INVESTIGATION OF THE CORROSION OF STEEL BY LEAD-BISMUTH EUTECTIC (LBE) USING SCANNING ELECTRON MICROSCOPY AND X-RAY PHOTOELECTRON SPECTROSCOPY

by

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ABSTRACT

Investigation of the Corrosion of Steel by Lead-Bismuth Eutectic (LBE) using Scanning Electron Microscopy and X-ray Photoelectron Spectroscopy

by

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Lead Bismuth Eutectic (LBE) has been proposed for use in programs for accelerator transmutation of waste. LBE is the leading candidate material as a spallation target and an option for the sub-critical blanket coolant. The corrosion of 316 and 316L stainless steels by LBE has been studied using UNLV’s facilities for Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS). We have compared exposed and unexposed samples and studied the differences. Some amount of surface contamination is present on the samples and has been removed by ion-beam etching. The unexposed samples reveal typical stainless steel characteristics: a chromium oxide passivation surface layer and metallic iron and nickel. The exposed samples show protective iron and chromium oxide growths on the surface. Oxygen takes many forms on the exposed samples, including oxides of iron and chromium, carbonates, and organic acids from subsequent handling after exposure to LBE. This is a research project in progress, and accomplishments to date include comparing and
confirming what is in the literature, as well as laying a strong foundation for further studies in this project.
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CHAPTER 1
INTRODUCTION

In proposed plans for accelerator transmutation of nuclear waste, Lead-Bismuth Eutectic (LBE) has been proposed for use in the transmuter, where it can serve two purposes: both as a spallation target (generating source neutrons from the incident proton beam) and as a blanket coolant (removing heat from fission of actinides and transmutation of fission products in nuclear waste).

The LBE circulates within stainless steel piping and containers. An absolutely critical question is whether stainless steel walls can be engineered to contain LBE for sufficient lifetime. It is known that the presence of small amounts of oxygen in such a system is beneficial in forming a passivation layer that inhibits corrosion. Lead and its oxides have been studied previously. (Koury et al.)

The Russians have many decades of experience with LBE coolant in their Alpha-class submarine reactors, having a significant development program and numerous test facilities. They have also performed laboratory studies of the reactions of LBE with US steels. Los Alamos scientists have reviewed these studies, in which several US steels [316 (tube), 316L (rod), T-410 (rod) HT-9 (tube), and D-9 (tube) and one Russian steel EP823 rod)] were corrosion-tested. Los Alamos scientists have built and are operating a medium-scale LBE materials test loop (MTL).

A variety of steel samples, some exposed to LBE for varying lengths of time and temperature, and some not exposed to LBE, have been examined in as-received condition. The results reported in this thesis consist of data taken on both exposed
and unexposed 316 and 316L stainless steels samples. The exposed samples were exposed to LBE for 3000 hours at 550 C.
CHAPTER 2

TECHNIQUES

Introduction

In our studies, we have employed scanning electron microscope (SEM), in which a high voltage focused electron beam strikes a solid sample, causing fluorescence in the x-ray spectral region. The X-rays are characteristic of the kind of atom and can be analyzed by a method known as energy dispersive x-ray (EDAX) spectroscopy. This instrument is capable of measuring elements from boron (Z=5) through uranium (Z=92), mapping the elemental analysis as a function of position.

![SEM Illustration](image)

Figure 1 SEM Illustration.

We have also performed x-ray photoelectron spectroscopy (XPS). XPS utilizes mono-energetic x-rays to irradiate a surface and eject electrons which are detected
and analyzed. XPS is a much more surface sensitive technique, looking at only the first several layers of atoms. Both techniques are described below.

![XPS Illustration](image)

Figure 2 XPS Illustration.

**Scanning Electron Microscopy**

Scanning Electron Microscopy uses 10-20 keV electrons to probe an object and resolve an image by detecting scattered electrons. The function of SEM is very similar to that of an optical microscope: photons are focused on an object by means of a series of lenses such that a magnified image of the object is observed through an eyepiece (Figure 3).

The amount of magnification from an optical microscope, or compound light microscope, is limited by the wavelength of the photons used. The Rayleigh’s criterion for just-resolvable images defines limit of resolution to a reasonable accuracy:

$$x_{min} = f \cdot \frac{1.22 \lambda}{D} \quad (1)$$

where $f$ is the focal length of the objective, $\lambda$ is the wavelength of light used, and $D$ is the diameter of the lens. For most objective lenses, the ratio $\frac{f}{D}$ is about 1.2, making $x_{min} \approx \lambda$. That means that the resolution of a microscope is approximately equal
Figure 3 A comparison of the components of an electron microscope (a) and a compound light microscope (b). (Wilson et al.)

to the wavelength of light used. For white light, one can achieve resolutions on the order of hundreds of nanometers. In the case of the SEM, the formula is the same except that the wavelength of the electrons is much smaller and varies depending on the energy of the accelerated electrons. Using the de Broglie relationship: (Somorjai)

\[ \lambda = \frac{h}{\sqrt{2mE}} \]  

(2)

where \( h \) is Planck’s constant, \( m \) is the particle mass (electron mass), and \( E \) is the kinetic energy of the electrons, the de Broglie wavelength of the electrons can be found. For this research the SEM anode was set to 15 kV, accelerating the electrons to an energy of about 15 keV and therefore, having de Broglie wavelengths of \( 10^{-11} \) m. This wavelength will, in theory, allow resolution of objects on that same order, with proper magnification. However, real SEM resolution is not that good because of lens aberrations, space charge, mechanical vibrations, electrical noise, finite conductivity, etc. Nonetheless, such high resolution was not necessary in our research since smallest objects we needed to resolve were conglomerates on the order of several hundred
nanometers in size. The electrons are focused by means of current loop magnets onto a surface and either get elastically back scattered or collide inelastically with electrons bound to the solid, causing a bulk electron to be ejected as a secondary electron. Either kind of electrons can be detected and used for imaging; however, in this work, only secondary electrons were used. Imaging works similarly to a television – the images are projected on to a fluorescent screen and different fluorescence intensities dictate whether a particular electron came from a high location (bright spot) or a low location. The sample has to be conducting to avoid local charge buildup and distorted imaging. All of the samples examined were steel, and conductivity proved to be substantial. In the case of poor conductivity, samples have to be either gold or carbon coated as part of their preparation before examination.

