materials for tailored applications [3][4,5].

High entropy alloys (HEAs), a new paradigm in alloy design strategy, with multiple principal elements demonstrate excellent mechanical, corrosion, wear, and creep properties while suppressing deleterious intermetallic formation [6,7]. In recent years, there are numerous reports on different HEA systems for a wide range of structural applications [7–9]. However, one of the major limitations in the development of these multi-component alloys using conventional vacuum arc melting technique is the severe elemental segregation [10,11]. Typically, elements with higher melting temperature segregate in the dendritic regions while elements with lower melting temperature are rejected into inter-dendritic regions resulting in non-homogeneous as-cast microstructure [12,13]. Homogenization of the as-cast HEA microstructure often involves tedious post-processing in the form of high temperature vacuum annealing for several hours to days [14,15]. In contrast, the inherent localized heating and rapid cooling (> $10^3$ K/sec) during additive manufacturing (AM) can suppress elemental segregation and phase separation. Further, net shaping using AM allows tuning of HEA properties by location for creating functionally graded materials (FGM) [16–18]. Thus, additive manufacturing can be highly efficient for the synthesis of multi-component alloy systems with minimum elemental heterogeneity or controlled heterogeneity [4,19,20]. There are several reports on additive manufacturing of HEAs including powder bed [21], LENS (laser engineered net shaping) [19], and SLM (Selective Laser Melting) [22]. However, there are very few reports and limited understanding of the degradation mechanism in additively manufactured high entropy alloys in terms of their wear, corrosion and tribo-corrosion behavior. Tribo-corrosion involves the synergistic combination of wear and corrosion.
resulting in accelerated material loss [23–26]. Tribo-corrosion is commonly seen in several applications including bio-implants, advanced energy conversion systems, hydraulic systems, nuclear power plants, chemical reactors, marine industries, heat exchanger, and deep-sea oil drilling rigs [27]. The presence of liquid media during wear involves complex interface phenomena of passivation, delamination and re-passivation. There are numerous studies on wear and corrosion behavior of high entropy alloys. However, to the best of the authors knowledge, there are no reports so far on the tribo-corrosion resistance of additively manufactured HEAs.

In the current study, tribo-corrosion behavior of an additively manufactured CoCrFeMnNi HEA was studied as a model alloy system and compared with its counterpart synthesized by conventional casting. Equimolar CoCrFeMnNi alloy is one of the most widely studied HEAs owing to its simple face centered cubic (FCC) structure, superior corrosion resistance and excellent mechanical properties. There are numerous reports on corrosion, wear, creep, microstructure, mechanical behavior, and processability of CoCrFeMnNi alloy [22,28–31]. Here, the reciprocating tribo-corrosion behavior of laser engineered net shaped CoCrFeMnNi high entropy alloy was studied in simulated marine environment.

4.3 Materials and Methods

4.3.1 Laser Engineered Net Shaping (LENS)

CoCrFeMnNi plates with dimensions of 29 mm × 10 mm × 10 mm were additively manufactured using laser engineered net shaping (LENS) on an OPTOMEC LENS 450 equipped with a 400W Nd:YAG fiber laser. Pre-alloyed CoCrFeMnNi powder with average particle size of 36.8 μm was delivered from the powder feeder to the melt pool through four co-axial nozzles. A standard low carbon steel plate with a thickness of 6.35 mm was used as the printing substrate. The standoff distance between nozzles and workpiece was kept at 8.89 mm to maintain deposition
efficiency and stability. The processing chamber was filled with high purity argon and the oxygen content was maintained below 10 ppm during printing. The processing parameters were optimized to obtain a fully dense part and are summarized in Table 4-1. Bi-directional scan strategy was used and the scan direction was rotated 90° for consecutive layers. In parallel, equimolar CoCrFeMnNi alloy ingot was synthesized by vacuum/argon arc melting using high purity elements (>99.9%). The as-cast CoCrFeMnNi was flipped and re-melted 5 times for homogeneity.

Table 4-1: LENS processing parameters for additively manufactured CoCrFeMnNi HEA

<table>
<thead>
<tr>
<th>Laser powder/W</th>
<th>Scan speed/(mm/min)</th>
<th>Z increment/mm</th>
<th>Hatching distance/mm</th>
<th>Powder feed rate/(g/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>762</td>
<td>0.35</td>
<td>0.4</td>
<td>6.5</td>
</tr>
</tbody>
</table>

4.3.2 Surface Analysis and Microstructure Characterization

Surface morphology, microstructural characterization and chemical composition of AM and as-cast CoCrFeMnNi HEAs were obtained using scanning electron microscopy (SEM, FEI Quanta-ESEM 200™) and energy dispersive spectroscopy (EDS). X-ray diffraction analysis using Rigaku Ultima III with 1.54 Å Cu-Kα radiation was performed to determine the crystal structure of the alloys. Electron backscattered diffraction (EBSD) analysis was performed to determine the grain size distribution and orientation. Surface topography and volume loss from tribo-corrosion was determined using non-contact white light interferometry (WLI) analysis using RTEC Instrument optical profilometer and analyzed with Gwyddion (version 2.55) software.

4.3.3 Tribo-Corrosion Test

Tribo-corrosion experiments were carried out on a reciprocating ball-on-flat tribometer (RTEC Instruments, Universal tribometer, San Jose, CA, USA) coupled with a potentiostat (Gamry Instruments, Ref-3000, Warminster, PA, USA). A schematic representation of the setup
and test-configuration is shown in Figure 4-1(a).

Figure 4-1: (a) Schematic representation of tribo-corrosion test setup showing the three-electrode cell (Ag/AgCl reference electrode, CoCrFeMnNi working electrode and Platinum wire counter electrode) coupled with the flat-on-ball reciprocating contact (Al₂O₃ and working electrode) in 3.5 wt.% NaCl environment; (b) Tribo-corrosion setup mounted on the universal tribometer; (c) As-built additively manufactured CoCrFeMnNi plates (build direction indicated by arrow) from which the tribo-corrosion cylindrical samples were cut out using electric discharge machining (EDM) to use as working electrode with dimensions of 6.35 mm diameter and 25 mm height.

Electrochemical cell for the tribo-corrosion test consisted of the HEA as working electrode (WE), platinum wire as a counter electrode (CE), and Ag/AgCl as a reference electrode (RE). All the electrodes were placed within proximity of 10 mm to increase sensitivity and reduce the ohmic drop as shown in Figure 4-1(b). The working electrode was cut from the as-built and as-cast plates of CoCrFeMnNi using electric discharge machining as shown in Figure 4-1(c). Alumina (Al₂O₃) counter-body was used in the form of a ball of radius 6.35 mm at different normal loads of 5 N, 10 N, and 15 N. The test frequency was varied over a wide range of 3Hz, 5Hz, and 9 Hz. In addition, tribo-testing was performed using silicon-nitride (Si₃N₄) counter-body to understand the effect of different interfaces in a tribo-system. Tribo-corrosion tests were carried out systematically in the following steps:

- Open circuit potential (OCP) for 3600 s at room temperature
• Reciprocating sliding initiated under OCP conditions for 1800 s and changes in coefficient of friction (COF) and OCP were continuously monitored

• After reciprocating sliding for 1800 s, OCP was stabilized for nearly 200 s

• All tests were repeated three times to determine reproducibility and obtain standard deviation for the measured data

4.4 Results and Discussion

4.4.1 Microstructural Characterization of LENS CoCrFeMnNi

The microstructure of laser engineered net shaped CoCrFeMnNi alloy is shown in Figure 4-2. Near full density was achieved in the LENS sample under optimized processing conditions. In Figure 2(a), some micropores (indicated by arrows) of size less than 10 µm were seen for the LENS sample due to evaporation of the constituent elements [30] and gas entrapment from melt pool turbulence [32]. Figure 4-2(b) shows the inverse pole figure (IPF) map of the LENS sample along the build direction with columnar grains of average size ~ 36.4 ± 23.4 µm. Microstructure of the as-cast CoCrFeMnNi alloy is shown in Figure 4-2(c), characterized by parallel columnar grains. The AM melt pool was semi-circular in shape with a diameter to depth ratio of 5:2 and overlap rate of 60% with the adjacent pool as shown in Figure 4-2(d). Elongated columnar grains growing towards the melt pool center were formed close to the vicinity of the melt pool boundary due to large thermal gradient (G) and varying solidification rate (R) as shown in Figure 4-2(e). Sub-grain cell structures with an average size of ~ 2-3 µm was observed within the melt pool (Figure 4-2(f)). In the longitudinal section of the sub-grain cells (Figure 4-2(g)), secondary columnar grains indicated side instabilities of the solid-liquid interface perpendicular to the primary growth direction with the transition of sub-grains from cellular to columnar growth [33]. High magnification EBSD analysis was performed to investigate fine sub-grain cells within the primary grains. The inverse pole figure and kernel average misorientation (KAM) maps are shown
in Figure 4-2(h) and 4-2(i), respectively. The IPF map clearly shows local misorientations in the interior of the grains (sub-grain cells). The local misorientation between sub-grain cell structures along the arrow shown in the IPF image was ~ 1.25 degrees as shown in the misorientation plot (inset of Figure 4-2(h)). Furthermore, many fine cell-like features in the size range of 2-3 µm were observed in the KAM map (Figure 4-2(i)) attributed to arrays of dislocations within the primary grains [34,35].

Figure 4-2: (a) SEM image of laser engineered net shaped CoCrFeMnNi alloy showing near full density microstructure with some micropores indicated by arrows; (b) EBSD IPF map along build direction showing columnar grains; (c) SEM image of as-cast CoCrFeMnNi alloy with columnar grains; (d) Optical microscopy (OM) image of the longitudinal section of the LENS sample; (e) magnified image of the square box area in (d) showing melt pool, columnar grains, and sub-grain cells; (f) SEM image showing transverse section of the sub-grain cellular structures; (g) SEM image showing the longitudinal section of the sub-grain cellular structures; (h) high magnification IPF image showing local misorientation within primary grains with the inset showing misorientation profile along the arrow; (i) corresponding kernel average misorientation (KAM) map indicating dislocations arrays along the cell boundaries.
4.4.2 Tribo-Corrosion at Room Temperature

4.4.2.1 Effect of Build Orientation on Tribo-Corrosion of AM CoCrFeMnNi

Anisotropy in mechanical behavior arising from the additive manufacturing microstructure [22], grain refinement, and grain-size distribution directly affect the wear behavior and consequently tribo-corrosion resistance. Three specific orientations investigated in this study are marked in Figure 4-3(a), including the build direction (BD), perpendicular to build direction (90° to BD), and 45° to BD. Tribo-corrosion of additively manufactured CoCrFeMnNi HEA was determined in these three directions. The results for coefficient of friction (COF) and OCP are shown in Figure 4-3(b) and 4-3(c), respectively. The OCP curves in Figure 4-3(c) were characterized by a sharp drop to more negative values as wear began followed by continuous change in OCP for the wear test duration and finally a jump to nobler value at the end of test indicating surface re-passivation. The sharp drops in OCP (Figure 4-3(c)) corresponded exactly to the spikes in coefficient of friction as shown previously for Ti6Al4V [36,37]. As OCP moved towards nobler values for the three orientations, both COF and wear rate decreased. The wear rate and wear volume loss are shown in Figure 4-3(d) and 4-3(e) for the three build orientations. The wear volume loss and wear rate along 45° to BD was found to be lowest at $9.28 \times 10^{-4}$ mm$^3$ and $5.9 \times 10^{-6}$ mm$^3$/Nm, respectively. Thus, 45° to BD showed better tribo-corrosion resistance with overall lowest COF, low wear rate and wear volume loss of the three directions studied. Therefore, the orientation of 45° to build direction was used for the remaining studies and compared with equiaxed as-cast specimen.
Figure 4-3: Effect of build orientation on tribo-corrosion behavior of additively manufactured CoCrFeMnNi at 5 Hz frequency and 5 N load in 3.5 wt.% NaCl at room temperature; (a) schematic representation of the three orientations studied; (b) coefficient of friction and (c) open circuit potential measurement in the three directions studied; (d) wear volume loss for the three build orientations; (e) wear rate for the three build orientations.
4.4.2.2 Effect of Reciprocating Frequency on Tribo-Corrosion of CoCrFeMnNi

