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Micro-Raman spectroscopic study of the corrosion of stainless steel by lead-bismuth eutectic

Brian D Hosterman

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MICRO-RAMAN SPECTROSCOPIC STUDY OF THE CORROSION OF
STAINLESS STEEL BY LEAD-BISMUTH EUTECTIC

by

Brian D. Hosterman
Bachelor of Science
Denison University
2001

A thesis submitted in partial fulfillment
of the requirements for the

Master of Science Degree in Physics
Department of Physics
College of Sciences

Graduate College
University of Nevada, Las Vegas
December 2006

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Nov. 17  2006

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Micro-Raman Spectroscopic Study of the Corrosion of Stainless Steel by Lead-Bismuth Eutectic

is approved in partial fulfillment of the requirements for the degree of

Master of Science in Physics

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ABSTRACT

Micro-Raman Spectroscopic Study of the Corrosion of Stainless Steel by Lead-Bismuth Eutectic

by

Brian D. Hosterman

Dr. John Farley, Examination Committee Chair
Professor of Physics
University of Nevada, Las Vegas

Lead-Bismuth Eutectic (LBE) has been proposed as a possible coolant and/or spallation target for the transmutation of nuclear waste. The corrosion of stainless steel from exposure to LBE must be understood if any transmutation scheme is to move forward. Annealed 316L, cold-rolled 316L, and D9 stainless steels corroded in a LBE environment were studied using Raman spectroscopy. Raman spectroscopy will allow identification of oxides within the corrosion layer. A micro-Raman system was constructed for these studies. The resulting Raman spectra from annealed 316L samples show evidence for the formation of Fe₃O₄, instead of Fe₂O₃, within the corrosion layer. The main feature at 670 cm⁻¹ matches well with the main peak of Fe₃O₄. Spectra from D9 samples show, in addition to a peak at 670 cm⁻¹, a second peak at approximately 606 cm⁻¹ that does not correlate to any oxide standards studied in this work. Raman spectra taken on iron, steel, and iron-silicon samples exposed to oxygen for short time periods also show evidence of Fe₃O₄ formation.
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ACKNOWLEDGMENTS

I would like to thank the following people whose assistance and support in this project has been invaluable and much appreciated: John Farley, Allen Johnson, Michael Pravica, David Shelton, Ning Li, Dale Perry, Amadeo Sanchez, James Norton, Daniel Koury, Umar Yuonas, Thao Ho Trung, Jenny Welch, John Kilburg, Bill O’Donnell, and Sandip Thanki. This work is funded through the University of Nevada, Las Vegas Transmutation Research Program administered through the Harry Reid Center for Environmental Studies and is gratefully acknowledged.
CHAPTER 1

INTRODUCTION

The Yucca mountain project will be the first permanent nuclear waste repository within the United States. It will have the capacity to store 77,000 tons of spent fuel. However, the site is expected to be filled by 2011 [1], and construction has not even begun because of various technical and political roadblocks. With more nuclear reactors being built, more repository sites similar to Yucca mountain will be required. Nuclear waste is already being stored at the Waste Isolation Pilot Plant (WIPP) near Carlsbad, New Mexico. However, this site is not a permanent storage facility and cannot accommodate all nuclear waste products.

Only a small percent, approximately one percent, of spent nuclear fuel presents major problems towards long term storage. The major constituent of spent fuel is uranium, which can be recycled or disposed as Class C low level waste. Plutonium and other minor actinides (neptunium, americium, and curium) have very long half lives, on the order of hundreds of thousands of years. The plutonium can be used as fuel, but this still leaves the minor actinides. Any storage facility must be durable for hundreds of thousands of years to accommodate the long lifetimes of these actinides. These actinides create problems because of the long term heat load and radiotoxicity.

Transmutation of nuclear waste from long lived products into shorter lived products will provide much relief to waste repositories. The transmutation process changes one element into another element through the neutron bombardment onto the waste. The extra neutrons make the element unstable, and fission occurs. The high atomic number waste decays into elements with a smaller atomic number. The goal of the
transmutation is to transmute all dangerous long lived elements into shorter lived products, which are inherently less dangerous to the environment.

By transmuting these actinides into shorter lived products, the radiotoxicity levels of spent nuclear fuel will decay orders of magnitude faster than the natural lifetimes of these elements. Figure 1 compares spent fuel toxicity levels with and without transmutation schemes. After transmutation, the radiotoxicity of the waste decays to levels below natural uranium ore in less than a thousand years.

![Toxicity Reduction of Transmuted Reactor Waste](image)

Figure 1 Radiotoxicity levels of nuclear waste with and without transmutation [2].

In addition, nuclear spent fuel includes plutonium, a possible weapons usable material. Storing plutonium on nuclear reactor sites raises proliferation concerns. Transmutation of the spent fuel reduces the proliferation potential of such waste.

**Lead Bismuth Eutectic**

Lead-bismuth eutectic (LBE) is a lead bismuth alloy containing 45 percent lead and 55 percent bismuth. An alloy of two components may cause the melting temper-
ature of the mixture to be less than either of the individual components. Adding lead to bismuth, for example, disrupts the crystal lattice of the bismuth, thus lowering the melting temperature of the mixture. A minimum melting temperature is reached at the 45:55 lead to bismuth ratio. A eutectic is the mixture with the necessary ratio between the two components that leads to the minimum melting temperature. Pure lead and pure bismuth have melting points of 327 and 271°C, respectively. The LBE melting point is only 123.5°C.

Lead bismuth eutectic presents much promise in the nuclear industry as a possible spallation target or a coolant. A spallation target produces neutrons when struck with protons. LBE has a low neutron capture cross section, allowing the neutrons to escape the LBE to be used for neutron bombardment in the transmutation process. LBE’s high thermal conductivity make it a good choice as a coolant to remove the large amounts of heat generated in a reactor environment. Unlike other potential coolants, such as sodium, LBE is inert with air and water. The low melting point, 123.5°C and high boiling point, 1670°C, allow for a wide range of operating temperatures.

A drawback of the LBE is that it corrodes steel. Any structural steel used in the construction of LBE facilities will experience corrosion upon long exposure to the LBE. For LBE to be a viable material in transmutation schemes, the corrosion layer must be minimized. Therefore, the mechanics of the corrosion process need to be understood.

The oxide layer formed during the corrosion process must be a protective layer. Pure iron under oxidation experiences an unprotective oxide layer, the common red rust, which easily flakes off to expose fresh iron, which then corrodes further. Stainless steel does not rust in air because of the protective chromium oxide layer formed. Unlike the iron oxide, which is very fragile, the chromium oxide layer retains its structure, protecting any further oxidation to the bulk material underneath the corrosion layer.
layer. In addition, the oxide layer should be able to recover from damage to the oxide surface. This allows for a self-healing corrosion layer. Because chromium oxidizes much faster than iron, chromium oxide will form over any scratches that may develop on a stainless steel surface.