As a result of the electrons bombarding a surface, x-rays are emitted with energies characteristic of the elements present in the sample. In a process labeled EDAX (Energy Dispersive X-ray), x-ray photons emitted from the sample are dispersed by a crystal and plotted as a function of energy. Peaks emerge from these plots that can be identified with tables or with software. The x-rays being analyzed come from the area being imaged, so elemental composition can be determined as a function of location on the sample. EDAX does not provide information about the chemical state of each element.

According to the universal curve (Figure 4), electrons with energies of 10-20 keV will penetrate tens of microns deep. Therefore, the electrons incident on the surface induce x-ray emissions from atoms at such depths. Because of this, EDAX sees through the surface which often contains unwanted contaminants. Even with no demanding sample preparation, EDAX will provide information preferentially about the bulk rather than the surface (first few atomic layers).
Figure 4 The mean free path of electrons in different solids as a function of kinetic energy. (Somorjai

**X-ray Photoelectron Spectroscopy**

Emission of electrons from the surfaces of materials induced by either a photon or another electron is one of the most successful ways of learning about composition, structure, and bonding at surfaces on an atomic and molecular scale. (Somorjai)

In x-ray photoelectron spectroscopy (XPS), electrons are photo-emitted from atomic core levels by use of mono-energetic (1.486 keV) x-rays. The x-ray source consists of an aluminum anode, where Al $K_{\alpha}$ photons are produced by electron beam bombardment of an aluminum target. The x-rays excite atomic core electrons on the sample, causing them to eject into vacuum with kinetic energies of

$$ KE = h\nu - E_b - \phi_s $$

(3)

where $h\nu$ is the energy of the incident photons, $E_b$ is the binding energy of the ejected electron, and $\phi_s$ is the spectrometer work function. (Perry) The electrons are
detected and their energies analyzed. A spectrum is plotted of electron counts per energy interval as a function of kinetic energy. Similar to SEM/EDAX, these electron kinetic energies are characteristic of the elements present: each element has its own unique spectrum. In a material composed of more than one constituent, the sum of the peaks from each element comprises the overall spectrum.

XPS has a few of its own advantages that makes it a unique and powerful method for analyzing materials. One of those advantages is its surface sensitivity. Even though x-rays can penetrate several microns deep into a material, the electrons that are analyzed come from just the top few atomic layers. This is because the inelastic mean free path of the electrons in a solid is very small, so only atoms near the surface emit electrons that can escape elastically. The inelastically scattered electrons contribute to the background. Therefore, XPS will provide data on just the top few atomic layers at the surface.

In XPS, electrons can be emitted by two processes: a radiative or non-radiative (also know as Auger) process. In the radiative process, an incoming x-ray photon causes the ejection of an electron. This creates a vacancy hole where the electron used to be. In the relaxation process, an outer shell electron falls into this hole, releasing its energy in the form of a photon. In the second, non-radiative process, the excess energy from the relaxation of the atom is transferred through the Coulomb interaction to another atomic electron, which is ejected. This process is called the Auger Effect. Like photoelectrons, Auger electrons serve as a means of elemental fingerprinting and show up as peaks in XPS scans. The emission of an Auger electron occurs about $10^{-14}$ seconds after the photoelectric emission, and they have kinetic energies equal to the difference between the initial ion binding energy and the final doubly charged ion binding energy. Also, Auger electron kinetic energy is independent of the initial state of ionization. (Moulder et al.) In most cases, depending on the
element, the Auger transition rate is faster than the radiative rate and therefore is more probable. (Crasemann)

Another useful aspect of XPS is the ability to scan elemental peaks to very high resolution (± 0.1 eV). This allows tracking of oxidation states of elements at the surface. Even though XPS probes binding energies in the range of inner core electrons, those energies shift as a result of changes in the chemical environment and the shift can be detected. The shifts in energy are related to charge transfer in outer electron levels. An electronically neutral element becomes oxidized by losing electrons, leaving it with a net positive charge. This causes electrons to be more tightly bound due to less charge sharing. In the case of oxidation, where an element has lost electrons, a shift to higher binding energy is observed. The degree of oxidation is then determined by the amount of peak shift. Oxidation is discussed in Chapter 4.

The XPS apparatus we used also had an ion beam milling (also known as ion sputtering) device attached to it. With the device, a beam of Ar\(^+\) ions can be formed and focused onto a material for surface ablation. This allows for sputter depth profiling (SDP) to be performed.

![Ar\(^+\) ions](image)

Figure 5 Ion Milling of the surface of a sample.

Though the sputter rate is difficult to determine, it can be approximated to tens
of nanometers per second. A good approximate measure to sputter rates can be found by inserting chips of silicon with an oxidized surface of known depth. By sputtering for short time intervals and taking x-ray data while watching for elemental peaks to change, a rate can be determined once the oxide layer is penetrated. Sputtering for short amounts of time (5 - 10 sec) can be done to clear away surface contaminants, while sputtering for longer times (30 - 300 sec) will etch deeper into the bulk.

Figure 6 X-ray analysis of an ablated surface.

Milling for increased time intervals can be executed, with XPS survey scans and high resolution elemental scans performed at each interval. This allows for elemental and chemical mapping as a function of depth.

It is worth mentioning here that some undesirable effects can and do occur from sputtering a surface with ions. The effects inevitably result in changes in the target material. Some of these effects include implantation of incident ions, changes in lattice structure, and, most importantly, chemical changes. (Vanselow et al.) Ions intermixing with a target obviously change the composition of a material. (Wachtman) Chemical changes can appear in the form of oxidation shifts from bonding creation or destruction. (Vanselow et al.) Though one can use an inert element such as Argon to bombard with, oxidation due to elevated oxygen partial pressures can occur. Stimulated oxide growth by this method usually results in an increase in sputter time.
(D.J. O’Conner et. al)

The effects mentioned above do not necessarily dominate the XPS/SDP environment. Nevertheless, when interpreting XPS/SDP data, they need to be considered.
CHAPTER 3
SAMPLE PREPARATION

Introduction

The 316 and 316L samples studied and reported on here were among a batch of steels corrosion-tested by scientists at the Institute of Physics and Power Engineering (IPPE) in Obninsk, Russia, under contract to Los Alamos National Laboratory (LANL). The samples were inserted in IPPE’s CU-1M non-isothermal LBE loop for time intervals of 1000, 2000, and 3000 hours at temperatures of 460 C and 550 C. The oxygen level in the LBE was maintained at 30-50 ppb.