The stability and regeneration of protective passive layer determines the rate of tribo-corrosion. To evaluate the stability of the protective passive layer for both AM and as-cast CoCrFeMnNi, 5 N normal load was applied at varying reciprocating frequency of 3 Hz, 5 Hz and 9 Hz. The tribo-corrosion results comparing both AM and as-cast samples are shown in Figure 4. The coefficient of friction along with corresponding OCP for AM CoCrFeMnNi are shown in Figure 4-4(a) and 4-4(b) respectively. At 3 Hz frequency (red plot), COF increased progressively as wear proceeded for 1800 s likely due to increase in surface roughness and wear area. There were minor fluctuations in COF and OCP at 3 Hz frequency which indicated that the tribo-layer remained intact during the test. However, at both 5 Hz and 9 Hz (blue and black plots, respectively), there was a drop in COF corresponding exactly with OCP jump towards nobler value. The peak observed in COF around 500 s confirmed the transition of wear from protective passive layer to the substrate. As wear proceeded beyond the dip with a new running-in-period, COF at both 5 Hz and 9 Hz continually decreased to a lower value as OCP increased to nobler values indicating less friction and better corrosion potential. The COF decreased in the order of 3 Hz (COF ~ 0.21 ± 0.04) > 5 Hz (COF ~ 0.15 ± 0.05) > 9 Hz (COF ~ 0.10 ± 0.03). The decrease in COF with increase in frequency may be attributed to decreasing surface interaction time with increasing reciprocating tangential force from 3 Hz to 9Hz. At 3 Hz frequency, a sharp drop in OCP at the beginning of the wear was observed (Figure 4-4(b)) without any sharp fluctuation till the end of wear before re-passivating for about 200 s. The absence of a clear and pronounced hump for 3 Hz may be attributed to enough time between cycle allowing worn protective passive layer to regenerate. For both 5 Hz and 9 Hz, the characteristic pronounced hump was seen after ~ 500 s of active tribo-corrosion, and both curves undulated and moved towards nobler OCP as wear
proceeded till the end. The hump in OCP at 9 Hz (black plot) began earlier and climb faster toward
the noble OCP as compared to 5 Hz frequency. This is in line with the fact that 9 Hz frequency
moving almost double the oscillation of 5 Hz, thus the protective passive layer was worn at a rate
faster than 5 Hz and creating a hump earlier. The evolution of nobler OCP as wear proceeded for
both 5 Hz and 9 Hz may be attributed to regeneration of the passive layer. The effect of frequency
on tribo-corrosion of as-cast CoCrFeMnNi is shown in Figure 4-4(c) and 4-4(d) for COF and OCP,
respectively. Similar trends were observed for all three curves at 3 Hz, 5 Hz and 9 Hz as AM
CoCrFeMnNi, having a dip at COF plots and corresponding hump at OCP curves at the same time.
The trend in average COF was 3 Hz (~ 0.17 ± 0.10) > 5 Hz (~ 0.15 ± 0.11) > 9 Hz (~ 0.12 ± 0.08),
identical to the trend observed for AM CoCrFeMnNi. For the OCP at 3 Hz, 5 Hz and 9 Hz
frequencies shown in Figure 4-4(d), the 3 Hz curve (red plot) showed a hump between 250 s and
710 s while it was in the range of 50 s to 230 s for 5 Hz and 9 Hz which were similar in behavior
to AM CoCrFeMnNi. The hump size was attributed to the stability, thickness and regeneration of
the protective passive layer in the region experiencing tribo-corrosion. To compare the total
material removal and rate of removal, Figure 4-4(e) and 4-4(f) shows a comparison of the wear
volume loss and wear rate of both AM and as-cast CoCrFeMnNi as a function of frequency. In
Figure 4-4(e), wear volume loss of the AM CoCrFeMnNi (black plot) shows a positive slope going
from 3 Hz to 5 Hz with a change in slope steepness going from 5 Hz to 9 Hz. This may be attributed
to the doubling of sliding distance 18.9 m to 31.5 m to 56.7 m going from 3 Hz to 5 Hz and 5 Hz
to 9 Hz, respectively. The wear volume loss of the as-cast CoCrFeMnNi (red plot) shows similar
trend to the AM specimen with a positive but steeper slope going from 3 Hz to 5 Hz, and similar
slope going from 5 Hz to 9 Hz indicating that material removal is at a higher rate than observed in
AM CoCrFeMnNi.
Figure 4-4: (a) Coefficient of friction (COF) and (b) open circuit potential (E_{ocp}) as a function of frequency in 3.5 wt.% NaCl at 5 N load for AM CoCrFeMnNi; (c) COF and (d) OCP as a function of frequency in 3.5 wt.% NaCl at 5 N load for as-cast CoCrFeMnNi; (e) wear volume loss for AM CoCrFeMnNi (solid black line) and as-cast CoCrFeMnNi (solid red line) as a function of frequency at a load of 5 N; (f) wear rate versus frequency for AM CoCrFeMnNi (dashed black line) and as-cast CoCrFeMnNi (dashed red line) at a load of 5 N showing increase of wear rate with frequency for both alloys and lower wear volume loss and wear rate of AM processed alloy.
The overall material removal for AM CoCrFeMnNi was about five times lower than as-cast CoCrFeMnNi at all frequencies. In Figure 4-4(f), the wear rate for the AM specimen (black dashed plot) showed similar trend to the wear volume loss, but a change in wear rate was observed for the as-cast specimen (red dashed plot) from 3 Hz to 5 Hz as compared to the range of 5 Hz to 9 Hz. This may be attributed to the changing contact mechanics and decreased interaction time with frequency as cited earlier. Overall, the wear rate of AM CoCrFeMnNi was about 4 times lower when compared with as-cast CoCrFeMnNi wear rate.

4.4.2.3 Effect of Applied Load on Tribo-Corrosion of CoCrFeMnNi

Most tribo-corrosion applications are prone to dynamic loading which leads to varying wear rate, fatigue, stress, reduced load bearing capacity and ultimately altered tribo-corrosion behavior. To evaluate the tribo-corrosion behavior of both AM and as-cast CoCrFeMnNi in a dynamic loading environment, 5 Hz reciprocating frequency was applied at varying normal loads of 5 N, 10 N and 15 N. The effect of load on tribo-corrosion behavior of AM and as-cast samples are shown in Figure 4-5. The coefficient of friction of AM CoCrFeMnNi Figure 4-5(a) shows a simultaneous dip in COF for 5 N, 10 N, and 15 N at exactly same time where OCP jumped towards nobler values as seen previously. All three curves showed a distinct transition from protective passive layer into substrate tribo-corrosion at different periods in a peculiar trend of 10 N > 15 N > 5 N in agreement with the OCP curve trends. As wear proceeds beyond the dip, COF of all three curves continually decreased to a lower value as OCP shift to nobler values indicating less friction, better corrosion potential and ultimately better stabilizing tribo-corrosion behavior. The average COF decreased in the order of 5 N (~ 0.20 ± 0.04) > 15 N (~ 0.19 ± 0.10)> 10 N (~ 0.18 ± 0.12). In Figure 4-5(b) at 5 N load (red plot), OCP of AM CoCrFeMnNi decreased at the beginning of wear and gradually moved upwards to form the characteristic hump.
Figure 4-5: (a) Coefficient of friction (COF) and (b) open circuit potential (E$_{ocp}$) as a function of load in 3.5 wt.% NaCl at 5 Hz frequency for AM CoCrFeMnNi; (c) COF and (d) OCP as a function of load in 3.5 wt.% NaCl at 5 Hz frequency for as-cast CoCrFeMnNi; (e) wear volume loss as a function of load for AM CoCrFeMnNi (solid black line) and as-cast CoCrFeMnNi (solid red line) at a frequency of 5 Hz; (f) wear rate as a function of load at a frequency of 5 Hz for AM CoCrFeMnNi (dashed black line) versus as-cast CoCrFeMnNi (dashed red line) indicating increase of wear volume loss and wear rate with increase in load for both samples with an exception for as-cast alloy showing reduction in wear rate at higher load.
After the hump, it gradually trended upwards to nobler OCP as wear proceeded until the end. OCP curves at both 10 N and 15 N (blue and black plots, respectively) followed similar trend with the hump starting earlier than 5 N. The variation in the hump size and span followed the order of 5 N > 15 N > 10 N may be attributed to work hardening near the surface as a result of doubling and tripling of the loading [35]. The COF and OCP simultaneously recorded for the as-cast CoCrFeMnNi are shown in Figure 4-5(c) and 4-5(d), respectively. At 5 N (red plot), COF decreased initially during the run-in period followed by rising to higher COF values as wear proceeds till the end. At both 10 N and 15 N, the curves were relatively smoother with overlapping COF indicating work-hardening and less passive layer regeneration to make two harder surfaces rubbing against each other. Thus, giving rise to a constant and low COF for the as-cast CoCrFeMnNi than AM CoCrFeMnNi. The trend in average COF was in the order of 5 N (~ 0.15 ± 0.12) > 10 N (~ 0.12 ± 0.05) > 15 N (0.11 ± 0.06), which is different to the trend observed for AM CoCrFeMnNi. OCP at 5 N, 10 N and 15 N of as-cast CoCrFeMnNi shown in Figure 4-5(d) had no pronounced hump as compared to the hump observed for AM CoCrFeMnNi. At a higher load of 15 N, the OCP shift towards more negative values may be due to increasing wear area in the tribo-corrosion environment. This was in line with the observed COF reducing as wear progressed because contact mechanics and stresses were modified as contact area was increased. This supports the effect of frequency study which hypothesized that the protective passive layer on the as-cast CoCrFeMnNi was not stable and virtually non-existent at higher loads. The wear volume loss for both the as-cast and AM CoCrFeMnNi shown in Figure 4-5(e) increased monotonically with increase in load but with different rate going from 5 N to 10 N and 10 N to 15 N as contact area and contact stresses are modified with increase in load. The overall material removal for the AM CoCrFeMnNi was about 6 times less as compared to as-cast CoCrFeMnNi at
all studied loads. In Figure 4-5(f), the wear rate for AM CoCrFeMnNi (black dashed plot) followed similar trend to the wear volume loss with a positive slope. The as-cast CoCrFeMnNi (red dashed line) showed an increase in wear rate from 5 N to 10 N, but a reduced wear rate going from 10 N to 15 N. This change in wear rate can be attributed to altered contact stress and contact mechanics under increased load without the protective oxide shielding the load at 15 N (as confirmed by change in wear mechanism from SEM). AM CoCrFeMnNi did not show a reduction going from 10 N to 15 N because the protective oxide remains to shield the load at 15 N (as confirmed by similar wear mechanism at 10 N to 15 N in SEM). The overall wear rate for AM CoCrFeMnNi was about 5 times less as compared to as-cast specimen at all loads. Both alloys showed higher material removal and wear rate as a function of load than frequency.

