

Investigation of Corrosion of Steel by Lead Bismuth Eutectic

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Abstract

A new research program has begun at UNLV in accelerator transmutation of waste. Lead Bismuth Eutectic (LBE) has been proposed for use in programs for accelerator transmutation of waste. The LBE acts both as a coolant and as a sputtering target. We have recently initiated a program to investigate the corrosion of steels by LBE. Corrosion products and chemical reactions will be identified using UNLV's facilities for SEM, XPS and XRD. The most recent experimental results will be reported.

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 coolant (removing heat from the nuclear waste) and as a spallation target (generating a neutron flux from the incident proton beam).

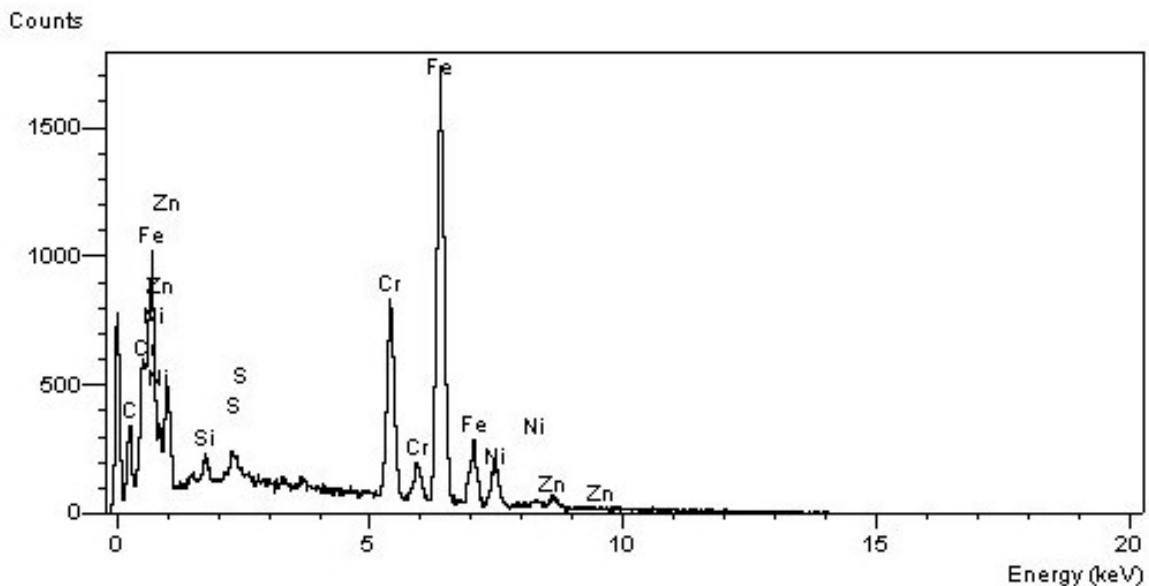
The LBE circulates within stainless steel piping and containers. An absolutely critical question is whether LBE can be engineered to be compatible with the stainless steel walls that contain it with sufficient lifetime. The deleterious process is the corrosion of stainless steel that has been in intimate contact with LBE. 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.

The Russians have 40 years of experience with LBE coolant loops in their Alpha-class nuclear submarines, and they have 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 are building and will operate a medium-scale LBE materials test loop (MTL).

The UNLV program began in June 2001. In our preliminary studies, we have reexamined a number of the same steel samples previously examined by the Russians. At UNLV we have employed a Scanning Electron Microscope (SEM), in which a high voltage focussed electron beam strikes a solid sample, causing fluorescence in the x-ray spectral region. The x-rays are characteristic of the kind of atom. This instrument is capable of measuring elements from boron ($Z=5$) through uranium ($Z=92$), mapping the elemental analysis as a function of position. It does not reveal speciation; i.e., it does not provide information about the chemical species. This shows the presence of oxygen (from oxides) and their spatial distribution, with a spatial resolution of about a micron. A variety of steel samples have been examined both before and after exposure to LBE for varying lengths of time and varying temperatures.

