An Electrochemical and Tribocorrosion Study on Austenitic High Nitrogen Steel in Orthopedic Applications

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THESIS

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DEDICATION

I would like to dedicate this work and the time invested in the completion of this thesis to my family: Grandma, Parents, my Wife and Siblings. This thesis is for the person who has been my support and motivation from day one: My Grandmother, Safia Sultana. It is her prayers and hearty wishes that I am able to complete this thesis. Lastly, I would also like to dedicate this thesis to all my friends and Dr. Mathew for his extremely kind mentorship.

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LIST OF ABBREVIATIONS

AHNS	AUSTENITIC HIGH NITROGEN STEEL
ASTM	AMERICAN SOCIETY FOR TESTING AND MATERIALS
BCS	BOVINE CALF SERUM
CoCrMo	COBALT CHROMIUM MOLYBDENUM
CE	COUNTER ELECTRODE
CoP	CERAMIC ON POLYMER
EIS	ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY
MoM	METAL-ON-METAL
MoP	METAL-ON-POLYETHYLENE
OCP	OPEN CIRCUIT POTENTIAL (V)
Rp	POLARIZATION RESISTANCE (OHMS•CM2)
RE	REFERENCE ELECTRODE
SS	STAINLESS STEEL
SEM	SCANNING ELECTRON MICROSCOPY
SCE	SATURATED CALOMEL ELECTRODE
THR	TOTAL HIP REPLACEMENT
Ti	TITANIUM ALLOY
WE	WORKING ELECTRODE
WLI	WHITE LIGHT INTERFEROMETRY

SUMMARY

Arthritis or rheumatism is the leading cause of disability. Majority of the patients, who goes through this disability, finds their solution by doing Total Hip Replacement (THR) surgery. More than 285,000 hip replacements are performed in the U.S. each year. It is estimated that by 2030 there will be an increment of 175% in the THR surgeries rising the numbers to 0.5 Million. Thus, these numbers portray the importance of hip replacement surgeries in the near future. Recently, there is a growing concern on the metal-on-metal (MoM) hip implants among the orthopedic clinicians and researchers. This is partially due to wear and corrosion behavior of the metals used for such implants, particularly their synergistic interactions lead to early failure and release of the metal ions to the host body. Majority of the hip implants are made of cobalt-chromium-molybdenum alloy (CoCrMo alloy), Ti6Al4V (Ti alloy) and Stainless Steel (316L). In the body, these implant metals are exposed to extremely complex and variable conditions, which can lead to degradation of the material and subsequent adverse biological reactions that has led to rise of many diseases and infections in the human body.

We hypothesized that Austenitic High Nitrogen Steel (AHNS) will have better electrochemical and tribocorrosion behavior than the other commonly used implant metals CoCrMo, Ti6Al4V and stainless steel (SS). AHNS will prove that it has strong wear and corrosion properties. Hence this study has two objectives: 1. To study the electrochemical characteristics of AHNS and compare with other commonly used implant alloys, CoCrMo, Ti6Al4V and stainless steel (SS). 2. To study the tribocorrosion behavior under tribocorrosion behavior under Potentiodynamic, Free Potential and Potentiostatic conditions in stimulated biological environment in order to verify the improvement in corrosion kinetics (from electrochemical test) under combined exposure to wear and corrosive joint environment of AHNS with CoCrMo alloy.

The findings of this investigation validate our hypothesis and suggest that AHNS shows better corrosion behavior compared to other traditional alloys in particular to CoCrMo. Electrochemical results exhibited the enhanced corrosion kinetics leading to a stable passive layer formation and better corrosion resistance of AHNS compared to CoCrMo alloy and Titanium alloy. Our studies shows that, AHNS exhibits better tribocorrosion behavior under Potentiostatic, free potential and potentiodynamic modes compared to traditional alloys. AHNS displayed more stable current conditions during mechanical stimulation as compared to CoCrMo.

In general, AHNS portrayed superior electrochemical and tribocorrosion behavior compared to other traditional alloys. The Nickel-free AHNS could be considered as a potential implant metal for orthopedic applications. Its superior corrosion and wear characteristics could assist in solving current concerns of the metal based orthopedic implants. AHNS has also proven to be a biocompatible metal and has shown superior properties for hard tissue implants. Current study will be extended to identify any other limitation of AHNS before considering an alternative implant metal, particularly in hip prosthesis application

1 CHAPTER 1: INTRODUCTION

1.1 Orthopedic Implants

An orthopedic implant is a medical device, surgically placed in a body to treat or replace a missing joint or bone and to support a damaged bone in the knees or hip. Orthopedic implants are designed in a way to provide mechanical stabilization to load bearing joints, that are conditioned to heavy mechanical stress, strain, and wear in the course of daily activities of a patient (1). Orthopedic implants plays vital role in restoring the function of an injured limb or body part, and helps in facilitating the pain relief. Theses implants are commonly used as prosthesis in hip, knee, and shoulder joints. Polymers, ceramics, and metals are the three most common types of materials used for designing and developing orthopedic implants (1). Metals like Titanium (Ti-6Al-4V), Cobalt Chromium (Co-Cr-Mo) & Stainless Steel (316L) are commonly used metal implants in orthopedic devices (2). The introduction of a foreign object in human body often leads to a risk of infection in the body, and orthopedic implants are not different. Orthopedic implants are often associated with microbial infections, which can lead to implant failure (3). In spite of these concerns, the need for orthopedic implants is great, particularly in the area of hip replacement, where these orthopedic implants play a vital role in the recovery of day to day movements in patients receiving total hip replacements.

1.2 Total Hip Replacements

Arthritis or rheumatism is the leading cause of disability among many fellow Americans (4). According to Center of Disease Control (CDC), 53 million American adults are suffering from Arthritis (4). Arthritis is a systemic inflammatory disease that develops by itself during the course of time in various joints of the human body. This is mainly caused by inflammation of one or more joints and is often referred as joint pain. This inflammation mainly occurs between the linings of the joints which are known as synovial membranes. The inflammation of joints leads to erosion of the bone cartilage and by overtime joints become loose and unstable. This leads to joint deformity and ultimately reducing the mobility of the person. Individuals with arthritis have severe limitation in function on a daily basis (4). Majority of the patients, who are suffering from this disability, consider Total Hip Replacement (THR) as the treatment strategy to overcome the difficulties. More than 300,000 hip replacements are performed in the U.S. each year (5). It is estimated that by 2030 there will be an increment of 174% in the THR surgeries rising the numbers to 0.5 Million (6). Thus these numbers defines the importance of hip replacement surgeries in the near future. Hip joint deterioration leads patients to extreme pain, stiffness in the joints and difficulty in walking. When these symptoms do not respond well to traditional treatments like physical therapy or pain medications, patients are then advised to undergo hip surfacing or total hip replacement. During this treatment, patients may receive hip implants which can consist of number of combinations. Hip implants can be divided into three major combinations: Metal on Polyethylene

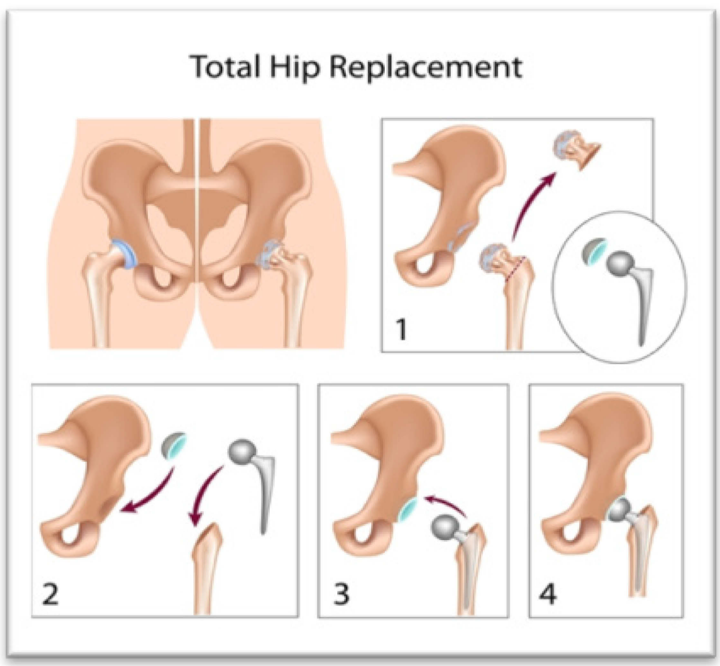

Figure 1: Hip replacement procedure [5] Courtesy of *American Academy of Orthopedic Surgeons* August (2015)

(MoP), ceramic on polyethylene or ceramic on metal (CoP or CoC or CoM) and metal on metal (MoM). Metal on Polyethylene (MoP) is made of metal ball and plastic socket. MoP due to its unique nature are more durable and versatile. They are known to have less wear and toxic issues in the human body. However, recent studies have shown that metal on plastic implants produced various instability problems in the patients who were more physically active and had high effects of metal ions and wear debris in the patient's body (7). Ceramic bearing implants are often used in younger patients due to its material characterization and toughness in the composition. They have proved to have better wear characteristics compared to other hip implants. While these are all good properties of hip implants, they are more prone to fractures and breaking during high stress due to the brittleness nature in the composition. They are harder to implant and replace during surgeries, due to the requirement of high quantity of removal rate in healthy bone because of size limitations (8). Thus, it leads to a more expensive option than other hip bearings. Another major combination in hip devices are metal on metal (MoM) hip implants in which both the ball and socket of the device is made of metal as shown in **Figure 1.** These metal implants have been extensively used in THR surgeries and hip resurfacing procedures among many patients. Metal on metal devices are generally expected to last longer than other hip implants due to the durability of the metal compared to other components. MoM is usually smaller in size, so they are easier to install and replace with smaller incision during surgeries. Since both surfaces of the components are hard without being brittle, they are less prone to scratching and wear. As all hip bearing implants have certain disadvantages, MoM is no different; there has been number of reports of high metal ion degradation in the human body due to interaction of metal alloys in biological environment. Thus, these are some major combinations of total hip replacement.

Nevertheless, THR has been extremely beneficial for patients, helping their quality of life with ease in mobility and providing them with utmost pain relief.

1.3 Current Problems in Total Hip Replacements

More than half of the world population over 65 years of age are suffering from different types of limb diseases and approximately quarter of the population over the age of 65 years are in constant need of medical care for joints and hip associated issues (9). There is a growing need for orthopedic advancement due to the rise of various joint and hip diseases. There has been a significant increase in failed joint replacements associated with osteolysis and bone defects. One of the most common reasons for implant failures is due to the aseptic loosening of components, citing almost 75% of failure rate (10). Biocompatibility of the device should be the key factor in the development of hip implants. Recently, as mentioned earlier number of studies in the orthopedics world has portrayed extensive metal debris being discharged by the implants when placed in the body. As with majority of non-natural materials in human system, orthopaedic implants also act as foreign bodies within the live cells and tissues. Thus, they are more inclined towards infection and other harmful diseases. The ejection of metal ions and debris from these implants increases the probability of having adverse infections in the body. Due to such issues in the implant, the lifespan of hip replacement implants have been reduced significantly. There has been a significant rise in the revision surgery for early failures of hip implants. The revision surgery is where health professional replaces the initial implant with another new implant. Thus, this causes economic burden to the patient, and reduces their functional mobility for significant time. One study suggested that patients disability level increased by having to experience pain and functional limitations due to the long wait times for hip revision surgery (11). Thus, hip replacement devices need to prove its success in the biocompatibility and longevity of the implant in the human body. Despite such medical advancements currently being explored, one of the key challenges in orthopedics is the engineering of an implant that incorporates bone healing properties with enhanced biocompatibility, and thus it helps in reducing biological related implant failures.

1.4 Metal On Metal Hip Replacement

In the recent years, there has been a tremendous growth in the development of hip and knee replacements. The earliest history goes back to 1891 for the development of hip implant fixation by Professor Themistocles Gluck who replaced the femoral head of the implant by using Ivory ball in Germany (12) . In 1940, an American Surgeon Dr. Austin T.Moore performed the first metallic hip replacement surgery at John Hopkins hospital (12). The prosthesis was designed to replace proximal twelve inches of a femur, with a custom made Cobalt-Chromium alloy Vitallium (12).