The LBE further compounds the corrosion problem because many of the stainless steel components are soluble in LBE. Dissolution corrosion can be especially dangerous in a LBE environment utilizing different temperature zones, such as a cooling loop with a hot and cold zone. Corrosion products may dissolve into the LBE at the hot zone and precipitate out at cold zones. This build up would eventually obstruct the LBE flow through the loop.

The Russians have much experience using LBE as a coolant in their nuclear class submarines. Rusanov et al. [3] performed weight change studies of the steels as well as measuring the oxide thickness. Their studies show that the amount of oxygen within the LBE system greatly affects the corrosion process.

Limitations of SEM, XPS, IR

Elemental composition of corrosion layers has already been well detailed using energy-dispersive x-ray (EDX) techniques at the scanning electron microscope facility and x-ray photoelectron spectrometry (XPS) [4]. Results from these techniques conclude that the surface preparation of stainless steel is very important to the corrosion process. Two different surface preparations, cold-rolling and annealing, were examined. Our studies show the superior corrosion resistance of the cold-rolled sample, which had a primarily chromium oxide layer of 1 \( \mu \text{m} \) thickness. The annealed sample had a complex oxide structure with iron oxide over a mixed chromium and iron oxide layer having a thickness of tens of microns. Sputter depth profiling was performed giving elemental composition as a function of depth within the oxide layer.

In a scanning electron microscope, the incident electrons knock out electrons from
the electron shells of atoms within the sample. The vacancy allows for an electron in a higher shell to fill the newly created hole. This process emits an x-ray with an energy corresponding to the energy difference between the electron levels. EDX displays these x-rays as a function of energy. The detected signals are well known and can quickly be identified by the software.

X-ray photoelectron spectrometry (XPS) is close to being the inverse process of EDX. Fixed energy x-rays are incident upon the sample, and electrons are ejected to the detector. Because electrons lose energy through collisions as they leave the sample, XPS is a very surface sensitive technique. Only the electrons close to the surface actually escape the sample with their original energy to be identifiable.

Because EDX and XPS measure energy differences corresponding to electron levels of atoms, these techniques can only identify the different elements within a sample. XPS does have the resolution to distinguish between different oxidation states. However, the realization of the actual chemical species often proves difficult. For example, the oxygen that exists in Fe$_2$O$_3$ and Cr$_2$O$_3$ have the same oxidation state. Thus, oxygen from these two sources appears the same in an XPS spectrum.

Raman spectroscopy gives information regarding the vibrational states of a molecule. Infrared absorption spectroscopy (IR) is another method of identifying vibrational states. Infrared spectrometers employ a light source that emits over a broad range of wavelengths. An absorption spectrum is measured from the absorption of specific frequencies that correspond to vibrational levels within the sample. Although infrared and Raman both measure vibrational information, selection rules determine whether a particular vibration is Raman-active and/or infrared-active. Infrared activity of a vibrational mode requires the dipole moment of a molecule to change during the vibration. Raman activity requires the polarizability of the molecule to change during the vibration. The polarizability and Raman activity will be detailed in the
following chapter.

Ignoring selection rules, which may rule out either Raman or infrared from detecting specific vibrations, Raman offers many advantages over infrared spectroscopy. Because infrared is a direct absorption of light of specific frequencies, the light source must be capable of emitting light matching the frequencies of the vibrations. The Raman effect, as will be explained in the following chapter, requires only an intense monochromatic illumination, easily produced by any laser system. Also, the optics within an IR system must be specialized to deal with the infrared spectrum whereas Raman systems often work in the visible range of the light spectrum. Another advantage of Raman is that water has a weak Raman signal, but a large IR absorption. Raman spectra of aqueous solutions do not suffer from interference from the water vibrations.
CHAPTER 2

RAMAN SCATTERING

The Raman effect, named for the Nobel prize work by Chandrasekhra Venkata Raman in 1928 [5], is an inelastic light scattering process due to the excitation or de-excitation of molecular vibrational states. Rayleigh scattering, the most common form of light scattering, involves the scattering of a photon with the same energy as the incident photon. In Raman scattering, the molecule can absorb some of the photon's energy, exciting a vibrational mode, resulting in a photon with less energy. Alternatively, the molecule, if already in an excited vibrational mode, can lose that energy, resulting in a photon with higher energy.

Raman scattering is an inherently weak process. Approximately 1 in $10^7$ of incident photons is inelastically scattered. This leads to the requirement that Raman systems must be very efficient at eliminating Rayleigh scattered light.

Raman scattering is typically non-resonant; meaning the energy of the incident light does not correspond to the energy difference of any pair of levels within the system. The incident photon excites the system to a virtual level and the system then decays to the ground state (Rayleigh) or an excited vibrational state (Raman). Resonance Raman scattering is a technique where the incident laser light equals the energy of a vibrational level. Raman signals for the resonant vibrational level are greatly enhanced. Unfortunately, finding a light source to match up with specific energy levels can prove difficult.

The spectral lines having a wavelength greater than the incident laser, resulting from excitation of vibrational modes, are called Stokes lines. The spectral lines
having a wavelength less than the incident laser, resulting from de-excitation of vibration modes, are called anti-Stokes lines. At room temperature, the majority of the molecules are not in vibrational excited states and Stokes signals will be dominant. Unless the experiment is devised in a way to thermally populate excited vibrational levels, anti-Stokes signals will be weak. Stokes and anti-Stokes scattering can be seen in Figure 2.

Figure 2 (a) Rayleigh scattering involves absorption and re-emission of a photon of the same energy. (b) Raman scattering involves the emission of a photon of lesser energy (Stokes). The vibrational level n=1 is excited. (c) Raman scattering involves the emission of a photon of higher energy (anti-Stokes). The vibrational level n=1 is initially excited and returns to the ground state after the photon scattering.

The spectra collected in this study are all Stokes signals, corresponding to an energy shift to a lower photon energy.

Because the Raman effect is only a shift in energy, any excitation wavelength can be chosen for the experiment, making the Raman system flexible in choosing the laser source. The experimental setup must only be capable at viewing spectral ranges close to the excitation line.
Classical Derivation

A classical treatment of light scattering shows the origin of the Raman effect. The electric field of the incident light with frequency $\nu_0$ can be written as

$$E = E_0 \cos 2\pi \nu_0 t.$$  \hspace{1cm} (2.1)

This electric field distorts the molecule because the positively charged nuclei pushes towards the negative pole, while the electrons are forced in the opposite direction. This induces an electric dipole in the molecule given by

$$P = \alpha E,$$  \hspace{1cm} (2.2)

where $\alpha$ is the polarizability of the molecule.

