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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

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

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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). 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, the fundamental understanding of the role of oxygen and passivating oxide layers is presently incomplete.

RESEARCH OBJECTIVES AND METHODS

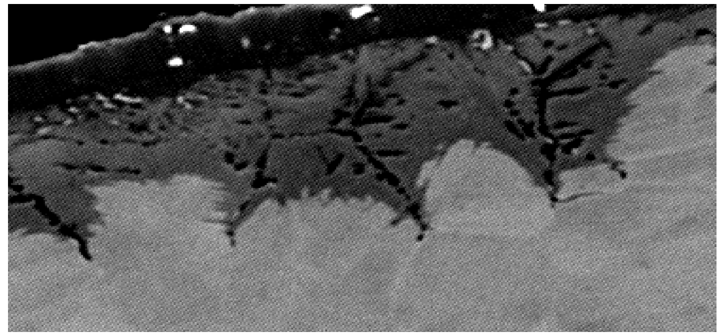
Steel samples have been characterized before and after exposure to LBE using different types of surface microscopy, including Scanning Electron Microscopy (SEM), Energy Dispersive X-ray analysis (EDX), Wavelength Dispersed X-ray, X-ray Photoelectron Spectrometry (XPS), and Sputter Depth Profiling. In past work, steel samples exposed to LBE at the Institute for Physics and Power Engineering in Obninsk, Russia, were examined using SEM and EDX. Samples with the same chemical composition but different surface treatments were compared, and cold-rolled samples were more corrosion resistant than annealed samples. Increased corrosion resistance was associated with changes in oxide layer thickness, morphology, and composition. These past results were published in the Journal of Nuclear Materials.

During the present reporting period, 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.

RESEARCH ACCOMPLISHMENTS

An analysis of the role of silicon in conferring corrosion resistance was published during the present reporting period. Silicon and its various oxides were found in the oxides of silicon-containing steels after exposure to LBE, with SiO_2 found near the oxide/metal interface, consistent with the formation of a layer between the metal and the oxide. Results were published in the Journal of Nuclear Materials.

A model was developed and presented at the AFCI materials working group March 2006 in Santa Fe. This model and supporting experimental results indicate that the conversion of the oxide layer on the austenitic steels from an initial compact thin layer to a porous thick multilayer occurs at localized failures of the thin oxide, with the formation of diffusion channels in the thick oxide. At the May 2007 Heavy Liquid Metals (HLM) Workshop in Rome, Italy, other researchers supported this model. Currently, a paper is being prepared on the application of the defect generated diffusion channel model to austenitic and ferritic/martensitic steels for nuclear applications.



Atom probe image of etched D-9. Note the high etch rate along grain boundaries and elsewhere. Also note the evidence of oxidation along the crystal planes in the metal.

Gas phase experimental results

The gas phase oxidation of steels has been examined at oxygen concentrations approximating those in LBE. This study determines the unique aspects of oxidation in LBE. For example, in the gas phase experiments on these steels, tin was sometimes observed at the surface. Tin has been implicated in temper embrittlement. In LBE, tin does not accumulate due to the solubility of tin in LBE. Conversely, nickel is depleted from the oxide layer that forms on the austenitic steels. In LBE, this nickel can dissolve. In the gas phase, Ni depletion was also observed, indicating that nickel must dissolve into the bulk metal in this case.

After 100 h of oxidation up to 10 microns of oxide is formed, which indicates a flux of oxygen onto the metal surface that is much higher than the oxygen control mechanism (CuO/Cu couple) would allow, suggesting that some other oxygen containing species is active. Of course water is a likely suspect, and experiments have been initiated to determine the role of water as an oxygen containing/transport agent in LBE. In summary, gas phase experiments have directed the project towards studies expected to give insight into the mechanisms of LBE corrosion of steel.

