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Fundamental and Applied Experimental Investigations of Corrosion of Steel by LBE under Controlled Conditions: Kinetics, Chemistry Morphology, and Surface Preparation

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Task 18

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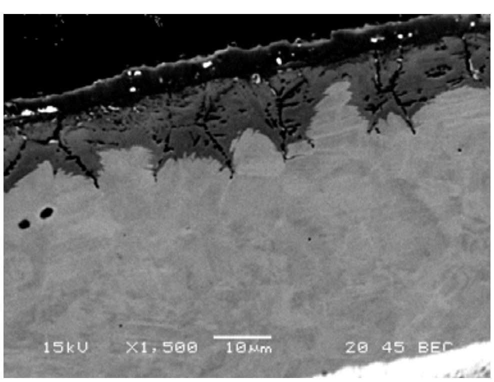
BACKGROUND

Advanced nuclear processes and facilities (e.g., transmutation of nuclear waste, fast reactors, and spallation neutron sources) impose special demands on materials, which must withstand high temperatures, high radiation fields, and chemical corrosion. Proposed schemes for transmuting nuclear waste require a non-moderating coolant such as lead-bismuth eutectic (LBE) or liquid sodium. While LBE corrodes most steels, small amounts of oxygen in the LBE greatly reduces the corrosion rate, and could ideally re-grow a damaged oxide layer in situ. The protective oxide layer would thus be self-healing. However, a fundamental understanding of the role of oxygen and passivating oxide layers is presently incomplete.

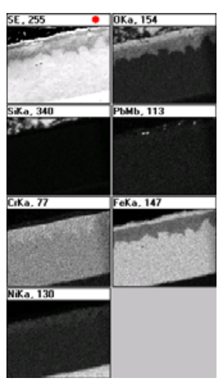
RESEARCH OBJECTIVES AND METHODS

The overall goal is to obtain scientific insight into the fundamental processes involved in the corrosion of steel by LBE. The experimental methods include characterization of steel samples before and after exposure to LBE using different techniques including: Scanning Electron Microscopy (SEM), Energy Dispersive X-ray analysis (EDX), Wavelength Dispersed X-ray (WDX), X-ray Photoelectron Spectrometry (XPS), Sputter Depth Profiling (SDP), X-ray Diffraction (XRD) and laser microRaman spectroscopy. These techniques have been previously used by this research group to probe the effect of surface preparation on corrosion-resistance of samples with the same chemical composition, and to examine the role of silicon in silicon-containing steel.

During the past year, gas-phase experiments were conducted in which steel samples were oxidized in glass capsules at elevated temperatures in a tube furnace. Corroded steel samples were analyzed from a variety of sources, including the Delta loop at LANL and samples corroded at UNLV in the gas phase experiments.

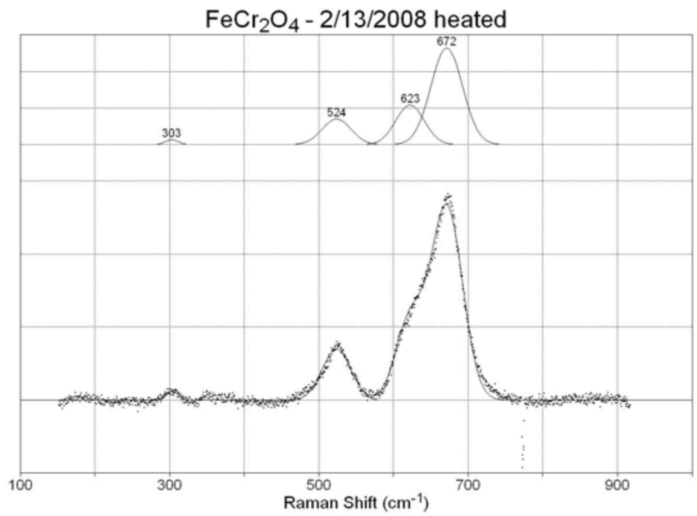


Back Scattered Image



Elemental Map

Transverse section of D9, a 316 class stainless steel. Note the large anisotropy in the growth of the thick inner oxide layer, showing obvious pathways for migration of oxidation reactants affecting the growth rate and morphology of the oxide layer.



Raman Spectrum of $FeCr_2O_4$

RESEARCH ACCOMPLISHMENTS

<u>Gas-phase experimental results</u>

Measurements have been made of the gas-phase oxidation of steel, using the tube furnace in the High Temperature Materials Exposure Facility in the UNLV Chemistry building. The goal is to clarify the differences between gas phase corrosion and corrosion by LBE. Oxidation of metal surfaces is carried out by the residual gas, which was characterized using a residual gas analyzer. The residual gas was determined to consists of much water vapor but little oxygen or hydrogen. The role of water as an oxygen carrier may be an underestimated factor in corrosion. These experiments are part of the doctoral dissertation of Thao Ho.

In other experiments, investigations were performed to determine whether alloys undergoing sputtering are chemically altered by the sputtering process. Such an artifact would reveal itself as a change from stoichiometric to non-stoichiometric composition during the sputtering process. Chromia (Cr_2O_3) was found to be affected minimally if at all, but hematite (Fe_3O_4) was significantly affected.