4.4.2.4 Effect of Counter Surface on Tribo-Corrosion of CoCrFeMnNi

The chemistry of contacting surfaces has already been established to affect the tribo-corrosion behavior of materials [40]. The protective passive layer on the AM CoCrFeMnNi plays a significant role in its tribo-corrosion behavior as seen in previous sections. Investigating the stability and regenerative properties of this protective passive layer by changing the contacting surface is critical to tribo-corrosion. To evaluate the effect of counter surface on the tribo-corrosion behavior of AM CoCrFeMnNi, 5 Hz reciprocating frequency was applied at normal load of 5 N against both Al₂O₃ (alumina) and Si₃N₄ (silicon nitride) counter surface balls. In Figure 4-6(a), the coefficient of friction and OCP of AM CoCrFeMnNi simultaneously recorded against Al₂O₃ and Si₃N₄ counter surface are shown. For Si₃N₄ (red plot), after about 250 s a transition point was reached indicating that the wear has moved from passive protective layer to underlying AM CoCrFeMnNi. COF against Si₃N₄ gradually increased and stabilized until the end of wear without undulating as compared to the Al₂O₃ curve which confirmed no regeneration in the protective
passive layer after been worn. For COF against Al$_2$O$_3$ (blue plot) curve, a dip corresponding to same time for the hump in the OCP curve was observed between 180 s to 500 s before a transition from protective passive layer to underlying AM CoCrFeMnNi. The time to wear out the regenerative passive layer against both counter surfaces indicated that AM CoCrFeMnNi against Al$_2$O$_3$ may have half of the wear rate as compared to Si$_3$N$_4$. As wear against Al$_2$O$_3$ proceeded, the COF undulated because the surface chemistry was continually changing to regenerate the worn oxide layer, thereby forming patches of oxides which resulted in altering the wear profile and consequently the COF. Eventually, the COF descended and stabilized to approximately same value as the Si$_3$N$_4$ curve. The OCP behavior of both counter surfaces against AM CoCrFeMnNi in Figure 4-6(b) showed an initial drop in OCP for both counter surfaces as wear started. For Si$_3$N$_4$ (red plot), OCP undulated continuously with amplitudes differing as much as 90 mV while keeping a relatively horizontal slope till the end of wear before re-passivating. This horizontal slope indicated that the absence of oxygen ions from the counter surface limited regeneration of stable oxide tribo-layer. Whereas for Al$_2$O$_3$ (blue plot), OCP climbed towards nobler values to form a hump between 100 s to 500 s, after which wear proceeded with the OCP curve shifting towards nobler values till the end of wear before re-passivation. This behavior was indicative that oxygen ions from the counter surface enhanced the regeneration and stability of the protective passive layer as wear proceeded. The wear depth profile of both Si$_3$N$_4$ and Al$_2$O$_3$ against AM CoCrFeMnNi is shown in Figure 4-6(c) with Si$_3$N$_4$ having almost double wear depth (~ -2.0 µm) than Al$_2$O$_3$ (~ -0.9 µm). The wider and deeper profile of the Si$_3$N$_4$ in comparison to narrow profile of the Al$_2$O$_3$ was consistent with their COF curves showing absence of re-passivation for the former and continuous re-passivation for the latter. The wear volume loss and wear rate for both counter surfaces are shown in Figure 4-6(d). Al$_2$O$_3$ against AM CoCrFeMnNi showed almost half the wear volume
loss and wear rate as compared to Si$_3$N$_4$ against AM CoCrFeMnNi.

Figure 4-6: (a) Coefficient of friction and (b) open circuit potential measurement of AM CoCrFeMnNi against Al$_2$O$_3$ and Si$_3$N$_4$ counter surfaces in 3.5wt.% NaCl with 5 N load and 5 Hz frequency for 1800 s of wear; (c) wear depth profile for AM CoCrFeMnNi against Si$_3$N$_4$ (red plot) and Al$_2$O$_3$ (blue plot) indicating deeper wear track against Si$_3$N$_4$; (d) wear volume loss and wear rate of both Si$_3$N$_4$ and Al$_2$O$_3$ against AM CoCrFeMnNi showing lower wear volume loss and wear rate of AM processed alloy against Al$_2$O$_3$ as compared to Si$_3$N$_4$.

4.4.3 AM and As-Cast CoCrFeMnNi Chronoamperometry and Wear Mechanism

4.4.3.1 Wear Mechanism of AM and As-cast CoCrFeMnNi

The surface morphologies of AM and as cast CoCrFeMnNi HEA after reciprocating tribo-corrosion are shown in Figure 4-7. All surface morphologies resultant from the effect of frequency were indicative of an abrasive material removal mechanism. But interestingly, a change of wear...
mechanism was observed as the load varied from 5 N to 15 N. Reciprocating sliding wear morphology of AM CoCrFeMnNi at 5 N in Figure 4-7(a), showed a typical abrasive wear with mild groves and deformation ridges parallel to the sliding direction with oxide pullout sections.

Figure 4-7: SEM micrograph showing wear track morphology as a function of load in 3.5 wt.% NaCl at 5 Hz frequency for 1800 s of wear for AM CoCrFeMnNi at (a) 5 N, (b) 10 N, and (c) 15 N load; wear track morphology of as-cast CoCrFeMnNi at (d) 5 N, (e) 10 N, and (f) 15 N load indicating stable and regenerative protective oxide formed on the AM CoCrFeMnNi resulting in its better tribo-corrosion behavior. Yellow arrows indicate reciprocating sliding direction.

For 10 N in Figure 4-7(b), a smoother profile with mild oxidative wear was seen because of increased normal load causing a polishing effect with smaller groves and ridges along with dark spots representing oxide pullout of micro sections of the wear morphology. For 15 N in Figure 4-7(c), similar abrasive wear with mild ridges, polishing and no presence of microcracks at high loads was observed. All three morphologies supported stable and regenerative protective passive layer formed on the AM CoCrFeMnNi leading to reduced wear mechanism and ultimately its better tribo-corrosion behavior. For the tribo-corrosion mechanism of as-cast alloy at 5 N and 5
Hz shown in Figure 4-7(d), abrasive wear morphology similar to the AM CoCrFeMnNi with mild ridges parallel to the sliding direction and micro oxide pullout sections were observed. At 10 N in Figure 4-7(e), oxidative wear morphology with larger sections of oxide pullout was observed as the combination of high load and corrosive environment deteriorated the protective passive layer and exposed the substrate. At 15 N in Figure 4-7(f), severe deformation ridges and a complete deterioration of the surface oxide led to severe abrasive wear indicating its poor tribo-corrosion behavior at high loads. Thus, AM showed better tribo-corrosion behavior and stable regenerative oxide than as-cast CoCrFeMnNi under varying loads, supporting the results of OCP and COF in the previous sections.

4.4.3.2 Chronoamperometry of AM and As-cast CoCrFeMnNi during Tribo-corrosion

Wear at dynamic potential gives a quantitative electrochemical contribution but lacks actual service operation representation, but most importantly may indicate passive layer stability at the working electrode (AM and as-cast CoCrFeMnNi). To evaluate the stability of the passive layer during tribo-corrosion, single forward potential sweep of 0.1667 mV/s was applied to the electrochemical cell while recording the resulting current. The chronoamperometry behavior of AM and as-cast CoCrFeMnNi at 5 Hz reciprocating frequency with an applied normal load of 5 N against Al₂O₃ (alumina) counter surface is shown in Figure 4-8. Using the chronoamperometry of AM CoCrFeMnNi without wear as the baseline, both AM and as-cast CoCrFeMnNi with wear showed a marked difference in the stability of the protective passive layer. Regular chronoamperometry of the AM CoCrFeMnNi without wear (corrosion only) in Figure 4-8(a) (blue plot) represented a baseline performance of protective passive layer stability in 3.5 wt.% NaCl. The single forward potential scan showed that the passive oxide remained intact for 1800 s without breakdown by anodic dissolution. For the chronoamperometry of AM CoCrFeMnNi during tribo-
corrosion (black plot) in Figure 4-8(a), as wear proceeds with the single forward potential sweep from cathodic to anodic region the current density measured remains flat line at zero. With less than $0.02 \times 10^{-4}$ A/cm$^2$ spike in current density at 1250 s, the current density starts to spike to higher values in a positive slope until it reaches $2.5 \times 10^{-4}$ A/cm$^2$ at the end of wear. This behavior indicated the stability of the protective amorphous oxide that passivated the surface of the AM CoCrFeMnNi. The spike in current density that returned to about zero represented the regenerative properties of this protective amorphous oxide. The absence of previously observed OCP hump and COF dip is because potential was controlled in the chronoamperometry experiment. For the chronoamperometry of as-cast CoCrFeMnNi during tribo-corrosion (red plot) in Figure 4-8(a), as wear proceeded with the single forward potential sweep from cathodic to anodic region, the measured current density was only flat line at zero for $\sim 30$ s before it rose to $\sim 1 \times 10^{-4}$ A/cm$^2$. This indicated that the protective passive layer had already failed as early as 30 s. At $\sim 375$ s, the current density increased undulating until $\sim 1000$ s where the slope became steeper and noisier till the end of wear with a final current density of $25 \times 10^{-4}$ A/cm$^2$. The final current density was about 10 times higher as compared with AM CoCrFeMnNi indicating the breakdown of the protective amorphous oxide from $\sim 30$ s till the end of wear without regeneration or stability after 1000 s. This behavior of the protective passive layer was consistent with the reports from previous sections. From Cottrell’s Eq. 4-1 [41] the change in electrode surface area ($A$) based on well-known redox reactions may be measured:

$$i t = \frac{n F A C_0 D_0^{0.5}}{r^{0.5} t^{0.5}}$$  (Eq. 4-1)

where, $i$ is current density, $t$ denotes time, $n$ is the stoichiometric number of the electrons transferred in the redox reaction, $F$ is the Faraday’s constant (96,485 C/equivalent), $A$ denotes the electrode surface area (cm), and $C$ and $D$ are the concentration (mol cm$^{-1}$) and diffusion constant.
of the electroactive species (cm s\(^{-1}\)) in the solution, respectively. Although calculating the electrode surface area using equation (1) is beyond the scope of this study, it supported the idea that increase in current density with time directly increased the surface area exposed. Therefore, the susceptibility of as-cast CoCrFeMnNi to tribo-corrosion has increased significantly with an increased electrode surface area exposed as wear proceeded.

Figure 4-8: (a) Chronoamperometry, and (b) coefficient of friction versus time during tribo-corrosion of AM and as-cast CoCrFeMnNi in 3.5wt.% NaCl showing protective amorphous oxide and lower COF for AM manufactured alloy; (c) wear profile of AM and As-cast chronoamperometry; (d) wear volume loss and wear rate of AM and As-cast chronoamperometry with tribo-corrosion. AM CoCrFeMnNi showing lower wear volume loss and wear rate of AM processed alloy against Al\(_2\)O\(_3\) as compared to Si\(_3\)N\(_4\).

The corresponding coefficient of friction simultaneously recorded for the chronoamperometry is shown in Figure 4-8(b). It was observed that current had a direct
relationship with COF with a monotonic rise at exactly same time which was in line with previous hypothesis of inverse relationship of open circuit potential and COF. AM CoCrFeMnNi maintained a lower and relatively constant COF (0.16 ± 0.13) as wear proceeded while as-cast specimen undulated at higher COF (0.22 ± 0.18) until the end of wear. In Figure 4-8(c), after chronoamperometric tribo-corrosion the wear profile for both AM and as-cast CoCrFeMnNi was obtained. The black plot (AM CoCrFeMnNi) had a depth of ~ 1.8 µm with a width of 284 µm without any significant pits along the wear profile. The red plot (as-cast CoCrFeMnNi) had a depth of ~ 4.0 µm with a width of 423 µm with pits along the wear profile and unworn surface of the wear profile. The wear volume loss and wear rate for both AM and as-cast CoCrFeMnNi are shown in Figure 4-8(d). AM CoCrFeMnNi showed less than half the wear volume loss and wear rate as compared to as-cast CoCrFeMnNi.