If the molecule is vibrating with frequency $\nu_m$, then the nuclear displacement can be written as

$$q = q_0 \cos 2\pi \nu_m t.$$  \hspace{1cm} (2.3)

For small amplitudes, $\alpha$ is a linear function of $q$, and can be expanded as

$$\alpha = \alpha_0 + \left( \frac{\partial \alpha}{\partial q} \right)_0 q + \ldots$$  \hspace{1cm} (2.4)

The partial derivative is evaluated at the equilibrium position.

Combining equations 2.1, 2.2, 2.3, and 2.4 gives

$$P = \alpha E_0 \cos 2\pi \nu_0 t$$
$$P = \alpha_0 E_0 \cos 2\pi \nu_0 t + \left( \frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 \cos 2\pi \nu_0 t$$
$$P = \alpha_0 E_0 \cos 2\pi \nu_0 t + \left( \frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 \cos 2\pi \nu_0 t \cos 2\pi \nu_m t$$
$$P = \alpha_0 E_0 \cos 2\pi \nu_0 t + \frac{1}{2} \left( \frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 \left[ \cos \{2\pi (\nu_0 + \nu_m) t\} + \cos \{2\pi (\nu_0 - \nu_m) t\} \right].$$  \hspace{1cm} (2.5)

The first term on the right hand side in Equation 2.5 is the elastic Rayleigh scattering term, and the Stokes ($\nu_0 - \nu_m$) and anti-Stokes ($\nu_0 + \nu_m$) terms are also apparent. The
coefficient of Raman terms shows that these Raman terms are non-zero only if there is a change in the polarizability when the molecule vibrates. If the polarizability does not change under molecular vibration, the vibrational mode is not Raman-active.

**Polarizability Tensor**

In real 3-dimensional molecules, Equation 2.2 needs to incorporate the \( x \), \( y \), and \( z \) directions. In matrix form, this is written as

\[
\begin{pmatrix}
P_x \\
P_y \\
P_z
\end{pmatrix} =
\begin{pmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{pmatrix}
\begin{pmatrix}
E_x \\
E_y \\
E_z
\end{pmatrix}.
\] (2.6)

The 3×3 matrix on the right hand side of Equation 2.6 is called the **polarizability tensor**. If any of the components of this tensor change during the vibration, then the vibration is Raman-active.

**Symmetry and Character Tables**

A full discourse on symmetry theory is beyond the scope of this paper. Numerous sources discuss the basics of group theory and its applications to vibrational systems [6] [7]. Terms from group theory are used throughout the discussion and analysis of data, which is common to the field of molecular vibrations. Therefore, a few concepts for a basic understanding will be introduced in this section.

Symmetry elements differentiate molecules into point groups. A symmetry element is a specific operation, such as a rotation, of the molecule that leaves the molecule indistinguishable from the original position. All the point groups have character tables that completely describe the point group’s symmetry elements, vibrational modes, and even Raman and infrared activity. As an example of a point group, the character table of the \( \text{C}_{2v} \) point group can be seen in Table 1.

Water, \( \text{H}_2\text{O} \), belongs to the \( \text{C}_{2v} \) point group. The top header row of the character table labels the point group, as well as the symmetry operations. The identity oper-
Table 1 The character table for the $C_{2v}$ point group.

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$\sigma_v(xz)$</th>
<th>$\sigma_v(yz)$</th>
<th>$T_z$</th>
<th>$\alpha_{xz}$, $\alpha_{yy}$, $\alpha_{zz}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td></td>
<td>$R_z$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td></td>
<td>$a_{xy}$</td>
</tr>
<tr>
<td>$B_1$</td>
<td>+1</td>
<td>-1</td>
<td>+1</td>
<td>-1</td>
<td>$T_x$, $R_y$</td>
<td>$a_{zz}$</td>
</tr>
<tr>
<td>$B_2$</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
<td>$T_y$, $R_z$</td>
<td>$a_{yz}$</td>
</tr>
</tbody>
</table>

Any possible vibration of a molecule can be represented in one of these irreducible representations. Herzberg's equations [6] can be used to determine the number of vibrations in each representation. For example, the water molecule has two $A_1$ vibrations and a single $B_2$ vibration.

The last two columns of the character table give the IR or Raman activity of the vibrations. A vibration is infrared-active if the vibration species contains a translational motion ($T_x$, $T_y$, $T_z$) and Raman-active if the vibration species contains an element of the polarizability tensor, $\alpha_{ij}$. For the water molecule example, the $A_1$ and $B_2$ species have translational and polarizability elements. Therefore, all three vibrational modes of water are infrared and Raman-active.

A total of 32 crystallographic point groups describe most molecular structures. In a purely mathematical sense, more point groups exist, but few molecules have
rotational symmetry, $C_n$, with $n > 6$. In addition to the identity $E$, $C_n$ rotations, and $\sigma$ mirror planes, there a total of five point group symmetry elements. The two other elements are the center of symmetry, $i$, and the rotation reflection axes, $S_n$.

Wavenumbers

Raman spectra are commonly denoted using a wavenumber (cm$^{-1}$) shift from the incident laser line. As the units imply, wavenumber is just an inverse centimeter. Wavenumbers can be converted from frequency, $\nu$, using

$$ wavenumber = \frac{\nu}{c}, \quad (2.7) $$

where $c$ is the speed of light in a vacuum.

The Raman shift, $\bar{\nu}$, can be calculated in wavenumbers using

$$ \bar{\nu} = \frac{\Delta \nu}{c} = \frac{\nu_i - \nu_s}{c}, \quad (2.8) $$

where $\nu_i$ and $\nu_s$ are the frequencies of the incident and scattered light, respectively. The Raman shift is just the difference in wavenumbers between the wavenumber position of the vibrational signal and the Rayleigh scattered signal.
CHAPTER 3

EXPERIMENTAL SETUP

The micro-Raman experiment was constructed mostly from available equipment. The major components of the system (laser, microscope, and monochromator) were already on hand. Minor purchasing was required to bring everything to an operational status. Figure 3 shows the major components of the assembled micro-Raman system. The laboratory in which this apparatus was built contained two previous Raman spectrometers. Neither system was ever fully optimized to give good data. This system was constructed to take advantage of the high quality Nikon microscope.