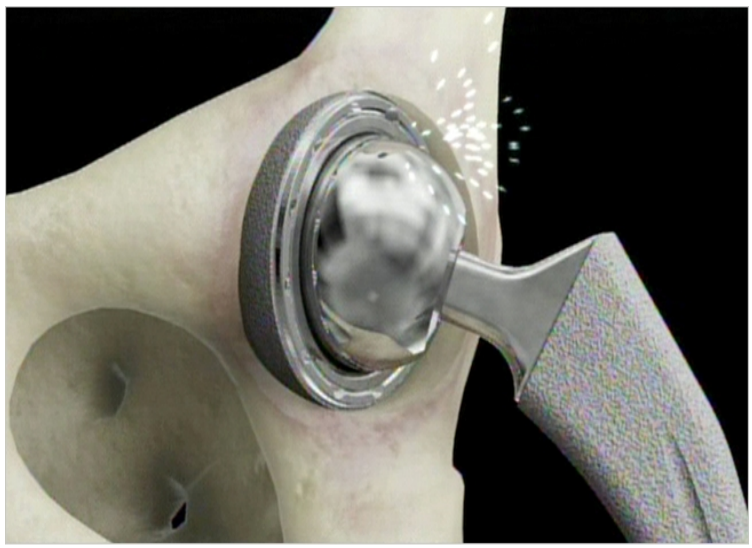

Figure 2: Metal Ion Debris [9] New York Times, March 9, 2010

Majority of today's hip implants are made of cobalt-chromium-molybdenum alloy (CoCrMo alloy), Ti6Al4V (Ti alloy) and Stainless Steel (316L) (13). Recently, there has been a growing concern on the metal-on-metal (MoM) hip implants among the orthopedic clinicians and researchers. This is partially due to wear, and corrosion behavior of the metals used for such implants, particularly their synergistic interactions lead to early failure and release of the metal ions into the host body as shown in **Figure 2**. In the human body, extremely complex and variable conditions are exposed to various metal implants leading to degradation of the material and causing hostile biological reactions. Thus it leads to rise of many infections and diseases in the body (14). Current studies have shown that some of the major orthopedic implant companies were forced to recalled their knee and hip replacement products by FDA due to various biological issues related to metal alloys (15). One of the key reasons for these recalls was due to fretting and corrosion of metal on metal.

One of the major issues that have been identified in patients who have had metal-on-metal (MoM) hip replacement implants include high rates of wear, particularly in cases where the implants have been malpositioned and those stemming from the release of metallic ions into the surrounding tissues and bloodstream as a result of metal ions being exposed in the blood stream (16,17). In order to reduce wear and control the amount of metal ions being excreted into the body due to lack of biocompatible metals, new hip replacement implants must be conceptualized (16,17). The most commonly used MoM materials are either Ti-alloys, which include alloys made out of titanium bases, or CoCrMo alloys (18,19). The performance of current MoM hip replacement devices reported over the last decade have been shown to have high biocompatibility in long-term implants, with implants lasting longer than they have in the past (18,19). For the older generation, a lifespan of 15 years after the implantation was previously considered sufficient, but with the vast advancement in technological proficiencies, such efforts are no longer deemed to be adequate (20). A shortened longevity period for a hip implant may be sufficient for younger patients who are still growing and in near future would need to be equipped with larger implant size, but for the older population, longer lasting implants with decreased side effects are vital to maintaining their overall health levels (18,21).

Passive layers formed on the surface of the metal alloys that helps in protecting the surface from degradation, are broken due to wearing process and metal ions being constantly released due to continuous metal on metal interactions in biological environment (22). A large number of metals release metallic ions during the course of time, and reducing these ions will help in the biocompatibility of the implant, and it will reduce the risk of failures in these implants (18). Thus, it will enable patients to be more satisfied with their implant in long term.

The first case of metal-related dermatitis was reported in 1966; since then, a growing number of reports of such cases have been published in the literature (23). By 1986, 42 such cases had been documented; 30 patients developed dermatitis in the setting of a static implant, whereas the remaining 12 patients with dermatitis had received a dynamic joint prosthesis (23). The condition of 18 (42.9%) of the 42 patients was diagnosed as "eczematous dermatitis" (23). Generalized eruptions in the form of erythema, urticaria, and vasculitis were also reported (23). In light of these findings, additional research is required regarding the potential need to limit the release of metallic ions in metal on metal hip implants and to enhance the life span of these implants.

One of the metals known as Austenitic High Nitrogen Steel (AHNS) have shown to have high corrosion resistant properties compared to other traditional alloys, and thus to understand in detail about this alloy, electrochemical and tribocorrosion study will be performed.

1.5 Hypothesis

We hypothesized that Austenitic High Nitrogen Steel (AHNS) will have superior electrochemical and tribocorrosion behavior than the other commonly used implant metals CoCrMo, Ti6Al4V and stainless steel (SS). AHNS will prove that it has strong wear and corrosion properties.

1.6 Thesis Aims

The Aims of this Study can be characterized into two parts:

1.6.1 Electrochemical Characterization

The first part of the study was to investigate the electrochemical characteristics of the Austenitic High Nitrogen Steels (AHNS) samples under biological conditions. Other alloys such as Cobalt Chromium, Titanium and Stainless Steel (316L) were also evaluated by electrochemical characteristics under similar conditions. The purpose of this study is to compare and analyze electrochemical characteristics of AHNS with other commonly used implant alloys, CoCrMo, Ti6Al4V and SS-316L steel.

1.6.2 Tribocorrosion

The second part of the study was to understand the tribocorrosion behavior under Potentiodynamic, Free Potential and Potentiostatic conditions in stimulated biological environment. The study was performed to verify the improvement in corrosion kinetics under combined exposure to wear and corrosive joint environment. The purpose of this study is to understand the tribocorrosion kinetics of AHNS with CoCrMo alloy.

2 CHAPTER 2: LITERATURE REVIEW

2.1 Concerns of Common Metals Used in Hip

The majority of hip implants are made of cobalt-chromium-molybdenum alloys (CoCrMo alloy), Ti6Al4V (Ti alloys), and chromium-nickel steel (Stainless Steel SS-316L) (13,14). In the body, the implants are exposed to extremely complex and variable corrosive conditions, which can lead to degradation of the material and subsequent adverse biological reactions. Corrosion is the degradation of materials properties by its surrounding environment leading to release of ions in the microenvironment. Corrosion is one of the most important studies that give us an overview as to the nature of failure of many dental and orthopedic implants. While each of these different metals has different associated wear rates, and each of these different metal alloys responds differently to a corrosive environment, it is important to explore each one individually, including titanium, Co-Cr-Mo and stainless steel.

2.1.1 Cobalt –Chromium-Molybdenum Alloys

Co-Cr-Mo alloys are known for their high levels of resiliency, particularly when treated with selective laser melting during the manufacturing process (24,25). The alloys have high melting points, high tensile strength, and a decreased potential for erosion, which makes them a preferred metal for use in the manufacture of many artificial joints including hips and knees (24,25). However Co-Cr alloys by themselves are known to have low ductility, leading to component fractures and resultant biocorrosion, which is the reason for the inclusion of molybdenum, or in many cases, nickel, carbon, or nitrogen may be incorporated to strengthen the alloy and reduce the potential for damage to the manufactured components (26). The inclusion of one or more of these elements helps in stabilizing the γ phase, the phase that has superior mechanical properties, in comparison with other phases of cobalt chromium alloys (27). CoCrMo alloys are also one of the most commonly used MoM bearing due to their high corrosion and wear resistance characteristics (30). Carbon plays an important part by being added in the formation of this alloy, by forming carbides in the microstructure. Carbides provide wear resistance and strength in the alloy by taking chromium and molybdenum from the nearby area during the solidification process. During articulation with a different surface, such as hip implant they may come under contact with a softer matrix and during body movement, two body grooving can take place where hard asperities (the carbides) comes in contact with their opposite surface leading to deep grooves. Thus, this can cause a release of metallic ions and wear debris in the surface.

Wear particles that are released from Co-Cr alloy tools and prosthetics may lead to an allergic reaction to the patient, patients may get skin eczema if they have sensitivity to any of the metals or elements used in the creation of the prosthetics themselves (31). Prosthetics and medical equipment's containing elevated nickel mass percentage, like Co-Cr alloys, must be avoided because of lower biocompatibility, as nickel is known to be the most common metal sensitizer in the human body (31).

Hallab, Merritt, and Jacobs (2001) detailed the issue of metal allergies in orthopedic patients (32). In their meta-analysis, the researchers noted relationships demonstrating a higher incidence of allergy to nickel, cobalt, and chromium among patients with poorly functioning implants than in patients with well-performing implants (33). A subsequent meta-analysis by Granchi, Cenni, Giunti, and Baldini (2012) supported this relationship noting "the probability of having a metal allergy was more than doubled in patients who had a failed replacement than in those with a stable replacement" (34). Similar to patients with allergies to other substances such as pollen, pets, etc., several studies have shown the majority of patients with metal allergies demonstrate reactions to more than one metal, rather than reacting to a single allergen (31). While nickel is the most often cited allergen, cobalt, and chromium sensitivities have also been cited as the causes of complications in hip and knee replacement surgeries (34).

2.1.2 Titanium and Titanium Alloys

One of the biggest advantages in the use of titanium and titanium alloys in medical devices is the strength that such metals offer (18). It has the strength of steel without the heavy weight behind it, being recorded as nearly 50% lighter in weight, titanium and its alloys are ideal for their use in surgical implant procedures (18). However, titanium is highly prone to be contaminated when exposed to hydrogen, nitrogen, and or oxygen, which effects the corrosion process in this metal, and thus the usage of this alloy maybe compromised in certain medical procedures (35) . Often titanium and its alloys are chosen as materials for metal plates or femoral stem implants because of its low modulus of elasticity (in comparison to other alloys); stainless steel has an elastic modulus which is 12 times the EM of cortical while the EM of titanium is six times that of cortical bone (36–38) .

Even though titanium-based implants are normally estimated to last ten years or more, its longevity is not certain, along with its insufficiency to integrate into the bone often occurs and leads to implant failure (39). Despite the primary health condition, surgery is required to address implant failure, which in turn involves increased risk, complications, and costs, all areas that could be further exacerbated depending on the primary health condition of the individual (40).

The main reason for implant failure that causes 60 to 70% of cases for revision surgeries, where the failure of the implant is the primary health condition is the aseptic loosening of the material (41,42). The success of an implant relies on its firm bonding or fixation of implant biomaterial to the bone, for ideal function and longevity, with new research being conducted in implant coating to work to reduce complications and increase the fixation of the implant (43).

Titanium alloys, were initially used for aeronautics, but due to their strong properties like biocompatibility, low modulus of elasticity, and superior corrosion resistance, they have been widely used in the biomedical field in the recent years (12). The presence of a strong oxide layer formed on the titanium surface, caused the osseointegration phenomenon, thus helping the development of titanium use in orthopedics (12,43). Titanium alloys are typically used in femoral necks and stems of orthopedic implants due to their low modulus of elasticity property affecting less shielding of bone (23). Thus, they are often used in low weight bearing surface compared to other alloys. Nevertheless, the osseointegrative bioactivity is still far from attaining a strong adhesive bond between the bone and implant, which has often led to mechanical instability and failures in various implant applications (23).

Titanium implants forms an oxide layer that helps it to assimilate with the living bone tissue. Though, Titanium is a good alloy in the integration with bone tissues, it causes adverse reactions to the human body such as inflammation and fibrosis, that has long term functional impact on the performance of titanium alloys (44). Apart from all these drawbacks titanium components tends to get condensed and covered by fibrous tissues of the living body after the implant has been placed (44). The extra cellular matrix in lengthier period could cause micromotion and due to the wear particles being generated at the surface of the implants thereby, causing in an inflammatory cascade leading to osteolysis which eventually would lead back to the aseptic losing and revision surgery of the implants (41,42). The Ti–6Al– 4V alloy has been employed for medical and dental implants; however, the cytotoxicity of vanadium has become an issue of concern (45). This has resulted in a further narrowing in the focus of new areas of research.

2.1.3 Stainless Steel 316L

It is common practice in orthopedics to employ the use of medical grade stainless steel (SS) 316L as a temporary implant (46). This material has mechanical properties relative to those of bone mineral, is easy to fabricate and is available at a lower cost than other materials that could be used for this practice (46). It has been reported that SS can corrode in vivo, leading to the discharge of metallic ions such as iron, chromium and nitrogen (7,8). Okazaki and Gotoh (2005) evaluated that a set of 20 patients who had gone through hip replacement (made of stainless steel) after 10-13 years, showed high levels of metal ions in the body fluid in comparision to those without an implant; nitrogen levels in the blood ~0.51 μg/L, in the plasma ~0.26 μg/L and in the urine 2.24 μg/L, along with Chromium levels in the plasma ~0.19 μg/L were all identified as greater than the control group (47). The corrosion and degradation products of the implant can lead to an inflammatory response locally and systemically in the individual (47).