Facility development

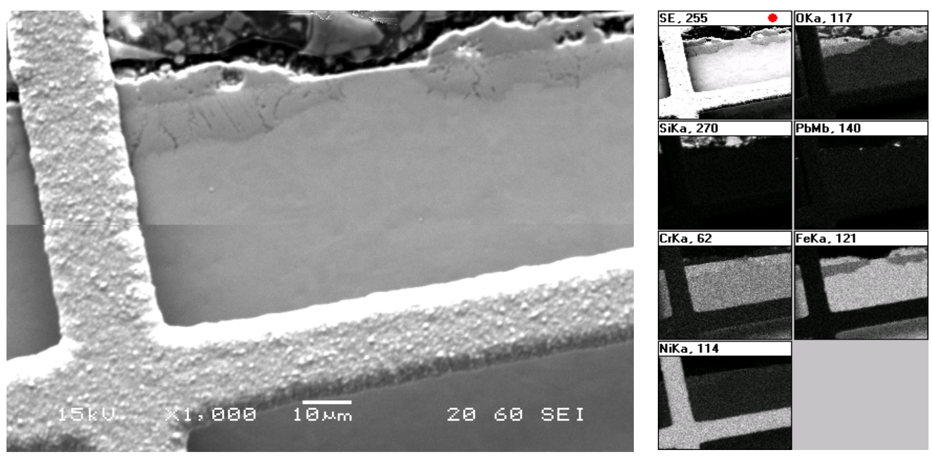
After the renovation of room 112C in the Chemistry building (CHE), the first experimental data came from an experiment in gas phase corrosion using a tube furnace. Steel samples were corroded by contact with controlled amounts of oxygen at elevated temperatures. The gas phase facility has produced valuable data for comparison with corrosion of steel by liquid metal. A clean bench has been installed in CHE 112C for handling liquid lead safely. A small liquid metal experiment is being assembled, and the lower section is now finished.

Analytical Techniques

In the last year, a laser Raman microscope was successfully developed, capable of performing Raman spectroscopy of sample surfaces with lateral resolution of a few microns, allowing detection of chemical species on the surface, whereas other analytical techniques (e.g., XPS or EDX) only provide elemental/oxidation state information. The laser Raman microscope can easily distinguish between the two oxides of iron, hematite (Fe_2O_3) and magnetite (Fe_3O_4), and was used in Hosterman's 2006 masters degree.

FUTURE WORK

Plans for Summer 2007 and later consist of continuation of work specified in previous work packages. The small liquid metal exposure facility will be completed, and physical, chemical, and corrosion LBE characterization will begin. Gas phase experiments will be continued with the use of the Oxygen Control System. These experiments are planned for completion in Fall 2007. They test the specifics of LBE corrosion verses standard gas corrosion of steel, and allow a clear indication of the differences induced by the LBE. Isotope labeling experiments turned out to be more difficult than planned. ^{18}O labeling studies following the experiments of Martinelli et al. (recently mentioned at the HLM conference in Rome) will be done on D9 and 316, and training on the required TOF-SIMS technique at the National ECSA and Surface Analysis Center for Biomedical Problems workshop will happen in August 2007. A joint paper has been planned using task work as well as investigations by the LANL and French groups to expand the model to include a broad array of structure steel corrosion phenomena in LBE.



D-9 shows failure of the thin oxide and formation of duplex oxide in localized patches. The iron moves outside the original metal surface to form Fe_3O_4 (as shown by Raman Spectroscopy) and the chromium stays in place to form an iron/ chromium oxide which undercuts the thin oxide.

ACADEMIC YEAR HIGHLIGHTS

- Brian Hosterman, M.S. thesis, UNLV Physics Department, "Micro-Raman Spectroscopic Studies of Corrosion of Steel by Lead-Bismuth Eutectic," December 2006.
- A. L. Johnson, J. W. Farley, D. Koury, B. Hosterman, J. Welch, T. Ho, L. Ma, and U. Younas; "Protective Oxide Layers on Austenitic Stainless Steel (316L and D9) in Molten Lead Service: Formation and Reformation, Structure and Dynamics," poster, Annual Meeting of the American Vacuum Society, San Francisco, CA, November 12-17, 2006.
- A.L. Johnson, J.W. Farley, L. Ma, O. Tschauner, D. Koury, T. Ho, B. Hosterman, and J. Welch, "HLM efforts at UNLV, USA: LBE Corrosion of D9 and Other 316-Group Steels," oral presentation, IV Workshop on Materials for HLM Cooled Reactors and Related Technologies, Rome, Italy, May 21-23, 2007.
- 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 duplex oxide formation," submitted, *Journal of Nuclear Materials*.
- T.D. Lane, C. Carr, J.W. Farley, A.L. Johnson, J.S. Welch, T. Ho, and D. Koury, "Formation of Oxide Layers in an Oxygen Controlled System," poster, Summer Undergraduate Research Experience, UNLV, Las Vegas, NV, August 11, 2006.
- P. Shafe, J. Farley, A. Johnson, D. Koury, and J. Welch, "Lead Bismuth Eutectic Corrosion Chamber Prototype," poster, Summer Undergraduate Research Experience, UNLV, Las Vegas, NV, August 11, 2006.

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