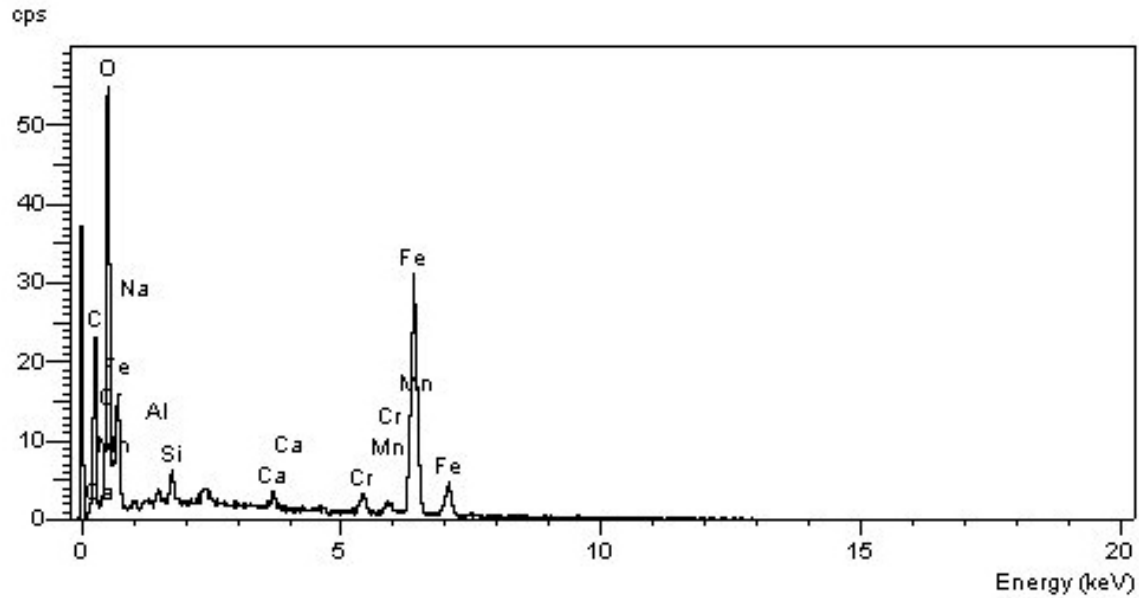
The surface analysis of the steel samples by the SEM yielded beautiful data on the surface morphology and elemental composition of the steel samples. Approximately 40 samples have been examined so far. The X-ray fluorescence spectrum includes characteristic peaks from such elements as Fe, Cr, Ni and Si. Oxygen peaks are very strong in steel samples that have been exposed to LBE, and are absent in unexposed samples. Our analysis has just begun. When our analysis is complete, it will allow identification of the elements present in the samples, and understand of the chemical reactions that give rise to such species.

A sample of 316 steel is composed mostly of iron, nickel, and chromium, with smaller amounts of other alloying elements: Si, Mn, and C. Our SEM data show semi-quantitatively the elemental composition of the surface and near-surface region. (SEM probes a deeper layer than XPS). The following SEM x-ray spectrum of a sample of 316 stainless steel tube before exposure to LBE, shows high abundances of chromium and iron, with a smaller amounts of nickel and a few other trace elements. The zinc peaks were surprising, but are



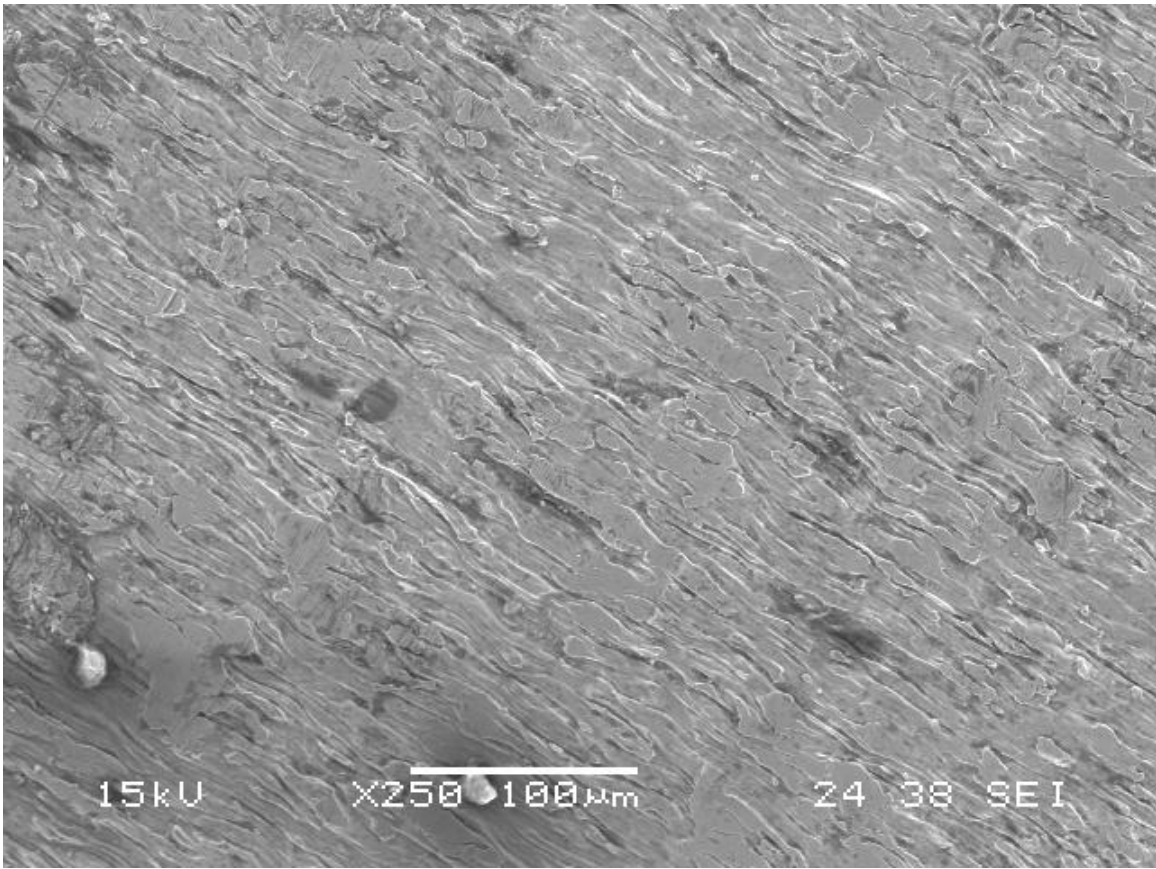
clearly present, and confirmed in the XPS data, discussed below. No oxygen peaks were observed in these SEM data, indicating that oxidation in the surface and sub-surface region is minimal. However, oxygen did appear in the XPS data, discussed below.