Addition of chromium (16%) to stainless steel, helps the metal alloy to be more corrosion resistant (48). 316L stainless steel chosen for surgical implants contain nearly 17 to 19% of chromium and 14% nickel (48). With the surgical implant, molybdenum is incorporated to the stainless steel alloy forming a protective layer protecting the metal from being exposed to an acidic environment (48). Moreover, in a solid solution state carbon element can also aid in achieving corrosion resistance (48).

Corrosion products have been linked with neoplasm as well as cessation in bone formation and growth, inflammation of the synovial membrane along with loosening of artificial joint implants (49). For example, a recent study reported that SS 316L emits corrosion products exceeding the non-lethal concentration and causes a disturbance by having a rapid increase in the osteoblastic alveolar cell cultures of the bone in a quantitable manner (47). Due to significant localized corrosion occurrence, for instance like pitting and crevice corrosion more than 90% of the stainless steel 316L implant materials were failed (47). Following the implantation period, intensity of corrosion attacks amplified and failure of the pit-induced fatigue was observed in the compression bone plate, the intramedullary nail cracked due to pit induced stress as a result of corrosion leading to nail edges and cracks being significantly pitted. (47).

In order to minimize the rate of corrosion as well as to reduce the metallic ions from being emitted, several attempts were made to alter the metal implant surface with ceramic coatings (1,48). A search of the extant body of literature shows that there was improvement in the bioreactivity, corrosion and wear resistance due to the ceramic coatings onto the metal alloys (1,48). Particularly, hydroxyapatite (HA) ceramic coatings on the metallic substrate draws distinctive response from the research communities due to its exceptional properties of biocompatibility and bioactivity (1). Hydroxyapatite is well recognized as the mineral substance of hard tissue such as bone, dentine and enamel and when it is used as a bone substitute material, it directly forms a bone bonding to hard tissues (1). Unfortunately, due to its weak mechanical reliability in terms of its poor fatigue resistance and tensile strength, its mismatched elastic modulus and the resultant stress shielding has to a certain extent caused limitations in its clinical applications (49).

2.2 Austenitic High Nitrogen Steel (AHNS) Introduction

As previously indicated, stainless steel is widely used as a biomaterial in the creation of medical implants due to its low associated costs in the manufacturing and machining process (50). As previously discussed, however, the nickel within basic stainless steel results in increased corrosion and wear, causing an increased presence of metal ions within the bloodstream, creating detrimental conditions for the recipient of the implant (50). These side effects can be particularly detrimental to patients, necessitating the exploration of the creation of other types of metal, or changes made to the composition of the metal in order to improve the overall stability, decrease corrosion, and decrease other associated adverse side effects. In order to reduce those adverse side effects, steps have been taken to remove the nickel used in the creation of the stainless steel alloys, replacing it with nitrogen, allowing for the creation of austenitic high nitrogen steel (50). While austenitic high nitrogen steel (AHNS) is a more appropriate metal for use in medical implants due to the lack of nickel and as such a decreased likelihood for adverse reactions on the part of the patient, AHNS is still classified as a form of stainless steel due to the materials used in the creation of the steel and the process employed (50). While AHNS is not as low cost as SS to produce, the benefits afforded by the lack of nickel used in the manufacturing process do outweigh the slightly higher cost; as a SS, however, AHNS is still a lower costing metal than other metals used in medical implants at this time (50). AHNS provides increased structural stability, decreases the potential corrosion, removes the potential for an allergic reaction to the nickel, offers greater strength to the structure, and decreases wear resistance (50). In addition, AHNS has higher biocompatibility than that of the SS 316L, a metal that also falls into the austenitic steel category (50). Despite the benefits of this particular metal as a biomaterial, there is still a great deal that is not yet known about the properties of AHNS (51). While it is known that the mechanical properties exhibited by AHNS are far superior to those of the more traditional options, the "microstructural and mechanical properties and the corrosion rate" while correlated to regions of processability during hot formation, are still being explored at this time (51). The use of the metal as a biomaterial is relatively new, occurring within the past two decades. The creation of the metal is a relatively new process, as is the use of AHNS in the medical field, resulting in a need for the completion of additional research in order to better understand how the material will hold up over time, under stress, and what corrosion and wear rates it may have. Research has indicated that the higher the heat and the greater the stress that the metal is subjected to, the more quickly the material starts to break down, resulting in corrosion and wear (51); as such, those in intensive physical routine activities may not benefit from the use of an implant made from this type of metal, further stressing the fact that there is still much to be learned regarding the use of this metal within the context of a medical implant. Further research is necessary to explore what effect, if any, these results will have on the use of the metal in the creation of implants. In spite of the need for additional research, the metal has been shown to reduce adverse side effects associated with other metals, and while it is perhaps still too early to be able to identify the long-term characteristics of the metal in its use in medical implants, the results of its use have been positive to date (52).

2.3 Corrosion

Corrosion refers to the deterioration of a given type of metal due to the reactions and interactions between that metal and its surrounding environment; in the case of implants, this refers to the reactions and interactions of the metal implant with the body, tissue, and fluids of the individual receiving the implant (53). More specifically, corrosion is "chemical oxidation comprising reduction reactions involving electron transport," which in turn "produces electrochemical degradation" (54). The amount and type of corrosion that can occur with a given biomaterial is largely dependent upon the type of material being used in the manufacture of the given object (55). It should also be noted that the type of implant likewise plays a factor in the type and amount of corrosion that can occur within the given object (55). As previously discussed, some corrode slower than others, while still others have various biofilms placed on them at the time of manufacture in order to further reduce the potential for corrosion in the device.

The corrosion of the metal implant occurs over time, based on the interactions between the metal in the implant and the implant environment are not the only factors that must be taken into consideration when exploring the type and amount of corrosion on the implant itself. Researchers have determined that the modularity of the implants likewise play a role in the type and amount of corrosion that will occur (56). The modularity of the implant refers to the total number of parts in the implant; the degree that the components can separate and recombine; thus, the greater total number of parts that are present in the implant, the higher the likelihood that the implant will be subject to corrosion (56). The corrosion of these different metals results in a host of byproducts that occur in different states and different sizes, again, dependent on the material being used and the modality of the implants, with each of these different factors resulting in detrimental effects on the host body (57). Over time, these metallic particles and metal ions continue to build in the body, dissolving in intracellular fluid, being internalized by surrounding tissue, migrating through the body via the bloodstream, and even accumulating within the brain

(57). Due to the size and nature of the migration of these byproducts through the body, many remain within the body of the individual instead of being flushed out of his or her system. The accumulation of metal ions and metallic particles in the body, will leads to local and systemic toxicity (57).

Corrosion of metal and metal alloy implants is, as such, a serious consideration when determining the best fit implant for the patient. At the same time, care must be taken to ensure that the implant is one that meets the needs of the patient. This further stresses the importance and necessity of the creation of an implant that works to address the detrimental aspects associated with corrosion while working to create an implant that is structurally sound, providing the necessary support and structure to the patient. Issues with corrosion have played a major role in current research, offering additional insights and means of improving the current devices being made, but still not fully addressing the problem as of yet. Corrosion is not, however, the only problem that must be taken into consideration when looking at potential areas of concern associated with medical implants; tribocorrosion must be taken into account as well.

2.4 Tribocorrosion

Metallic implant degradation occurs when electrochemical dissolution and mechanical/ physical wear are combined (58). This process, known as tribocorrosion, in layman's terms, refers to the process that occurs within the medical implant as a result of degradation due to the combination of corrosion and wear on the implant (58). Tribocorrosion is one of the primary reasons that MoM joint replacement implants fail 15 to 20 years following insertion (54). Basic wear on the joint is discussed in greater detail in the next section; however, when combining basic wear of the implant with the corrosion of implant material result is an increased toxicity within the body. As the metal becomes more corroded, the surface of the implant changes, providing the potential for increased wear (54). As the individual uses the joint, wear occurs, rubbing down the material further, providing the potential for further corrosion (54).

As with corrosion, there are secondary detrimental effects that can occur as a result of the presence of tribocorrosion. Not only are the potential toxicities that occur gradually with the presence of the medical implant and described in the section on corrosion a possibility, there are other, more immediate, detrimental effects that are a possibility (59). When tribocorrosion occurs, the most likely means through which it will be identified is as a result of an adverse reaction in the tissue surrounding the implant. This may manifest as an area of inflammation, a potential fever, soreness, swelling, or general discomfort (59). While it is possible that this may be caught in advance through a routine checkup, due to the variations in time of use during which tribocorrosion may occur, resulting from variations in type of implant, type of materials within the implant, location of the implant, and amount of wear and corrosion of the implant itself, the individual is more likely to identify the tribocorrosion through resultant discomfort.

This is not to state that tribocorrosion is not a serious concern, but rather to indicate the myriad factors that are associated with the identification and diagnosis of tribocorrosion. Failure to address tribocorrosion or to notice the inflammation in local tissue surrounding the implant can result in tissue necrosis, osteolysis, and even aseptic lymphocyte-dominated vasculitis-associated lesions (59). Tribocorrosion, once it starts to occur, has the potential to lead to a host of concerns for the individual and has the potential to compound further the other detrimental effects associated with use of the current array of medical implants available. While, ultimately, the only resolution to the matter is surgery to replace the implant itself, there are additional factors that must be taken into consideration, and each case must be carefully evaluated to determine the appropriate course of treatment, based on metal level testing, site assessment, and the potential for secondary health concerns, among other care aspects (59). The tribocorrosion will vary based on how active the individual is, other health concerns of the individual, and other health statuses of the individual. Furthermore, each patient will react in a different manner to the implant, its use, and the resultant side effects of tribocorrosion. Still a further difficulty arises from the fact that the potential is present for tribocorrosion to occur in all current metal and metal alloys used in medical implants at this time as, even if a protective barrier is put in place to reduce the potential for corrosion, this does not prevent the potential for wear, and patients who receive a medical implant do so in order to be able to continue to continue their activities of daily living. Tribocorrosion testing can distinguish the relationship between corrosion and wear (60).

2.5 Wear and Tear

The result of mechanical movement on the implant surfaces is known as wear (61). Basic wear on the medical implant occurs as a result of the different components rubbing against one another, or against other bones in the body (54). The more a given joint is used, the more the bone wears down; the same holds true for MoM implants (54). Furthermore, depending on the type of activity being done, the wear pattern will be different. This holds true for all types of bones, from dentition to the bones in the feet and to the workings of the very joints themselves (62) . While such wear and tear plays a seminal role in forensic exploration, these patterns of wear displayed on normal bones are equally likely to be found on MoM implants, though the frequency of wear may be decreased due to the tensile strength of the implants depending on the type of implants, the material they are made from, and the frequency of the action being completed. Metal ionic and particulate debris resulting from in vivo degradation of total hip replacement and as well as joint replacement components are recognized as one of the key factors in reducing the longevity of these joint and hip reconstructions, and the overall success of the procedure (63).

As previously discussed, when combined with corrosion, wear and tear of the medical implants can create further complications for the individual.(54). As the metal wears down, this provides a greater surface, one not previously treated against corrosion, on which corrosion can occur. As more corrosion occurs, the wear can become greater due to a breakdown in the metal. The result is that the presence of wear in the implant works to further compound the potential for corrosion and vice versa. Wear and tear is common in the use of any manufactured item with moving components; in this case, as the joint operates, the different pieces rub against one another. As these components are not biologic components, the body cannot affect this outcome, and can only work to process the associated debris. Lastly, wear can lead to the damage of the film formation in the contact area of the metal alloy, and thus this could lead to the exposure of metal surface to the electrolytic environment, affecting the corrosion resistance of the alloy.

3 CHAPTER 3: ELECTROCHEMICAL STUDY

3.1 Introduction

Corrosion is an electrochemical process of oxidation and reduction reactions. Corrosion of metals in aqueous solutions is defined as electrochemical process. Occurrence of corrosion leads to the discharge of electrons by oxidation process of the metal which is taken up by the elements by reduction process in the oxidizing solution. Because of the electronic current in the oxidation reaction, through electrical configuration these could be measured as well as controlled. Thereby, controlled electrochemically experimented methods could be applied to describe the corrosion characteristics of metal and metal components in the presence of different electrolyte solutions. In order to understand the enhanced wear and mechanical characteristics of austenitic high-nitrogen steels (AHNS) electrochemical testing was conducted under American Society for Testing and Materials (ASTM) standard G61. Corrosion behavior was evaluated with Gamry made potentiostat (G700) in a custom made corrosion cell (made of acrylic) under Bovine Calf Serum (BCS) to simulate in-vivo conditions.

