

Corrosion of Stainless Steel 316L and ASTM F75 Cobalt Chromium Alloy during Immersion Testing in Silver Salt Solutions

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Abstract

This study evaluates the potential effects of silver salts on biocompatible metals used for prostheses during the chemical reduction process to produce a silver antimicrobial layer on the metal's surface. Samples of two biocompatible metals were obtained: Stainless Steel 316L and ASTM F75 Cobalt Chromium Alloy. Three different silver salts were also acquired: silver nitrate, silver sulfadiazine, and silver chloride. Specimens of each metal were cut to size using a 4-1/2 inch aluminum oxide, 40 grit, cut off wheel for metal, attached to a Dewalt Angle Grinder. The biocompatible metal samples were then subject to either Solution 1, water with 10.0 µg of silver salt per liter of water, or Solution 2, water with 20.0 µg of silver salt per liter of water. Some samples were left untreated for comparison. The samples were removed from the solution after 5 days, rinsed, and examined using SEM. From these images, the corrosion of the metal, the increase in corrosion associated with the increase in silver salt concentration, as well as the differences between each of the metal and salt solution combinations was observed. These images can be found in the Results section of this report.

Keywords:

Materials Engineering, Stainless Steel 316L, ASTM F75 Cobalt Chromium Alloy, Silver Nitrate, Silver Chloride, Silver Sulfadiazine, Corrosion, Immersion Testing.

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Introduction

Statement of Purpose

Medical Prostheses comprise a large portion of modern health care. Infections remain one of the most common serious complications of these devices. One method of prevention is to

deposit antimicrobial metal, such as silver, prior to insertion. Chemical reduction is one approach being used, which involves putting the biocompatible metal in contact with a solution including an antimicrobial metal composition.¹ Silver salts are suitable compounds for facilitating the deposition of silver onto the biocompatible material, such as stainless steel or cobalt chromium. The purpose of this project was to determine if during this chemical reduction process, the salt compound would cause corrosion to the biocompatible material while the silver is being deposited, thus weakening the prosthesis.

Justification

Chemical reduction is a method of applying an antimicrobial silver coating to prostheses. The prosthesis is placed in a solution that contains a silver compound. While the silver particles are being deposited, the salt compounds are moving freely in the solution. It is important to know whether or not these compounds are having adverse effects on the prosthesis metal. Although the metals used have been engineered to be highly corrosive resistant, they are not flawless and are still vulnerable to some corrosion. Stainless steel is susceptible to localized corrosion by chloride ions and reduced sulfur compounds. Biocorrosion is a major issue for cobalt-based alloys. Once the prostheses are placed in the body, they will corrode further. As a material starts to corrode, the dissolution of metal will lead to erosion which in turn will eventually lead to brittleness and fracture of the implant. There are many health hazards associated with corroded implant material in the body, for example, cobalt can cause Anemia B inhibiting iron from being absorbed into the bloodstream. It is important to reduce corrosion as much as possible to increase the longevity of implants. This includes decreasing possible corrosion from occurring during the implant preparation.

Background

Antimicrobial Activity of Silver

Silver is one of the oldest known antimicrobials. Its antimicrobial activity has been recognized by clinicians for over 100 years. Metallic silver is relatively unreactive; however, when exposed to aqueous environments some ionic silver (Ag^+) is released. The positively charged ionic form is highly toxic for microorganisms but has relatively low toxicity for human tissue cells. It simultaneously attacks sites within the cell to inactivate critical physiological functions such as cell-wall synthesis, membrane transport, nucleic acid synthesis and translation, protein folding and function, and electron transport, which is important in generating energy for the cell. Without these functions, the bacterium is either inhibited from growth or killed. Because it affects so many different functions of a microbial cell, it is effective against a broad spectrum of microorganisms. Resistance to antimicrobial silver would be difficult to develop because an organism would have to undergo simultaneous mutations in every critical function within a single generation to escape the silver's effects. Spontaneous mutations are as it is, so the probability of multiple dependent mutations in the same generation of microbes is extremely unlikely.²

Materials Used

ASTM F75 Cobalt Chromium Alloy

The main components that make up the chemical composition of ASTM F75 is about 28% chromium, 6% molybdenum, less than one percent of a number of elements such as manganese, iron, nickel, and titanium, and then balanced in the end by cobalt, which turns out to be about 65% cobalt. CoCrMo alloys are widely used for medical prosthetic implant devices.