![Diagram of micro-Raman experimental setup](image)

Figure 3 Micro-Raman experimental setup.
A Lexel RamanIon krypton ion laser acts as the excitation source. The main lasing line of the krypton ion laser is at 647.1 nm. The power output is adjustable, but for experiments in this research, was usually set to 70 mW. However, optical components such as the spatial filter and beamsplitter cut out a large amount of light. Only 1.5 mW, approximately, is incident upon the sample. The krypton ion laser was selected over an available argon ion laser (main lasing line at 514.5 nm) because of the lower power of the krypton ion laser. Because some samples are sensitive to heating effects, the lower power is more desirable. The higher energy per photon of an argon laser would more easily heat the sample. If the use of the argon laser is needed, incorporating the argon laser into the system would not be too difficult.

A spatial filter cleans up the frequency profile of the laser beam. The spatial filter is a Newport 910 series five-axis spatial filter. A lens focuses the laser onto a pinhole. The size of the hole in the spatial filter will affect the focused spot size at our sample. Currently a 10 micron pinhole (Newport 910PH-10) is used, although other sizes can easily be installed in the spatial filter. A second lens is placed at the focal distance away from the pinhole to collect and collimate the light from the pinhole. The beam size after the collimating lens is about 2 mm.

After the beam is cleaned with the spatial filter, the laser light enters a port on the Nikon MM-40 Measuring Microscope where a mostly transparent beamsplitter reflects a portion of the light down through the objective to the sample. The microscope objective focuses the laser onto the sample. The objective also acts to collect the scattered light from the sample. This light then travels up the microscope, through the beamsplitter, and exits through a separate port on the microscope.

A 50X and 20X objective was used for data collection. A quick experiment was performed to determine the focused spot size of the laser. The intensity of the 647.1 nm Rayleigh scattered light was recorded as a function of the spot position as the spot
was moved perpendicularly to the edge of a razorblade. First, the laser was focused on the edge of the razorblade. Then the spot was moved away from the edge along the surface. This position was set at zero, and using a micrometer with half micron divisions, the spot was incremented towards the edge. The signal should be expected to remain mostly constant until the spot reaches the edge of the blade. There may be some variance in the signal because of imperfections in the surface of the razorblade. As the spot moves off the surface of the razorblade the signal should begin to fall off to zero. Afterwards, the signal should remain at a minimum as the laser is no longer incident upon the surface of the blade.

Figure 4 shows the results of this experiment using the 50X objective. As is clearly evident from the graph, the spot begins leaving the razorblade edge at 17 microns and is completely off at 20 microns. This places an upper bound on the spot size at 3 microns in diameter. The 20X objective has a larger spot size, approximately 10 microns. Figure 5 shows the results from the same experiment performed with the 20X objective.

The highly transparent beamsplitter was selected to allow for minimal loss of signal from our sample due to reflection. The laser output is intense enough that even the small amount that gets to our sample after reflection from the beamsplitter is sufficient for strong signal.

The eyepiece on the microscope allows for a visual guide when focusing the laser onto a desired area of the sample.

The sample stage of the microscope has micrometers in all three dimensions and will allow a wide range of sample sizes. A glass slide is as easily accommodated as a sample with a thickness of one inch or more. The micrometers allow adjustments accurate to a half micron.

A holographic notch filter is used to filter out the 647.1 nm light due to Rayleigh
Figure 4 The Rayleigh scattered light signal of the 647.1 nm laser focused through the 50X objective as a function of position along the surface of the razorblade. The spot size can be inferred from this graph at 3 microns.

scattering of the laser source. A crucial necessity of any Raman system is its ability to reject stray light. Due to the weak Raman signal, the equipment is meant to be very sensitive to any light, so the Rayleigh signal must be removed. If allowed into the spectrometer, this light would saturate the CCD and overwhelm any weak Raman signal. Even though the grating inside the monochromator can be adjusted away from the 647.1 nm line, the Rayleigh signal is so strong that it completely fills nearby wavelengths, making it impossible to see signals less than one hundred wavenumbers from the Rayleigh line. In fact, when this light does hit the CCD, the signal remains for a time before eventually decaying away. Even with the notch filter, the smallest wavenumbers viewable without getting Rayleigh signal is about 150 cm\(^{-1}\) from the Rayleigh line. The effect of the notch filter can be seen in many of the spectra at a grating position of 665 nm. Signals cut off drastically below 150 cm\(^{-1}\).

A double convex lens is used to focus the light onto the slits of the monochromator.
Figure 5 The Rayleigh scattered light signal of the 647.1 nm laser focused through the 20X objective as a function of position along the surface of the razorblade. The spot size can be inferred from this graph at approximately 10 microns.

A 1 cm diameter aperture is placed in front of a 68 mm focal length lens to best match the $6.4 \times f/number$ of the monochromator. The $f/number$ of an optical system is given by

$$f/\text{number} = \frac{f}{A}, \quad (3.1)$$

where $f$ is the focal length of the lens and $A$ is the apertured diameter of the light. With this setup, the circular signal slightly overfills the first mirror within the monochromator.

The monochromator is a Horiba Jobin Yvon TRIAX 550 with a 55 cm focal length and 1.55 nm/mm dispersion. The TRIAX 550 is fully automated by a computer through a GPIB interface. The entrance port has an adjustable 2 mm slit. With the exception of the neon spectra used for calibration, all data collected had the slits open to 0.2 mm. The spectrometer contains three gratings mounted on a turret. The
1200 lines/mm grating with a blaze angle at 500 nm was used throughout the data collected for this work. The software allows full automation of the grating position and slit opening.

The grating within the spectrometer diffracts the light and a select spectrum of light falls onto a Princeton Instruments Spec-10 liquid nitrogen cooled charge-coupled device (CCD) detector. The CCD is cooled to a temperature of -120°C to minimize any dark current on the detector. The CCD is model 100BR, a back-illuminated 1340 × 100 imaging array with 20 × 20 μm pixels. The chip has an imaging area of 26.8 × 2.0 mm. The CCD has the highest quantum efficiency in the range of 600-900 nm, which is ideal for measuring Stokes scattering from the 647.1 nm excitation line.

A section of the TRIAX 550 to which the CCD mounts was replaced due to incompatibility with the Princeton Instruments detector. Diagrams of the part were received from Jobin Yvon and the aluminum part was machined in the UNLV Department of Physics machine shop with a Haas CNC machine. The part was then anodized to prevent stray light reflection inside the monochromator. The anodization process consisted of electropolishing in nitric acid followed by submersion in a heated dye bath. This gives the surface of the aluminum a flat black finish that has low reflectance to avoid any stray light reflection within the monochromator.