3.2 Materials and Methods:

3.2.1 Specimens:

The samples (n=3) of AHNS, CoCrMo alloy, Ti6Al4V alloy, Stainless Steel (control) were used (12 mm diameter and 7 mm thick), and exposed area were mechanically polished to have mirror like surface with a Ra value below 20 nm. The chemical compositions of the tested samples in weight % are displayed in **Table 1.**

Table 1: Chemical Composition (in wt. %)

Material Composition	Fe	Cr	Mn	Mo	C	N	Co	Ti	Al	Ni	V	Others
AHNS	64.12	18	14	3	0.13	0.75	-	-	-	-	-	
Co-Cr-Mo	-	27.63	0.7	6.04	0.24	-	64.6	-	0.02	-	-	0.77
Titanium	0.16	-	-	-	0.004	0.008	-	89.62	6.1	-	4	0.108
Stainless Steel	62	16.72	1.18	2.05	0.08	-	-	-	6	12	-	

3.2.2 <u>Electrochemical testing:</u>

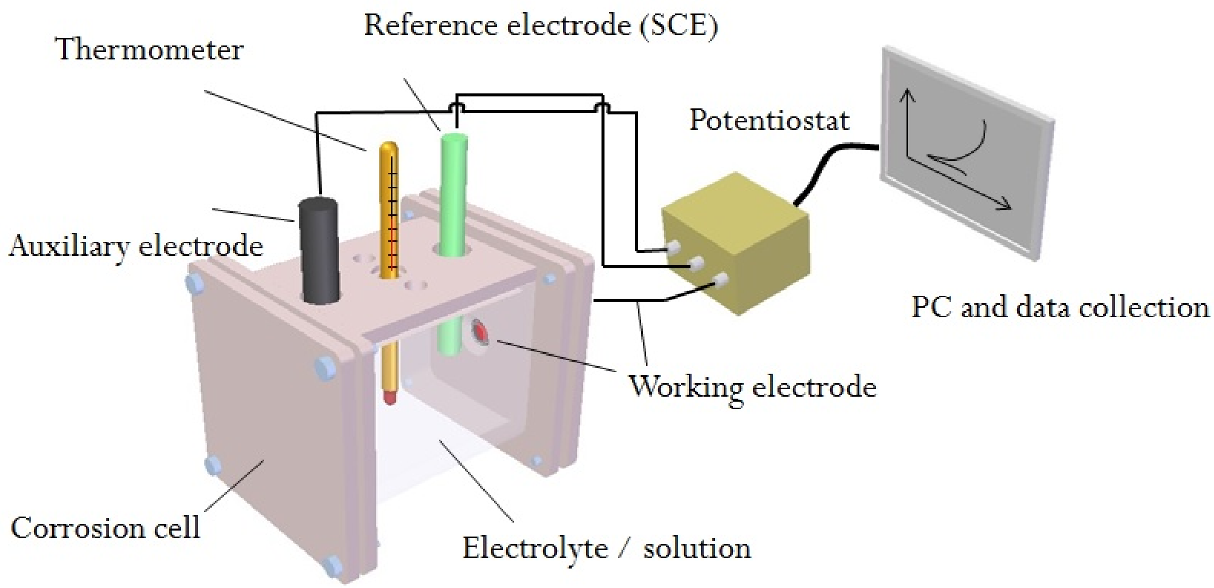

Figure 3: Electrochemical Test Setup

The electrochemical tests were conducted on samples with specially made corrosion cell and a Gamry made potentiostat (G700) was used and test protocol was based on the American Society for Testing and Materials (ASTM) standard G61 as shown in **Figure 3**. The exposed area of the material was 0.385 cm^2. The standard three electrode electrochemical set up was used: working electrode (WE), reference electrode (RE) and graphite rod: counter electrode (CE)

Electrolyte used in the experiment was bovine calf serum (BCS) with Protein content of 30 g/L. It mimics the synovial fluid conditions of the human body at pH 7.4. The temperature of the experimental solution was upheld at 37 ± 1º C to imitate the human environment. Gamry potentiostat (G300) was connected to a computer to extract data, and to study the corrosion measurements of the electrochemical test. A specific protocol was applied for electrochemical testing, which includes initial potentiostatic cleaning followed by an open circuit potential measurement, electrochemical impedance spectroscopy (EIS) test and finally the Potentiodynamic test (**Figure 4**).

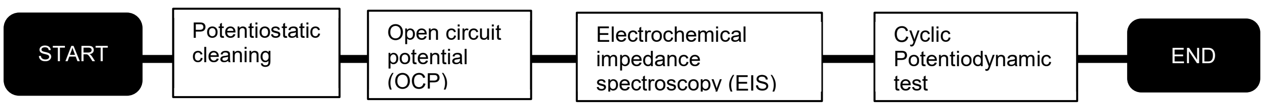

Figure 4: Electrochemical Test Protocol

Open Circuit Potential (OCP) ran for 600s to study the measurement of the corrosion tendency (Potential) vs. time length. EIS was conducted at E_{corr} with AC potential amplitude of ± 10 mV within a frequency range from 100 kHz to 0.001 Hz. During the potentiodynamic scan, the initial potential was -0.8 V to 1.8 V vs. SCE. The electrochemical parameters corrosion potential (E_{corr}), corrosion resistance (I_{corr}) were estimated from polarization curves by the Tafel method. EIS data were used to fit in an equivalent electrical circuit with modified Randles circuit (using Echem Analyst, Gamry) and polarization resistance (R_p) and Capacitance (C_f) were estimated. The model was checked for the goodness of fit of below 0.002. The data was analyzed using Origin software.

3.2.3 Surface characterization

Morphological characterization of the surface was carried out using different techniques. A white light interferometry microscope (WLI) (Zygo New View 6300) was used for capturing three-dimensional (3D) surfaces of the untouched (baseline) of the samples. These images help in understanding the changes and damaged surface of the metal alloy. The roughness of the surface was analyzed using the Zygo equipment as well. Scanning Electron Microscopy (SEM) images were used to observe the alloy microstructure and film composition.

3.3 Results and Discussion

3.3.1 Potentiodynamic data and Corrosion kinetics

The polarization curves for the tested metals are presented in **Figure 5**. The potentiodynamic curves results exhibited the enhanced corrosion kinetics leading to a stable passive layer formation and better corrosion resistance of AHNS compared to traditional alloys. The potentiodynamic curves displays the samples corrosion resistance after the samples has been corroded by analyzing the energy being moved from cathodic to anodic region, helping in determining the corrosion resistance of the sample. Estimated corrosion potential (Ecorr) and corrosion current (Icorr) are displayed in **Figure 6(a)** and **(b)** respectively. The corrosion potential and corrosion current were analyzed by using Tafel extrapolation. For AHNS the Ecorr value are more noble potential than other metal alloys. Compared to CoCrMo and SS alloy, AHNS shows low corrosion current; however it is higher than Ti alloy showing the qualitative ranking of the stability of passive films. According to Faradays law, the corrosion rate is directly proportional to corrosion current. Also, AHNS had higher pitting potential compared to all other alloys.

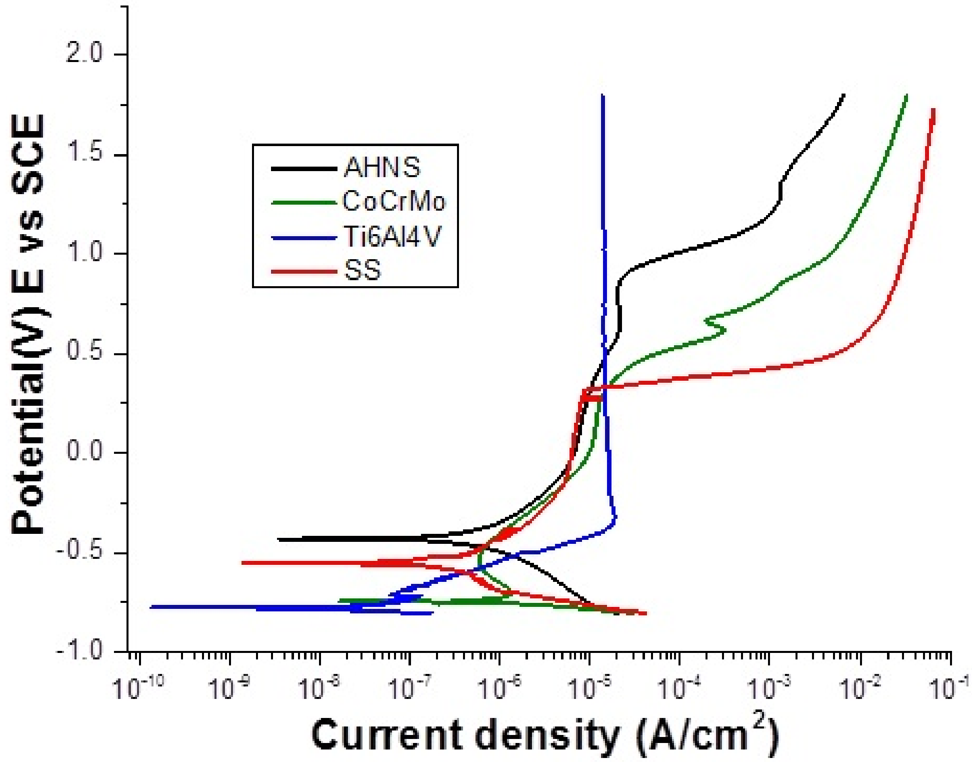

Figure 5: Polarization Curves of AHNS in comparison with CoCrMo, Ti6Al4V and SS (316L)

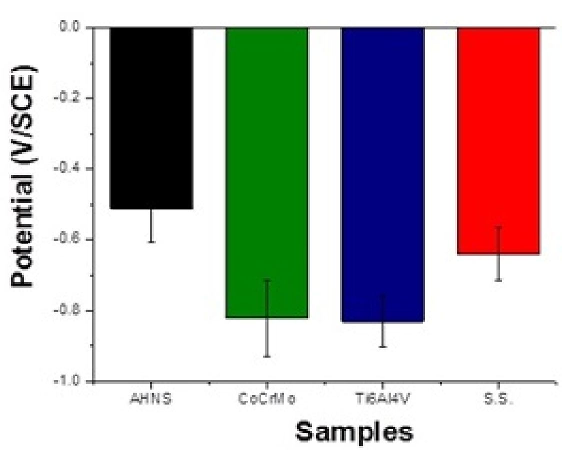

Figure 6a: Corrosion Potential (Ecorr) of AHNS in comparison with CoCrMo, Ti6Al4V and SS (316L)

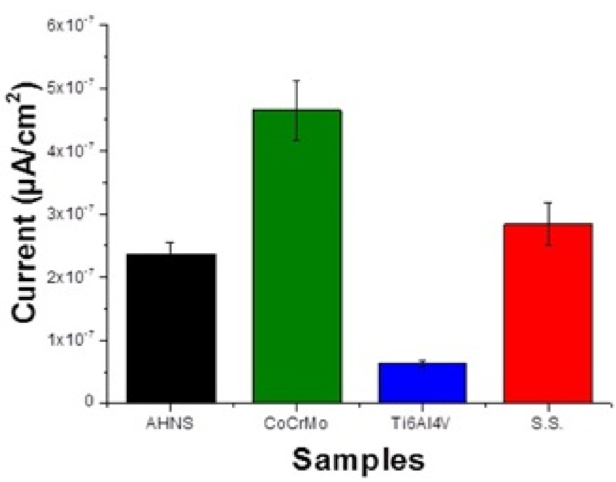

Figure 6b: Corrosion current (Icorr) of AHNS in comparison with CoCrMo, Ti6Al4V and SS (316L)

3.3.2 Electrochemical Impedence Spectroscopy

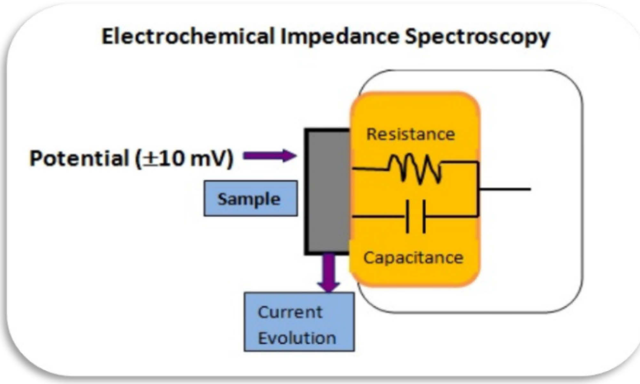

Figure 7a: EIS; Equivalent Circuit Model: Randles Circuit

The electrochemical impedance spectroscopy (EIS) technique was developed for characterizing electrochemical reactions at the electrolyte and metal interface. Thus, this technique helps in assessing the interfacial changes from the effect of protein at the metal surface. An equivalent electrical circuit model for the electrochemical process was used to analyze EIS data. This helps to understand the electrochemical kinetic parameters such as polarization resistance (Rp) and capacitance (C). The electric circuit used for this testing was modeled by Randall circuit. **Figure 7a** shows the schematic diagram of the EIS testing.