Knee implants, metal-to-metal hip joints, and dental prosthetics frequently use this alloy. The alloys are especially used where high stiffness or a highly polished and extremely wear resistant material is required. It has an ultimate tensile strength of 655 MPa and a rotating beam fatigue limit of over 10 million cycles at 610 MPa before any heat treatments.³

Stainless Steel 316L

The main components that make up the chemical composition of stainless steel 316L is about 17% chromium, 13% nickel, 3% molybdenum, 2% manganese, and less than one percent of a number of elements such as nitrogen, sulfur, and carbon, and then balanced in the end by iron, which turns out to be about 63% iron. Stainless steel 316L is used for surgical and medical tools, medical implants including pins, screws, and orthopedic implants such as total hip and knee implants, and a number of other applications. Stainless steel 316L exhibits better resistance to general corrosion, creep, and pitting than conventional nickel chromium stainless steels. It has an ultimate tensile strength of 558 MPa and a 0.2% yield strength of 290 MPa.⁴

Silver Nitrate

Silver nitrate is an inorganic compound with a chemical formula of AgNO_3 . It is a water-soluble silver salt, about 2.16 kg/L at 20°C. It has a molar mass of 169.87 g/mol. It is used as a precursor to prepare silver-containing nanoparticles or complexes, silver plating, as well as other applications. Silver nitrate has been exploited as an antiseptic agent for decades.⁵

Silver Chloride

Silver chloride is a compound with a chemical formula of AgCl . This compound has a low solubility in water, about 0.0016 g/L at 20°C. It has a molar mass of 143.32 g/mol. It is used as an antimicrobial agent for long-term preservation of drinking water in water tanks and in some personal deodorant products. It is also used in bandages and wound healing products, as well as a number of other uses.⁶

Silver Sulfadiazine

Silver sulfadiazine is a compound with a chemical formula of $\text{C}_{10}\text{H}_9\text{AgN}_4\text{O}_2\text{S}$. This compound has a low solubility in water, less than 1 part in 10,000. It has a molar mass of 357.14 g/mol. Silver sulfadiazine was developed in 1968 as a prophylactic therapy for infections in burn wounds. The compound ionizes in wound fluids to provide a reservoir of silver ions which can provide a sustained antimicrobial effect with action against a great deal of known pathogenic strains.⁷



Figure 1: The three silver salts that were used from left to right are silver sulfadiazine, silver nitrate, and silver chloride.

Corrosion

A very important requirement for bioimplants is that they should have very high corrosion and wear resistance. They need to be able to withstand the preparation process as well as the highly corrosive body environment and varying loading conditions. The failure of bioimplants due to corrosion has remained one of the most challenging clinical problems faced. Corrosion is the gradual degradation of materials by electrochemical attack. It has been well accepted that the tolerable corrosion rate for metallic implant systems should be about 2.5×10^{-4} mm/yr. The most common forms of corrosion that occur are uniform corrosion, intergranular, galvanic and stress corrosion cracking, pitting, and fatigue corrosion. The two physical characteristics which determine implant corrosion are thermodynamic forces which cause corrosion either by oxidation or reduction reaction and the kinetic barrier such as surface oxide layer which physically prevents corrosion reactions.⁸

Pitting is the most common form of corrosion arising from the localized breakdown of the passive film. Many engineering alloys such as stainless steel are useful only because of

passive films, which are thin oxide layers that form naturally on the metal surface and greatly reduce the rate of corrosion of the alloys. Breakdown of these films result in accelerated dissolution of the underlying material. When the attack initiates on an open surface, it is called pitting corrosion. This form of pitting corrosion will only occur in the presence of aggressive anionic species. It is autocatalytic, which means that once a pit starts to grow, the local conditions are altered such that further pit growth is promoted.⁹ Pitting corrosion can lead to accelerated failure of the implant by acting as an initiation site for cracking.

Stainless steel 316L is recommended by ASTM for implant fabrication because it contains less carbon, which decreases the chance of forming chromium carbide that generally results in intergranular corrosion. Lowering the carbon content also makes this type of steel more corrosion resistant to chloride-bearing solutions. However, stainless steel is susceptible to localized corrosion by chloride ions and reduced sulfur compounds.⁸ Studies on retrieved implants show that more than 90 percent of the failure of implants of stainless steel 316L are due to pitting and crevice corrosion attack.¹⁰

Cobalt based alloys have better mechanical strength, elastic modulus, abrasion resistance, and corrosion resistance compared to stainless steel. The chromium in these alloys provides the essential corrosion resistance. Cobalt also contributes to the corrosion resistance which makes cobalt-chromium alloys to have excellent corrosion resistance. Biocorrosion of this alloy is one of the major problems to be dealt with as there is larger release of metal ions which causes adverse effects.⁸