High quality, high reflective laser mirrors are used to guide the beam across the table. Newfocus 5901 silver mirrors direct the light to the microscope. Any loss here is inconsequential because of the great intensity of the laser output. Thorlabs laser mirrors coated with their BB01, a proprietary film, designed for greater than 99% reflectivity in the wavelength range of 400-800 nm, direct the light into the monochromator. The high reflectance mirrors are used here to keep as much of the weak Raman signal as possible and minimize stray light problems.

Data collected by the CCD is displayed through Princeton Instruments WinSpec
software. The software monitors the detector temperature and controls the detector functions. The software has peak finding functions, which were used for wavelength calibration described in the following section.

Software and Calibration

The WinSpec software that controls the CCD does not communicate with the Jobin Yvon software controlling the monochromator. The data collection software does not recognize the position of the grating within the spectrometer. The JY software controlling the grating position allows a desired wavelength to be centered on the CCD. However, the system cannot be trusted to be at the same position when the grating position has been changed and then brought back to position. The data collection software also does not know anything about the dispersion of the grating. WinSpec has built in calibration functions that allow known wavelength positions to be entered for pixel numbers of the detector. The software will then perform a polynomial fit to these points to span the entire range of the detector. The calibration can be performed in any units (nm, cm$^{-1}$) and displayed in another desired unit. All the necessary conversions are performed by the software.

A neon gas penlamp was used to create a calibration spectrum for the data collection software. The spectral lines of neon are well known and easily identifiable. Neon is an ideal source because the wavelength range for neon lines correlates very well to Raman shifts from the 647.1 nm krypton ion laser. Ferraro et al. [6] contains a well diagramed spectrum of strong neon lines that trivialized the identification of neon spectrum from the pen lamp. The lines used for calibration purposes of any spectrum centered at 665 nm or 700 nm can be seen in Table 2.

An uncalibrated spectrum of neon at a grating position of 700 nm can be seen in Figure 6. A quick look at the spectrum presented in Ferraro et al. [6] shows that the three visible lines are, from left to right: 692.95, 703.24, and 717.39 nm.
<table>
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<td>671.70</td>
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<td>692.95</td>
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<td>703.24</td>
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Table 2 Neon lines used for calibration of Raman spectrum at grating positions of 665 nm and 700 nm [6].

A peak finding function of WinSpec gives the exact pixel value for a peak. The known wavelength was calibrated to these peaks and a polynomial fit calculated. Figure 7 shows the same spectrum with these calibration points entered into WinSpec. After Winspec performs the polynomial fit, the line positions are 692.97, 703.20, and 717.41 nm.

Figure 6 Uncalibrated neon spectrum at a grating position of 700 nm.
To test the viability of using neon as a calibration source, an argon source was examined. A calibration was created using neon at a grating position of 700 nm. Using the same grating position, a spectrum from an argon pen lamp was obtained in order to compare positions of argon lines in the region to literature values. The gathered spectrum can be seen in Figure 8. Experimental results using the neon calibration compared to literature values can be seen in Table 3 and show that the neon calibration works very well.

For the argon and neon pen lamps, a focusing lens was not used. The lamps were mounted at the input port of the microscope, where the laser would normally enter the microscope, allowing the lamp to be the illuminating light source on the sample. The neon lamp is too intense for the detector if mounted directly in front of the monochromator. Even at 100 ms exposure time, the shortest acquisition time, saturation limits of the detector are reached when the lamps are mounted in front of the slits. Mounting the pen lamps to act as a illuminating source also means that the

Figure 7 Neon spectrum calibrated using the three visible neon lines.
Figure 8 Argon spectrum at a grating position of 700 nm.

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Table 3 Argon gas discharge spectrum at a grating position of 700 nm. The wavelength was calibrated using neon emission lines at the same position.

light scatters off the sample and follows the exact same path as light scattered from the exciting Kr ion laser. While using neon as a calibration source, the slits were opened to only 0.1 mm to provide even narrower lines for better calibration points. A neon spectrum taken with the monochromator grating positioned at 665 nm can be seen in Figure 9. The visible lines are 653.3, 659.9, 667.8, and 671.7 nm. Most of the data taken in this research was done at this grating position of 665 nm. The majority of Raman data for the oxides that interest this research are in this region. Without changing the grating position, the same neon calibration spectrum can be
Figure 9 Neon gas discharge spectrum at a grating position of 665 nm. Spectrum is calibrated using the four visible lines. This calibration spectrum is used for any data taken at a grating position of 665 nm.

used for all collected data. The grating did require periodic adjustment, usually to make adjustments to the notch filter. A new neon calibration spectrum was taken after the grating was brought back to the 665 nm position.

A future significant software upgrade may allow the camera and spectrometer to communicate so that this step can be eliminated from the data analysis process. However, computer and operating system upgrades will also be required, making the upgrade a non-trivial task.

Background and Baseline Fitting

Stray light always appears in any signal. Although this background is small, it may contain features that can be misinterpreted as Raman signal. To remedy this problem, a spectrum is first taken with the laser turned off but the spectrometer slits open. This procedure allows any stray light existing outside the spectrometer to fall on the CCD. The acquired spectrum is saved as a background spectrum and
subtracted from any subsequent spectra. A new background must be taken whenever the grating is moved. Furthermore, as backgrounds may vary from day to day, a new background spectrum is taken each day.

Care must be taken to not confuse random noise with a real signal. Many Raman signals are very weak, and subtracting an old background spectrum can easily create artifacts similar to actual Raman signal.

Many of the acquired spectra have flat baselines after background subtraction and the Raman signals are easily distinguished from the background. However, a few acquired spectra needed a polynomial fit to better view the spectral lines from the messy background signal. If a background fit was necessary, a second order fit was performed using data points in the pixel range of 200 to 1200 and subtracted from the signal. These low and high pixel ranges are not included in the polynomial fit because of unpredictable behavior. At low wavenumbers, usually below 200 cm⁻¹, the notch filter drastically cuts into the signal. Many spectra also just fall off sharply, or even spike, at the high pixel limits of the CCD. An example of a background requiring a fit can be seen in Figure 10, which shows the Raman spectrum from chromium oxide powder.

The large background signal from many of the corroded stainless steels can be slowly reduced by the focused laser spot. Figure 11 shows a spectrum from a fresh spot on a D9 corroded sample. Using the 50X objective, the incident laser eventually eliminates this background. Figure 12 shows the same spot from Figure 11 on the D9 sample after approximately two hours of illumination from the laser. Even though the units on the y axis are arbitrary, they are provided to give a scale of the substantial background removed during this process. After removal of the sample from the laser, the background will eventually return to the sample.
Figure 10 Raman spectrum from Cr$_2$O$_3$ standard. The problematic baseline requires a polynomial fit to better investigate the Raman lines.