We received the samples in as-is condition. The samples were a 8 mm in diameter tube (6 mm ID) for the 316 and 8 mm diameter rod for the 316L. All samples were roughly 10 cm in length upon receipt.

Austenitic Steel

There are over 10,000 different types of steel, the type dictated by the purpose for which it will serve. They all fall into either of two categories, carbon steels or alloy steels. Stainless steels fall under the alloy classification and are the most common steels. The main components are iron, chromium, and nickel. (Moore et al.) Stainless steels are classified as ferritic, martensitic, or austenitic, based on alloying components (and the amount of each) and their lattice structures. The primary requirement for a steel to be classified as stainless, is that it have a chromium content greater than or \( \approx 11.5 \) % by weight. Austenitic alloys, which we are interested in, have a chromium content of 16.00-18.00 % by weight. They also contain nickel (10.00-
14.00 % by weight), whereas martensitic and ferritic steels do not. The added nickel helps stabilize austenites and makes them especially corrosion resistant. (Baumeister et al.) They are most useful for instrument construction because of their toughness, ductility, and resistance to corrosion. Austenitic steels comprise the 200 and 300 series of stainless steels, including 316 and 316L. Of the 300 series, 316 is most resistive to corrosion attacks. (Moore et al.) It has been reported that austenitic steels have higher oxidation resistance in LBE due to their relatively high chromium content. (Fazio et. al)

It needs to be noted also that the difference between 316 and 316L is carbon content. The “L” in 316L stands for “low carbon”. In 316 the carbon content is 0.08 % (by weight) while in 316L it is 0.03 %.

Cutting

To prepare a sample for SEM/EDAX analysis, they were first placed in a vice, and pieces about 5-10 mm were cut using either a Dremmel tool with a aluminum oxide blade or an abrasive cutoff saw. The cutoff saw was only used for the rods, as they tended to rapidly wear out the Dremmel blades. Samples were wrapped with copper foil before being placed in the vice, to reduce contamination.

Both of these techniques proved adequate for analysis of the outer wall of the samples. In later studies, attempts were made to measure oxidation thickness by viewing the samples’ cross sections in the SEM. According to several articles (F. Barbier, A. Rusanov; H. Glasbrenner et al) the oxidation layer thickness should be very thin, 1-2 μm, possibly less, for austenitic steels. To make an accurate measurement of the oxide layer, one can view the cross section with the SEM while taking x-ray data from EDAX. This is done by gradually moving closer to the edge of the cross section while watching the peaks from EDAX change from bulk signatures to oxide layer signatures, namely, watching for oxygen to appear.
The above mentioned methods of cutting proved to be too damaging in that they either crumbled the oxide layer or smeared it into the cross section. Accurate measurements were impossible with this technique, and other methods of cutting had to be used.

Polishing

The next method used was to polish the end of a steel sample with diamond grit powder. By successive 5-minute polishing sessions, moving to a higher (finer) grit each round, samples became very smooth and shiny. The highest grit used was 1 \( \mu m \) diamond powder. Though this method seemed hopeful, it proved also to not be the answer. The polishing appeared to have smeared the oxide layer into the cross section.

We attempted to embed a thin piece of a sample, cut with a Dremmel tool, in an epoxy, and then tried polishing the steel/epoxy cross section. It was hoped that the embedding would provide stability to the oxide layer. The only issue with the epoxy was poor conductivity for SEM examination. By using a fine nickel screening that would cover the sample and wrap around it, charge buildup was found to be minimal. The edge of the metal, a piece of the edge cross sectional area, was then examined through the screen. This method also seemed to be fruitless, as no accurate measurements of the oxide layer were made.

Low-Speed Diamond Saw

The next technique used was to cut through the samples with a low-rpm, linear precision saw. This type of cut provides a minimum amount of damage to samples. Using a Buehler Isomet saw with a diamond wafering blade in operation at Los Alamos National Lab (LANL), clean and careful cuts were made on two 316L steel rods. SEM inspection revealed that the cuts appeared to be indeed clean. From our
measurements, the oxide layer appears to be on the order of a micron. Data taken with sputter-depth profiling confirm this.

Cleaning

Once cut, steel samples were cleaned with methanol and, in some cases, placed in an ultrasonic bath for five minutes. The purpose of cleaning was to remove any contamination from cutting products as well as incidental handling.

Figure 7 Cross-section view of surface contamination on a sample (not to scale).

The methanol and ultrasonic bath proved to be adequate cleaning for SEM analysis but not for XPS analysis. This is because, as previously mentioned, XPS analysis is highly surface sensitive. Therefore, surface contamination is more prominent. Dealing with surface contamination issues with XPS is discussed in CHAPTER 6 - XPS Results.
CHAPTER 4

CORROSION THEORY

Introduction

The corrosion mechanism of the LBE/steel system is not completely understood. There have been experiments carried out to examine LBE corroded steel, with only qualitative results reported. Specifically, only elemental identification in the corrosion layers and chemical speciation of a few of those elements have been performed. A detailed description of the chemical and thermodynamic process by which different steels react when in intimate contact with LBE has yet to be provided. There are, however, several preliminary ideas about preserving the steel surfaces and models describing the whole LBE/steel chemical behavior.

Reduction/Oxidation Reactions

In a typical oxidation corrosion environment, an electrochemical process resembles a galvanic cell, an electrochemical cell which operates a spontaneous reduction-oxidation (redox) reaction, where reacting species exchange electrons to form products. In a redox reaction, one of the reactants is oxidized, meaning that it gives up electrons, increasing its oxidation number. The other redox reactant is reduced, meaning that it accepts electrons, decreasing its oxidation number. The species is oxidized by an oxidizing agent, which itself is the reduced species. The oxidized species is the reducing agent. (Atkins)

Consider two representative elements, A and B. The chemical equation representing the sum of reduction and oxidation half-reactions, in which electrons appear
explicitly, are written as

\[ A(s) \rightarrow A^{m+} + me^- \] (1)

\[ B^{n+} + ne^- \rightarrow B(s) \] (2)

where \( m \) and \( n \) are the oxidation numbers. The net equation is just the sum of the two, properly balanced so that electrons cancel and charge is conserved.

\[ nA(s) + mB^{n+} \rightarrow nA^{m+} + mB(s) \] (3)

In this redox reaction, element A is oxidized and is the reducing agent, while element B is reduced and is the oxidizing agent.