4.4.4 Tribo-Corrosion Mechanism of AM CoCrFeMnNi HEA

The tribo-corrosion removal of AM CoCrFeMnNi HEA in 3.5 wt.% NaCl was influenced by several mechanisms as established in the previous sections. To study the synergy in play, tribo-corrosion of AM CoCrFeMnNi as the working electrode in 3.5 wt.% NaCl at 5 Hz reciprocating frequency with an applied normal load of 5 N for a stroke length of 3.5 mm at room temperature against 6.35 mm diameter Al₂O₃ counter-body for 1800 s after 3600 s OCP stabilization was modeled. In Figure 4-9(a), both counter surface and AM CoCrFeMnNi HEA were immersed in the corrosive 3.5 wt.% NaCl environment for 3600 s to achieve stable open circuit potential (OCP), the native oxide on the surface of this passive AM CoCrFeMnNi grew at kinetics currently unresolved until a certain thickness was reached at Figure 4-9(b). This native oxide grown into a protective passive layer with bilayer structures consisting of a defective oxide (native layer) adjacent to the metal and an outer layer formed from reaction of metal cations with NaCl species.
in the solution to form the secondary layer. This protective passive layer like an amorphous oxide possessed semiconductor properties which made it a charge resistant barrier, and this charge resistance led to limited growth in thickness. This charge resistance insulated the working electrode from exchanging electrons with the solution, and thus protected the AM CoCrFeMnNi from corrosion which is a charge transfer dependent process. Just before beginning wear in Figure 9(b), OCP was already achieved and thickness was considered maximum or near maximum. At the start of wear with the application of load and first run-in cycle, the protective passive layer developed cracks from the stress. The sudden exchange of charges piled up on the metal-oxide interface accounted for the initial sharp drop in potential. As the charge difference disappeared and the oxide layer regenerated, the potential returned to nobler values. OCP values prior to wear could not be achieved because of newly induced stress and deformations in this amorphous oxide layer. Amorphous wear results in less friction than wear in the crystalline phase because of the absence of grain boundary density, thus COF while in the amorphous oxide resulted in considerably lower COF values. At Figure 4-9(c), as wear proceeded and the amorphous oxide thickness reduced to a critical thickness at approximately half the size of the hump, the charge insulation properties of the amorphous oxide started to breakdown to allow charge transfer between working electrode (AM CoCrFeMnNi) and the electrolyte (NaCl). As the hump begins to descend to more negative OCP from reduced charge insulation, the COF increased to mark the end of amorphous wear. A transition to the highest COF value corresponding to the most negative OCP value marks the transition interface believed to be the roughest because of fresh asperities exposed. As wear proceeded beyond the hump and transition, a new run-in cycle occurred at the AM CoCrFEMnNi-Al₂O₃ interface. As the oxygen ions from the alumina (Al₂O₃) continuously deposited on the surface of the AM CoCrFeMnNi to alter the surface chemistry by formation of new oxide layer,
COF reduced and OCP shifted towards nobler values (Figure 4-9(d)). As wear proceeded till the end, both OCP and COF were stable at lower friction and nobler OCP to indicate stable tribo-corrosion behavior of AM CoCrFeMnNi in 3.5 wt.% NaCl environment. After wear ended in Figure 4-9(e), OCP increased to values before wear indicating re-passivation of the exposed area which took about 200 s.

![Figure 4-9: Tribo-corrosion model of AM CoCrFeMnNi in 3.5wt.% NaCl at room temperature at 5 Hz reciprocating frequency and 5 N normal load for 1800 s after 3600 s of open circuit potential stabilization against Al₂O₃ counter-surface; Al₂O₃ and AM CoCrFeMnNi (a) at the beginning of 3600 s open circuit stabilization; (b) at the end of 3600 s open circuit stabilization; (c) at 100 s of active tribo-corrosion; (d) at 1100 s of active tribo-corrosion; (e) after active tribo-corrosion in the re-passivation phase.]

4.5 Conclusion

In summary, we looked at how metallurgical processing fundamentally affected the tribo-corrosion behavior of additively manufactured and as-cast CoCrFeMnNi HEA in corrosive 3.5 wt.% NaCl at room temperature. Fundamental external stimuli that altered tribo-corrosion rates
such as change in load, reciprocating frequency, counter-body and corrosion current was applied to deduce the following conclusions:

- Orientation of the build direction with respect to the sliding direction yielded difference in the COF and OCP depending on the resultant microstructure (45 to BD being the best in this study). Thus, when considering build direction of AM parts, designers need to orient the tribo-corrosion surface based on grain size and microstructure anisotropy.

- For the effect of frequency, COF decreased with increase in reciprocating frequency while OCP moved towards nobler values as wear proceeded. The wear rate of AM CoCrFeMnNi was about 4 times less as compared to the as-cast CoCrFeMnNi at all frequencies.

- Load had more effect on overall wear rate and material removal of both AM and As-cast CoCrFeMnNi than the effect of frequency, and significantly more severe for the protective amorphous oxide of as-cast alloy than the AM CoCrFeMnNi.

- Effect of counter surface on the tribo-corrosion behavior of AM CoCrFeMnNi HEA showed that counter surface rich in oxide ions can help restore passive layer compared to counter surface deplete in oxide ions during tribo-corrosion. Thus, chemistry of the counter surfaces played significant role in the tribo-corrosion behavior of CoCrFeMnNi.

- Chronoamperometry of both AM CoCrFeMnNi and as-cast CoCrFeMnNi during tribo-corrosion revealed that the regeneration and stability of the protective passive layer on the surface of the AM CoCrFeMnNi was about 10 times better than as-cast CoCrFeMnNi.

- Both AM and as-cast had similar material removal mechanism of abrasive wear with AM having lower wear volume loss and lower wear rate than as-cast.

4.6 References


1.


CHAPTER 5
TRIBO-CORROSION DEGRADATION OF EUTECTIC HIGH ENTROPY ALLOY AND
DUPLEX STEEL AT ELEVATED TEMPERATURE

5.1 Abstract

Degradation of heat mediums by the combined action of elevated temperatures and tribo-
corrosion remains a detrimental downtime for the energy, process, and especially regulated
industries. Eutectic high entropy alloy (AlCoCrFeNi2.1) with desirable properties wield the
potential to deliver this critical degradation resistance over presently used stainless steels. Here we
account on the weld joint heat affected zone microstructural stability, pitting resistance, and tribo-
corrosion degradation resistance of AlCoCrFeNi2.1 high entropy alloy in comparison to duplex
stainless steel 2205 at room temperature, 50°C and 100°C in deionized water. Overall,
AlCoCrFeNi2.1 high entropy alloy showed excellent microstructural stability, excellent tribo-
corrosion degradation resistance, one order magnitude lower wear volume loss, one order
magnitude lower wear rate, and lowest COF when compared to duplex steel 2205. Also, the
stability of AlCoCrFeNi2.1 at 50°C suggests that a balance between flow conditions, temperature
and pressure can effectively lower the tribo-corrosion degradation of present stainless-steel
constructed heat exchange medium in service. These results pave the way to inclusion of HEA as
a material selection alternative to solving elevated temperature tribo-corrosion degradation
particularly in regulated industries seeking extended service life and process safety.

5.2 Introduction

The importance of heat exchange media in every process industry requires that the posses
a high degradation resistance particularly in regulated industries [1]. Metals been the most reliable
thermal conduction material finds use in construction of this heat exchangers in the form of tubular
and plate forms depending on the fluid systems [2,3]. Exposing the metal to a sandwich variation in flow transients, pressure pulsations, temperature variation gradients and tribo-corrosion tends to accelerates the degradation of the heat exchange medium [4,5]. With ubiquitous application in automotive, aeronautical, power generation, chemical processes, industrial cooling systems, offshore platforms, nuclear power plants, and petrochemical hydrocracker units, it remains paramount to resolve the degradation resistance of heat exchange mediums. Material selection considerations of heat exchange mediums are centered mainly around corrosion resistance, wear resistance, tribo-corrosion resistance, thermal conductivity, material strength, cost and reliability in service [6]. Although heat exchange mediums are the most common and relatable examples, similar elevated temperature tribo-corrosion mechanism occurs for thermo-hydraulic systems, oil rig drilling, mining, pump and impellers, and upstream-downstream pumping [7,8].

Tribo-corrosion degradation exacerbated by operating temperature and temperature gradient variation diminishes presently used structural steel alloys in the process fluid [9–11]. High entropy alloys (HEAs) representing a new paradigm in alloy development is based on alloying multiple principal elements in near equimolar proportions [12–14]. This alloying route gives rise to four core effects namely, solid solution strengthening, high configurational entropy, cocktail effect and severe lattice distortions [15,16]. These core effects invariably enhance the mechanical properties, wear properties, corrosion properties, oxidation properties, microstructural properties and thermal properties depending on the alloying elements[17,18]. The added control of tailoring synthesis-properties-performance of these high entropy alloys prompts exploring the degradation mechanism of established high entropy alloy system such as AlCoCrFeNi$_2$ in an elevated temperature tribo-corrosion environment.

Here we report on the tribo-corrosion response and microstructural stability of
AlCoCrFeNi\textsubscript{2.1} HEA at room temperature, 50°C and 100°C and compared to duplex stainless steel 2205 (DS2205) in deionized water. These alloys were selected because of their dual phase microstructure, corrosion resistance and wear resistance that has been established in literature [19–23]. Although, actively been researched are the wear, corrosion, mechanical properties, microstructural stability and degradation of both alloys, there is no knowledge of elevated temperature tribo-corrosion degradation of AlCoCrFeNi\textsubscript{2.1} and DS2205 [24–27]. We establish the degradation behavior of AlCoCrFeNi\textsubscript{2.1} and DS2205, microstructural stability, and then explored the tribo-corrosion resistance of both alloys with the effect of reciprocating frequency, effect of load and effect of temperature. AlCoCrFeNi\textsubscript{2.1} showed excellent microstructural stability, low wear volume loss, low wear rate, excellent corrosion resistance, regenerative passivity and ultimately better tribo-corrosion resistance when compared with DS2205.

5.3 Materials and Methods

5.3.1 Sample Preparation

Multiple principal elements of Al-Co-Cr-Fe-Ni with 99.99% purity were alloyed into ingots with a chemical composition of AlCoCrFeNi\textsubscript{2.1} using vacuum/argon arc melting. While duplex stainless steel DS2205 (UNS 31803) was prepared according to ASTM A815 specification which includes hot rolling of the as-cast. Cylinders of 6.34 mm diameters and 35 mm length was prepared from the AlCoCrFeNi\textsubscript{2.1} and DS2205 ingots using wire electric discharge machine (EDM) from Kent USA for the tribo-corrosion experiment. The flat bottom of the cylinder was polished up to 1200-grit abrasive paper and then polished on 1 \(\mu\)m diamond suspension to reveal a mirror surface finish before cleaning in acetone. Cylinder walls were sealed using acrylic nail polish to prevent galvanic coupling between the tribo-corrosion surface and cylinder walls when exposed to the tribo-corrosion environment.
5.3.2 Microstructure Characterization and Surface Analysis

Microstructural characterization was performed using scanning electron microscopy (SEM) in FEI Nova-NanoSEM 230™. Samples cut along same cylinder length were used to determine the elemental composition, phase fraction and crystal structure of the alloys using energy dispersive spectroscopy (EDS), electron backscatter diffraction (EBSD) and x-ray diffraction (XRD) analysis in Rigaku Ultima III (Rigaku, Tokyo, Japan), respectively. The surface topography of the wear scars was examined using white light interferometry. Wear volume loss was calculated from image analysis of 3D optical micrographs using Gwyddion software. The wear tracks were further analyzed in SEM to identify material removal mechanism.