Figure 11 Raman spectrum of a fresh spot on a D9 stainless steel tube exposed for 1000 hours at 550°C.
Figure 12 Raman spectrum of the same spot on the D9 stainless steel tube exposed for 3000 hours at 550°C. The laser was incident upon the sample for approximately 2 hours. The signal to noise ratio is now enough to see the Raman signal.
In order to analyze the oxide composition of corroded stainless steels, the spectra of oxide standards must be known. The collective vibrational states of oxides are unique and can be used for identification of unknown oxides in steel samples. Standards were selected that could likely be found as corrosion products in corroded stainless steel samples. Because iron and chromium are the major elements within stainless steel, iron and chromium oxides were first selected to be studied.

The data collected from other experimental methods such as EDX and XPS will help guide selection of oxide standards to study.

The Fe\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{3}O\textsubscript{4}, and Cr\textsubscript{2}O\textsubscript{3} powder standards are brand Alfa Aesar and are greater than 99.9% pure.

**Hematite (Fe\textsubscript{2}O\textsubscript{3})**

Hematite is the common oxide known as rust. The spectrum of Fe\textsubscript{2}O\textsubscript{3} is well known [9]. The signal from this spectrum is very strong and easily seen. The sample is red, and the red laser scatters well from this sample. This sample was always used when any changes were made to the system, to ensure that the system performed as expected. Also, fine tuning of any optical components of the experimental setup could be accomplished by examining the effect on the Fe\textsubscript{2}O\textsubscript{3} signal.

The oxide powder was crushed into a pellet using a press. The spectrum from a one minute exposure can be seen in Figure 13. The lines agree well with literature values. The spectral line position of this work is compared with previous work in...
Figure 13 Fe₂O₃ spectrum at a grating position of 665 nm. Exposure time: 60 seconds.

Table 4. The 292 and 299 cm⁻¹ doublet is not resolved in this data. Hematite belongs to the $D_{3d}$ crystal space group. A total of seven phonon lines, two $A_{1g}$ and five $E_g$ modes should be visible.

A large feature exists at the 1320 cm⁻¹ region due to a second order overtone of an unallowed vibration. This feature can be seen in Figure 14. Some sources claim that this feature arises from a two magnon scattering process [9]. A magnon is a collective spin excitation of the electrons within the crystal lattice. However, other work has shown that this is not the case. The extensive work done by McCarty et al. [10] and Massey et al. [11] on this peak at high temperatures and varying pressures concludes that the peak must arise from a second order vibration of approximately 660 cm⁻¹.

The laser power, through heating of the sample, can affect the position of the lines [9] [12]. The lines taken in this research agree well with literature values for laser powers that do not induce heating effects.
Figure 14 Fe$_2$O$_3$ spectrum at a grating position of 700 nm. The large feature at 1300 cm$^{-1}$ is seen. Exposure time: 60 seconds.

Magnetite (Fe$_3$O$_4$)

Magnetite gives a spectrum with a significantly weaker signal than hematite. Fe$_3$O$_4$ belongs to the $O_h$ crystal space group and has five predicted Raman bands consisting of three $T_{2g}$, one $E_g$, and one $A_{1g}$ line. The strongest line exists at approximately 670 cm$^{-1}$. A spectrum of magnetite powder placed on a microscope slide can be seen in Figure 15. The large feature is at 665 cm$^{-1}$. This is consistent with other sources as to the position of this feature, considering the disagreements as to the exact position of the main magnetite feature [13]. Two other small features appear at 227 and 295 cm$^{-1}$. These features do not agree well with the two other Fe$_3$O$_4$ lines presented by De Faria et al. Although as that work shows, there is disagreement on this spectrum. These lines do correlate well with the strongest Fe$_2$O$_3$ lines and most likely arise from small amounts of heating due to the laser. The two other lines De Faria et al. [9] measured are at 301.6 and 513 cm$^{-1}$. These features are very small.
Table 4 Fe₂O₃ spectrum at a grating position of 665 nm.

<table>
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<td></td>
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<td>497.1</td>
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<td>611.3</td>
<td>611.9</td>
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and are most likely just not detectable by this system.

Upon sufficient heating, magnetite will decay into hematite in a process known as martitization. Shebanova et al. [14] and de Faria et al. [9] study the heating effects on magnetite using Raman spectroscopy. Their studies show Fe₂O₃ lines growing into the Fe₃O₄ spectrum as the temperature is raised. The change is permanent. As the temperature is reduced, the Fe₂O₃ lines remain in the spectrum.

A magnetite sample was also created in a manner similar to the creation of the hematite pellet through a pressing process. The pressing process must have created enough heat to degrade the magnetite into hematite. Under optical microscope, red spots appear throughout the surface of the pellet. The magnetite pellet spectrum can be seen in Figure 16. Many of Fe₂O₃ lines are present. This is clear evidence of the martitization process that occurs during the pressing of the pellet.

**Chromium Oxide (Cr₂O₃)**

Chromium oxide is the protective layer on stainless steel that passivates and protects the surface. The powder standard was placed upon a microscope slide. The spectrum for this sample is seen in Figure 10. Since this spectrum shows a very poor increasing baseline, a second order polynomial fit was applied and subtracted from
Figure 15 Fe$_3$O$_4$ spectrum at a grating position of 665 nm. Exposure time: 60 seconds.

the data. Only data from pixels 200 to 1200 was used in the polynomial fit. The chromium oxide signal with the second order polynomial fit subtracted can be seen in Figure 17. The Raman lines visible are detailed in Table 5. These lines are in relatively good agreement with literature [15].

A spectrum of uncorroded cold-rolled 316L stainless steel can be seen in Figure 18. Stainless steel resists corrosion because of the protective chromium oxide layer that forms over the bulk material. Cr$_2$O$_3$ lines should be present within this spectrum. The chromium lines from the standard were weak however, and the system just may not be capable of seeing a thin chromium oxide layer on the stainless steel.
Figure 16 $\text{Fe}_3\text{O}_4$ spectrum at a grating position of 665 nm. Exposure time: 60 seconds. This sample was pressed into a pellet. The visible hematite lines are indicative of heating effects during the pressing of the pellet. The single magnetite line is labeled with a $M$.

Figure 17 $\text{Cr}_2\text{O}_3$ spectrum at a grating position of 665 nm. A second order polynomial fit was applied and subtracted from the spectrum.
Table 5 Cr$_2$O$_3$ Raman lines measured in this work compared to work done by Mougin et al.