Broader Impacts

My senior project investigates the corrosion of stainless steel and cobalt chromium when submerged in a silver salt solution. The importance of this is that cobalt chromium and stainless

steel are used as prostheses and are submerged in silver salt solutions prior to being introduced into the body to create a silver coating that has antimicrobial properties. Implant infections are one of the major complications of prosthetic devices, and the hope is that silver coatings will reduce this. Studies have shown that silver exhibits rather broad-spectrum antimicrobial activity. The anti-infective effects of silver are multifactorial and affect a large spectrum of bacterial and fungal species. Silver ions bind irreversibly to functional proteins on the cell membrane, transmembrane transport proteins and extra- and intracellular enzymes, inhibiting multiple functions including the respiratory chain and the development of biofilm.¹¹ These antimicrobial properties are found in small concentrations of silver, while much higher concentrations produce a toxic effect on human and animal cells. Because I will be working with materials that are to be used in the body and I am investigating how to make implants safer by reducing infection, health and safety is a major realistic constraint for my project.

Three different silver salt solutions were utilized, comprised of three different silver salts: silver chloride, silver nitrate, and silver sulfadiazine. The differences in corrosion caused to the biocompatible material by these solutions was investigated. I am interested in determining which of the different ions in each solution will cause the least corrosion to the cobalt chromium and stainless steel samples while the silver coating is being formed. The ions in the silver salts will likely cause different levels of corrosion in the stainless steel than in the cobalt chromium. For example, I expect that silver chloride will have more of an adverse effect on the stainless steel samples than the cobalt chromium samples. Stainless steels and nickel alloys are unlikely to resist all breakdown by pitting when exposed to bodily fluids, or other media containing chloride, indefinitely.¹² This investigation into which method is best for silver coating application brings up another realistic constraint, manufacturability.

Experimental Procedure

Sample Preparation

Identifying Biocompatible Metal Alloys

When the cobalt chromium samples and stainless steel samples were obtained, it was unknown what the exact alloys were. To determine the chemical composition, a handheld Innov-X Systems X-Ray Fluorescence (XRF) Spectrometer was used, as shown in Figure 2. The data obtained for the cobalt chromium alloy and stainless steel alloy are shown below in Table I and Table II.



Figure 2: XRF was used to determine the composition of the stainless steel and cobalt chromium alloys.

Table I: Average Chemical Composition of CoCr Alloy

Cobalt	65.4%
Chromium	27.4%
Molybdenum	6.2%
Manganese	0.8%

Table II: Average Chemical Composition of Stainless Steel Alloy

Cobalt	65.4%
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Chromium	27.4%
Molybdenum	6.2%
Manganese	0.8%

Using these chemical compositions, standards were consulted and we were able to identify the exact alloys of the samples. The cobalt chromium alloy is ASTM F75 cobalt chromium alloy, and the stainless steel was found to be stainless steel 316L.

Cutting the Samples

Before cutting the samples, they had to be cleaned. The outside was covered in paint and dirt, so the outside of the rods were rubbed smooth with 150 grain, fine surface preparation sand paper, as seen in Figure 3. The stainless steel 316L rods and the ASTM F75 cobalt chromium alloy rods had different diameters. To compensate for this, we cut the samples



Figure 4: Paint and dirt was removed from the samples using fine grain sand paper.



Figure 3: The metal alloy samples were cut using a cut off wheel attached to an angle grinder.

to ensure they each had the same surface area, and therefore the same amount of area exposed to the silver salt solution. The samples were cut using a 4-1/2 inch aluminum oxide, 40 grit, cut off wheel for metal. It was attached to a Dewalt Angle Grinder, as seen in Figure 4. The stainless steel samples had a diameter of 16 mm and a length of 2 cm. The cobalt chromium rods have a smaller diameter, so they were

cut to a longer length. These samples had a diameter

of 10 mm and a length of 4 cm. This gave the stainless steel and cobalt chromium samples similar surface areas, 1407.4 mm² and 1413.7 mm² respectively.

Immersion Testing Procedure

Test Set-Up

The picture below shows the testing arrangement for one metal alloy and silver salt combination. ASTM G31-72 Standard Practice for Laboratory Immersion Corrosion Testing of Metals was taken into account while developing this test. The different aspects are discussed further below.