5.3.3 Elevated Temperature Tribo-Corrosion Test

Elevated temperature tribo-corrosion experiment was performed using a linear reciprocating inverted ball-on-flat setup as shown in Figure 5-1. The reciprocating tribo-corrosion setup was mounted on a RTEC Instruments tribometer (RTEC San Jose, CA, USA) coupled with a Gamry potentiostat (Gamry Warminster, PA, USA) as seen in Figure 1(a). 6.35 mm diameter alumina ball was held in a resin cast at the bottom with the top of the ball aligned with the center of the polished alloy cylinder. Both sample and counter-body were held for 3600 s in deionized water to achieve open circuit potential (OCP) stability. The red terminal in Figure 1(d) indicates the working electrode (cylindrical AlCoCrFeNi2.1/DS2205 sample), the blue terminal indicates the counter electrode (platinum wire), and the green terminal indicates the reference electrode (Ag/AgCl electrode). All three electrodes are within 10 mm of each other as stipulated by ASTM standard for correction of electrolyte resistance in electrochemical tests (STP 1056) to reduce ohmic overpotential [28]. 100 ml of deionized water was measured used to immerse sample, counter-body and electrodes for each tribo-corrosion experiment. The effect of load on alloy tribo-
corrosion performance was measured at three temperatures room temperature (22 °C), 50 °C and 100 °C temperature with 5 Hz frequency at 3.5 mm stroke length while varying the load to 5 N, 10 N and 15 N for 1800 s of wear after 3600 s of open circuit potential stability. The effect of frequency on alloy tribo-corrosion performance was studied also at the 3 temperatures identified by varying the reciprocation frequency from 3 Hz to 5 Hz and 9 Hz while keeping the load fixed at 5 N. After the wear test, the sample was left in the deionized water to measure the open circuit potential for another 300 s for surface re-passivation. Three tribo-corrosion tests were performed for each condition to obtain the statistical average and standard deviation in wear volume loss and wear rate.

Figure 5-1: Tribo-corrosion experimental setup. The electrochemical cell was setup on a linear reciprocating tribometer within a heating module to achieve simulating elevated temperature tribo-corrosion of heat exchanger medium; (a) Tribo-corrosion experimental setup with RTEC Universal tribometer coupled to a Gamry potentiostat, (b) Tribo-corrosion and heating module assembly, (c) Immersed tribo-corrosion cell (d) Schematic representation of the elevated temperature tribo-corrosion setup.

5.4 Results and Discussion
5.4.1 Structural and Electrochemical Characterization

Microstructural characterization of both AlCoCrFeNi\textsubscript{2.1} HEA and DS2205 is shown in Figure 5-2. The backscattered secondary electron (BSE) micrograph shown in Figure 5-2(a) represents the overall as-cast microstructure of AlCoCrFeNi\textsubscript{2.1} HEA. The microstructure consists of lamellar arrangement of dark and light contrast solid solution phases that corresponds to B2 and L\textsubscript{12} phases, respectively [22,29]. The B2 phase contained nano-sized precipitates (white spots) as shown in the high magnification image (inset in Figure 5-2(a)) These nano-precipitates were previously reported to be Cr-rich [22,30]. Figure 5-2(b) shows the EBSD phase map with lamellar structure of B2 (yellow color) and L\textsubscript{12} (blue color) along with some coarse B2. The volume fraction was determined to be approximately 71% for L\textsubscript{12} phase and 29% for B2 phase. The B2 lamellae with thickness of \(~2-3\) µm are distributed in the L\textsubscript{12} matrix. Figure 5-2(c) shows the X-ray diffraction (XRD) of AlCoCrFeNi\textsubscript{2.1} HEA with the higher intensity peaks indicating the L\textsubscript{12} phase and lower intensity peaks indicating the B2 phase (consistent with the EDS phase fraction analysis). Backscattered secondary electron (BSE) micrograph of DS2205 ferritic-austenitic stainless steel in Figure 5-2 (d) shows elongated ferritic and austenitic phases. The dark grey contrast phase is the \(\delta\) phase (Ferrite-BCC) and the light grey contrast is \(\gamma\) phase (Austenite-FCC). From the EBSD phase map in Figure 5-2(e), it was observed that \(\delta\) phase had 48% and \(\gamma\) phase had 52% (approximately in equal amount) with lamellar structures. XRD analysis of DS2205 in Figure 5-2(f) shows peak intensity of both \(\delta\) phase and \(\gamma\) phase in agreement with the microstructure and EBSD phase map.

Electrochemical characterization of both AlCoCrFeNi\textsubscript{2.1} HEA and DS2205 in Figure 5-2(g) through 5-2(j) was conducted as a function of temperature in deionized water. The open circuit potential (OCP) of AlCoCrFeNi\textsubscript{2.1} HEA at room temperature (RT), 50°C and 100°C shown in
Figure 5-2(g) indicates a consistent shift toward nobler values as temperature increases. This can be attributed to temperature assisted passivation as the OCP at 50°C attain faster stabilization than room temperature OCP. Although OCP shifts to nobler values as temperature increases from 50°C to 100°C, the OCP curve at 100°C can be seen to be rougher than 50°C and RT. This characteristic roughness of the curve can be attributed to the instability of the passive layer as a continuous film-formation and film-diffusion interplay proceeds at higher temperature. Occasional spikes and dips on the 100°C curve can be attributed to film-diffusion events that successfully rupture the passive layer before re-passivation. Figure 5-2(h) shows the OCP of DS2205 at same RT, 50°C and 100°C with similar trends as the AlCoCrFeNi2.1 HEA. Notably, the shift towards nobler OCP values as temperature increases for DS2205 leads to significantly less noble OCP curves and unstable OCP fluctuations when compared to AlCoCrFeNi2.1 HEA OCP. Electrochemical Impedance spectroscopy (EIS) for AlCoCrFeNi2.1 HEA shown in the Nyquist plot in Figure 5-2(i) indicates a consistent reduction in arc radius as temperature increases, indicating a reduction in polarization resistance with increase in temperature. The Nyquist plot for DS2205 in Figure 5-2(j) follows similar suit having a decrease in arc radius as temperature increases. A comparison in the arc radius at same temperature for both AlCoCrFeNi2.1 HEA and DS2205 indicates that AlCoCrFeNi2.1 HEA has an overall higher polarization resistance than DS2205 at all temperatures. Notably, the Nyquist plot for DS2205 at 100°C was characterized with a semicircular plot with a diagonal diffusive tail at lower frequency. The semicircular region on the left signifies the coupling between double layer capacitance and DS2205 surface kinetic effects at frequencies faster than the physical process of diffusion. The diagonal diffusive tail (shown in the inset) indicates diffusion effects at higher temperatures and lower frequencies. This diagonal diffusive tail supports the OCP behavior of DS2205 at higher temperature. Overall, AlCoCrFeNi2.1 HEA exhibited a better and more stable
surface passivation when compared to DS2205 at all temperatures investigated in deionized water.

Figure 5-2: Microstructural and Electrochemical characterization of AlCoCrFeNi\textsubscript{2.1} HEA and DS2205. (a) BSED image of AlCoCrFeNi\textsubscript{2.1} HEA showing L1\textsubscript{2} and B2 phases in light and dark contrasts respectively; (b) EBSD phase map showing AlCoCrFeNi\textsubscript{2.1} HEA volume fraction of the two phases.
phases; (c) X-Ray diffraction pattern showing a dual phase AlCoCrFeNi$_{2.1}$ HEA crystal structure; (d) BSED image of DS2205 showing austenite and ferrite phases in light and dark contrasts respectively; (e) EBSD phase map showing volume fraction of the two phases; (f) X-Ray diffraction pattern showing a dual phase DS2205 crystal structure; (g) Open circuit potential plot for AlCoCrFeNi$_{2.1}$ HEA at room temperature, 50°C and 100°C for 3600 s; (h) Open circuit potential plot for DS2205 at room temperature, 50°C and 100°C for 3600 s; (i) Nyquist plot for AlCoCrFeNi$_{2.1}$ HEA at room temperature, 50°C and 100°C; (j) Nyquist plot for DS2205 at room temperature, 50°C and 100°C.

5.4.2 Effect of Temperature on Tribo-Corrosion

To investigate the effect of temperature on the tribo-corrosion response of both AlCoCrFeNi$_{2.1}$ and DS2205, open circuit potential (OCP) and coefficient of friction (COF) during the tribo-corrosion test were recorded simultaneously with a load of 5 N and oscillation frequency of 5 Hz at RT, 50°C and 100°C as shown in Figure 5-3. For AlCoCrFeNi$_{2.1}$ HEA coefficient of friction during tribo-corrosion in Figure 5-3(a), at room temperature and 50°C the COF both show similar behavior with an average COF of 0.195 ± 0.012 and 0.181± 0.015 respectively. At a higher temperature of 100°C, a different COF phenomenon was observed to follow similar trend as the RT and 50°C until about 1000 s before transitioning to a higher value with an average COF of 0.254 ± 0.094. With ~25°C increase from RT to 50°C, the COF can be said to follow same trend with a general reduction in COF after the run in period of about 600 s, but increasing from 50°C to 100°C shows same run in trend before transitioning at 1000 s. For AlCoCrFeNi$_{2.1}$ HEA open circuit potential during tribo-corrosion in Figure 5-3(b), we can observe that the OCP show the characteristic tribo-corrosion curve. At room temperature, the OCP is steady with minor spikes throughout the active wear event, while at 50°C and 100°C we see a different curve which transitions to nobler OCP at approximately same time the COF run-in period is completed. These three OCP curves are fundamentally indicate how temperature assists the repassivation event at all three temperatures. At room temperature, slower repassivation kinetics during active wear yields a curve that runs smoothly due to temperature.
Figure 5-3: (a) Coefficient of friction (COF) and (b) open circuit potential (E_{ocp}) as a function of temperature at 5 Hz frequency and 5 N load for AlCoCrFeNi_{2.1} HEA; (c) COF and (d) OCP as a function of temperature at 5 Hz frequency and 5 N load for DS2205.

While at 50°C and 100°C, a much faster repassivation kinetic during active wear yields a curve that undulates with a shift towards nobler OCP. These faster kinetics may also be responsible for the rate of repassivation after wear following a trend of 100°C > 50°C > RT. For DS2205 coefficient of friction during tribo-corrosion in Figure 5-3(c), the COF at room temperature had an average of 0.403 ± 0.018, while the average COF at 50°C and 100°C was 0.315 ± 0.014 and 0.394 ± 0.021 respectively. Thus, the trend in average COF was 50°C < 100°C < RT, which can be attributed to the passivation kinetics being optimum to create a stable passivation layer at 50°C when compared to 100°C and RT. For DS2205 open circuit potential during tribo-corrosion in Figure 5-3(d), room temperature and 50°C OCP showed a steady horizontal curve with no spikes throughout the active
wear event. While at 100°C we see a different curve trending towards nobler OCP from the onset of wear. These trends are similar to what was observed for AlCoCrFeNi$_{2.1}$ HEA at all three temperatures. Overall, AlCoCrFeNi$_{2.1}$ HEA showed a stable tribo-corrosion response with desirable repassivation and lower coefficient of friction when compared to DS2205 at all temperatures.