Aqueous Corrosion

One of the most common forms of corrosion is aqueous corrosion. Aqueous corrosion can occur in many forms. For all types of aqueous corrosion, it is well known that the process proceeds by an electrochemical mechanism. An anodic and cathodic reaction must occur, very similar to that of an electrochemical cell. Oxidation takes place at the anodic site, while reduction takes place at the cathodic site. These two reactions must take place simultaneously, as the electrons gained in the reduction process are provided by the oxidation process. If the electrons from oxidation cannot be consumed, the anodic reaction does not take place.

One familiar form of this type of corrosion is the oxidation of iron alloys, or rusting. A piece of iron with water on it exposed to atmosphere serves as a good example of rusting. In the scenario, iron atoms on the surface of the metal in contact with the water serve as the anodic site. The iron is oxidized (ionized) in the following fashion

\[ Fe(s) \rightarrow Fe^{2+} + 2e^- . \] (4)

The surface of the water in contact with atmosphere serves as the cathodic site. Here, both oxygen and hydrogen ions (from acid solutions) are reduced. The oxygen
molecules are dissolved in solution to form hydroxide, and hydrogen gas is produced by the reduction of the hydrogen ions. The two reduction reactions are

\[
O_2 + 4e^- + 2H_2O \rightarrow 4OH^- \tag{5}
\]

and

\[
2H^+ + 2e^- \rightarrow H_2. \tag{6}
\]

In the case in which the iron is only partially exposed to the solution, such as water droplets on a piece of steel, there is often separation of anodic and cathodic sites, with the latter at the water/atmosphere boundary where there is oxygen available. In between the two is where, in this system, rust would form. The iron ions bond with hydroxide ions in solution and precipitate out, forming various insoluble mixtures of iron, oxygen, and H. A few of these are Fe(OH)\(_2\), FeO·OH, and Fe\(_2\)O\(_3\)·H\(_2\)O. (Scully) (Oxtoby et al.)

Since steels are widely used structural materials, much has been learned about rusting. Many techniques have been developed for use either in the manufacturing stages, such as experimenting with different alloys in different quantities, or in the post-manufacturing stage, such as covering steels with paint or other protective material. (Oxtoby et al.)

**Dissolution Corrosion by LBE**

It is known from experience that LBE attacks steel surfaces, corroding them severely and rapidly. The type of corrosion that occurs is dissolution corrosion. This corrosion occurs mostly because the base and major alloying components of steels are soluble in LBE. Those elements include nickel, chromium, and iron, listed in decreasing order of solubility. It has been found that adding a small amount of oxygen, on the order of tens of ppb, to the LBE will greatly reduce the steel corrosion. Lead and bismuth are chemically more inert than the major alloying elements of steel,
namely, the elements listed above, because they all have higher molar free energies of formation for oxidation. Therefore, it is possible to form chromium and iron based oxidation layers at the LBE-steel interface that can passivate the steel surface. With proper oxygen control, a self-healing protective oxide film forms. The oxide layer protects the metal substrates by greatly reducing diffusion, as diffusion rates of the alloying elements in oxides are negligibly small. The oxide, however, reduced by the LBE at the interface, but it reaches a local equilibrium and the iron concentration is at equilibrium. (He et al.) (Li) This reduction process is discussed below.

The oxygen level must be carefully maintained by a technique called active oxygen control. If not enough oxygen is present in the coolant, the protective oxide films on the steel surfaces aren’t formed, therefore permitting dissolution corrosion as mentioned above. If too much oxygen is present, exceeding solubility, then solid lead and/or bismuth oxides can form from the overabundance of oxygen. Such oxides contaminate the coolant and can precipitate out in cool regions, possibly clogging the flow of coolant. Another problem that will occur if the oxygen levels are not properly maintained is reduction of the oxide layers until they are thin enough such that diffusion of substrates is considerable. The main idea behind active oxygen control is by properly controlling oxygen levels, the reduction process can be kept at an equilibrium between the formation and dissolution of oxides. (Li)

The popular description of the actual corrosion mechanism of the LBE/steel system, as proposed by several papers, is described here. Multi-phase oxide scales are formed due to different diffusion rates in alloying components, which occurs as a result of different solubilities of the alloys in LBE. Three different layers form on the steel surfaces: an outer magnetite (Fe₃O₄) which is on top of the original surface and consists mostly of iron and oxygen, an intermediate spinel Fe²⁺(Fe³⁺₁₋ₓ Cr³⁺ₓ)₂O₄(+Ni), and an innermost layer which is an oxygen diffusion zone with spinel formation along
grain boundaries. (Glasbrenner et al.) (Barbier et al.) (Fazio et al.) (He et al.)

The proposed mechanism for the layering goes as follows: oxygen in the LBE first reacts with iron and chromium to form the Fe-Cr spinel. Oxygen can diffuse through this layer and further react with steel elements to form more spinel-like structures. Due to the inward diffusion of oxygen, the Fe-Cr spinel grows inward, forming the innermost layer mentioned above. Iron diffusion outward is what accounts for the outer magnetite layer, which grows on the surface. Chromium diffusion occurs more slowly which accounts for its presence only in the inner layers. In those regions, the chromium content is roughly 1.5 times higher than its concentration in the bulk. This is due to iron depletion. (Glasbrenner et al.)

Dissolution occurs if too little oxygen is available for an oxide layer with iron. In this regime, the concentration of iron in LBE is equal to its saturation level, meaning the iron concentration is at an equilibrium. (Li) The concentration of the iron is

$$\log(c_{Fe}) = 6.01 + \frac{-4380}{T},$$

where $T$ is temperature in Kelvin. If sufficient oxygen is present and the oxide is formed, the reaction that takes place at the interface is a reduction reaction with lead as the reducing agent.

$$Fe_3O_4 + 4Pb \rightarrow 3Fe + 4PbO$$

The concentration of iron in this situation is now determined by the following:

$$\log(c_{Fe}) = 11.35 - \frac{12844}{T} - \frac{4}{3}\log(c_O),$$

where $c_O$ is the concentration of oxygen. The point where these two functions of iron concentration equal each other determines the minimum oxygen concentration to form the oxide layer. The ideal oxygen concentration is actually beyond this point (at higher concentrations) such that the iron concentration is significantly lowered and the oxidation corrosion rate is minimized. (He et al.) (Li)
The data and conclusions reported in this work are in good agreement with this model. It should be noted, however, that much work has yet to be done to fully test this model.
CHAPTER 5

SCANNING ELECTRON MICROSCOPY RESULTS

Introduction

Data obtained using the SEM apparatus comprised the initial steps in this research and helped form some preliminary ideas about the corroded samples. Combining imaging with x-ray detection allowed for elemental mapping of samples. This provided interesting information on samples that appeared inhomogeneous in the images. The results reported in this chapter are from data taken on 316 stainless steel.