The results from this EIS model, polarization resistance (Rp) and capacitance (C) are presented in **Figure 7(b)** and **(c)** respectively. AHNS shows slightly low Rp and higher capacitance values than the CoCrMo and the Ti-alloy. EIS data can also be analyzed using Nyquist and Bode plot. These plots help in determining the corrosion kinetics by using frequency and impedance. A Nyquist and Bode plot displays the variation of impedance as a function of frequency of the two layers that are formed at the interface of metal and electrolyte during the corrosion process. In **Figure 8(a)** Nyquist plot, Titanium has a very steep curve, and as well as better corrosion kinetics in **Figure 8b** for having higher impedance. AHNS, however, is not the best in terms of impedance and Nyquist graph, and that is because AHNS weakness is, it does not form a lot of film formation. Therefore, AHNS will not portray strong results in resistance and capacitance of EIS data. Titanium has best corrosion kinetics for higher impedance.

Titanium has big stable film. Therefore it is very steep. AHNS never forms any film. Ideally any metal alloy would like to have higher resistance and lower capacitance, which will provide impedance to be higher.

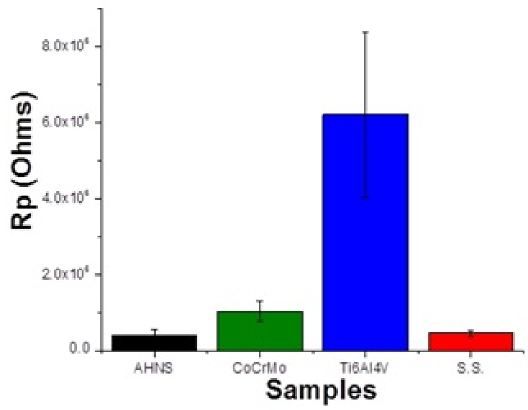

Figure 7b: Polarization Resistance (Rp) of AHNS in comparison with CoCrMo, Ti6Al4V and SS (316L)

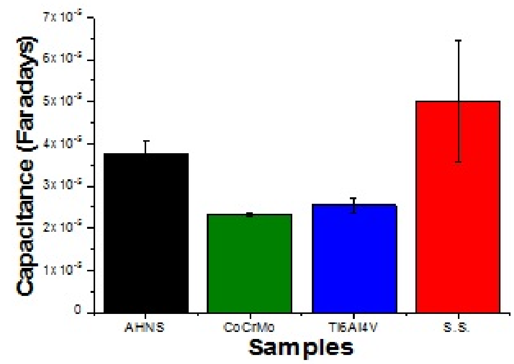

Figure 7c: Capacitance (C) of AHNS in comparison with CoCrMo, Ti6Al4V and SS (316L)

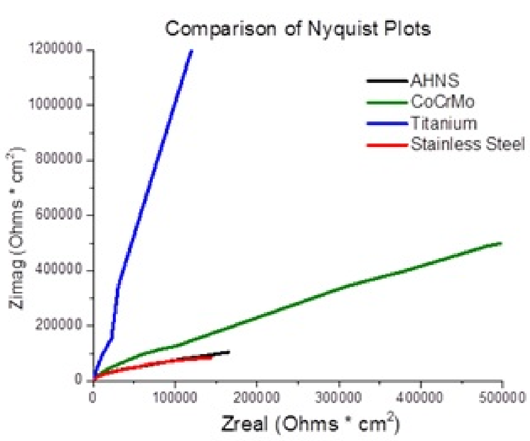

Figure 8a: Nyquist Plot of AHNS in comparison with CoCrMo, Ti6Al4V and SS (316L)

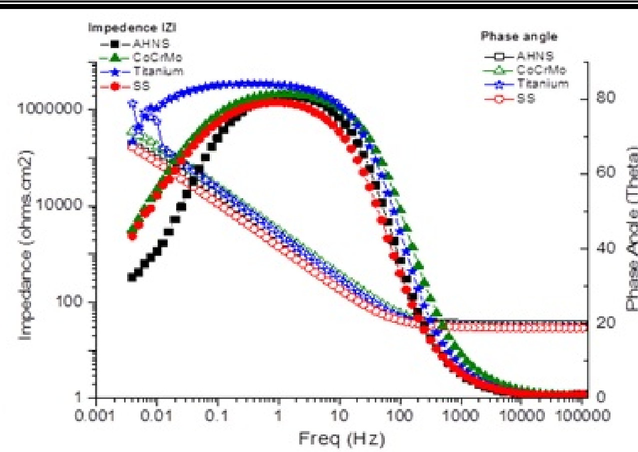

Figure 8b: Bode Plot of AHNS in comparison with CoCrMo, Ti6Al4V and SS (316L)

3.3.3 Surface characterization

Alloy surfaces were characterized using white-light-interferometry and scanning electron microscopy (SEM). White light interferometry microscope (Zygo) images of AHNS were captured before and after the electrochemical corrosion test (Figure 9a). These images were used to capture three-dimensional (3D) surfaces of the untouched (baseline) and of the samples in order to understand the changes on the damaged surface. In Figure 9a surface analysis after corrosion testing portrayed that AHNS did not show evidence of severe pitting formation (Ra values are only increased by 5%). Figure 9b shows that scanning electron microscopy (SEM) images also depicted no signs of pitting formation on the surface after going through electrochemical tests. The images under various zoom focus (x300, x1000 and x3000) shows that the surface was not corroded and had very minimal pits.

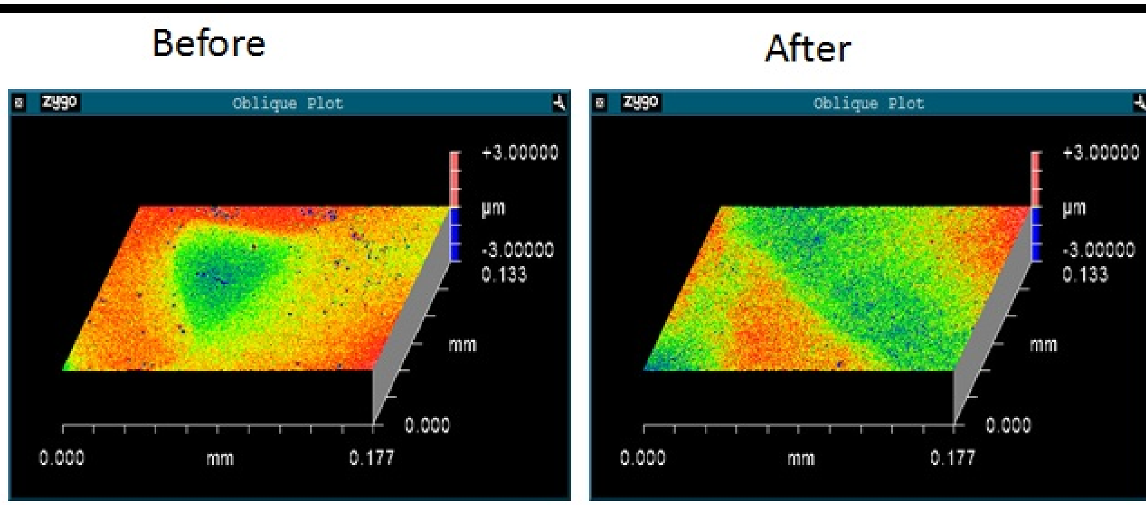

Figure 9a: White light Microscopy Images of AHNS Before and After Corrosion

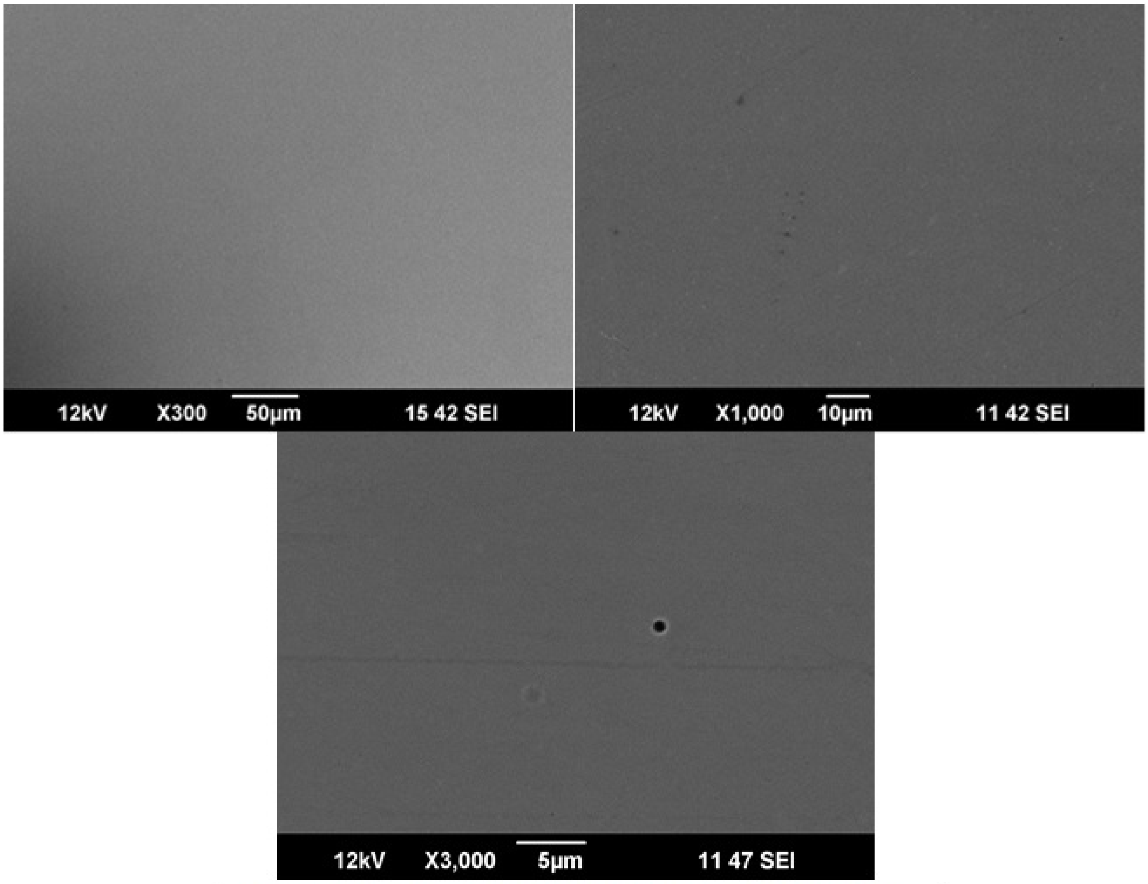

Figure 9b: Scanning Electron Microscopy Images of AHNS After Corrosion (x300, x1000 and x3000)

3.4 Summary

The study suggests that AHNS is electrochemically better compared to the traditional alloys in particular to CoCrMo. In the polarization curves (**Figure 5**), AHNS has the highest pitting potential curve compared to all the other alloys. Potentiodynamic test was performed on the samples to analyze the corrosion resistance of the sample under potentiodynamic conditions. AHNS shows stable film formation and resistance compared to all the other traditional alloys. Overall, Titanium is well known for its plateau formation, but still, AHNS displays better characteristics than all the alloys. Titanium is determined as good alloy because of its passive filming layer, and therefore it demonstrates a vertical graph in the polarization curves compared to other alloys. AHNS Passivation and repassivation kinetics under anodic conditions demonstrate the satisfied trends in the overall corrosion behavior. This might assist to overcome the inferior corrosion kinetics of AHNS to CoCrMo, as indicated by low Rp and high capacitance compared (from the EIS test at Ecorr). Titanium has one of the best corrosion kinetics for higher impedance. SS and AHNS have low corrosion kinetics, and that is due to less film formation. Titanium film formation is very strong and stable compared to all the other alloys. Therefore, its Nyquist plot was very steep, and bode plot showed higher impedance and phase angle. However, once the passive film is removed from Titanium, it has high tendency of corrosion potential. One the other hand, AHNS does not form any passive film formation or oxide layer, which is one of the key factors of this alloy.