5.4.3 Dynamic Load and Frequency Tribo-Corrosion Degradation Rate

The dynamic degradation conditions of turbulent flow existing on both shell-side and tube-side at varying elevated temperature was simulated using varying load from 5 N, 10 N and 15 N and varying reciprocating frequency of 3 Hz, 5 Hz and 9 Hz. The resultant tribo-corrosion wear volume loss and wear rate are shown in Figure 5-4 and Figure 5-5 respectively. For the effect of frequency, Figure 5-4(a) shows the wear volume loss of AlCoCrFeNi$_{2.1}$ HEA for reciprocating frequency of 3 Hz, 5 Hz, and 9 Hz at RT, 50°C and 100°C. It can be observed that increasing the frequency from 3 Hz to 5 Hz generally leads to a steeper increasing slope in wear volume loss at all three temperatures, but further increase from 5 Hz to 9 Hz generally leads to a reduced slope in wear volume loss. This trend can be attributed to low reciprocating frequency at 3 Hz allows for ample time to repassivate the worn surface between cycles, but insufficient time between reciprocating cycles at a higher reciprocation frequency of 5 Hz leads to less repassivation and consequently higher wear rates. The decrease in the slope from 5 Hz to 9 Hz can be attributed to reduced material removal as the surface interaction time decreases with increasing reciprocating tangential force (faster removes less). Overall, less material is removed at 50°C than RT and 100°C at all three frequencies, and this trend is similar to the COF trend observed in section 5.3.3 because of the relative stability of the passive layer at the corresponding temperature. For the effect of temperature on DS2205 in Figure 5.4(b), similar trend observed for the AlCoCrFeNi$_{2.1}$ HEA at all
temperature was seen. DS2205 showed one order magnitude higher material removal than AlCoCrFeNi_{2.1} HEA at all temperatures.

Figure 5-4: Wear volume loss at RT, 50°C and 100°C as a function of reciprocating frequency and load for of AlCoCrFeNi_{2.1} HEA and DS2205; (a) wear volume loss for of AlCoCrFeNi_{2.1} HEA at 3 Hz, 5 Hz and 9 Hz; (b) wear volume loss for of DS2205 at 3 Hz, 5 Hz and 9 Hz; (c) wear volume loss for of AlCoCrFeNi_{2.1} HEA at 5 N, 10 N and 15 N (d) wear volume loss for of DS2205 at 5 N, 10 N and 15 N

For the effect of load on AlCoCrFeNi_{2.1} HEA in Figure 5-4(c), with a general increase in wear volume loss as load increased from 5 N to 15 N, similar trend in wear volume loss was observed. Similarly, for the effect of load on DS2205 in Figure 5-4(d), the monotonic increase in material loss was observed as load increased. Overall, AlCoCrFeNi_{2.1} HEA had the lower tribo-corrosion
wear volume loss at all frequency, load and temperatures investigated. The trend in material volume loss during tribo-corrosion was $50^\circ C < \text{RT} < 100^\circ C$, and it can be credited to favorable passivation kinetics $50^\circ C$, regular passivation kinetics at RT, and detrimental temperature induced passivation dissolution and instability at $100^\circ C$.

The corresponding wear rate for the effect of frequency and load for both AlCoCrFeNi$_{2.1}$ HEA and DS2205 shown in Figure 5-5 reveals a strong dependence on temperature for the wear rate experienced by both alloys. For AlCoCrFeNi$_{2.1}$ HEA wear rate at varying reciprocating frequency of 3 Hz, 5 Hz and 9 Hz in Figure 5-5(a). An increase in wear rate from 3 Hz to 5 Hz was observed for all temperatures, and a subsequent decrease in wear rate from 5 Hz to 9 Hz follows the decreased interaction and decreased material removal hypothesis. For DS2205 wear rate in Figure 5-5(b), wear rate reduced with increasing temperature as the material removal mechanism changed from two body abrasive wear at room temperature, to polishing at $50^\circ C$, and back to three body abrasive wear at $100^\circ C$. For the effect of normal load on the wear rate of AlCoCrFeNi$_{2.1}$ HEA in Figure 5-5(c), increasing load from 5 N to 15 N had a similar trend at both RT and $50^\circ C$. But a reverse trend was observed with the wear rate as load was increased at $100^\circ C$, this can be attributed to the passive layer losing its load bearing capabilities at higher temperature, and possible softening of the near surface as increasing load leads to increased frictional heating of the contact surface. For the effect of load on DS2205 in Figure 5-5(d), similar behavior was observed at both RT and $50^\circ C$ with a decrease in wear rate as load increased from 5 N to 10 N, and a further increase in wear rate going from 10 N to 15 N. This change in wear rate can be attributed to the changing contact mechanics of the ductile DS2205 as load moves from 5 N to 15 N. At $100^\circ C$ the wear rate increased monotonically from 5 N to 15 N, this can be credited to the unstable passive layer at $100^\circ C$. Overall, AlCoCrFeNi$_{2.1}$ HEA showed about one order of
magnitude lower and stable tribo-corrosion wear rate when compared to DS2205 at all temperatures, frequencies and loads investigated.

5.4.4 Wear Mechanism of AlCoCrFeNi$_{2.1}$ HEA and DS2205

Surface morphologies of AlCoCrFeNi$_{2.1}$ HEA and DS2205 wear tracks after tribo-corrosion at RT, 50°C and 100°C with 5 Hz frequency and 5 N normal load are shown in Figure 5-6. As temperature changed from room temperature (RT) to 50°C and 100°C, the wear
mechanism significantly changed to indicate passive layer stability at the temperatures investigated. Figure 5-6(a) shows the surface morphology of AlCoCrFeNi2.1 HEA at RT with a characteristic two body abrasive wear as can be deduced from the multiple abrasive groves aligned along the reciprocating sliding direction. The abrasive ridges appear to be shallow without pile-up on the edge of the wear track. The two body abrasive wear track at room temperature supports the results previously seen for COF, wear volume loss, and wear rate. In Figure 5-6(b), the surface morphology of AlCoCrFeNi2.1 HEA at 50°C shows a characteristic polishing wear without significant groves along the sliding direction. This polished wear track is consistent with the low wear rate, low wear volume loss and reduced COF observed at 50°C for AlCoCrFeNi2.1 HEA. Figure 5-6(c), the surface morphology of AlCoCrFeNi2.1 HEA at 100°C shows discontinuous tribo layer with multiple patches of dislodged oxides in the middle of the contact area and polished surface towards the edge of the wear track. This morphology at 100°C indicates oxidative wear at higher temperatures, and the unstable COF which increases as tribo-corrosion proceeds supports the oxidative wear characteristics. For DS2205 surface morphology at room temperature shown in Figure 5-6(d), two body abrasive wear was observed with similar morphology to AlCoCrFeNi2.1 HEA at room temperature. The wear track for DS2205 was wider, and had deeper groove than the AlCoCrFeNi2.1 HEA wear track. This wider track and deeper grooves account for the order of magnitude increase in the wear volume loss, the increased COF and the higher wear rate reported in the previous sections. At an elevated temperature of 50°C, the tribo-corrosion wear morphology shown in Figure 5-6(e) can be characterized as a polishing wear. The wear track appears to be polished while maintaining a visible microstructure of γ phase and δ phase within the wear track. Considerable pile up on the edge of the wear track is consistent with the ductility of DS2205, and the significantly low COF at 50°C is consistent with the smooth and polished wear track. The wear
track is significantly wider than AlCoCrFeNi$_{2.1}$ HEA wear track at 50$^\circ$C, which accounts for the increased wear volume loss and wear rate of DS2205 at 50$^\circ$C when compared to AlCoCrFeNi$_{2.1}$ HEA. At 100$^\circ$C in Figure 5-6(f), the surface morphology of DS2205 revealed a three body abrasive wear mechanism of material removal.

The ploughing seen on the wear track is characteristic of a trapped third body dislodged during the tribo-corrosion event. This leads to an incomplete groove as can be seen on the wear track. The edge pile up at 100$^\circ$C is noticeably more than the edge pile up at 50$^\circ$C, this suggests thermal softening at higher temperatures for DS2205 elevated temperature tribo-corrosion. This wear morphology is consistent with the increase COF at 100$^\circ$C for DS2205, also consistent with the reduced wear volume loss of just slightly higher than wear volume loss at 50$^\circ$C, and the reduced wear rate. The width of the wear track is significantly larger than that of 100$^\circ$C, and the micro-cutting and
ploughing of DS2205 removes more material than the tribo layer dislodged volume. Overall, AlCoCrFeNi$_{2.1}$ HEA showed a much stable wear morphology, smaller worn area and ultimately better tribo-corrosion resistance than DS2205 at all the temperatures and conditions investigated.

5.5 Conclusion

In retrospect, heat affected zone degradation and elevated temperature tribo-corrosion of eutectic high entropy alloy (AlCoCrFeNi$_{2.1}$) was studied in 3.5 wt.% NaCl and deionized water respectively. Results were compared with DS2205 under identical conditions, and the following conclusions may be drawn from the results obtained:

- AlCoCrFeNi$_{2.1}$ HEA showed a stable tribo-corrosion response with desirable repassivation and lower coefficient of friction at RT, 50°C and 100°C temperatures when compared to DS2205.

- With AlCoCrFeNi$_{2.1}$ HEA showing one order of magnitude lower wear volume loss and one order of magnitude lower wear rate than DS2205, the trend in material volume loss during tribo-corrosion was 50°C < RT < 100°C for both alloys.

- The stability of both AlCoCrFeNi$_{2.1}$ HEA and DS2205 at 50°C suggests that a balance between flow conditions, temperature and pressure can effectively lower the tribo-corrosion degradation of heat exchangers in service.

5.6 References


CHAPTER 6

STRESS CORROSION SUSCEPTIBILITY OF FCC HIGH ENTROPY ALLOY IN
SIMULATED MARINE ENVIRONMENT

6.1 Abstract

Although cables and wires in stress corrosion susceptible application such as marine anchors, bridges, and excavation reinforcements can benefit from tailored alloying such as high entropy alloys, there is a lack of studies in this area. Here, we report on the corrosion behavior under uniaxial tensile stress for Al$_{0.1}$CoCrFeNi high entropy alloy using a novel stress accelerated electrochemical measurement setup. Results show characteristic drop in open circuit potential with yield stress, flow stress and ultimate tensile stress as the high entropy alloy wire is loaded uniformly in a uniaxial direction at a tensile stress of 600 MPa. The corrosion current density increased by three orders of magnitude with ~ 150 mV drop in corrosion potential to less nobler values from unstressed to stressed state. The direction of applied stress and resulting slip lines clearly confirm that macroscopically brittle fracture resulted from microcracking on the $\{111\}$ microfacets in a zigzag manner for FCC Al$_{0.1}$CoCrFeNi HEA. The mechanism of accelerated corrosion was determined to be surface passivation breakdown which created pit initiation sites on the exposed surface and culminated into rapid pitting propagation along the loading direction. The characteristics open circuit potential signature revealed by the novel stress corrosion susceptibility measurement can be developed into non-destructive continuous corrosion monitoring methods for early failure identification of tensile wire applications.

6.2 Introduction

Degradation of wires and cables in marine environment, cable-stayed bridges, and suspendomes from the simultaneous stress and corrosion of the engineered component leads to
loss of performance, efficiency and ultimately failure [1]. The combined action of stress and corrosion accelerates the degradation mechanism beyond the individual degradation action especially for passive metals [2,3]. Stripping the adherent passive oxide on the surface of the alloys leads to exposure of the bare underlying metal [4,5]. This increases the alloys susceptibility to corrosion which could form pits that act as stress concentration sites during loading. These sites culminate during the loading events to reduce the design performance and useful life. Tailored passive alloys have been shown to possess regenerative passivity that help resist corrosion susceptibility in aggressive environments [6,7]. Developing tailored alloys with acceptable degradation resistance leads to high entropy alloys as a paradigm of specifically desired tailored mechanical, microstructural and corrosion properties.