Data and Results

The surface images (Figures 8 and 9) and the EDAX spectral data show that the surface of the corroded sample is covered by oxygen-containing compounds, presumably mostly iron oxide. This is also indicated by the XPS data, which will be discussed below. Samples exposed for shorter times and/or cooler temperature (450 C) show a morphology consisting of some areas covered by oxides, and other areas uncovered. This is shown in Figure 10.

EDAX spectra taken on the uncovered areas reveal significant differences from those of the covered areas. The x-ray spectrum of an uncovered area is shown in Figure 11. The level of chromium in the uncovered area is much higher than the level of chromium in the covered area, shown by the spectrum in Figure 12. While chromium is present in the uncovered (but not covered) areas, oxygen is present in the spectra of both areas. For the covered area, the chromium is presumably covered by iron oxides, as it is consistent with the data on the completely covered 316 steel.
In short, chromium oxides are present in the uncovered (but not covered) areas, while iron oxides are present in both covered and uncovered areas. XPS studies are used to investigate the detailed chemical states of the surface species. The studies are discussed in the next chapter.

The EDAX spectra include characteristic peaks from such elements as iron, chromium, nickel and silicon. Oxygen peaks are very strong in steel samples that have been exposed to LBE, and they are absent in unexposed samples. This demonstrates the existence of protective oxide layers on the surface of exposed samples.

As mentioned earlier, a sample of 316 steel is composed mostly of iron, nickel, and chromium, with smaller amounts of other alloying elements: silicon, manganese, and carbon. Our SEM data show semi-quantitatively the elemental composition of the surface and near-surface region (SEM probes on the order of a micron in depth). The EDAX spectrum of a sample of 316 stainless steel tube before exposure to LBE.
Figure 9 The surface of the exposed, corroded 316 steel sample is drastically different when viewed at the same magnification as Figure 8.

(Figure 13) shows high abundances of chromium and iron, with a smaller amount of nickel and a few other trace elements. The zinc peaks were surprising, but are clearly present, and confirmed in the XPS data, discussed below. No oxygen peaks were observed in these SEM data, indicating that oxidation in the surface and sub-surface region is minimal. However, oxygen did appear in the XPS data, as discussed below. Figure 14 is a spectrum taken from an identical tube that has been exposed to LBE for 3000 hours at a temperature of 550 C, the longest and hottest exposure in a number of tests. For the exposed sample, the spectrum (Figure 14) shows high abundances of iron and oxygen, with very little chromium. This suppression of chromium in the exposed sample is confirmed in the XPS data, which are discussed below.
Figure 10 SEM of a 316 steel sample exposed to LBE for 2000 hours at 450 C shows some uncovered areas where the original surface is still visible.

Figure 11 EDAX spectrum of an uncovered area on a 316 steel, exposed for 2000 hours at 550 C.
Figure 12 EDAX spectrum of a covered area on a 316 steel, exposed for 2000 hours at 550 C.

Figure 13 EDAX spectrum of 316 steel sample, not exposed to LBE.
Figure 14 EDAX spectrum of 316 steel sample, exposed to LBE for 3000 hours at 550 C.
CHAPTER 6

X-RAY PHOTOELECTRON SPECTROSCOPY RESULTS

Introduction

Most of the research in this thesis is based on the use of XPS. With the ability to track oxidation states as well as sputter-depth profile, much more has been learned about the nature of corrosion on our samples. By comparing high resolution peaks obtained of individual elements to documented peaks of known oxidation states and species, most of the elements present have been characterized. XPS studies of 316 and 316L stainless steels also reveal more interesting details on the differences between exposed and unexposed samples.

It is noteworthy to mention XPS spectra calibration. Typically, XPS spectra will shift due to the problem of charging, especially on insulating samples. When a poorly conducting sample acquires a steady state charge, binding energies in the sample can shift by as much as several electron volts above their true value. Therefore, to insure accuracy in binding energies, all of the XPS spectra need to be calibrated using an internal standard, or reference peak, of known binding energy. For the following data, adventitious carbon was used as the reference, assigned a binding energy of 284.6 eV.

Preliminary Results

The preliminary studies of 316 consisted of survey scans on both exposed and unexposed samples, as well as individual high resolution scans of carbon, oxygen, iron, chromium, nickel, lead, bismuth, and silicon. On the unexposed steel (Figure 15), we find the expected surface dominance of chromium over iron and nickel, as
one expects for a passivated surface. No lead or bismuth is seen. However, we were surprised by the levels of zinc. On the exposed sample (Figure 16), we see the suppression of chromium with respect to iron as seen in other corroding stainless steel systems. We also see some residual lead and bismuth.

Figure 15 XPS survey scan of 316 steel sample not exposed to LBE (before ion milling).

The strongest peaks in both surveys, carbon and oxygen, are also surprising (especially carbon). As XPS is sensitive to only the first few atomic layers of a sample, we conclude that those layers are mostly those two constituents. The cause of the high surface carbon and oxygen content is possibly due to contamination of the samples from handling, as they are strong in the both the exposed and the unexposed samples. High resolution scans of carbon and oxygen, as well as sputter-depth profiling
Figure 16 XPS survey scan of 316 steel sample, exposed to LBE for 3000 hrs at 550 C (before ion milling).

(discussed below), serve to help determine their origins.

High resolution scanning of the carbon 1s peak of the uncorroded sample (Figure 17) shows a less oxidized carbon species on the surface than on the corroded sample (Figure 18). This carbonaceous species may be either generated during the LBE exposure or during subsequent handling. The peak to lower binding energy ($\approx 285$ eV) is consistent with aliphatic carbon, which suggests that it is from handling. Sputter-depth profiling reveals that the carbon peaks do not maintain strength and shape with depth. This suggests that the origin of carbon on the metal surface is a contaminant, as well as a corrosion product.

In Figure 19, the oxygen (and other edges) shows corresponding shifts to higher binding energy on the exposed sample, as compared to the unexposed sample (Figure 20). Although oxygen shows up mostly as a consequence of oxidation, there is some
Figure 17 XPS high-resolution scan of carbon 1s line on 316 steel sample, not exposed to LBE (before ion milling).

evidence that it also has some contaminant related (discussed below).