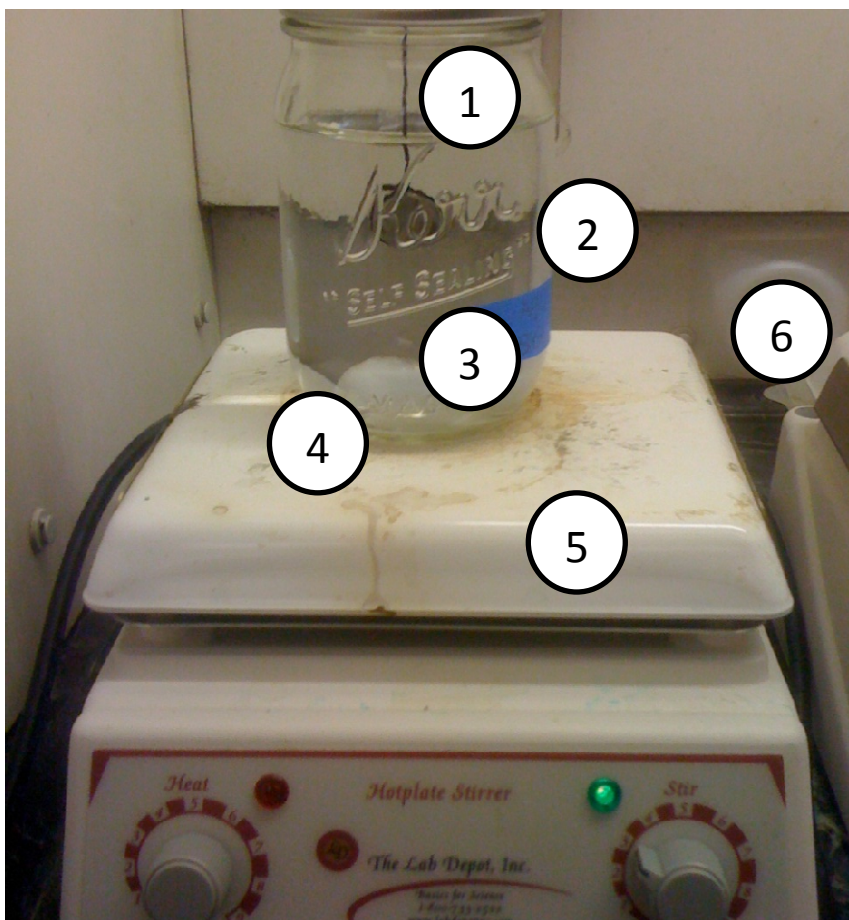


Figure 5: Testing set-up for one metal and silver salt combination.

1. **Suspension:** To keep the metal sample suspended in the solution, a popsicle stick was laid across the top of the container. Hemp string was tied around the popsicle stick and then around the sample. This held the sample above the stirring rod and below the solution surface.
2. **Container:** 16 oz (473 mL) Mason Jars were used to hold the solution, samples, and stirring rods. These worked just as well as a beaker would have.
3. **Sample:** The samples were Stainless Steel 316L and ASTM F75 Cobalt Chromium Alloys. These are discussed in detail in the Introduction.
4. **Solution:** The solution consisted of silver salt and deionized water. The three silver salts that were used, silver nitrate, silver chloride, and silver sulfadiazine, are discussed in

detail in the Introduction. To make each test consistent, all of the deionized water for all tests done at each concentration came from the same batch. The solutions being tested are discussed in detail in the Tests Performed section.

5. **Stirring:** To keep the silver salts from settling on the bottom of the container, a stirring rod was placed in the container and the container was placed on a stir plate. Prior to testing, the stirring rods were coordinated to the same speed by counting the number of turns per minute. This helped ensure the speed of the solution in each container would be similar. The heating capabilities of the stirring plates were not utilized.
6. **Environment:** As an added safety precaution, all testing was done under a fume hood.

Tests Performed

There were two concentrations of silver salts tested; Concentration 1 which is 2.8×10^{-8} moles of silver salt per liter of water, and Concentration 2 is doubled, 5.6×10^{-8} moles of silver salt per liter of water. The test lasted 5 days. Both metal samples were exposed to Concentration 1 and Concentration 2 of each of the 3 silver salts (12 tests total). All of the Concentration 1 tests were done together, and then all of the Concentration 2 tests were done together. This means that there were 6 tests running in each of the two test periods, as seen in Figure 6. The solution for one concentration of one silver salt for the stainless steel test and the cobalt chromium alloy test was mixed together and then poured into their individual containers. For example, for Concentration 1 of silver sulfadiazine, 5 liters of water had 50 μg of silver sulfadiazine mixed in and then 425 mL was poured into a container for the stainless steel and then 425 mL was poured into another container for the cobalt chromium alloy. Silver nitrate had 4.756 μg of compound per liter of water and silver chloride had 4.013 μg of compound per liter of water. For

Concentration 2 of silver sulfadiazine, 5 liters of water had 100 μg of silver sulfadiazine mixed in and then 425 mL was poured into a container for the stainless steel and then 425 mL was poured into another container for the cobalt chromium alloy. Silver nitrate had 9.512 μg of compound per liter of water and silver chloride had 8.026 μg of compound per liter of water. The solutions were made in larger batches so that the scale measuring the weight of the silver salt would be more accurate.