<table>
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Figure 18 Uncorroded cold-rolled 316L stainless steel at a grating position of 665 nm. The chromium oxide layer is most likely too thin to be detected by the system.
CHAPTER 5

RAMAN SPECTRA OF CORRODED SAMPLES

With a library of vibrational spectra of known oxides, unknown corroded samples can be studied to determine the corrosion products formed during the corrosion process.

A Rusted Iron Sample

A quick experiment was devised to test the viability of studying in situ a metal sample after corrosion. A piece of iron was left in water until it had a reddish colored oxide, the common rusting reaction. This experiment was not well controlled. The iron just sat in a water-filled cup for a period of about a week. No controls on the temperature of the corrosion environment were done. The spectrum from this sample is shown in Figure 19. The spectrum resembles lepidocrocite (\(\gamma\)-FeOOH) spectrum. \(\gamma\)-FeOOH is a common iron hydroxide formed during the rusting process of iron containing metals due to water. The main features are at 244.4, 373.9 cm\(^{-1}\) with smaller features at 523.7 and 646.8 cm\(^{-1}\). This is in very good agreement with the spectrum taken by De Faria et al. [9] These results are expected from the material, pure iron, and the water environment where corrosion occurred. It was somewhat surprising not to see the formation of Fe\(_2\)O\(_3\) as the major corrosion product.

LBE Corroded Stainless Steel

Many small samples were cut from lengths of stainless steel samples that had been exposed to LBE for 1000 to 3000 hours at a temperature of 550°C. The size of all the cut samples is approximately a centimeter long and a centimeter in diameter.
The exposure to LBE was done at IPPE in Russia under contract from Los Alamos National Lab [3]. The Russians corroded a number of different stainless steels for various temperatures and exposure times in their LBE loop. The steels studied here are a 316L tube that was annealed, a 316L rod that was cold-rolled, and D9. The atomic weight percent composition of the 316L stainless steel is Cr 17.3, Ni 12.1, Mo 2.31, Mn 1.8, Si 0.35 and C 0.2 with the rest being iron. D9 stainless steel contains a chromium and nickel weight percent of 15 and 15, respectively. In addition, a small amount of titanium, around 0.2 percent, is added to the steel. D9 steel is believed to better resist the radioactivity of nuclear environments. These samples are some of the same samples as studied by Johnson et al [4].

The first stainless steel is from a hollow 316L tube and was selected for its relatively thick oxide layer, which is on the order of 10-30 \( \mu m \) [4]. The thicker oxide would produce a larger Raman signal from the corrosion layer. The steel was annealed. Scanning electron microscope images taken on cross sections of the sample show an
average corrosion thickness of approximately 10 microns.

The Raman spectrum of this sample can be seen in Figure 20. The peak is located at 667 cm\(^{-1}\) which correlates to the Fe\(_3\)O\(_4\) peak. Also, it is noted that none of the Fe\(_2\)O\(_3\) peaks exist in the spectrum. The conclusion is that iron oxide in the form of Fe\(_3\)O\(_4\), and not Fe\(_2\)O\(_3\), is formed during the corrosion of the steel by LBE.

The spectrum from a 316L stainless steel tube that had been exposed to LBE for 3000 hours at a temperature of 550°C can be seen in Figure 21. This sample was also annealed similar to the 1000 hour sample above. The feature at 670 cm\(^{-1}\) corresponds well to the main Fe\(_3\)O\(_4\) peak.

316L rod samples that were cold-rolled instead of annealed were also exposed at IPPE. A sample exposed for 3000 hours at 550°C can be seen in Figure 22. Unfortunately, no Raman peaks are detected in this spectrum. SEM studies by Johnson et al. [4] conclude a corrosion layer of only 1 micron thickness. The thin oxide layer may just be undetectable by the system.
Figure 21 Raman spectrum of the annealed 316L stainless steel tube exposed for 3000 hours at 550°C.

According to unpublished work by Johnson et al., the corrosion layer of D9 shows a duplex oxide layer of iron oxide over an iron and chromium oxide layer. A D9 stainless steel sample exposed to LBE for 3000 hours at a temperature of 550°C can be seen in Figure 23. The peak at 673 cm$^{-1}$ matches the usual Fe$_3$O$_4$ peak. In addition, there is another peak at approximately 606 cm$^{-1}$. The spectrum of a D9 sample exposed for only 1000 hours at 550°C is shown in Figure 24. This 1000 hour sample does not show the second peak at 606 cm$^{-1}$.

The second peak located at 606 cm$^{-1}$ could be evidence for chromite, FeCr$_2$O$_4$. Johnson et al. have shown large amounts of chromium contained in the corrosion layer, and chromite is a likely candidate. Literature on chromite Raman spectra is inconsistent, and samples of chromite need to be attained and studied before further conclusions are made. An online database compiled by the RRUFF project contains three FeCr$_2$O$_4$ spectra, each showing two main peaks of slight variance [16]. One Raman peak falls at a similar position as Fe$_3$O$_4$ around 670 cm$^{-1}$, while the second
smaller peak is in the 600 cm$^{-1}$ region. Unfortunately, other literature studying chromite does not agree with the aforementioned peaks. Table 6 lists Raman data from previous work on FeCr$_2$O$_4$.

Steel and Iron-Silicon Samples Exposed to Oxygen at 550°C.

A variety of samples were exposed in a vacuum-sealed, quartz tube at a temperature of 550°C for 100 hours. The samples were strung on a stainless steel wire and situated on one end of the tube. A pellet of copper and copper oxide was placed within the other side of the tube in an attempt to control the amount of oxygen within the system. After exposure, small regions of the corrosion layer that developed on the samples was sputtered through to reveal the bulk material.

The samples placed within the experiment were: D9, EP823, Fe, Fe(1), Fe(2), and Fe(3). EP823 is a common stainless steel. Fe is just a pure iron sample. The Fe(1), Fe(2), and Fe(3) samples are iron-silicon samples containing approximately 1,
Figure 23 Raman spectrum of D9 stainless steel tube exposed for 3000 hours at 550°C.

2, and 3% silicon. Johnson et al. [20] performed EDX and XPS studies on similar iron-silicon samples corroded in an LBE environment.

All of the iron-silicon steels show strong Fe$_3$O$_4$ signals whereas this signal is very weak on the D9 and EP823 samples. The signal located around 670 cm$^{-1}$ in all of these corresponds well with the main Fe$_3$O$_4$ peak. A form of iron oxide is expected to be the major corrosion product. However, none of the samples show any signs of a Fe$_2$O$_3$ oxide layer.