Sputter-Depth Profiling

Ion-beam milling and depth profiling were performed for durations of 5, 25, and 85 seconds on 316 and 316L stainless steels. The corroded subjects were exposed to LBE for a duration of 3000 hours at 550 C. The results of subsequent high resolution scans are below.

It needs to be noted, before further remarks on ion-beam milling, that the bombardding $\text{Ar}^+$ may slightly alter a material (see Chapter 2). However, 85 seconds, the longest sputter interval performed, is not a very long sputter time and any alterations due to ion bombardment is minimal.
Carbon

Carbon 1s in the 316 on both the exposed and unexposed (Figures 21 and 22) samples shows no change in structure with depth. However they get slightly weaker. The unexposed sample shows two peaks. The weaker of the two, at lower binding energy ($\approx 283.2$ eV), is possibly from $\text{Ar}^+$ but more likely from metal carbides. Carbides are formed from anionic or reduced carbon. A good carbide candidate would be silicon carbide, SiC, found at 282.5-283.4 eV.

In the exposed 316L sample (Figure 23), carbon 1s is similar to the 316 exposed sample. In the unexposed 316L sample (Figure 24), again carbon 1s shows similar behavior as 316, although at low sputtering times (5 sec) the weaker carbide peak is not present. A possible explanation to this would be that surface contamination has
Figure 19 XPS high-resolution scan of oxygen 1s line on 316 steel sample, exposed to LBE for 3000 hrs at 550 C (before ion milling).

not yet been removed.

Oxygen

Oxygen 1s in the exposed 316 (Figure 25) has two peaks. One of them is more intense and is at a lower binding energy of 530.7 eV. It could come from similar species as that of the unexposed sample. The other, less intense peak has a binding energy of 532.7 eV. This binding energy puts it in between two peaks that are present in the unexposed sample. This energy is consistent with polyesters (possibly contaminant related), metal sulfates, and some carbonates. Some organic and silicon compounds exist in this region as well.

Oxygen 1s in the unexposed 316 sample (Figure 26) shows at least two peaks with
Figure 20 XPS high-resolution scan of oxygen 1s line on 316 steel sample, not exposed to LBE (before ion milling).

A possible third, less intense peak that showed up at 5 sec sputtering time. This third peak, at a binding energy of about 534 eV, is consistent with organic acids such as polyesters and maleic acids. At the longer sputtering times only the two peaks at lower binding energies show up. The lower energy peak at ≈ 530.7 eV is consistent with chromium oxides (529.7-530.8 eV) as well as FeO(OH) (530.1-531.8 eV). No oxides are reported at the second peak, at 531.7 eV. However, some carbonates show up here, such as Na$_2$CO$_3$ (531.5-531.8 eV).

Exposed 316L (Figure 27) has single oxygen 1s peak at about 531 eV. It grows and narrows a little with sputtering. Unexposed 316L (Figure 28) also has a single peak at about 530.5 eV but in this case it shrinks significantly and broadens with sputtering. This peak is consistent with metal oxides. Also, similar to unexposed
316, there may be a weaker peak around 532 eV.

Iron

The main iron peak that has been studied in this project is the 2p state. Exposed 316 (Figure 29) displays a rather complex Fe 2p\textsubscript{3/2,1/2} spectrum, as compared to that of the unexposed (Figure 30). In the exposed spectrum, there exists a metallic component at low binding energies that appears at longer sputter times (25-85 sec), located at about 707.7 eV. The peak at higher binding energy, centered around 710 eV, is consistent with iron oxide or other species of oxidized iron. The unexposed sample shows constant metallic iron at all depths studied.

Fe 2p for exposed 316L has several peaks (Figure 31), similar to those of the 316 exposed. One of them is the metallic peak growing with sputter time and the other is the oxidized iron peak, which remains constant throughout the sputtering. On the unexposed sample (Figure 32), oxidized iron shows up at 710.2 eV for the low sputter time (5 sec). It is a relatively weak peak and therefore we conclude that sputtering has probably not completely cleared the surface impurity layer. At the higher sputter times (25 and 85 seconds) we again see a metallic iron structure.

Chromium

Two peaks appear in high resolution spectra of chromium on exposed 316 (Figure 33), the doublet peaks Cr 2p\textsubscript{1/2} and Cr 2p\textsubscript{3/2}. Cr 2p\textsubscript{1/2} and Cr 2p\textsubscript{3/2} on exposed 316 are very weak. The larger of the two, near 577 eV is consistent with chromium oxide, Cr\textsubscript{2}O\textsubscript{3} (576.5-577.1 eV). It appears to narrow with sputtering. On the unexposed sample the chromium shows up mostly unoxidized with the main peak at 574.4 eV (Figure 34). This is the classic 2p signature of chromium and it remains constant throughout sputtering. In the literature, Cr\textsubscript{2}O\textsubscript{3} shows up in the innermost part of the steel-oxide covering, just outside the bulk of austenitic steels. It’s predicted that
with further sputtering this layer rich in \( \text{Cr}_2\text{O}_3 \) will be found (see Chap. 7).

\( \text{Cr} 2p_{3/2} \) on the exposed 316L (Figure 35) shows up as a broad peak at all sputter depths, with its intensity increasing with depth. This peak is much stronger than that of the 316 steel. On the unexposed 316L steel (Figure 36), \( \text{Cr} 2p_{3/2} \) shows up in the form of chromium oxide at low sputter depths, as expected, and shifts towards its metallic form with prolonged sputtering.

Nickel

The nickel \( 2p \) signature on the exposed 316 is very weak (Figure 37). In fact, it is nonexistent at 5 sec of sputtering; however, a small bump appears at \( \approx 853 \) eV, consistent with metallic nickel (852.0-853.8 eV), at longer sputter intervals. On the unexposed 316, Ni \( 2p_{3/2} \) shows up around 853 eV (Figure 38).

On the exposed 316L sample (Figure 39), Ni \( 2p \) is again very weak, if present at all. A small “kink” in the spectral baseline occurs at \( \approx 853 \) eV. Nickel is not seen on the unexposed sample (Figure 40) at 5 sec of sputtering, but shows up in metallic form rather strongly at 25 and 85 sec of sputtering.