This next spectrum was 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.



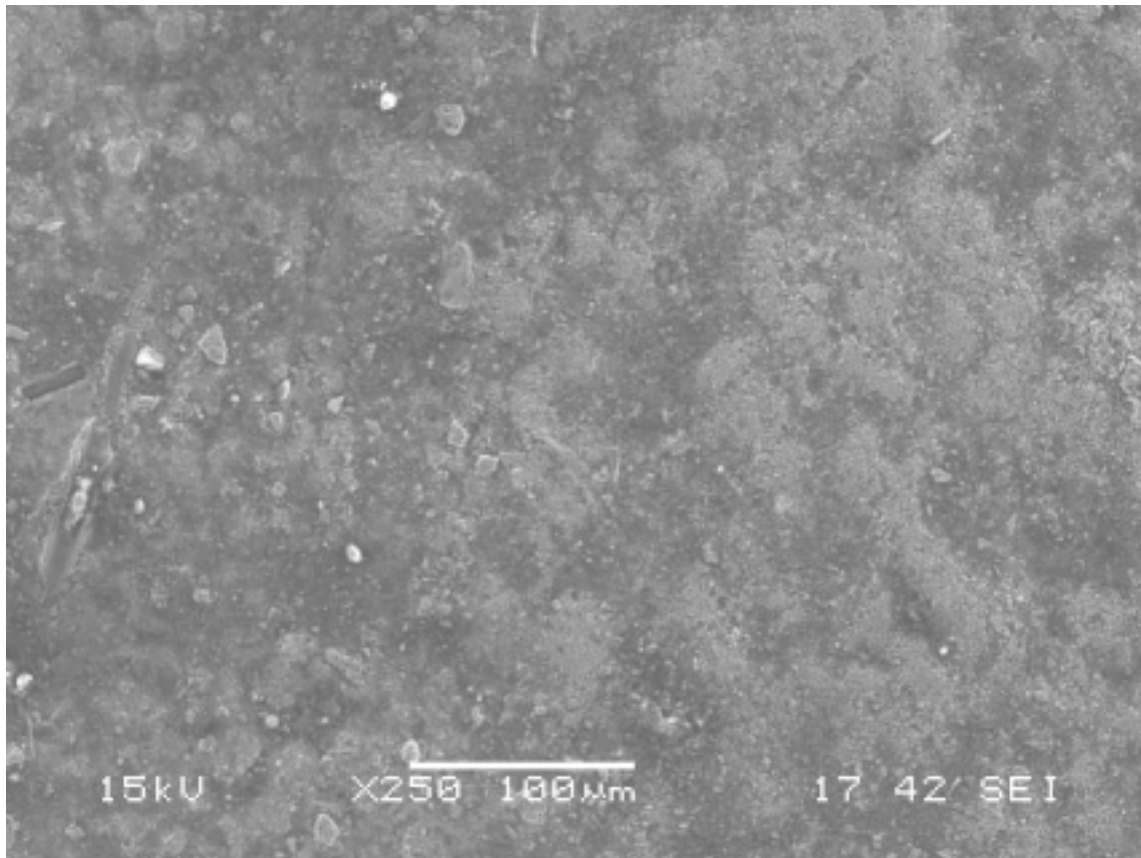
For the exposed sample, the spectrum shows high abundances of iron and oxygen, with very little chromium. This suppression of chromium in the exposed sample is confirmed in the XPS data, discussed below.

Also quite useful from the SEM data were the images of the surfaces. The first image is of the unexposed 316 steel.



SEM analysis of the surface of the unexposed 316 sample reveals the fresh steel surface before exposure to LBE.

