PROJECT TITLE: In-Situ X-ray Spectroscopic Studies of the Fundamental Chemistry of Pb and Pb-Bi Corrosion Processes at High Temperatures: Development and Assessment of Composite Corrosion Resistant Materials.

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RECIPIENT: Illinois Institute of Technology
3300 South Federal Street
Chicago, Illinois 60616

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CONTACT: Carlo Segre
Professor of Physics &
Associate Dean for Graduate Admissions, Graduate College
Illinois Institute of Technology

Voice: 312.567.3498 Fax: 312.567.3494

Carlo.Segre@iit.edu <http://www.iit.edu/~segre>

Research Progress

Shanshan Liu completed her dissertation in December 2009 and the final 2009-3 MRCAT run saw the successful first run of experiments supported by the NRR-CAT collaboration and the ATR project. These data are currently being analyzed by students at IIT. In addition, the 2009-3 run saw a general user experiment for Small Angle X-ray Scattering accepted for beam time at Sector 12-BM. We participated in this experiment which was headed by Prof. G.R. Odette of UCSB. These data are being processed now.

Project Accomplishments

Over the course of this project, we have a number of accomplishments. The following list is presented as a summary statement for the project. Specific details from previous Quarterly Reports follow.

1. We established that it is possible to use EXAFS to study the interface layer between a material and the liquid Pb overlayer. We have discovered that molybdenum grows a self-limiting oxide layer which does not spall even at the highest temperatures studied. There have been 2 publications resulting from these studies.
2. We have fabricated a high temperature environmental chamber capable of extending the Pb overlayer studies by varying the incident x-ray beam angle to perform depth profiling of the Pb layer. This chamber will continue to be available to nuclear materials program researchers who wish to use the MRCAT beam line.

3. We have developed a collaboration with researchers at the Paul Scherrer Institute to study corrosion layers on zircalloy. One publication has resulted from this collaboration and another is in progress.
4. We have developed a collaboration with Prof. G.R. Odette of UCSB in which we studied the local structure of Ti and Y in nanoclusters found in oxygen dispersion strengthened steels. There are two publications in progress from this collaboration and we have extended the project to anomalous small angle x-ray scattering as well as EXAFS.
5. We have promoted the use of EXAFS for the study of nuclear materials to the community over the past 4 years and we have begun to see an increase in demand for EXAFS from the community at the MRCAT beam line.
6. This grant was instrumental in nucleating interest in establishing a new Collaborative Access Team at the Advanced Photon Source, the Nuclear and Radiological Research CAT (NRR-CAT). The co-PI (Jeff Terry) is the lead investigator on this project and it has been approved by the APS Scientific Advisory Committee for further planning. The status of the NRR-CAT project is being discussed in a series of workshops in 2009-2010 and has received exploratory funding from INL. This funding is being used to provide beam time and support at MRCAT for NRR-CAT related experiments. This will continue through 2010 as the development of a full NRR-CAT proposal develops.

We believe that this has been a very successful project whose impact will continue to be felt for a number of years. Not only will there be additional publications coming from the work supported directly by this grant but the establishment of NRR-CAT will have a significant impact on the field of nuclear materials research for decades to come.

2006 Highlights

Over the summer 2005 run at the Advanced Photon source, we used 6 days of beam time to study *ex-situ* samples of 316 stainless steel, molybdenum and spinel which had been exposed to lead at 1000C for 5 hours and 50 hours under argon atmosphere. Because of the *ex-situ* nature of the experiments, the lead was found to be in an oxidized state on the samples when measured.

For the 5 hour exposures, both the molybdenum and stainless steel showed significant attack by the Pb. The spinel seemed relatively unaffected. For the 50 hour exposures, the stainless and molybdenum showed significant flaking of the surface and the spinel also appeared to have some surface contamination.

The EXAFS measurements were conducted on all the 5 hour samples and the stainless steel at 50 hours where we measured both the material which flaked off the surface and the residual materials on the surface of the sample. The other 50 hour samples were measured in November, during the 2005-3 run.