In recent years, there has been tremendous research interest in multi-principal element alloys (also known as high entropy alloys (HEAs)) because of better property control over conventional alloying techniques [8–11]. Among the various alloy groups, Al$_x$CoCrFeNi system has been particularly interesting because of the versatility in terms of tuning of microstructure and the corresponding properties. Minor variation in Al content transforms the microstructure from a single phase face centered cubic (FCC) alloy (for x=0.1) to complex phase mixtures (for x=0.3, 0.5) to a single-phase body centered cubic (BCC) structure (for x=1.0) [12–15]. In particular, the single-phase FCC Al$_{0.1}$CoCrFeNi alloy has been widely studied because of its exceptional corrosion resistance [16–18], remarkable phase stability [19], high resistance to irradiation damage [20] and excellent weldability [21]. Although stress corrosion cracking is used for understanding the corrosion behavior of components exposed to stress and corrosive environments, the challenge with such an approach is the inability to determine and predict the dynamic corrosion rate at different stress levels. This information is important for fundamentally understanding the
detrimental effects of applied stress on corrosion behavior, as well as necessary in determining the application worthiness of this new class of emerging alloys in the marine environment. However, the corrosion behavior of this alloy under external applied stress is not well understood and has not been reported.

Here, we demonstrate a novel stress accelerated electrochemical (SAE) measurement setup to measure the change in corrosion potential and corrosion current density, and we report on corrosion mechanisms at different applied stress levels for a model single-phase Al$_{0.1}$CoCrFeNi HEA. This approach aided understanding the mechanism of stress accelerated corrosion breakdown of surface passivation layer, pit initiation, and rapid pit-propagation along the loading direction. The setup and methodology may be applied to a wide-range of material systems for designing highly corrosion resistant alloys.

6.3 Materials and Methods

6.3.1 Alloy Synthesis

Five-component Al$_{0.1}$CoCrFeNi high entropy alloy ingot was synthesized by vacuum/argon arc melting using high purity elements (>99.9%). Al$_{0.1}$CoCrFeNi ingot was rolled to 99.7% strain to produce a 2 mm diameter cylindrical wire. The sample was annealed at 1200°C for 20 h to produce a fully recrystallized test sample.

6.3.2 Microstructural Characterization

Surface morphology, microstructural characterization and chemical composition of Al$_{0.1}$CoCrFeNi HEA were obtained using scanning electron microscopy (SEM, FEI Quanta-ESEM 200™) and energy dispersive spectroscopy (EDS). Further, electron backscattered diffraction (EBSD) was performed to confirm the grain orientation and crystal structure. Post stress-corrosion
experiment, the wire rolling surface was characterized in FEI-Quanta environmental scanning electron microscope (SEM).

6.3.3 Stress Accelerated Electrochemical Measurement

A schematic of the test setup is shown in Figure 6-1. Ambient air tensile test was conducted with a relative humidity of 22% and at a strain rate of \(2 \times 10^{-6}\) s\(^{-1}\). A three-electrode cell configuration was used for measuring the electrochemical response from loading Al0.1CoCrFeNi using a Gamry potentiostat (Gamry Warminster, PA, USA). A saturated calomel electrode (SCE) was used as reference electrode, high density graphite as counter electrode and the Al0.1CoCrFeNi high entropy alloy as the working electrode. The electrolytic cell was filled with 3.5 wt\% NaCl solution and appropriate connections were made. Controlled uniaxial tensile loading was applied to the SAE module using ADMET eXpert 4000™ professional table-top micro tensile testing machine (MTTS). The HEA wire sample was allowed to attain stable open circuit potential (OCP) before SAE testing and subsequently potentiodynamic polarization test was carried out at a rate of 0.16 mV/s.

![Figure 6-1: Schematic of stress accelerated electrochemical (SAE) measurement setup showing the HEA wire connected as the working electrode, graphite used as counter electrode and saturated calomel used as the reference electrode. Uniaxial loading was applied using ADMET eXpert 4000™ professional table-top tensile testing machine with a load cell capable of varying the applied stress over a wide range.](image-url)
6.4 Results and Discussion

6.4.1 Microstructural Characterization

HEA wire schematic and electron backscattered diffraction (EBSD) images along the different directions, pole figures, and the engineering stress-strain curves are shown in Figure 6-2.

Figure 6-2: (a) Schematic of the high entropy alloy (HEA) wire obtained after cold rolling, wire drawing and static recrystallization annealing treatment showing the rolling direction (RD) and normal direction (ND); (b) EBSD image of the HEA wire along the rolling direction (RD); (c) EBSD image of the HEA wire along the normal direction (ND); pole figures along the (d) rolling direction (RD) and (e) normal direction (ND); (f) engineering stress-strain curve for the high entropy alloy with the yield point and ultimate tensile strength (UTS) marked on the curve.

In Figure 6-2(a) along the wire drawing length of the HEA, EBSD is taking in the rolling direction (RD) and perpendicular to the rolling direction along the normal direction (ND). The EBSD map of RD in Figure 6-2(b) shows large plastic deformation with no preferred wire drawing texture. Although significantly smaller grains are seen on the EBSD map of ND in Figure 6-2(c), it shows similar plastic deformation and no preferred wire drawing texture. Both Figure 6-2(b) and 6-2(c) shows significant amount of annealing twins with ~ 10 µm width. The microstructure of the wire was homogenous and characterized by equi-axed strain-free grains. The pole figures confirming uniform distribution of grains along the principal crystallographic axes are shown in Figure 6-
2(d) and 6-2(e). The absence of wavy cup rims from wire drawing correlated with uniformly distributed grains and balanced combination of rolling and recrystallization. Engineering stress-strain curve obtained from ambient air tensile test with a relative humidity of 22% and at a strain rate of $2 \times 10^{-6}$ s$^{-1}$ is shown in Figure 6-2(f). The values for yield strength and ultimate tensile strength were similar to those reported in literature for bulk alloy of the same composition [22].

6.4.2 Stress-Corrosion Degradation

After confirming the ambient values of yield strength and ultimate tensile strength, stress accelerated corrosion experiments were carried out by mounting the Al$_{0.1}$CoCrFeNi wire in the SAE module. Corrosion response of the HEA wire under no external applied stress ($\sigma$=0) was recorded in terms of the corrosion potential ($E_{corr}$) and corrosion current density ($i_{corr}$), the unstressed $E_{corr}^{\sigma=0} = -235 \pm 16$ mV and $i_{corr}^{\sigma=0} = 16 \pm 6.5$ nA/cm$^2$ based on six measurements for samples prepared from the same batch. Subsequently, the electrochemical response while the sample was subjected to uniaxial tensile loading was recorded. Figure 6-3(a) shows the engineering stress-strain curve of the wire measured in the SAE module during stress-corrosion measurement. The change in open circuit potential (OCP) as the wire was deformed is shown in Figure 6-3(b). The first potential drop in OCP of $\sim 30$ mV was seen at the onset of plastic deformation ($\sigma$=242 MPa). This small potential drop was followed by recovery in OCP as stress was increased up to 700 MPa, where a sharp drop of $\sim 225$ mV ($E_{OCP}^{\sigma=700} = -500$ mV) was observed. This was immediately followed by a second potential recovery regime during which the OCP remained stable at -400 mV (vs SCE). The sample was stressed up to the ultimate tensile limit of 755 MPa at which point a third potential drop of $\sim 37$ mV was recorded. Correlating the drop in open circuit potential to engineering stress-strain curve identified three distinct mechanical response events namely; yield stress at 242 MPa, flow stress at 700 MPa and ultimate tensile stress...
at 755 MPa. The magnitude of potential drop was small at yield stress. At a point between yielding and ultimate tensile strength (UTS), corresponding to an elongation of ~16% We attribute the degree in open circuit potential drop to the fraction of passivated surface frayed by cracking, thus larger fractions to larger drop and vice versa. While we attribute the recovery after each mechanical response event to regenerative passivation along the damaged surface passivation and passivation of freshly exposed area as engineering strain increases. These observations were consistent for all six tests, thus indicating that there may be a critical stress value between yield and ultimate tensile strength (UTS) at which the rate of nucleation of deformation induced surface cracking leads to accelerated corrosion. A fresh HEA wire was loaded to a tensile stress of 720 MPa (which is 35 MPa below the ultimate tensile limit) and subjected to potentiodynamic polarization as shown in Figure 6-3(c) to record the corrosion current density and corrosion potential. The $i_{corr}^{720} = 4.7 \pm 0.65 \, \mu A/cm^2$, which was roughly 300 times higher corrosion current density compared to the undeformed HEA wire. The corrosion potential ($E_{corr}$) was -392 mV (vs SCE) in the stressed condition, which represents a 157 mV drop towards less noble value compared to the undeformed wire. We attribute the reduction in corrosion potential and the increase in corrosion current density between the unstressed and stressed state to be as a direct result of unstable and non-continuous surface passivation in the stressed state. The corrosion current density increased to less noble values with three orders of magnitude and more than 150 mV drop in corrosion potential represents significant acceleration in corrosion behavior for same alloy previously reported to have exceptional corrosion resistance in the undeformed state. Similar tensile stress-corrosion degradation has been reported for FCC alloys such as austenitic stainless steels [23], Cu-Zn and Cu-Au alloys [24], and pure Cu [25], and Fe-Cr-Ni [26] in Cl⁻ environment.
6.4.3 Degradation Mechanism

The surface of the wire post stress-corrosion experiment shown in Figure 6-4(a) was observed to have multiple cracks normal to the loading direction as shown in the 10X magnified inset. Surface cracks and exposure of underlying base metal, akin to characteristic mud-cracking appearance. Figure 6-4(b) of the elemental scans performed using energy dispersive x-ray spectroscopy of the cracked area reveals that the surface oxide had discontinuous cleavage-like cracks, exposing the underlaying material to the electrolyte and consequent accelerated corrosion during the stress-corrosion experiment. High magnification SEM images of the stress-corroded regions indicates breakage of the surface passivation layer as seen in Figure 6-4(c) and Figure 6-4(d). The propagating crack tips coalesced and formed corrosion pits as shown in Figure 6-4(c). High magnification images of a large pit are shown in Figure 6-4(d) and Figure 6-4(e). The direction of applied stress and resulting slip lines are clearly visible in Figure 6-4(f). The similar behavior was reported for stress corrosion cracking of FCC austenitic stainless steel in Cl⁻ solution at slow strain along the 〈110〉 and 〈100〉 orientation by Magnin et al. 1995 [27]. Thus, confirming that macroscopically brittle fracture results from microcracking on the 〈111〉 microfacets in a...
zigzag manner for FCC Al$_{0.1}$CoCrFeNi HEA (and general FCC alloys). These slip planes and sharp boundaries contributed to the preferred pit nucleation sites that accelerated the corrosion of the stressed region.

![Image of bulk morphology and corrosion microstructure](image)

Figure 6-4: (a) Low and high magnification SEM images of the HEA wire after the corrosion test showing surface oxide cracking; (b) EDS images showing discontinuity of the surface oxide and exposure of underlying metallic substrate; (c) corrosion pits growing due to the coalescence of surface cracks; (d) large surface crack; (e, f) high magnification SEM images showing slip steps inside the corrosion pit.