Lead

As expected, lead is not found in either of the unexposed steels (Figures 42 and 44). It does show up in small proportions on both of the exposed steels as two peaks, Pb \( 4f_{5/2} \) and \( 4f_{7/2} \) (Figures 41 and 43). Lead shows up more oxidized nearer the surface (5 sec sputtering) and shifts to lower binding energy with sputtering depth. This is consistent with the literature, from the standpoint that lead is oxidized in the model. (Li) Metallic lead is reported at binding energies of 136.4 eV to 137 eV. Lead oxide (PbO) is reported at 137.8-138.1 eV.

Exposed 316L shows similar traits to exposed 316 with metallic lead growing with depth. It is, however, much more evident on 316L.
Bismuth

Like lead, bismuth does not show up on either unexposed sample (Figure 46). There does happen to be a peak at \( \approx 154 \text{ eV} \) that is possibly the signature of Si 2s. There are two peaks corresponding to a Bi 4\( f_{7/2,5/2} \) doublet on the exposed 316 sample (Figure 45). At low sputtering (5 sec) the peaks have shoulders slightly shifted to higher binding energies (oxidized bismuth). With sputtering those shoulders subside, leaving peaks at 163.2 eV and 157.5 eV. These agree with reported values for metallic bismuth.

Exposed 316L also has two bismuth components (two on each peak of 4\( f \) doublet) that are much more evident on this steel. Again, the peak to lower binding energy is the metallic form and the the peak to higher binding energy is is oxidized form, consistent with Bi\(_2\)O\(_3\) at 158.6-159.8 eV. The oxidized peak falls off with sputtering.

Silicon

Silicon 2\( p \) is not present on the unexposed 316 (Figure 48), and may only be present on the unexposed 316L in trace amounts (Figure 50). The questionable Si 2\( p \) peak on 316L, consistent with SiO\(_2\) (103.1-103.6eV), disappears with sputtering.

Both exposed samples (Figures 47 and 49) have peaks for SiO\(_2\) at low sputtering, and they both decrease with sputtering depth. It is possible that silicon is diffused out of the bulk via oxidation and segregated to the corrosion layer surface.

It is well known that adding silicon to certain stainless steels, namely those which are martensitic, reduces the growth rate of the oxide layer, improving its resistance to oxidation. (Barbier et al.)
Figure 21 XPS high-resolution scan of carbon 1s peak on 316 steel sample, exposed to LBE for 3000 hours at 550 C.

Figure 22 XPS high-resolution scan of carbon 1s peak on unexposed 316 steel sample.
Figure 23 XPS high-resolution scan of carbon 1s peak on 316L steel sample, exposed to LBE for 3000 hours at 550 C.

Figure 24 XPS high-resolution scan of carbon 1s peak on unexposed 316L steel sample.
Figure 25 XPS high-resolution scan of oxygen 1s peak on 316 steel sample, exposed to LBE for 3000 hours at 550 C.

Figure 26 XPS high-resolution scan of oxygen 1s peak on unexposed 316 steel sample.
Figure 27 XPS high-resolution scan of oxygen 1s peak on 316L steel sample, exposed to LBE for 3000 hours at 550°C.

Figure 28 XPS high-res scan of oxygen 1s peak on unexposed 316L steel sample.
Figure 29 XPS high-resolution scan of iron $2p_{3/2,1/2}$ peaks on 316 steel sample, exposed to LBE for 3000 hours at 550 C.

Figure 30 XPS high-resolution scan of iron $2p_{3/2,1/2}$ peaks on unexposed 316 steel sample.
Figure 31 XPS high-resolution scan of iron $2p_{3/2,1/2}$ peaks on 316L steel sample, exposed to LBE for 3000 hours at 550 C.

Figure 32 XPS high-resolution scan of iron $2p_{3/2,1/2}$ peaks on unexposed 316L steel sample.
Figure 33 XPS high-resolution scan of Chromium $2p_{3/2,1/2}$ peaks on 316 steel sample, exposed to LBE for 3000 hours at 550 C.

Figure 34 XPS high-resolution scan of Chromium $2p_{3/2,1/2}$ peaks on unexposed 316 steel sample.
Figure 35 XPS high-resolution scan of Chromium $2p_{3/2,1/2}$ peaks on 316L steel sample, exposed to LBE for 3000 hours at 550 C.

Figure 36 XPS high-resolution scan of Chromium $2p_{3/2,1/2}$ peaks on unexposed 316L steel sample.
Figure 37 XPS high-resolution scan of Nickel $2p_{3/2,1/2}$ and peaks on 316 steel sample, exposed to LBE for 3000 hours at 550 C.

Figure 38 XPS high-resolution scan of Nickel $2p_{3/2,1/2}$ peaks on unexposed 316 steel sample.
Figure 39 XPS high-resolution scan of Nickel $2p_{3/2,1/2}$ peaks on 316L steel sample, exposed to LBE for 3000 hours at 550°C.

Figure 40 XPS high-resolution scan of Nickel $2p_{3/2,1/2}$ peaks on unexposed 316L steel sample.
Figure 41 XPS high-resolution scan of Lead $4f_{7/2,5/2}$ peaks on 316 steel sample, exposed to LBE for 3000 hours at 550 C.

Figure 42 XPS high-resolution scan of Lead $4f_{7/2,5/2}$ peaks on unexposed 316 steel sample.
Figure 43 XPS high-resolution scan of Lead $4f_{7/2,5/2}$ peaks on 316L steel sample, exposed to LBE for 3000 hours at 550 C.

Figure 44 XPS high-resolution scan of Lead $4f_{7/2,5/2}$ peaks on unexposed 316L steel sample.
Figure 45 XPS high-resolution scan of Bismuth $4f_{7/2,5/2}$ peaks on 316 steel sample, exposed to LBE for 3000 hours at 550 C.

Figure 46 XPS high-resolution scan of Bismuth $4f_{7/2,5/2}$ peaks on unexposed 316 steel sample.
Figure 47: XPS high-resolution scan of Silicon $2p_{3/2,1/2}$ peaks on 316 steel sample, exposed to LBE for 3000 hours at 550 °C.

Figure 48: XPS high-resolution scan of Silicon $2p_{3/2,1/2}$ peaks on unexposed 316 steel sample.
Figure 49 XPS high-resolution scan of Silicon $2p_{3/2,1/2}$ peaks on 316L steel sample, exposed to LBE for 3000 hours at 550 C.