Figure 6: All of the tests at each solution were performed at the same time.

Humans generally have plasma levels of silver of about 0.2 to 10 parts per billion. This correlates to 0.2 to 10 $\mu\text{g}/\text{L}$. 300 parts per billion or 300 $\mu\text{g}/\text{L}$. has been associated with toxic symptoms including argyria in gingiva and cheeks, nephrotic syndrome, and leukopenia. 4 mg/L results in rapid cell death.¹³ The concentrations of silver salts being used in this test are well below the toxic level of silver, where no symptoms will be observable.

The test will determine if some salt compounds cause more corrosion than others, if the stainless steel alloy or the cobalt chromium alloy will be more adversely effected by the salt compounds, and if there is an observable difference between Concentration 1 samples and Concentration 2 samples.

Results

To be able to see if any corrosion occurred, a scanning electron microscope, the SEM FEI Quanta 200, was used to look at areas of the surface of each sample. Images and observations were then made of the conditions of the surfaces.

The first images that were taken were of the surface of the control samples of Stainless Steel 316L, which were not exposed to Concentration 1 or Concentration 2. In Figure 7(a), you can see the average area of the control samples. You can see the striations from sanding the surface, but there is no pitting or evidence of corrosion. Sporadically, small depressions were observed in the surface, as seen Figure 7(b).

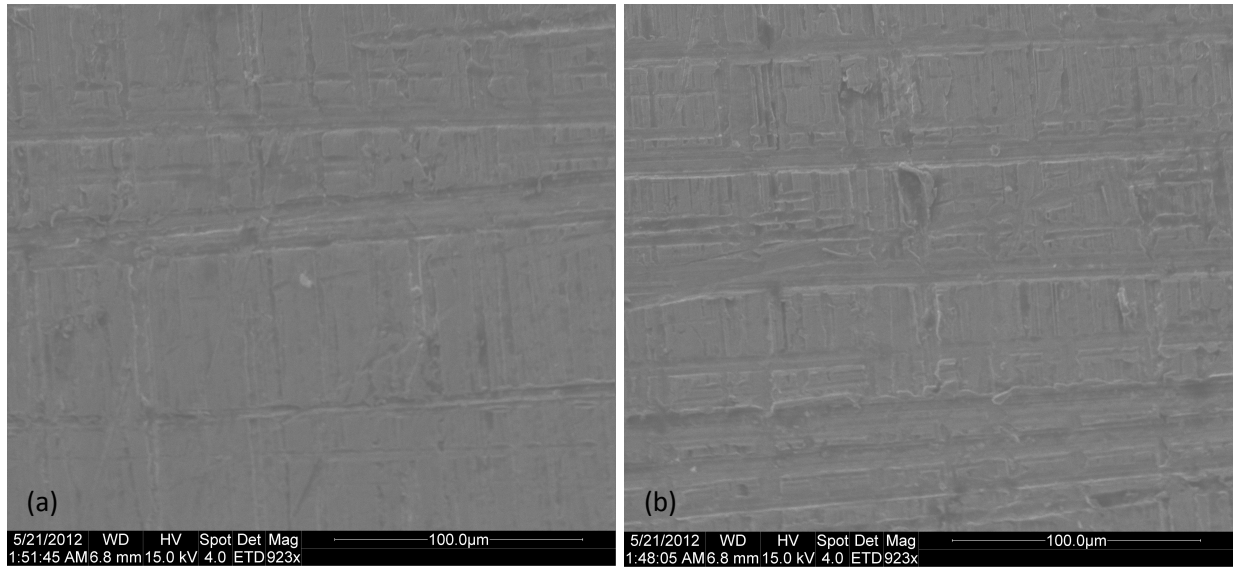


Figure 7(a),(b): Images of the surface of the control samples.