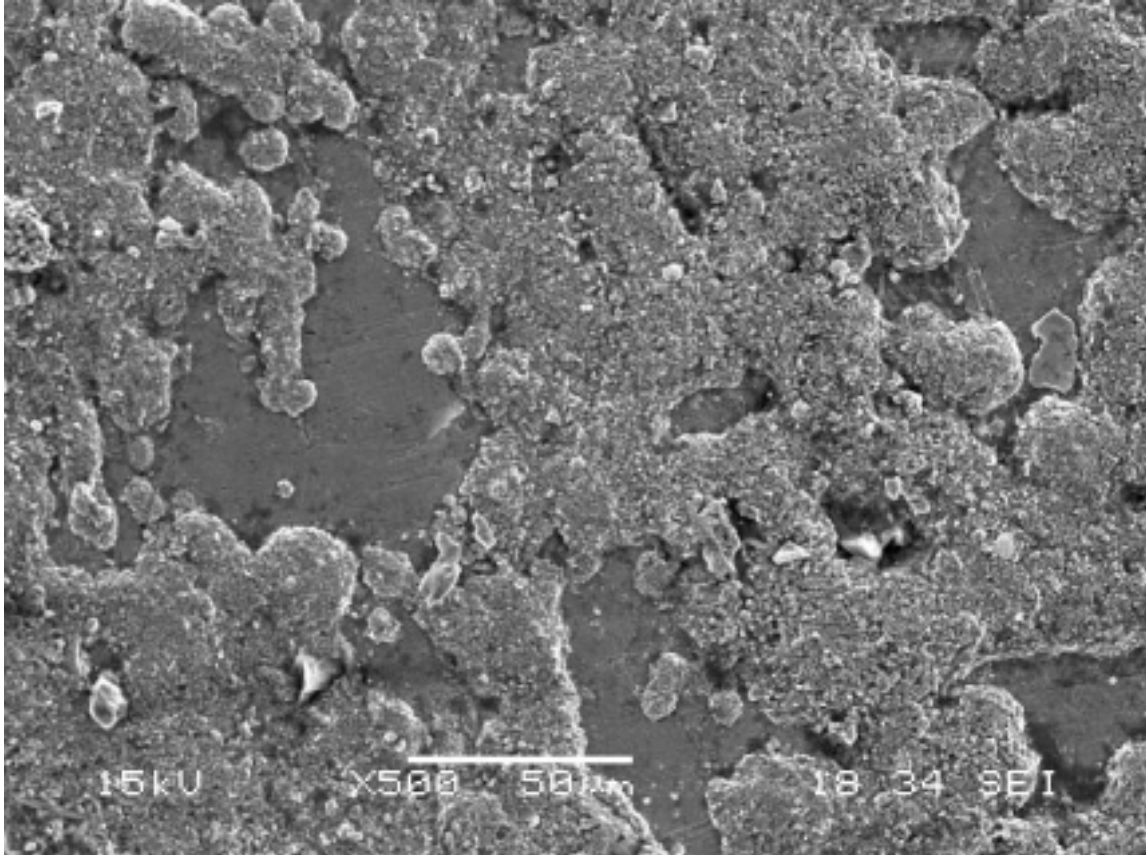
The next image is of the corroded 316 steel.



The surface of the exposed, corroded sample is drastically different when viewed at the same magnification.

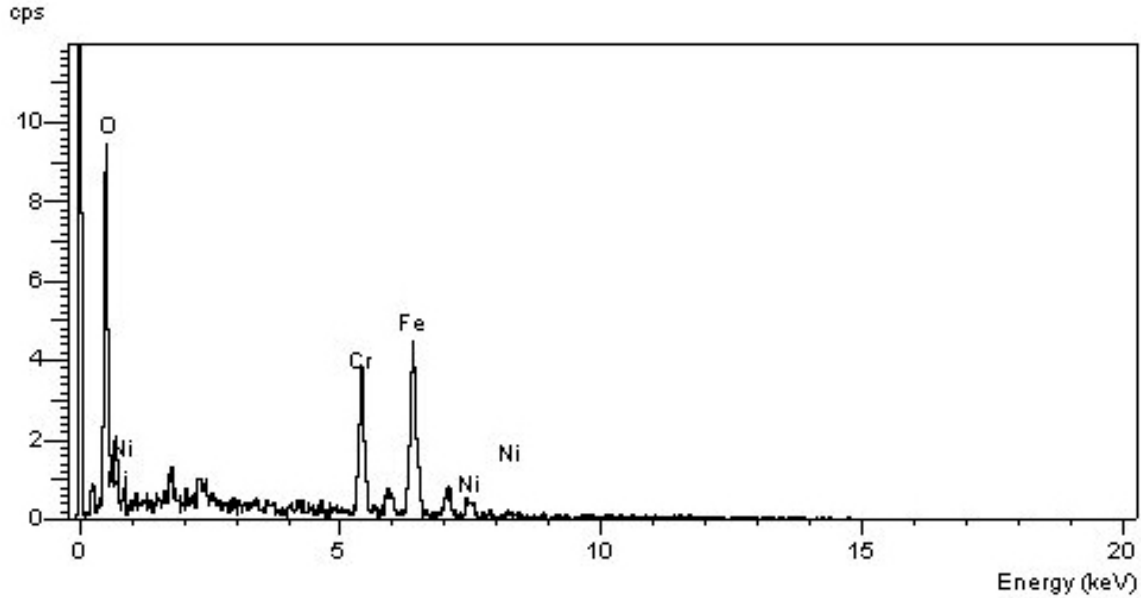
The surface images and the x-ray spectral data show that the surface of the corroded sample is covered by oxygen-containing compounds, presumably mostly iron oxide. This is also indicated by the XPS data, discussed below.