The Raman spectrum of the Fe(3) sample can be seen in Figure 31. This spectrum is very similar to the Russian sample from Figure 20 and is perhaps the most interesting results from these spectra. A sputtered area of this same sample can be seen in Figure 32. The Fe$_3$O$_4$ peak cannot be seen in this spectrum. The sputtered area spectrum suggests that the iron oxide was completely sputtered through. This sample was sputtered for 232 minutes, removing approximately 12 $\mu$m of material.

The spectrum from the sputtered area on the D9 sample, Figure 34, also shows...
Figure 24 Raman spectrum of D9 stainless steel tube exposed for 1000 hours at 550°C.

that the oxide layer was sputtered through.

Table 6 Previous work on FeCr$_2$O$_4$ is inconsistent. *Chen et al. do not assign vibration species to these three peaks.

<table>
<thead>
<tr>
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Figure 25 Raman spectrum of Fe exposed for 100 hours at 550°C.

Figure 26 Raman spectrum of a sputtered area on Fe exposed for 100 hours at 550°C.
Figure 27 Raman spectrum of Fe(1) steel exposed for 100 hours at 550°C.

Figure 28 Raman spectrum of a sputtered area on Fe(1) steel exposed for 100 hours at 550°C.
Figure 29 Raman spectrum of Fe(2) steel exposed for 100 hours at 550°C.

Figure 30 Raman spectrum of a sputtered area on Fe(2) steel exposed for 100 hours at 550°C.
Figure 31 Raman spectrum of Fe(3) steel exposed for 100 hours at 550°C.

Figure 32 Raman spectrum of a sputtered area on Fe(3) steel exposed for 100 hours at 550°C.
Figure 33 Raman spectrum of D9 steel exposed for 100 hours at 550°C.

Figure 34 Raman spectrum of a sputtered area on D9 steel exposed for 100 hours at 550°C.
Figure 35 Raman spectrum of EP823 steel exposed for 100 hours at 550°C.

Figure 36 Raman spectrum of a sputtered area on EP823 steel exposed for 100 hours at 550°C.
CHAPTER 6

CONCLUSIONS

A micro-Raman system was successfully constructed. This apparatus provides a wealth of *in situ* data on real world samples. Even though the apparatus is intended for corrosion research, the system is very flexible and allows micro-Raman studies on virtually any sample. For example, a different group has already begun using the system to take Raman data on samples within a Merrill-Bassett diamond anvil cell. The sample region of these diamond anvil cells is only about 100 microns in diameter.

Spectra of many standards have been measured and agree well with previous work. Fe$_3$O$_4$ has a very strong signal which is easily detected. The spectrum of Fe$_3$O$_4$ is weaker, although the main line at 670 cm$^{-1}$ is not too difficult to find. The Cr$_2$O$_3$ standard has a large background that must be fitted and subtracted from the spectrum.

The simple experiment on a pure iron sample rusted in water indicates that a iron hydroxide, $\gamma$-FeOOH, is produced instead of Fe$_3$O$_4$.

Iron oxide in the form of Fe$_3$O$_4$ appears in almost every corroded stainless steel sample. Only the 316L rod sample gave an empty spectrum, most likely being a result of an oxide layer that was too thin to detect by the system. The D9 spectrum contains a second peak located at 606 cm$^{-1}$ that could potentially be evidence of FeCr$_2$O$_4$. A few sputtered areas on the gas phase samples also do not show evidence of the Fe$_3$O$_4$ peak. However, with the corrosion layer being completely sputtered through, it is not expected detect the Fe$_3$O$_4$ peak. There is no evidence for Fe$_2$O$_3$ existing as a corrosion product in any of the spectra from corroded stainless steels.

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Fe$_2$O$_3$ is a much more intense spectra than Fe$_3$O$_4$ spectra. If Fe$_2$O$_3$ existed within the corrosion layer in any significant amount, it would be detected by the system.

The ability to distinguish between different iron oxides, such as Fe$_2$O$_3$ and Fe$_3$O$_4$, is an advantage of Raman over other methods of investigation. Knowing that magnetite is formed over hematite in the corrosion process provides some more insight into understanding the corrosion products of stainless steel.

With the exception of the D9 sample, nothing other than Fe$_3$O$_4$ was detected on LBE corroded stainless steels. XPS and EDAX studies have shown evidence of chromium within the corrosion layer. Chromium oxide is another expected corrosion product. Without seeing a chromium oxide layer on top of an uncorroded stainless steel, a conclusion cannot be made as to whether or not a chromium oxide layer exists on any corroded stainless steel. The system may not be capable of detecting small traces of oxides.

**Future Work**

The library of oxide standards needs to be expanded. Many other possible oxides could form within corrosion layers. Silicon oxide needs to be studied. The iron-silicon steels could very likely form SiO$_2$ within the corrosion layer. A few attempts were made to find the Raman spectrum of SiO$_2$ by studying blank microscope slides and a fractured piece of quartz. No signal was identifiable from the noise.

Spinel oxides such as iron chromite, FeCr$_2$O$_4$, also need to be acquired and studied. The D9 3000 hour sample shows an interesting second peak that could be evidence for FeCr$_2$O$_4$. Cunha et al. [21] studied 316L corrosion from a pressurized water reactor environment. They reported a corrosion layer containing NiCr$_2$O$_4$.

The data collected on the corroded samples was from the surface of the samples. Sputter depth profiling similar to XPS studies can be performed using Raman as the analysis technique. Hamilton et al. [22] performed depth profiling of oxidized iron
foil and oxidized stainless steel. Similar experiments performed on the LBE corroded samples will provide valuable information about the corrosion layers. In addition, with only a three micron spot size, cross sections of these corroded stainless steel samples can be studied.

Constructing this system has been a very challenging and rewarding process. Improvements will be made to the system. For example, the beamsplitter used in the microscope has a thickness of approximately two millimeters. Reflection of the laser occurs from the front and back surfaces creating unwanted interference patterns in the focused spot. Applying an anti-reflection coating to one surface of the beamsplitter will improve the focused spot size of the laser.

The future for this experimental apparatus is very promising, not only for research related to this work, but other research desiring Raman data. The system is capable of taking data on nearly any sample. The samples studied in this work covered a large range. The gas phase samples were very small, approximately two to four millimeter square samples having a one millimeter thickness. Large samples such as the Fe$_2$O$_3$ and Fe$_3$O$_4$ pellets, which were contained within the pressing chamber, had a height of approximately two centimeters. The 50X objective has enough working distance to examine the sample region in a Merril Basset diamond anvil cell.
REFERENCES


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