During the same period, we brought our vacuum deposition into working order and made initial Pb film depositions on a Mo substrate. Our initial sample was prepared and measured during the 2005-3 run in order to determine the conditions under which we could probe the film and substrate separately by changing the incident angle of the beam.

Figure 1

Figure 1 shows data on 316 stainless steel exposed to Pb at 1000C (black) flaked off corrosion layer (red), iron oxide (green) and Fe metal foil (blue) for comparison. Clearly there is a significant amount of iron in the flaked off material, indicating that at 50 hours and 1000C, we would be able to observe the first stages of corrosion in the *in-situ* experiments. Note that the edge structure of the sample and the flakes shows an intermediate character between Fe metal

and Fe oxide. The similarity between these two spectra is indicative of the fact that we are likely probing only the reacted surface of the stainless steel at the 20 degree incident angle.

Figure 2

Figure 2 shows incident intensity-normalized data taken on the Mo coated with a thin, evaporated layer of Pb at 45 and 15 degree incident angles. The lower intensity at the smaller angle is indicative of the shallower probe depth. At the lower energy of the Fe edge, this effect is more pronounced.

Figures 3a-c show the effects of corrosion on 316L steel, molybdenum and spinel samples exposed to Pb vapor at 1000°C for 50 hours. The 316L steel is most affected by the Pb vapor, showing severe flaking from the surface and a distinct layer of Pb. The molybdenum, on the other hand, shows no flaking but a change in surface color. Finally, the spinel shows virtually no effect of the Pb vapor.

Figure 3a: 316L Stainless Steel exposed to Pb at 1000°C (50x magnification)

Figure 3b: Molybdenum metal exposed to Pb vapor at 1000°C.

Figure 3c: Surface of spinel, exposed to Pb vapor at 1000°C.

Figure 4: Comparison of Pb fluorescence on three substrates exposed to Pb vapor at 1000°C. Spinel clearly has the least residual Pb on the surface.

The visual inspection is borne out by the measurement of Pb fluorescence intensity as a function of material (Figure 4).

In the 2006-1 run at the Advanced Photon Source, we used 4 days of beamtime for our first *in-situ* high temperature experiments. The purpose of these experiments were to:

1. Test the capabilities of the high temperature furnace insert with Kapton windows (see Figure 5);
2. Perform preliminary experiments of Pb reaction with a metal surface in a Helium atmosphere;
3. Take EXAFS spectra of the same sample processed at a series of high temperatures in inert atmosphere;
4. Measure reactivity of Mo metal with Pb and residual oxygen by EXAFS.

These experiments showed that we would be able to reach *in-situ* processing temperatures up to 900°C without melting the Kapton windows. Data was taken at room temperature after heating to desired maximum temperature. We have begun to analyze these data and have submitted abstracts to two conferences, the 5th International Conference on Synchrotron Radiation in Materials Science (SRMS-5) and the winter 2006 American Nuclear Society meeting in Albuquerque, New Mexico. A poster was presented at the May 2006 Advanced Photon Source User Meeting.

Figure 5: Experimental setup for *in-situ* experiments on the MRCAT beamline. The system was successfully raised to 900°C.

The fluorescence spectra of the Pb-coated Mo sample were measured at various temperatures *in-situ*. By integrating the counts under the Pb K α fluorescence line, we were able to determine that the quantity of Pb remains relatively constant as a function of temperature. This indicates that the Pb has, indeed, reacted with the Mo surface and is not volatile even at the high temperatures measured (Figure 6).

The radial distribution functions obtained from the Mo edge XAFS data after each heating step show that the Mo surface remains largely metallic but with an additional short-range order forming with high temperature processing. Each data set was fit using a pure Mo metal model (in the range $1.6\text{\AA} < R < 5.6\text{\AA}$) and this fit was subtracted to obtain a qualitative measure of the change in the low-R intensity as a function of processing temperature. Figure 7 shows the residual $k^3\chi(R)$ for selected temperatures. The low-R peaks exhibit a systematic growth in intensity to a maximum at 750°C but disappear at higher temperatures. This may indicate that a self-limiting mechanism is present in this system.