<u>Facility development</u>

Progress continued on the construction of the apparatus for the Liquid Metal Corrosion Experiment, which will be able to expose steel samples to either LBE or sodium.

ACADEMIC YEAR HIGHLIGHTS

- Dan Koury, doctoral dissertation, "Characterization of the Mechanism of Duplex Oxide Growth on Austenitic Stainless Steels 316 and D9 in Oxygen-Controlled Lead-Bismuth Eutectic (LBE)," August 2008 (expected).
- Brian Hosterman, doctoral dissertation, "Studies of corrosion of steel by laser microRaman spectroscopy," August 2009 (expected).
- Thao Ho, doctoral dissertation, "XPS studies of Si in Fe/Si alloy steel in corrosion of steel by LBE," August 2009 (expected).
- A.L. Johnson, D. Koury, J. Welch, T. Ho, S. Sidle, C. Harland, B. Hosterman, U. Younas, L. Ma, and J.W. Farley. "Spectroscopic and microscopic investigation of the corrosion of D-9 stainless steel by lead-bismuth eutectic (LBE) at elevated temperatures. Initiation of thick oxide formation," *Journal of Nuclear Materials* (in press, 2008).
- A. Johnson, "Heavy Liquid Metal efforts at UNLV, USA: LBE Corrosion of D9 and other 316-group Steels," presented at the IV Workshop on Materials for Heavy Liquid Metal Cooled Reactors and Related Technologies, Rome, Italy, May 21-23, 2007.

The Oxygen Control System (OCS) from Germany's Karlsruhe Lead Laboratory was used for initial experiments, and very low oxygen concentrations were recorded.

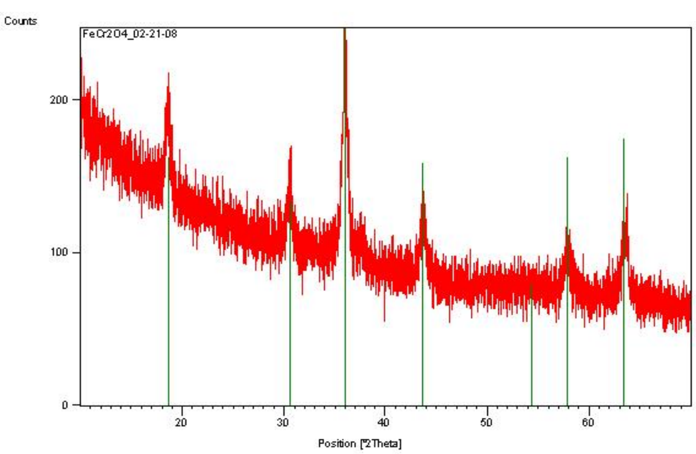
Characterization of samples

Oxide layers were studied using high-resolution XPS with sputter depth profiling, revealing the extent of oxidation as a function of position within the oxide layer.

A new capability in microRaman spectroscopy was built by physics graduate student Brian Hosterman in order to examine the Raman spectra of compounds relevant to corrosion. Raman studies can distinguish between different chemical species by their characteristic vibrational spectra. For example, Fe_2O_3 can be distinguished from Fe_3O_4 by its Raman spectrum. The Raman microscope gives a lateral spatial resolution of the order of a few microns.

Synthesis of standards

Chemical characterization of the species involved in corrosion can be revealed by microRaman studies, in which the spectrum of an unknown compound is matched to a library of spectra of standards. Standards have been purchased when possible, but some standards have been synthesized in the laboratory. Spinels (compounds with formula XY_2O_4) are of special interest because they are believed to form part of the metal oxides under investigation. Spectra of standards have been measured, and are in good agreement with literature values. The crystal structure of the oxide layers can be determined by X-ray diffraction. The XRD spectrum of $FeCr_2O_4$ is illustrated (below, right). The lattice spacings derived from analysis of this spectrum agree with literature values.



XRD Spectrum of $FeCr_2O_4$

Outcomes

A model of the LBE corrosion process is emerging, incorporating theoretical and experimental results from UNLV laboratory results and elsewhere. Several of the presentations at the May 2007 Heavy Liquid Metals Workshop in Rome, Italy were based on the new insights. UNLV has contributed the observation that localized failure in the initial oxide layer leads to formation of duplex/complex oxide structures. Scientific collaboration with Los Alamos National Laboratory has continued. Steel samples exposed to LBE at LANL have been analyzed by the UNLV group.

FUTURE WORK

Future work includes expansion of this program to studies covering the effect of liquid sodium on structural materials.

Faculty
Allen Johnson, Principal Investigator, Assistant Professor, Department of Chemistry
John Farley, Professor, Department of Physics

Students
Thao Trung Ho, Graduate Student, Department of Chemistry
Dan Koury and Brian Hosterman, Graduate Students, Department of Physics and Astronomy
Jenny Welch and Tim Lane, Undergraduate Students, Department of Physics and Astronomy
Noah Kapley (Undergraduate; Western Kentucky University) and Zara Fewsmith (Local high school volunteer), Summer 2007 Students

Collaborators
Ning Li, LBE Project Leader, Los Alamos National Laboratory
Peter Hosemann, Visiting Scientist, Los Alamos National Laboratory