Figure 50 XPS high-resolution scan of Silicon $2p_{3/2,1/2}$ peaks on unexposed 316L steel sample.
CHAPTER 7

OTHER STUDIES

In other similar studies, much of what is reported is verified in our work for austenitic type stainless steels. Included in the austenite category are 316 and 316L, which is what this thesis reports. Some groups did very similar studies, namely their steel samples were exposed for durations and temperatures very close to those of our steels. Others did different temperatures and/or different durations.

H. Glasbrenner et al. report that austenitic steels develop an oxide layer thickness of about 2 μm after being exposed for 3000 hours at 550 C. An inspection of the exposed samples revealed a golden shiny surface which is indicative of a thin oxide layer. The color darkens with exposure time but remained shiny up to the 3000 hour mark. They claim that an oxide layer of such thickness is still substantial to prevent dissolution attacks for at least the 3000 hour exposure time. The techniques they employed were weighing of test specimens, X-ray spectral microanalysis, metallurgical examination, and EDAX analysis on cross-sections of the samples.

F. Barbier and A. Rusanov performed similar studies on several types of steel, one being 1.4970 austenitic steel. They exposed samples in LBE at 300 C and 470 C for up to 3116 hours. The austenitic steel showed the greatest resistance to oxidation in LBE. They report that no signs of corrosion damage occurred in the maximum exposure time and temperature. They claim the austenitic steel exhibited no nickel depletion even though it has a high solubility in lead alloys, as reported by several others. X-ray maps and concentration profiles from the oxide/bulk interface show
no change in the distribution of the elements, therefore dissolution did not occur. They measured an oxide layer \( \ll 1 \, \mu m \) which apparently provided protection against corrosion. They calculated the oxide layer from weight change measurements, as SEM did not detect it. The techniques they used were SEM/EDAX, X-ray diffraction spectroscopy (XRD), and weight analysis.

C. Fazio et al. performed tests on 316L at 300 C, 400 C, and 476 C for times of 700, 1200, 1500, and 5000 hours. The report the austenitic steel, the 316L, exhibited acceptable resistance to oxidation corrosion. At the two colder temperatures with the longest exposure, a thin oxide layer formed (\( \ll 1 \, \mu m \)). EDS (EDAX) analysis showed oxide composition of mostly iron, chromium, and oxygen. Some nickel enrichment was also detected. At 1200 hours at higher temperatures of 464 C and 476 C, 316L showed a slightly thicker and nonuniform layer of oxidation growth, ranging from 2 to 4 \( \mu m \). Nickel enrichment at the oxide/metal interface was again detected. Using XRD, they report composition of the corrosion products corresponds to \( \text{Fe(Fe}_{1-x}\text{Cr}_x)_2\text{O}_4 \).

All three papers mentioned above report the multi-layer oxide formation as mentioned in Chapter 4, under “Dissolution Corrosion by LBE”. The layers are: an outer magnetite (\( \text{Fe}_3\text{O}_4 \)), an intermediate spinel \( \text{Fe}^{2+}(\text{Fe}^{3+}_{1-x}\text{Cr}^{3+}_x)_2\text{O}_4(+\text{Ni}) \), and an innermost oxygen diffusion layer.

Also reported in the above papers, \( \text{Cr}_2\text{O}_3 \) shows up in the innermost part of the steel-oxide covering, just outside the bulk of austenitic steels. It is predicted that with further sputtering this layer rich in \( \text{Cr}_2\text{O}_3 \) will be found.

According to Li and Barbier et al., nickel has the highest solubility and therefore we predict it to be the first alloying element diffused out of the bulk and dissolved into the LBE. At a first look, our data seem to agree with that claim. However, Glasbrenner et al. claim that nickel is in the deepest regions of the oxide layer and at the oxide-bulk interface. These data neither prove or refute these claims, as
sputter-depth profiling has not been performed for long enough intervals to reach the bulk materials.

Lead shows up more oxidized nearer the surface (5 sec sputtering) and shifts to lower binding energy with sputtering depth. The oxidation of lead is consistent with reports from Li and He et al.
CHAPTER 8

CONCLUSION

The results reported in this paper represent a solid first few steps in understanding the mechanism of LBE/steel corrosion. Much more work can and will be done as this research continues. What has been primarily accomplished thus far is obtaining the data to compare to and match similar studies and then proceed farther in such studies.

From our SEM/EDAX studies we know that exposed samples are covered with oxides, as indicated by strong oxygen peaks. Unexposed samples do not have significant oxygen peaks. Furthermore, among the exposed samples we know some areas are covered more densely with oxides. On such samples, uncovered or lightly covered areas show chromium signatures similar to that of an unexposed sample, whereas covered areas show little if any chromium. Iron and oxygen are strong in both the covered and uncovered areas, suggesting different oxide layer thicknesses (very thin oxide layering in the uncovered areas).

From our XPS studies we see quite different data. Due to the surface sensitivity of XPS (first few atomic layers), we initially see very similar peaks on both exposed and unexposed samples. In the spectra, carbon and oxygen both show up quite strong. At first look this seems very surprising since EDAX does not show much for the existence of carbon, and oxygen only showed up on the exposed samples. While keeping in mind that XPS and EDAX probe significantly different depth regions, this is what initially led us to consider the existence of surface contaminants. After ion-beam milling, the XPS spectra changed drastically.
Iron shows up mostly in metallic form on the unexposed samples and mostly oxidized on the exposed samples, as expected. Also, oxidized iron remains constant throughout sputtering (up to 85 sec) on the exposed samples. Metallic iron shows up with depth on the exposed samples. Chromium is similar to iron, but is much weaker in oxidized form on the exposed 316. However, on the exposed 316L sample oxidized chromium is much stronger. We expect to see Cr$_2$O$_3$ on stainless steels (especially on the unexposed samples), as it is the passivating component under atmospheric conditions. It shows up oxidized on the surface of the unexposed samples and shifts to metallic form with sputtering. We also expect, as mentioned in other studies, to see weak signals from nickel on the exposed samples. This is because nickel has the highest solubility in liquid metals. We do indeed see weak nickel peaks, if at all, on the exposed samples. On the unexposed samples it shows up in metallic form. Lastly, residual lead and bismuth appear on the exposed samples but not on the unexposed. On the exposed samples, lead and bismuth appear in both oxidized (PbO and Bi$_2$O$_3$) and metallic form. They are both more oxidized on the surface and shift to metallic form with sputtering.

In the future we plan further study of corroded steel samples by conducting corrosion experiments of our own and exercising different material-analysis techniques. Two techniques that we plan to utilize are micro-Raman spectroscopy and x-ray diffraction.
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