Next, the samples that were exposed to Concentration 1 were observed. There was not a significant difference between the control samples and the samples from Concentration 1. The majority of the area was clear, as was the case with the control samples, as seen in Figure 8. Figure 8 is an image of the surface of ASTM F75 Cobalt Chromium Alloy which was exposed to silver sulfadiazine, Concentration 1. The same striations from the sand paper are visible but there are no noticeable pits. There were still intermittent areas in which indents in the surface were found. However, these indentations did not appear to be the same as in the control samples. Figure 9 is an image of the surface of ASTM F75 Cobalt Chromium Alloy which was exposed to silver chloride, Concentration 1. The indent appears to be deeper than the depressions found in the control samples. These pits were found on the surfaces of both the Stainless Steel 316L and the ASTM F75 Cobalt Chromium Alloy samples. Figure 10 shows a more magnified image of a pit in the surface of Stainless Steel 316L exposed to silver nitrate, Concentration 1.

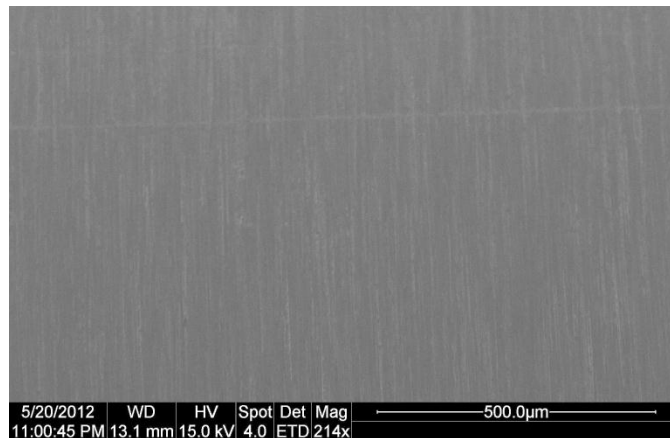


Figure 8: Cobalt chromium alloy surface after exposure to Concentration 1 showing no apparent corrosion.

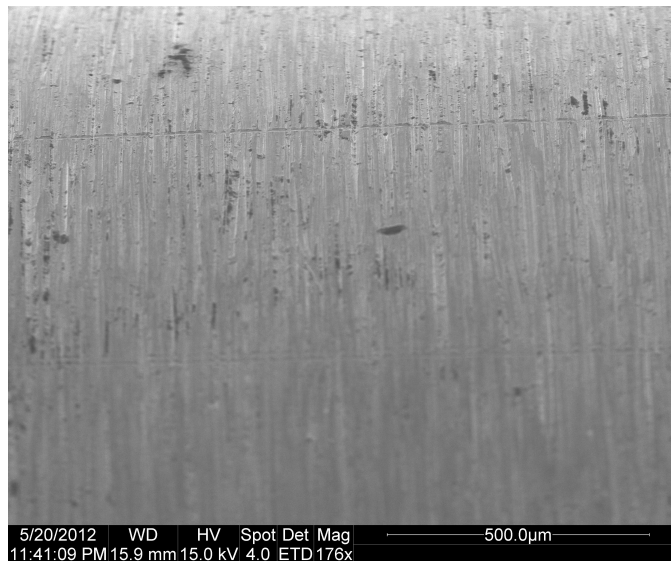


Figure 9: Cobalt chromium alloy surface after exposure to Concentration 1 showing some visible pits.



Figure 10: A pit in the Stainless Steel 316L, Concentration 1.

After visual inspection of the images produced with the SEM, there did not seem to be a difference between the corrosion experienced two types of metal samples. Also, there did not

appear to be any observable difference between the three types of silver salts used. The effects of the testing seemed to be consistent with every sample from each test that used Concentration 1.

The surfaces of the samples that were exposed to Concentration 2 were then examined. Figure 11 shows the surface of the ASTM F75 Cobalt Chromium Alloy sample that was exposed to silver sulfadiazine, Concentration 2. The same pits were still visible, similar to the surface of ASTM F75 Cobalt Chromium Alloy which was exposed to silver chloride, Concentration 1 as seen in Figure 9. Stainless Steel 316L after exposure to silver sulfadiazine, Concentration 2 and ASTM F75 Cobalt Chromium Alloy after exposure to silver chloride, Concentration 2 showed similar pitting patterns.