We will have another *in-situ* experimental run in August 2006, where we plan to study the effect of a thin Mo coating on the surface of electropolished 316L stainless steel compared to uncoated steel. Future plans include deposition of a spinel coating on 316L in collaboration with Dr. Beihai Ma of Argonne National Laboratory.

Figure 6: Integrated fopresence peak of Pb as a function of temperature. The dashed line is shown as a guide to the eye.

Figure 7: Residual $\kappa^3\chi(R)$ after removing Mo metal fit for samples treated at different temperatures: as deposited (—); 700°C (---); 750°C (- · -); 800°C (· · ·) and 900°C (- - -).

2007 Highlights

In the 2006-3 run at the Advanced Photon Source, we used 4 days of beamtime to measure the 316L stainless steel coated with Mo deposited by a commercial vendor. Figure 8 showing the data at the Fe edge for various temperatures indicates that the Mo film is not protecting the stainless steel and in fact we noted visually that the Mo foil is not adhering to the stainless steel at the high temperatures.

The design of our new high temperature measurement station is completed and parts are being procured. Figure 9 shows a schematic of this system. It includes a liquid nitrogen dewar

for rapid cooling of the sample and a load lock for rapid exchange of samples without breaking containment.

Figure 8

Figure 9

Analysis of the data from the molybdenum-lead high temperature experiments is continuing and is to be presented at the GNEP Materials Workshop in July, 2007. Figure 10 shows the result of the XANES analysis for Mo metal coated by Pb. The dominant oxide species

is MoO_2 at low temperatures. At intermediate temperatures, MoO_3 grows in and then disappears to be replaced by MoO_2 once again.

Figure 10: XANES fractions of MoO_2 and MoO_3 as a function of temperature for Mo metal coated by Pb.

Figure 11 shows the results of the XANES analysis for the 316L stainless steel with a 1 micron Mo sputtered film coated by Pb. The trend for MoO_3 is identical with a growth at intermediate temperatures followed by a conversion to MoO_2 . The difference in this sample is that the Mo film is spalling from the 316L surface and is therefore becoming more oxidized than was the Mo metal surface shown in Figure 1. The decline of the MoO_3 is well-correlated with the melting point of this compound. It is reasonable to suppose that as it melts, MoO_3 becomes more susceptible to dissolution in the Pb overlayer or conversion to MoO_2 . With the new chamber, we expect to be able to obtain more complete results, including being able to determine whether the Mo is being dissolved in the Pb overlayer.

Figure 11: XANES fractions of MoO₂ and MoO₃ as a function of temperature for 316L stainless steel with a sputtered Mo metal film coated by Pb.

2008 Highlights

In our initial XANES studies of ODS steels in collaboration with Dr. G. Robert Odette (U.C. Santa Barbara) we have measured both the Ti and Y edges of steel samples as well as powder sampled used to prepare the ODS steels. Both data sets show interesting correlations between the commercial ODS steels and the as-milled powders. Once the powders are annealed or heated and pressed to form a solid sample, the Ti and Y edges change to an apparently more oxidized state (see Figure 12).

Figure 12: Comparison of the Ti XANES showing similarity between the commercial ODS alloy (MA957), the as-received steel powder, and the as-milled steel/Y₂O₃ powder sample and the difference in the steel powder annealed at 1150C.

As a result of a collaboration with scientists from the Paul Scherrer Institute of Zurich, Switzerland, initial experiments on the corrosion layer of Zircalloy was accepted for publication in *Corrosion Science*. In the 2008-1 run at the Advanced Photon Source, these researchers, collaboration with the PI, were able to perform much more extensive grazing incidence experiments on the Nb in 20 μ m and 3 μ m thick corrosion layers on Zircalloy. The experiment was conducted at the MRCAT beam line (Sector 10-ID) using a custom rotation stage. We successfully obtained data at angles from 0.2° to 45° and were able to see changes in oxidation state of the Nb as a function of depth probed in the surface layer.