Samples exposed for shorter times and/or cooler temperature (450C) show a morphology consisting of some areas covered by oxides, and other areas uncovered. This is visible in the SEM image below.

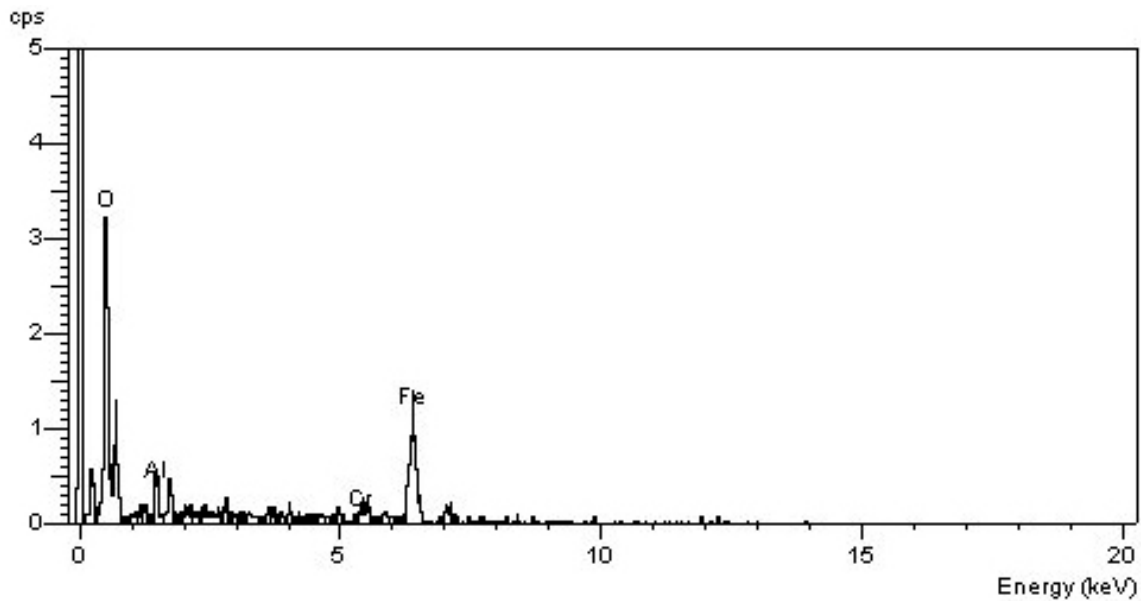


The image above is another 316 steel sample exposed to LBE for 2000 hours at 450 C. X-ray analysis was performed on different, highly localized areas. A quick glance shows that some areas are covered with corrosion, presumably iron oxide.

X-ray spectra taken on the uncovered areas reveal significant differences from those of the covered areas. The x-ray spectrum of a uncovered area is shown below.



The level of Cr in this spectrum is much higher than in the spectrum of the covered area, shown below.