Although AHNS shows lower width in Bode plot due to no oxide film formation in the alloy, it has inherent nitrogen which is constantly supplying nitrogen ions at all times. Therefore, impedance test is not a suitable determination for corrosion resistance as it focuses mostly on the corrosion resistance of a metal alloy film. Overall, electrochemical testing displayed noble characteristics of AHNS regarding corrosion resistance. In order to understand more on corrosion kinetics of AHNS, we need to further analyze this alloy under tribocorrosion conditions which will help us understand the tribocorrosion mechanisms and synergistic interactions of wear and corrosion.

4 CHAPTER 4: TRIBOCORROSION

4.1 Introduction

Tribocorrosion test assists to study corrosive behavior of the metal samples under combined exposure to wear and corrosion. In this study, the pins of AHNS, CoCrMo alloy, and Ti6Al4V were undergone tribocorrosion tests- potentiodynamic mode. Other tribocorrosion tests such as free potential and potentiostatic mode were conducted on AHNS and CoCrMo alloys only. The electrolyte used in the test was BCS with a protein concentration of 30g/L. Tribological contact conditions were pin-on-ball configurations (alumina ball-28mm diameter on flat of surface of the metal pin). Load applied was 16N, and amplitude of rotating cycle was $\pm$ 30° and frequency of 1Hz. A combined study of wear and tribocorrosion was employed to study the performance of AHNS, under simulated joint environment.

4.2 Materials and Methods

4.2.1 Specimens:

Three samples of AHNS, CoCrMo, and Ti6Al4V (diameters of 14 mm dia and 7 mm thick) were used to conduct this study. However, Titanium alloys were only used for potentiodynamic study. Samples exposed area were mechanically polished with silicone carbide grinding papers to get a mirror like finish (Ra < 25 nm). Prior to testing each sample was ultrasonically cleaned with Isopropanol (70%) for fifteen minutes and washed with deionized water. These samples were then dried using nitrogen air stream.

4.2.2 Tribocorrosion Testing

Tribological testing was conducted on a custom made testing apparatus (**Figure 10a**). Tribocorrosion cell consist of an electrolyte chamber, a cylindrical metal pin which in contact with rotating ball. The electrolyte solution was maintained at the body temperature of 37 ± 1º C. The test apparatus contained a cylindrical metal pin which had its contact conditions on pin-on-ball configurations (alumina ball-28mm diameter on flat of surface of the metal pin). The ball's rotating cycle was + 30 at a normal load of 16N. The frequency of the oscillation was controlled at 1 Hz. The standard 3 electrode model (Counter electrode, Reference electrode and Working electrode) as shown in the electrochemical study was employed in this study as well. Graphite rod was used as counter electrode (CE), SCE was used as reference electrode (RE), and the mounted metal sample in the system was used as the working electrode (WE).

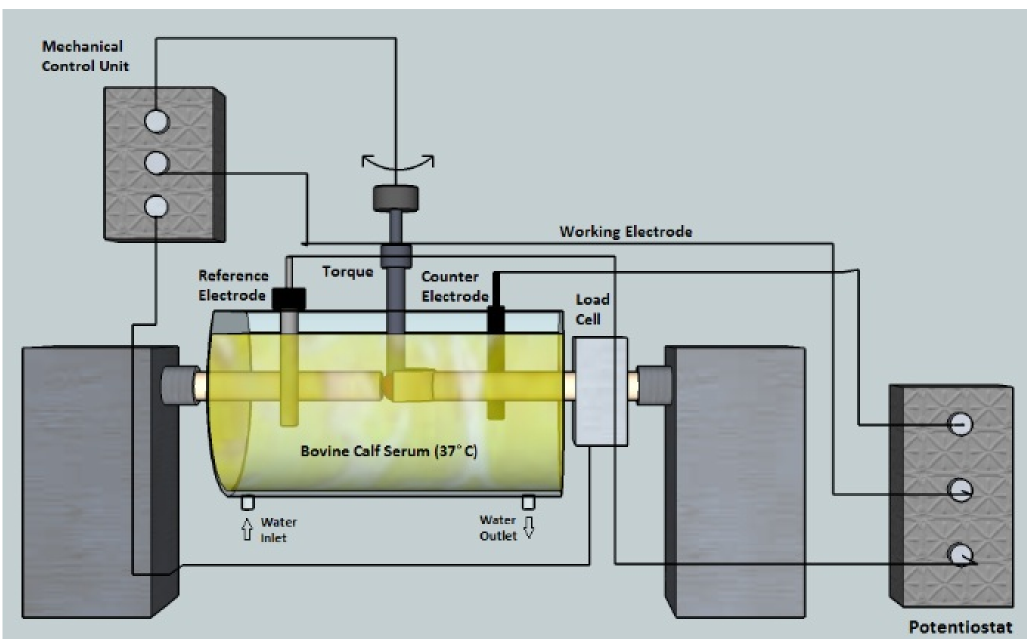

Figure 10a: Tribocorrosion Test Setup

Standard tribocorrosion test protocol was used for running these tests (**Figure 10b**). Initially, OCP was run for 300s to check the connections, and then a second OCP was monitored for 1800s to stabilize the system. Then, an EIS test was performed to examine the properties of oxide film formed on the alloy surfaces. The frequency range (100 kHz-0.005 Hz) was used as measurements for EIS test, with AC sine wave amplitude of ±10 millivolts oscillating around its corrosion potential before sliding. After OCP was run for 5000s for sliding friction, and after sliding second EIS, measurements were performed to examine the tribocorrosion exposure after the sample has gone through sliding to study the surface chemistry/conditions. Lastly, a final OCP ran for 1800 secs for potential stabilization. The samples were then removed and cleaned with deionized water per the standard before storing them. Three types of tribocorrosion experiments were conducted: 1. Potentiodynamic 2. Free potential 3. Potentiostatic.

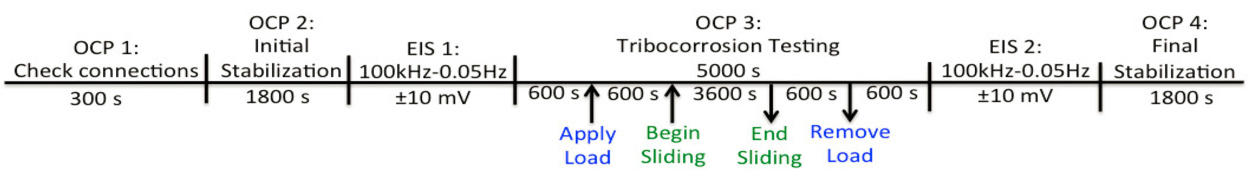

Figure 10b: Tribocorrosion Test Protocol

4.2.3 <u>Surface Characterization</u>

Images were taken before and after the corrosion to evaluate the physical changes and corroded surface of the samples after undergoing tribological corrosion mechanisms by using white-light interferometry microscope (Zygo). Inside and outside scar images were taken on the samples to compare the changes in roughness by understanding the effect of sliding on these samples.

4.3 Results and Discussion

4.3.1 Tribocorrosion data: Potentiodynamic mode

The potentiodynamic curves during tribocorrosion are presented in **Figure 11(a)** and **(b)**. Interestingly, the shift of the potentiodynamic curves to the high current region is very minimal in the case of AHNS. **Figure 11(b)** shows that AHNS tribocorrosion curve has a very similar pathway to corrosion curve even after going through sliding mechanism. This is highly unusual compared to other traditional alloys. One of the prime reasons for such behavior in the graph could be due to the presence of high nitrogen in this alloy. Thus AHNS exhibit superior corrosion kinetics under tribocorrosion compared to CoCrMo alloy and Ti alloy. AHNS displays better Icorr values since the corrosion current of AHNS during sliding is much better than CoCrMo and Titanium alloys. It has lower equilibrium potential and thus it could be due to the minimal film formation in AHNS alloy compared to other two alloys. AHNS has very less film formation on its surface, and thus it could have higher corrosion potential due to less resistance to sliding mechanism.

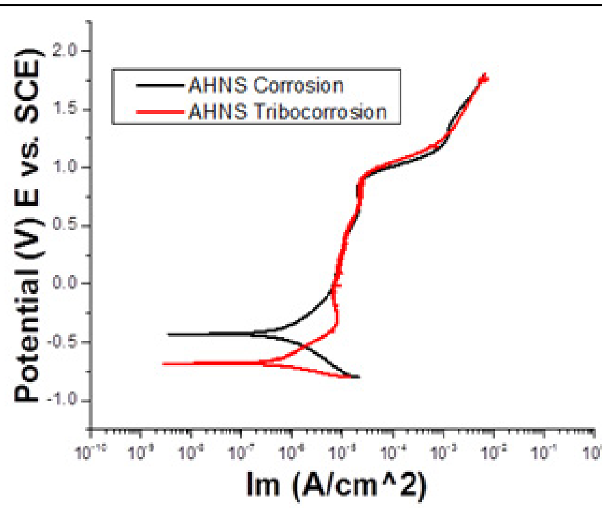

Figure 11a: Potentiodynamic curves for AHNS: Corrosion vs. Tribocorrosion

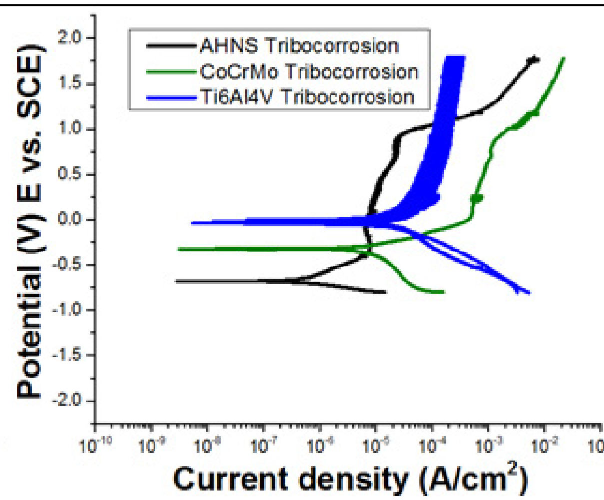

Figure 11b: Potentiodynamic curves under tribocorrosion conditions for AHNS, CoCrMo alloy and Ti6Al4V

4.3.2 Tribocorrosion data: Free potential mode

Tribocorrosion tests under free potential mode were performed. During this test, zero potential is applied and the variation in potential is observed as a function of sliding. Free potential mode helps in assesing the material behavior during pure tribological conditions. **Figure 12** shows the evolution of OCP under free potential mode between AHNS and CoCrMo. AHNS portrays low current compared to CoCrMo and shows better corrosion potential as well. Corrosion potential helps in determining that AHNS is exhibiting less electrons movement between the surface and the solution and thus less metal ions are being dissolved in the system compared to CoCrMo.

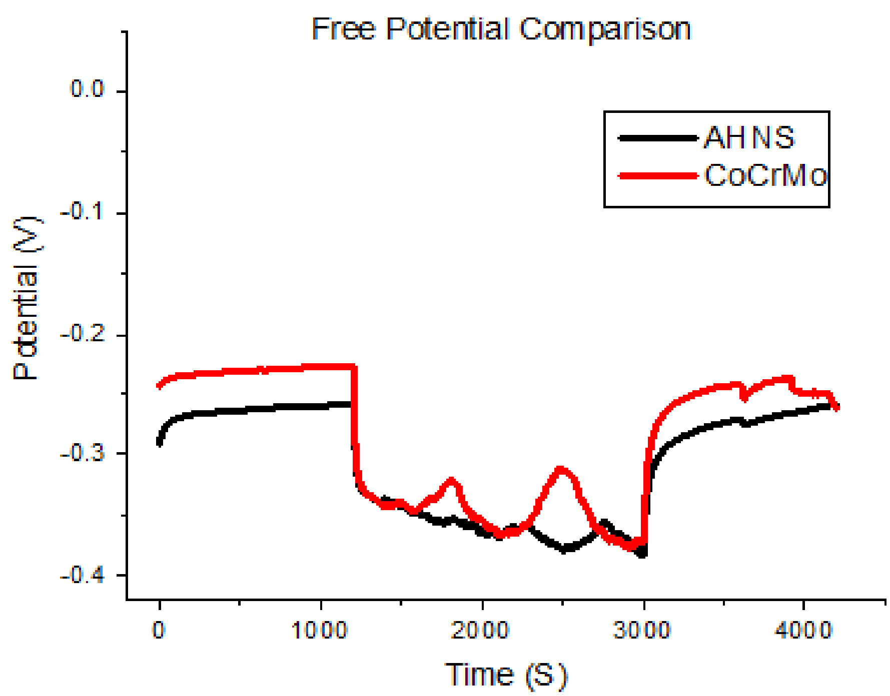

Figure 12: Free Potential mode OCP comparison of AHNS and CoCrMo.