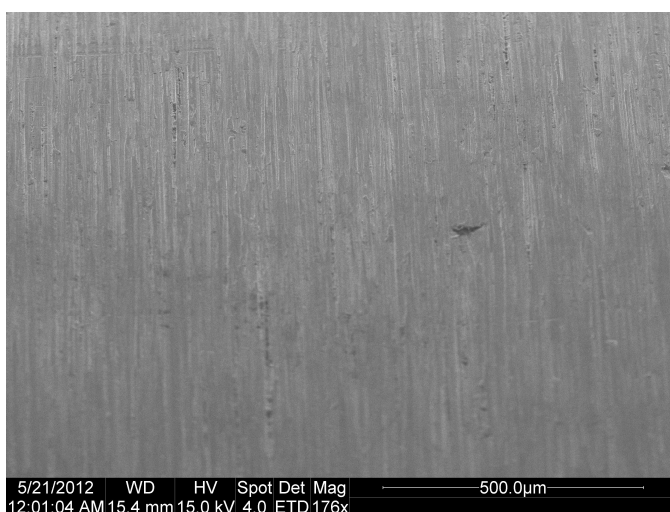


Figure 11: Surface of ASTM F75 Cobalt Chromium which displayed some pitting after exposure to Solution 2.

Some differences were observed between these samples and the control samples as well as the samples from Concentration 1. In some of the silver salt and biocompatible metal combinations, the indentations in the surface appear more frequently than in the Concentration 1 samples. Figure 12 is an image of the surface of an ASTM F75 Cobalt Chromium Alloy after exposure to silver nitrate, Concentration 2. There is a noticeable increase in the amount of pits in the surface of the material.

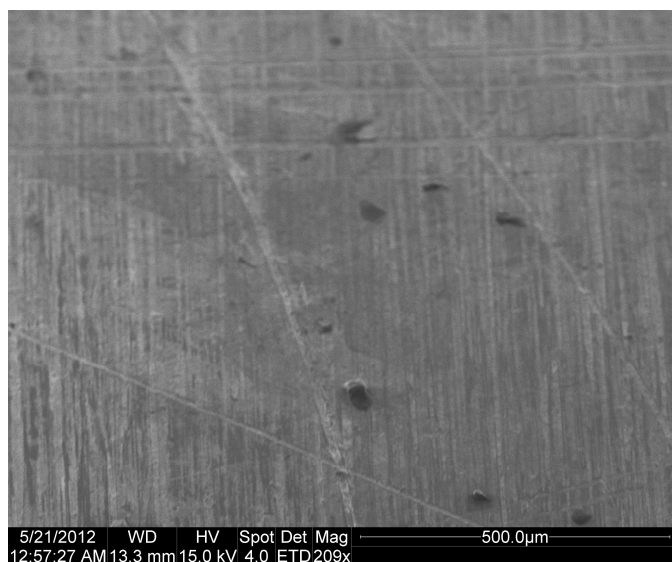


Figure 12: Cobalt chromium alloy after exposure to Concentration 2 with increased amounts of pitting.

This increase in pitting was apparent in some of the Stainless Steel 316L samples that were exposed to Concentration 2 as well. Figure 13 is an image of the surface of Stainless Steel 316L after exposure to silver nitrate, Concentration 2 and Figure 14 is an image of the surface of Stainless Steel 316L after exposure to silver chloride, Concentration 2. In this image, the pits are along striations in the surface. Both images show more pitting that was visible in the combinations at Concentration 1.

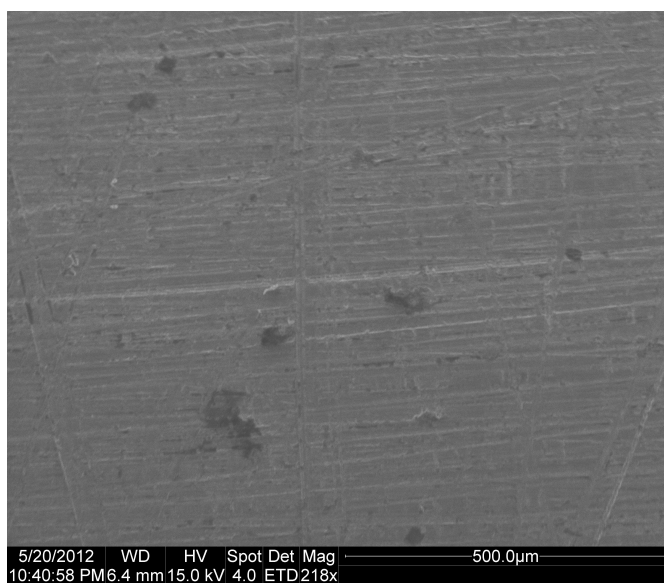


Figure 13: Stainless steel after exposure to Concentration 2 showing increased pitting.