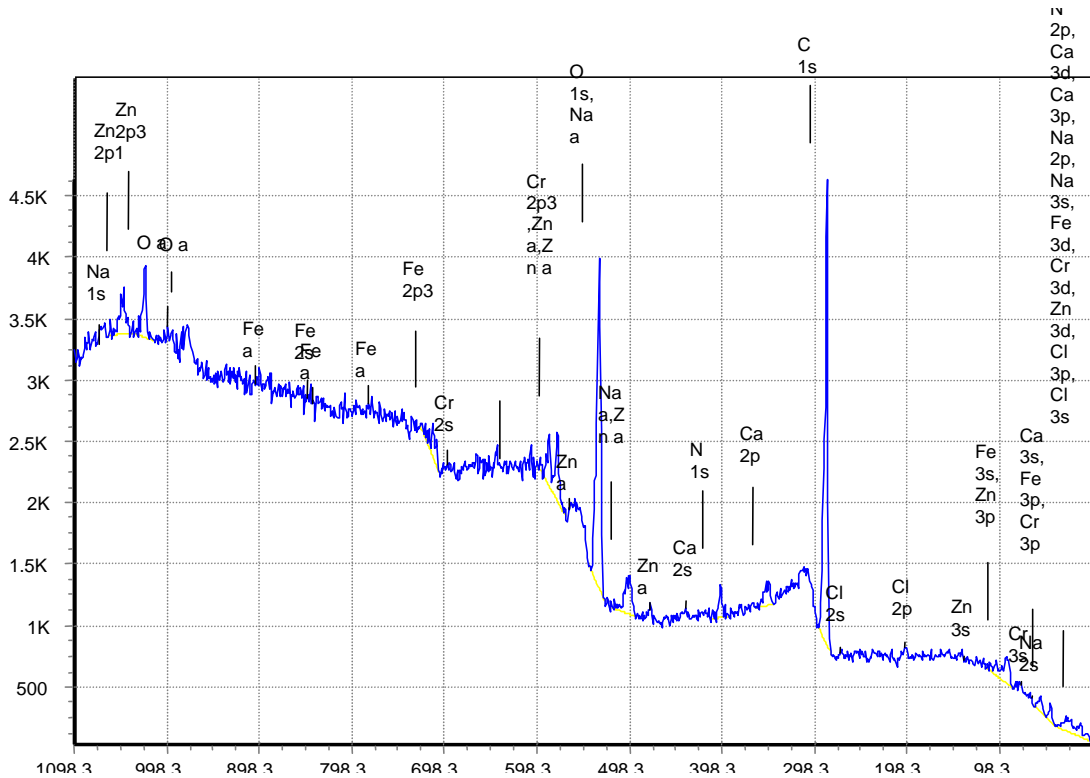
While chromium is present in the uncovered (but not covered) areas, oxygen is present in the spectra of both areas. For the covered area, the Cr is covered by iron oxides. This is consistent with the data on the completely covered 316 steel.

In short, chromium oxides are present in the uncovered (but not covered) areas, while iron oxides are present in both covered and uncovered areas. In the future XPS studies will be used to investigate the detailed chemical states of the surface species.

XPS spectrometry has a number of capabilities in regards to studies of corrosion. XPS allows the determination of the atomic composition and oxidation state of the top few nanometers of a sample, where the corrosion is initiated and takes place. Further, the sample can be insulating, as corrosion products have a tendency to be. Lastly, the level of modification of the sample surface during analysis is lower in XPS than in some competing techniques.

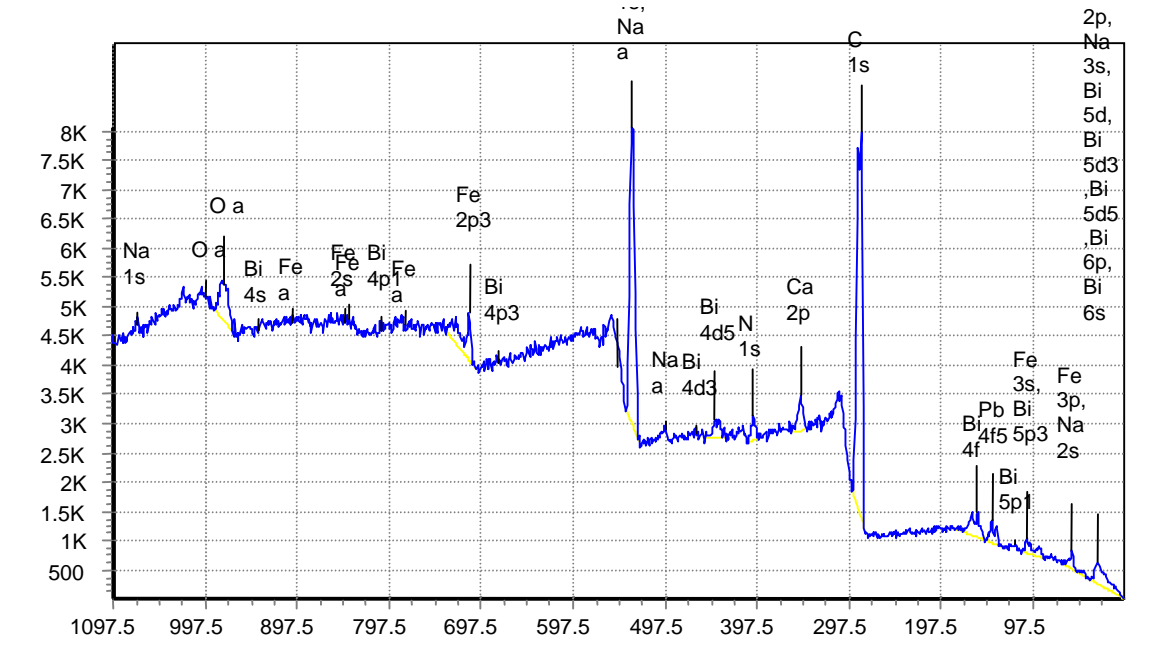
We have done some preliminary studies of 316 stainless steel both before and after exposure to Lead Bismuth Eutectic (LBE).