### 6.5 Conclusion

In this study, we investigated the stress-corrosion susceptibility of Al$_{0.1}$CoCrFeNi high entropy alloy in 3.5 wt.% NaCl. In conventional stress corrosion cracking the electrochemical signals are not recorded as the specimen is stressed to failure. But in this novel approach with static and dynamic stress application with electrochemical monitoring, results reveal insights into corrosion initiation at different levels of applied stress. The developed methodology may be useful in determining the electrochemical response for a wide range of materials in corrosive environments.
6.6 References


[27] Magnin T, Chambreuil A, Bayle B. The corrosion-enhanced plasticity model for stress
CHAPTER 7
SUMMARY AND FUTURE WORK

7.1 Overall Summary

High entropy alloys (HEAs) are a new class of five or more principal element materials that offer great opportunities in the search for advanced alloys that bear unique compositional properties to satisfy structural and functional usage. HEAs exhibit attractive material properties such as excellent corrosion resistance, high strength/hardness, outstanding wear resistance, exceptional high-temperature strength, good structural stability, and oxidation resistance. These attractive properties are attributed to four core effects namely; high entropy effect, sluggish diffusion effect, severe-lattice distortion effect and cocktail effect. High entropy alloys with exceptional wear resistance and corrosion resistance hypothetically should show exceptional tribo-corrosion resistance, but a knowledge gap unfilled in research of the tribo-corrosion resistance of this high entropy alloys exist. Conversely, investigations into understanding the mechanism of tribo-corrosion resistance of this high entropy alloys promises to unlock alloy development of superior alloy systems that will satisfy material application in harsh environments. This research work was geared towards seeking answers to initially formed hypotheses as summarized below:

- Excellent corrosion resistance and wear resistance of the BCC high entropy alloy translated to better tribo-corrosion resistance in simulated physiological environment.
- High entropy alloy formed from all biocompatible elements yields an alloy with regal osteointegration and biocompatibility.
- Anisotropy from additive manufacturing of high entropy alloys resulted in a preferred orientation with the build direction and consequently a preferred orientation for tribo-corrosion resistance.
- Refined microstructure and homogeneous elemental distribution resulting from rapid cooling during additive manufacturing promotes superior tribo-corrosion resistance of high entropy alloys.
• With increase in temperature, the tribo-corrosion resistance of dual phase high entropy alloy reduces as temperature goes from room temperature to 50 °C because of thermally assisted passivation, but as temperature goes from 50 °C to 100 °C tribo-corrosion resistance reduces because of thermally accelerated degradation (diffusion) of the protective passive layer.

• Dual phase high entropy alloy maintains its microstructure, phase fraction and corrosion resistance along the welded heat affected zone. This can be attributed to the severely distorted lattice of the high entropy alloy retarding microstructural variation along the heat affected zone of weldments.

• Corrosion susceptibility of high entropy alloy in a stress-corrosion environment results from the cracking of the protective passive layer perpendicular to the tensile loading direction. Thus, creating a region where corrosion is accelerated with coalesced pitting that eventually culminates into fracture.

Culminating the knowledge gathered from the hypothesis tested in the various chapters, a sensor that use bio-electrochemical responses to sense implant degradation was proposed. By combining the mechanochemical degradation response of the high entropy alloy wire to sense stress induced degradation, the electrochemical response to sense corrosion degradation, and the combined wear-corrosion response to sense tribo-corrosion degradation, the working principle of a bio-electrochemical sensor was proposed.

7.2 Future Work

With the knowledge contribution gained from these investigations of high entropy alloy tribo-corrosion, the following are tangential pathways that could be further evaluated for gaining insight into resistance mechanism and application worthiness of this high entropy alloys.

• A comparison of the tribo-corrosion resistance of BCC, FCC, and dual phase high entropy alloy under similar conditions can be used to develop of a material selection library on the tribo-corrosion resistance of high entropy alloys. This library will be a guide to alloy development experts in designing for tribo-corrosion resistant applications.

• The wealth of data generated during this study can be used as the feed data to developing machine learning algorithms that will aid sensor development for the monitoring, analyzing and early identification of tribo-corrosion degradation of materials in service.
• This study demonstrated a strong correlation between the dependence of open circuit potential and coefficient of friction. This correlative dependence can be further investigated to determine if friction can be controlled by electrochemically tailoring the parameters that favor friction reduction or controlling tribo-corrosion degradation generally.

• A tangential pathway could be explored towards tribo-corrosion resistance of ion-irradiated high entropy alloys. This will aid development of high entropy alloys that can satisfy grid-to-rod fretting application, and will be beneficial to understand how the science of introduced defects can directly intensify or deter tribo-corrosion.

• We demonstrated that the tribo-corrosion resistance and biocompatibility of MoNbTaTiZr was suitable for bio-implantation, a further study can try to establish weight reduction of the MoNbTaTiZr high entropy alloy by varying the composition of the heavy refractories. Alternative fabrication methods such as additive manufacturing could be explored for functionally grading and weight reduction of the MoNbTaTiZr while maintaining the most biocompatible and tribo-corrosion resistant surface.
A.1 Microstructural Characterization

Figure A.1 shows scanning electron microscopy (SEM) image and energy dispersive spectroscopy (EDS) elemental mapping of equiatomic MoNbTaTiZr high entropy alloy. Appendix Figure A1(a) shows the SEM microstructure with bright contrast representing the major BCC phase (dendrites) and dark contrast representing the minor BCC phase (inter-dendritic region). Elemental distribution for the as-cast alloy was obtained using EDS as seen in Appendix Figure A1(b) through A1(f). The dendritic region was rich in Ta and Mo while the inter-dendritic region was rich in Ti, Nb and Zr. This segregation may be attributed to the difference in melting point of the constituent elements, with higher melting temperature ($T_m$) elements such as Ta ($T_m = 3017$ °C) and Mo ($T_m = 2617$ °C) in the dendritic arms and remaining elements segregating to the interdendritic region. This illustrates the stabilization of solid solution phases due to high configurational entropy of mixing. Phase separation of $\beta$-phase (Zr-Ta) into Zr-rich and Ta-rich phases at 1747 °C is thermodynamically driven as predicted by their binary phase diagram.

Figure A.1: (a) SEM image of MoNbTaTiZr high entropy alloy with bright contrast (dendrites) indicating major BCC phase and dark contrast (inter-dendrites) indicating minor BCC phase; Energy dispersive spectroscopy (EDS) elemental mapping showing the distribution of (b) Ta, (c) Mo, (d) Ti, (e) Nb, and (f) Zr.
A.2 Equivalent Circuit Elements Obtained by Fitting of Nyquist plots

The impedance data was confirmed using Kramer-Kronig transform to satisfy linearity, causality, stability, and finiteness. The equivalent circuit consisted of the reference electrode (R.E), solution resistance ($R_{\text{soln}}$), passive layer resistance ($R_{\text{pass}}$), passive layer capacitance ($C_{\text{pass}}$), pore resistance or passive layer stability ($R_{\text{pore}}$), passive layer constant phase element ($C_{\text{c}}$), polarization resistance ($R_{\text{p}}$), electrochemical reaction constant phase element ($C_{\text{p}}$), m and n are the constant phase element coefficients respectively (0 = imperfect capacitors while 1 = perfect capacitors), and the working electrode (W.E). The values of the equivalent circuit elements for the two alloys at room and body temperatures are summarized in Table A.1.

A.3 Apatite Formation on the Surface of MoNbTaTiZr High Entropy Alloy

The wear tracks on the surface of MoNbTaTiZr high entropy alloy at 9 Hz frequency and 5 N normal load is shown in Figure A.2(a) while 5 Hz frequency and 15 N normal load is shown in Figure A.2(b). The data obtained from point EDS at the spots marked on the wear tracks with a star are summarized in Table A.2. The presence of Ca, O and P is indicative of CaO and CaP formation which are precursor to apatite formation on the MoNbTaTiZr surface.

![Figure A.2: SEM micrograph showing EDS spot location for MoNbTaTiZr (a) 9 Hz frequency 5 N wear track and (b) 15 N load 5 Hz wear track.](image-url)
Table A.1: Equivalent Circuit Element values for modified REAP2CPE fit for MoNbTaTiZr and SS304 in SBF at room temperature (25 °C) and body temperature (37 °C).

<table>
<thead>
<tr>
<th>Equivalent Circuit elements</th>
<th>MoNbTaTiZr at Room Temperature</th>
<th>MoNbTaTiZr at 37 °C</th>
<th>SS 304 at Room Temperature</th>
<th>SS304 at 37 °C</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Value</td>
<td>Error</td>
<td>Value</td>
<td>Error</td>
</tr>
<tr>
<td>Rsoln (ohm*cm²)</td>
<td>7.31</td>
<td>1.82 × 10⁻³</td>
<td>6.99</td>
<td>125.82 × 10⁻³</td>
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<tr>
<td>Rpass (ohm*cm²)</td>
<td>1.6</td>
<td>781.08 × 10⁻³</td>
<td>7.40</td>
<td>507.80 × 10⁻³</td>
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<tr>
<td>Rp (ohm*cm²)</td>
<td>137.10 × 10³</td>
<td>1.79 × 10⁻³</td>
<td>21.39 × 10³</td>
<td>1.34 × 10⁻³</td>
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<tr>
<td>Rpore (ohm*cm²)</td>
<td>17.73</td>
<td>245.39 × 10⁻³</td>
<td>1.23 × 10⁻³</td>
<td>17.78 × 10⁻³</td>
</tr>
<tr>
<td>Cpass (F/cm²)</td>
<td>8.32 × 10⁻⁶</td>
<td>13.42 × 10⁻⁹</td>
<td>22.34 × 10⁻⁶</td>
<td>121.61 × 10⁻⁹</td>
</tr>
<tr>
<td>Cp (S*s⁻¹/cm²)</td>
<td>9.63 × 10⁻⁶</td>
<td>15.54 × 10⁻⁹</td>
<td>84.19 × 10⁻⁶</td>
<td>8.17 × 10⁻⁶</td>
</tr>
<tr>
<td>Cc (S*s⁻¹/cm²)</td>
<td>16.35 × 10⁻⁶</td>
<td>23.20 × 10⁻⁹</td>
<td>23.78 × 10⁻⁶</td>
<td>443.32 × 10⁻⁹</td>
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<tr>
<td>n</td>
<td>884.1 × 10⁻³</td>
<td>3.06 × 10⁻⁶</td>
<td>384.9 × 10⁻³</td>
<td>3.06 × 10⁻⁶</td>
</tr>
<tr>
<td>m</td>
<td>874.9 × 10⁻³</td>
<td>61.53 × 10⁻³</td>
<td>839.2 × 10⁻³</td>
<td>3.30 × 10⁻⁵</td>
</tr>
</tbody>
</table>

Table A.2: Elemental distribution (at. %) for spot EDS on wear tracks of MoNbTaTiZr

<table>
<thead>
<tr>
<th>Elements (at. %)</th>
<th>9Hz 5 N Wear track</th>
<th>15N 5Hz Wear track</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>5.62 ± 0.06</td>
<td>0.74 ± 0.07</td>
</tr>
<tr>
<td>Ti</td>
<td>6.00 ± 0.06</td>
<td>5.47 ± 0.06</td>
</tr>
<tr>
<td>Ta</td>
<td>5.44 ± 0.04</td>
<td>4.57 ± 0.04</td>
</tr>
<tr>
<td>Ca</td>
<td>2.69 ± 0.10</td>
<td>5.71 ± 0.06</td>
</tr>
<tr>
<td>O</td>
<td>61.47 ± 0.10</td>
<td>68.35 ± 0.09</td>
</tr>
</tbody>
</table>