4.3.3 Tribocorrosion data: Potentiostatic mode

Tribocorrosion tests under potentiostatic mode were performed as well. Potentiostatic mode is performed on application of fixed potential, and the density of the current is observed as a function of sliding during the test. Potentiostatic mode testing helps in understanding the estimation of corrosion loss during tribocorrosion testing. **Figure 13** shows the evolution of current density during the tribocorrosion process of AHNS and CoCrMo. AHNS displays more stable conditions during mechanical stimulation as compared to CoCrMo. Though the current is very similar between both the alloys. CoCrMo current density displayed high fluctuations in the current and larger voltage drop compared to AHNS. Higher fluctuations in the current states the system to be less stable, thus allowing larger flow of electrons between the metal and the electrolyte. Due to high electrons flow in the system, there is a high driving force for metal dissolution. Thus, AHNS displayed superior anti-corrosive behavior with respect to current levels during sliding conditions under this test.

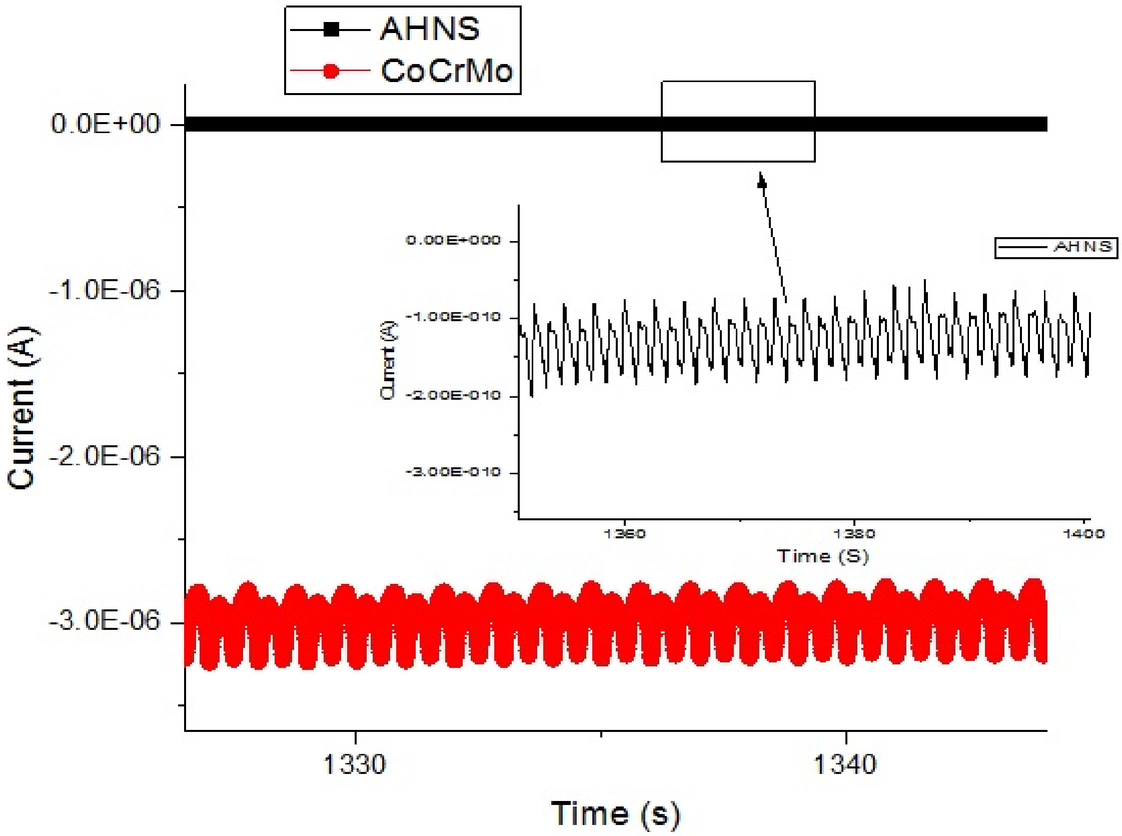

Figure 13: Potentiostatic mode comparison of AHNS and CoCrMo.

4.3.3.1 Total Weight Loss

During tribocorrosion, weight loss and synergistic relationship between wear and corrosion under potentiostatic conditions, were measured and analyzed by using Stack and Abdulrahman et. al (64) proposal. The following equation describes the total weight loss (Kwc):

$$Kwc = Kw + Kc, \quad [1]$$

where Kwc is the total weight loss due to the combined interactions of mechanical (wear) and chemical (corrosion) degradation, hence Kw is the entire weight loss as a result of (mechanical) wear, and Kc is the entire weight loss caused by corrosion.

Kc as defined earlier was the weight loss due to corrosion, and it can be estimated using Faraday's Law(65):

$$\mathrm{Kc} = \frac{M \times i \times t}{n \times F} \qquad [2]$$

here "M" constitutes as the atomic mass of metal alloy or its comparable weight in g/mol, " i " constitutes as current density in $\mathrm{A/cm^2}$, " t " constitutes as complete duration of test in seconds and 'n'constitues the amount of electrons. F is Faradays constant (96500 $\mathrm{C/mol^{-1}}$). 'n' is the number of electrons involved in the corrosion process but for simplicity of this study we used n = 2, although n could be 2+ or 3+.

Kwc, total weight loss can be estimated using the below equation:

$$\mathrm{Kwc} = \mathrm{V} \times \mathrm{D} \qquad [3]$$

Where 'V' is the estimation of total material loss volume during tribocorrosion process, and this is obtained through Zygo images, and 'D' is the density of the metal alloy.

Once, Kc and Kwc is calculated from Equation [2] and [3] respectively, Kw can be calculated by using the Equation [1]. Therefore, based on the equations above wear and corrosion mechanisms can be classified by using Stack and Abdulrahman et al proposal (64), the ratio of weight loss due to corrosion (Kc) and weight loss due to wear (Kw) can be defined as follows:

" $\mathrm{Kc/Kw} < 0.1$ Wear [4]

$0.1 \leq \mathrm{Kc/Kw} < 1$ Wear–corrosion [5]

$1 \leq \mathrm{Kc/Kw} < 10$ Corrosion-wear [6]

$\mathrm{Kc/Kw} \geq 10$ Corrosion. [7] "

4.3.4 Tribocorrosion data: Wear Data

The total wear volume in an electrochemical tribocorrosion study can be determined by analyzing the worn material measurement before and after an experiment. The total wear can be characterized as the loss due to corrosion (electrochemical oxidation), the mechanical wear volume, and the loss due to the synergistic effect. In this study, AHNS portrayed significantly lower weight loss in wear compared to CoCrMo (**Figure 13**). The reason for such low weight loss is due to lack of oxide layer in AHNS alloy. AHNS has a very minute oxide layer compared to other alloys, and therefore it has lower tendency of weight loss during corrosion sliding. The formation and reformation of passive film plays a key role in accelerating the total weight loss. CoCrMo alloys shows inferior mechanical properties due to the elimination of passive oxide film, therefore there is an increase in ion exchange between the electrolytic environment and surface of the bare metal alloy (66).

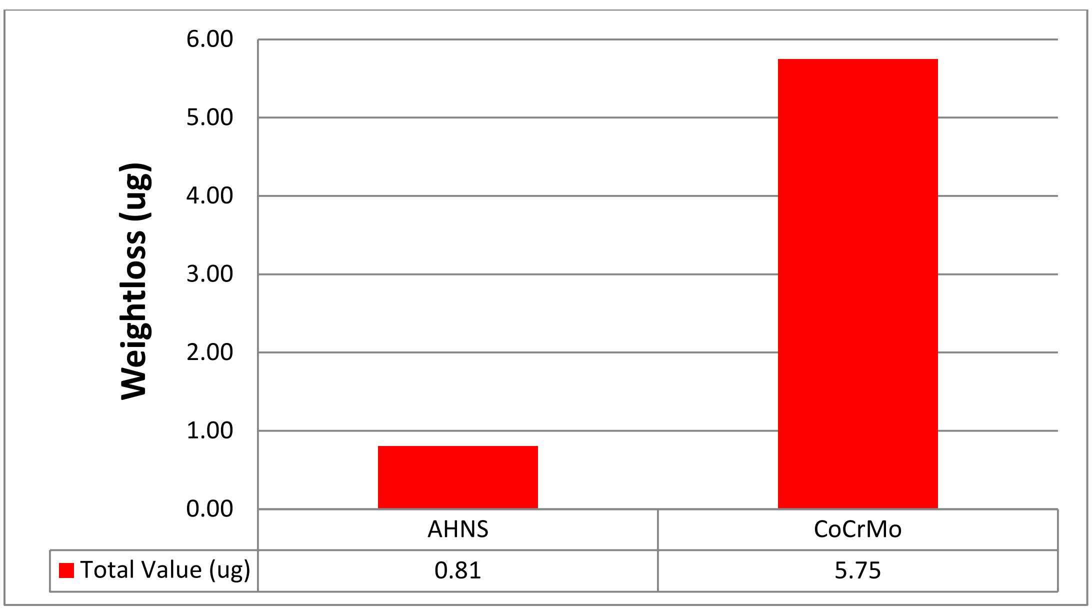

Figure 13: Wear Loss data of AHNS and CoCrMo after Tribocorrosion

Table 2 shows the total weight loss for both the metal alloys under potentistatic conditions. The weight loss due to corrosion in table 2 is much higher for CoCrMo as compared to AHNS. This could be due to the constant rubbing of the ball with the metal surface during sliding, which could affect the passive oxide film on the metal alloy and thus allowing ion exchange between the bare metal alloy surface and the electrolytic environment during the test. As stated above the ratio for Kc/Kw was used to understand and analyze the degradation mechanism between two alloys. According to Stack and Abdulrahman et al proposal (64), both alloys fit into equation [5] synergistic range ($0.1 \leq Kc/Kw < 1$), where both wear and corrosion plays a vital role in the degradation of the sample. In both cases, AHNS portrays lower values compared to CoCrMo, and hence we can determine that AHNS have better wear and corrosion properties compared to CoCrMo.

Table 2

Sample	***Kwc (ug)***	***Kc (ug)***	***Kw (ug)***	***Kc/Kw***
CoCrMo	**5.75 ± 1.95**	**2.69 ± 0.87**	**3.06 ± 1.1**	**0.877**
AHNS	**0.81 ± 0.13**	**3.81E-05 ± 0.9E-05**	**0.81 ± 0.21**	**4.76E-05**

4.3.5 Surface Analysis

White light interferometry microscope (Zygo) images of AHNS and CoCrMo were captured before and after the tribocorrosion test (**Figure 15**). The surface of AHNS shows better scar properties compared to CoCrMo, and thus this is due to low wear loss during tribocorrosion study.