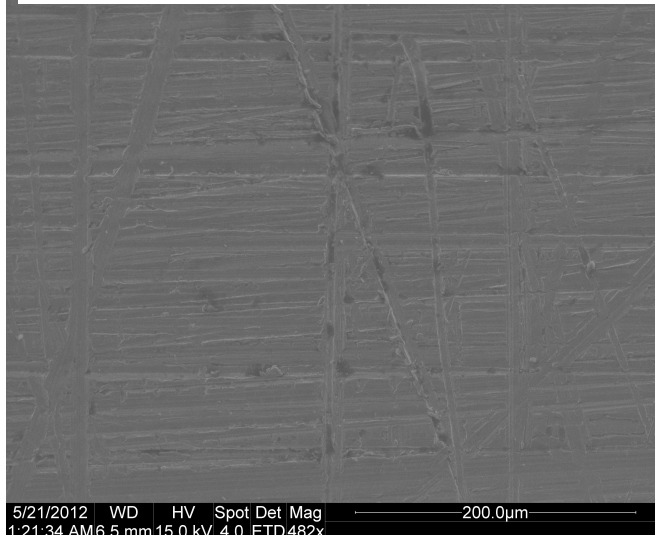


Figure 14: Stainless steel after exposure to Concentration 2 showing increased pitting.

After observing the SEM images of all the samples from Concentration 2, silver sulfadiazine seems to have the smallest impact on both of the biocompatible metals. It also did not show any increase in the amount of defects from Concentration 1 to Concentration 2. For both the stainless steel alloy samples and the cobalt chromium alloy samples, increasing the concentration of silver nitrate increased the frequency of the surface defects observed. Silver chloride had a greater impact on the stainless steel alloy samples than the cobalt chromium alloy sample.

Discussion

In the images obtained from the SEM, there is a correlation between the location of the striations in the surface from the sanding process and the locations of a lot of the surface defects in the material. These striations increase the amount of surface area exposed create surfaces that

can trap corrosive ions. These defects greatly accelerate the formation of defects. In a real prosthesis however, the surface metal would be much smoother, which would likely decrease the amount of corrosion on the surface.

Pitting corrosion is very common in these two types of alloys. As stated in the Introduction, pitting corrosion, the breakdown of the passive oxide layer, occurs in the presence of anionic species. When silver sulfadiazine, $C_{10}H_9AgN_4O_2S$, dissolved in the water, it is unknown how the many elements would have recombined or if they would recombine. From the low levels of corrosion experienced, it can be assumed that silver sulfadiazine must not have created highly aggressive species. Further testing of the solution after the chemical reduction process would provide the actual species present.

When silver chloride, $AgCl$, dissolved in the water, the solution would contain Ag^+ to be deposited on the metal surface and chloride ions, Cl^- . Cl^- is an acid anion which is small and has high diffusivity, it interferes with passivation, and it is ubiquitous as a contaminant. It is well known that chloride solutions are among the most aggressive and corrosive to metals. The chloride ion combines with chromium in the passive layer, forming soluble chromium chloride. The chromium dissolves exposing the underlying material. Silver chloride was more corrosive to the Stainless Steel 316L sample than the ASTM F75 Cobalt Chromium Alloy sample.⁹ Stainless steel is particularly susceptible to localized corrosion by chloride ions. ASTM F75 Cobalt Chromium Alloy contains higher amounts of molybdenum, an alloying element that increases resistance to chlorides.¹²

When silver nitrate, $AgNO_3$, dissolved in the water, the solution would contain Ag^+ to be deposited on the metal surface and nitrate ions, $AgNO_3^-$. Nitrate is an oxyanion, which is also electronegative. Just as described for the corrosion due to chloride, the potential difference

between the anode and the cathode facilitates corrosion and the size of the difference determines the rate of corrosion.

ASTM F75 Cobalt Chromium Alloy had been engineered to have better mechanical strength, abrasion resistance, and corrosion to that of stainless steel. The cobalt provides added corrosion resistance that is not present in stainless steels. This supplementary benefit enabled ASTM F75 Cobalt Chromium Alloys not to corrode in more solutions than Stainless Steel 316L.

Conclusions

Analysis of the corrosion data collected from this study has led to the following conclusions:

- ASTM F75 Cobalt Chromium Alloy was more corrosion resistant than Stainless Steel 316L.
- Silver sulfadiazine preformed the best out of the silver salts tested for causing the least amount of corrosion during the chemical reduction process.
- I suggest using alternative methods for depositing the silver layer onto prostheses, such as ionic plasma deposition.

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