Survey scan of uncorroded 316 stainless:



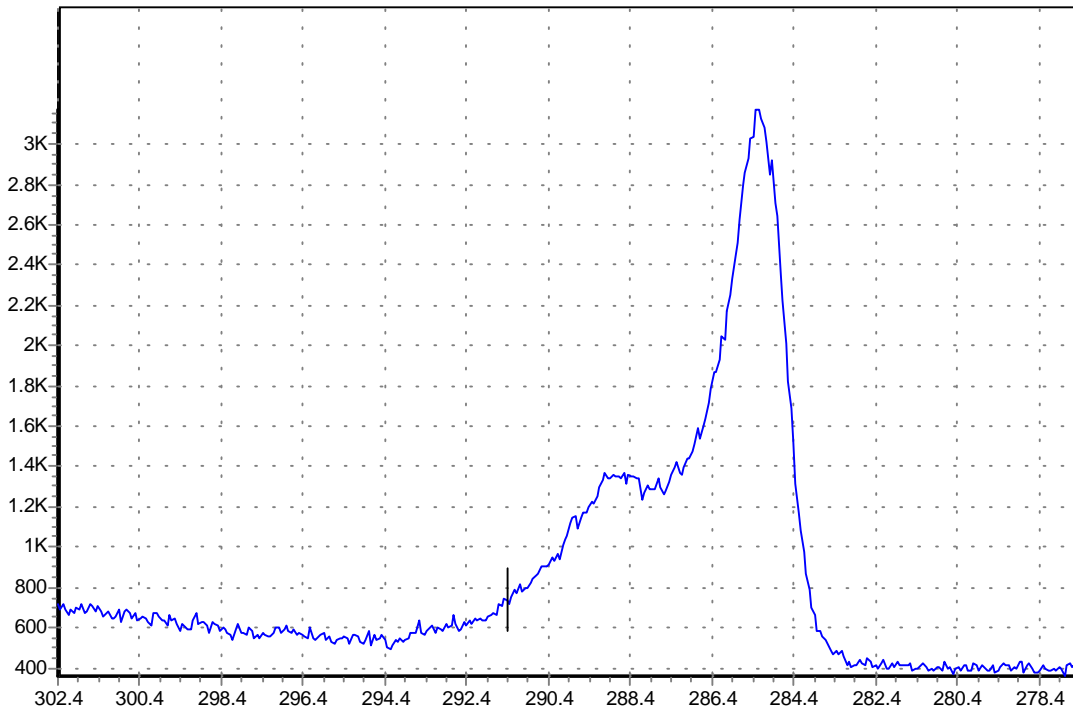
We find the expected surface dominance of Cr over Fe and Ni, as one expects for a passivated surface. No Pb or Bi is seen. We were surprised by the levels of Zn.

Survey scan of corroded 316 stainless:



In this spectrum we see the suppression of Cr with respect to Fe as seen in other corroding stainless steel systems. We also see some residual Pb and Bi. Further information can be obtained by looking at peak profiles.

The carbon 1s peak of the uncorroded sample shows much less highly oxidized carbon species on the surface:



as verses the corroded sample:

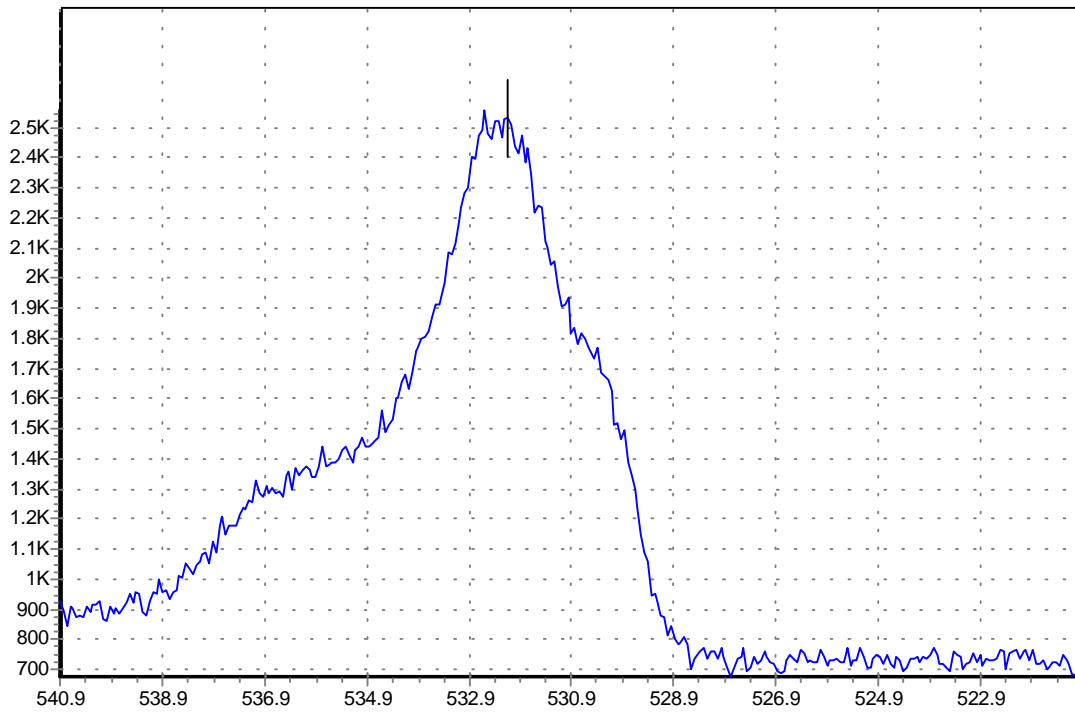


This carbonaceous species may be either generated during the LBE exposure or during subsequent handling. Sputter depth profiling will be done to see if the carbon composition

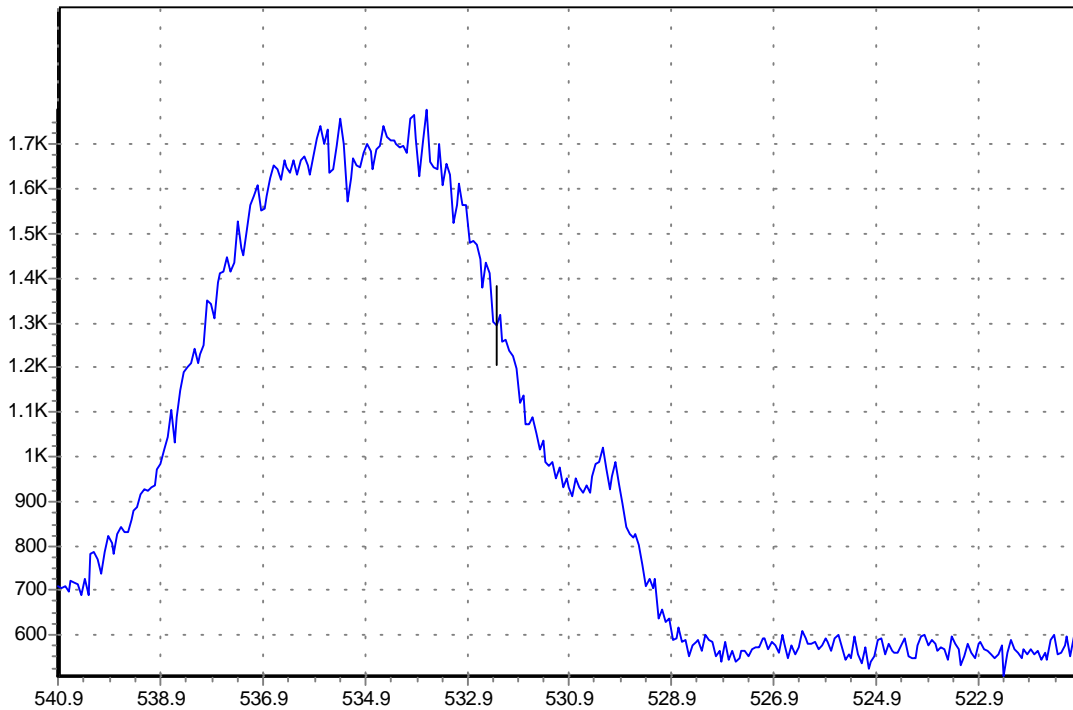
appear to be fairly constant through the corroded layer.

The oxygen (and other edges) show corresponding shifts to higher binding energy:

O1s uncorroded:



O 1s corroded:



Studies of the oxidation states of the major species of the steel candidate both before and after LBE exposure are expected to yield significant insight into the mechanisms and possible remedies for corrosion during exposure.

Analysis of the metal species is continuing. Our research program will also entail future analysis of samples using the X-ray Photoelectron Spectrometer (XPS) and the X-ray Diffraction apparatus (XRD) at UNLV. Our long-term goal is to fill in some very important gaps in our understanding of the chemistry of corrosion in the LBE/steel system. For example: what are the chemical species created during the corrosion process? What are the chemical reactions occurring? What is the morphology of the interface at both the macroscopic and microscopic scale? How do these reactions depend on temperature and the presence of trace elements? What is the heterogeneity of the corrosion process in a LBE system? What are the chemical species involved in the reaction as corrosion products? What about oxides of contaminant metal ions that may leach from the stainless steel during the course of the reaction of the LBE at the interface? Which metal ions are involved, and which chemical form do they exhibit? What is the oxidation state of each of the elements? What is the electronic structure of each of the elemental ions? What is the magnetic configuration of each of the appropriate ions? Is there any evidence for passivation at the interface of the reaction of the LBE with the steel substrate? Answering these questions is necessary in order to understand the corrosion process, and hence to be able eventually to engineer the system in order to control or minimize the various corrosion processes in the LBE/steel system.

Acknowledgment

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