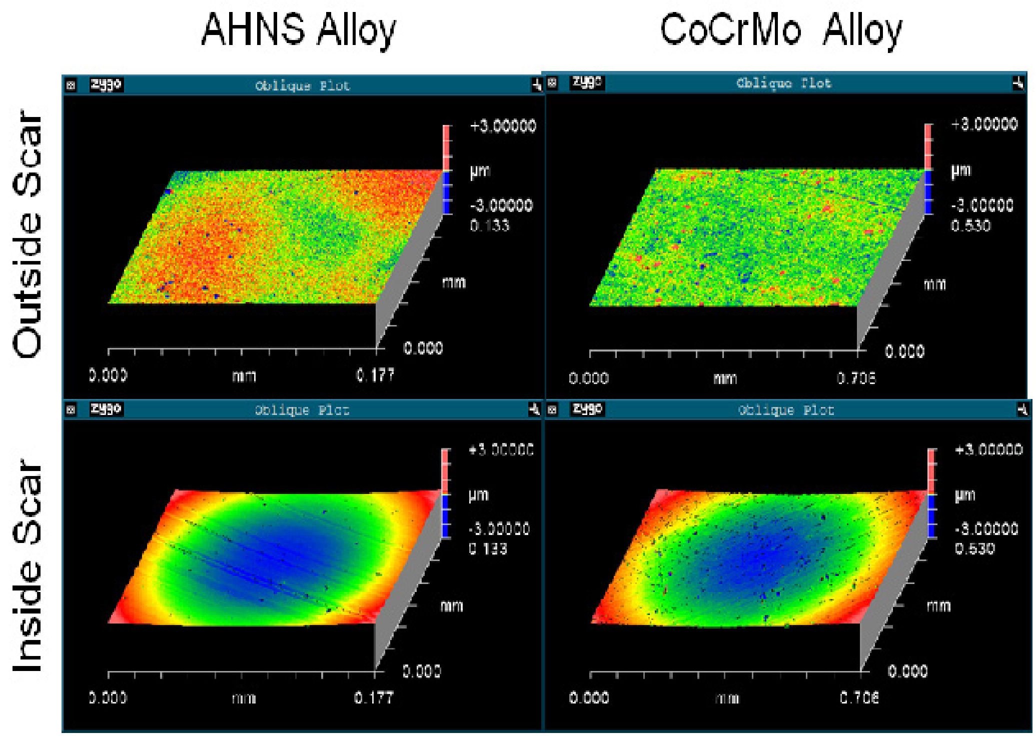

Figure 15: Zygo Images of AHNS alloy and CoCrMo both inside and outside the wear region

4.4 Summary

During tribocorrosion exposure, AHNS, exhibit an exceptional behavior of minimal shift of the potentiodynamic curve to the high current region (**Fig. 11a**). Compare to other alloys, AHNS exhibits better tribocorrosion behavior (**Fig. 11b**). In **Figure 12**, AHNS portrays low current compared to CoCrMo and shows better corrosion potential as well. In **Figure 13**, AHNS displayed more stable current conditions during mechanical stimulation as compared to CoCrMo. This is partly due to AHNS having superior corrosion kinetics compared to other alloys. AHNS key factor is its formation of strong adherent flow of nitrogen during the friction of two surfaces. Schematic Diagram (**Figure 16)** has been developed to demonstrate the influence of passive film during wear/tribocorrosion mechanism of the metal alloys. Prior to sliding, the metal alloy is being protected by an oxide film formation.

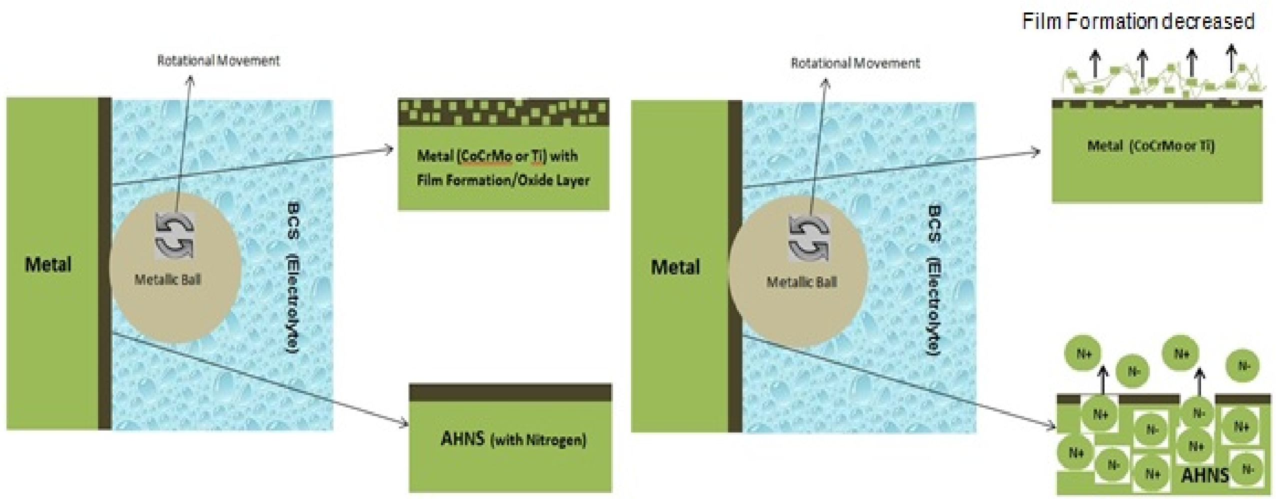

Figure 16: Schematic Diagram of AHNS during Tribocorrosion (Before and After)

During the sliding, the majority of passive film formation is removed and there is an exposure in the surface of the metal alloy, and thus exchange of ions between metal alloy and electrolyte occurs. While in the phase of sliding majority of the metal alloys exhibit some amount of debris, and thus the new surface of the metal alloy is attacked which increases the total weight loss. However, AHNS has adherent supply of nitrogen which helps in preserving the characteristics of the metal alloy and reduces the wear debris in the corrosion kinetics. AHNS key factor could be its constant supply of nitrogen during sliding, which helps in better wear and corrosion properties compared to other traditional alloys.

Hence, AHNS displayed lower wear loss data compared to CoCrMo and had better 3-D surface images as seen in figure 13 and 14 respectively. Also as seen in table 2, synergistic interactions of wear and corrosion is significantly lower in AHNS compared to CoCrMo. This is due to the influence of mechanical and chemical degradation during tribocorrosion testing, and thus formation and reformation of the passive film accelerates high amount of total weight loss in other alloys like CoCrMo or Ti compared to AHNS.

5 CHAPTER 5: CONCLUSIONS

5.1 Reasons for the Enhanced behavior of AHNS

When considering the toxicity of metals for clinical study, the study indicated that AHNS had less chromium than CoCrMo. As CoCrMo is known for the high amount of chromium present, this is unsurprising. Chromium has specific properties, including the ability to annihilate proteins, which can have an adverse effect on the human body. AHNS displayed high levels of iron (Fe) and manganese (Mn) as compared to traditional alloys; these levels are essential for strength and ductility of an implant (67). The materials used for orthopedic implants, particularly in cases where the implant has load bearing applications, must show greater corrosion resistance in the human environment, increased wear and fatigue resistance, higher ductility and must display minimal cytotoxicity (68,69).

Chromium is primarily responsible for the high passivation ability of many alloys (70). Chromium has also been recently tested as a high carcinogenic cancer material for the body fluids. Patients who had MoM hip replacement surgeries presented with various side effects due to levels of cobalt and chromium found in their bloodstream (71). According to the FDA, side effects of chromium toxicity are nausea, vomiting, nerve damage, thyroid and cardiovascular disorders (72). Despite these side effects, a small amount of chromium is needed for the stability of the material, and that is why AHNS has about 18% chromium (Table 1). On the other hand, nickel has proven to be toxic to the human body if released. There is a great deal of evidence indicating that elevated amount of nickel ions in the tissue could cause genotoxic and mutagenic actions or in interaction with the skin resulting in an immensely widespread contact allergy (73) and cancer (74). The compilation of nickel in the body through prolonged exposure can result in fibrosis of the lungs, diseases of the renal and cardiovascular system (75). The nickel toxicity in stainless steel has resulted in high volume of health risks on the human body and hence, nickel-free stainless steel would aid in reducing these hazards and are believed to be in the development phase as the next generation of metallic implant materials. Due to these harmful properties of nickel ions being released from stainless steel, AHNS can be viewed as a potential material for orthopedic implant.

Nitrogen is considered to be a very strong austenite forming element, one that has been successfully used to replace nickel, resulting in large improvements in the mechanical properties of the metal and increases in the corrosion resistance of stainless steels (76). Nitrogen plays an important alloying component as AHNS alloy in respect to the corrosion resistance and strength (77,78). Nitrogen leads to elevation in the high strength of stainless steels without disturbing its ductile or tough character (79). Busher and Fisher et al. (80) studied the mechanical, chemical, and tribological properties of AHNS; this metal showed extremely high strength, high ductility, and superior corrosion resistance. Due to adding nitrogen, there has been reports of considerable elevation in the stability of the passive film, pitting resistance, crevice and intergranular corrosions along with stress cracking corrosion in certain media. (50).

AHNS had a higher pitting potential because the addition of nitrogen resulted in favorable properties by elevating the potential at which pitting corrosion takes place along with reducing the metastable pits (81) and helps in aiding the rate at which passivation occurs after the failure of the passive film. (50). AHNS has a better sliding wear resistance compared to its other alloys; a potential reason for this could be the presence of the nitrogen, as it is known to improve the sliding wear resistance of austenitic stainless steels (50). The trace element of nitrogen in AHNS alloy has an important effect in the wear resistance by increasing the initial hardness of the surface and the strain-hardening behavior. It also increases the fatigue life of the implant (82,83).

AHNS has a higher composition of manganese which could be another reason it has better corrosion kinetics. Manganese is incorporated to additionally improve the nitrogen content, and is also a nickel replacing alloy element (50). Manganese (Mn) also causes a rise in the solubility of nitrogen (84). Mn is an important element for the growth and development of human health, and is therefore biocompatible. Molybdenum improves nitrogen solubility, causing an increase in the corrosion resistance behavior (84). Molybdenum has also shown initialization of film formation in the metal implants (84). The discharge of ions from nickel into the living tissues can be expected when they are used as implants. Hence, development of nickel-free steels for use in the production of implants designed for longer life span implantation is very vital. Because of the resilient nature of nitrogen to elevate the stability of austenite, mechanical characteristics and corrosion resistance of steels, AHNS can solve the nickel and chromium problem in the medical implants industry.

5.2 Limitations of the work

There were few limitations in the current study. Smaller sample size (n=3) was used to test each alloy. The testing was done in a time frame of 2 years. So each alloy was tested with a significant time difference totaling the 2 years' time frame. The tribological system used in the study was pin on ball configuration; which does not replicate in vivo environment completely, as it is complex and duplicating it precisely is highly difficult. This study did not have SEM images after tribocorrosion for AHNS, which could have validated our wear and corrosion total weight loss data. In future, complete tribocorrosion testing with 316L and Titanium alloys will need to be tested in order to understand the difference between various alloys in terms of tribocorrosion mechanisms. In addition, this study will need to be extended to modify the test system with more relevant environment, by including variations and stress loads. An enhanced understanding of dominant tribocorrosion interactions is necessary to further improve AHNS wear data in vivo system. Lastly, further studies are required to understand the clinical issues of the metal alloy.

5.3 General Conclusions

Fixing of orthopedic implants like joint and hip implants has been one of the most challenging and toughest problem encountered by orthopedic surgeons and patients for past several years. As the patients' population for orthopaedic reconstructions is growing with an alarming rate, the development and enhancement of metal alloys with structural and biological potentials to reduce bone healing deficiencies and defects would be highly desired. Fixation of these defects could often be accomplished by direct biological fixation through helping tissues develop around the surfaces of the implants or via creating implants that are structurally strong and less corrosive in human body. Therefore the enhancement of implant integration would bring enormous benefits.

The results of this investigation suggest that commercial austenitic high-Nitrogen steel (AHNS) shows better corrosion behavior compared to other traditional alloys in particular to CoCrMo. Its superior corrosion and wear characteristics could assist in solving current concerns of the metal based orthopedic implants. AHNS has also proven to be a biocompatible metal and has shown superior properties for hard tissue implants (83). Current study will be extended to identify any other limitation of AHNS before considering an alternative implant metal.

Lastly, to understand implant behavior, analysis of failed implants is highly required, while the in-vitro investigations fundamentally lack the corresponding connection to an actual case, thus challenging the realistic imitation of the in-vivo study. Hence, to understand and comprehend the mechanism of true corrosion at the implant/biological interface and to reduce the gap among in-vivo and in-vitro studies, combined efforts by multi-disciplinary groups such as nanomedicine, biomaterials and engineering should be formed.

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02/15- Present ***Development Engineer***

- Leading development engineering tasks for new combination products i.e. pre-filled syringes with Biologics and Pharmaceutical drugs.
- Responsible for managing the functional tests of the product for clinical studies and for commercial product launch within US.
- Collaborate with cross functional teams to develop product requirements, design requirements, use cases, design outputs, design inputs, specifications, verification plans and functional testing per the design control method.

Baxter Healthcare, Round Lake IL

05/13- 2/15 ***Engineer***

- Worked in the renal core team focusing on the research of treatment methods for patients with end stage kidney disease.
- Developed protocols and reports for technical studies, verification testing and coordinating with manufacturing for device builds at Baxter production facilities.
- Contributed to design history file (DHF) remediation for the life cycle management of medical devices, which includes PFMEA, RACT, Manufacturing Control Plans, Validation & Verification studies.

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