The primary graduate student on the project (Shanshan Liu) attended the ANS meeting in June and presented two posters on our work. We submitted one manuscript, on the measurement of Mo-O species as a function of processing temperature in contact with lead metal, to the Journal of Nuclear Materials for this conference.

The environmental chamber has been tested at high temperature and is vacuum tight. The support table base has not yet arrived from the manufacturer but should be available in early November. Final drawings for the upper support system have been completed and have been sent out for bid. Figure 13 shows the chamber and the complete support table. It has been designed so that the entire assembly can be rolled into the experimental hutch on a pallet jack and dropped into place on kinematic mounts. This will permit us to realign the entire system quickly.

Figure 13

The results of our data analysis on the ODS steel nanoclusters indicate that the titanium in the ODS steel samples moves from being a BCC substituent in the as-received powder to the yttrium-containing nanoparticulate inclusions in the annealed samples. This is in contrast to the commercial alloys studied, which show a significant amount of BCC substituent even after consolidation.

2009 Highlights

We have taken some final Ti-edge data for the manuscript on oxygen dispersion strengthened steels. We were missing experimental data on some titanium oxide standards. The measurement of a cubic TiO standard was expected to show features similar to those found in our annealed powders, however, it is more similar to anatase (TiO₂) and thus indicates that the titanium oxide present in the samples is more like a TiO defect structure first identified in 1968. These are the final data required for the manuscript. This work was included in an invited talk at the TMS meeting in February 2009 given by our collaborator, G.R. Odette.

The TiO data obtained in Fall 2008 were confirmed at the MRCAT Bending Magnet line. The XANES of the TiO standard matches extremely well with the XANES of the Ti in the ODS steel samples. The EXAFS of the TiO standard, however is not at all like that of the Ti in the ODS steels and also unlike the expected EXAFS of TiO based on the crystallographic structure. This apparent contradiction was finally resolved by realizing that in the TiO standard, there are a significant number of defects (up to 12%) which are ordered in the TiO monoclinic structure. Because of these defects, the local environment of the Ti is really significantly more disordered than the average crystallographic structure would indicate. There are two Ti-O paths at very similar distances which interfere to give a much smaller peak in the $\chi(R)$. In the ODS, on the other hand, we see well-ordered TiO. This new insight has permitted us to complete the manuscript on the ODS steels. We have requested beam time at Sector 11-BM for high resolution diffraction of the TiO standard.

The co-PI, Jeffrey Terry has been asked by the Advanced Test Reactor and the Nuclear Engineering group at Argonne National Laboratory to head an effort to build a sector at the Advanced Photon Source dedicated to the study of nuclear materials, including hot cells. A Letter of Intent was submitted and the scientific case and conceptual design was presented to the APS Scientific Advisory Committee in January 2009 where he was given approval to begin looking for funding to construct the beamline. The proposed Nuclear and Radiological Research Collaborative Access Team (NRR-CAT) will initially be using MRCAT to perform synchrotron experiments starting in Fall 2009.

We completed assembly of the high temperature environmental chamber on the new positioning table. The heater element and vacuum systems were tested offline and we identified some additional modifications which needed to be made to the table for better operation. In March, we were able to test the new chamber and table on the 10-ID beamline with Pb-coated Mo samples. The heater worked up to 900C successfully and data were obtained at 18 degrees incident angle. We identified 2 problems which limited our experiment to only a few scans at

the 18 degree incident angle. These were (1) an obstruction by the sample holder which needs to be redesigned to permit grazing incidence x-rays, and (2) a vacuum leak in the vacuum isolation jacket which prevented the sample stage from being cooled rapidly from high temperatures. The former will be resolved by our designing a new sample holder. The latter required our sending the sample stage back to the manufacturer for warranty repair. We expect it to be returned in summer 2009.

The manuscript on Pb-coated Mo was accepted and will appear in print in July 2009. Its archival reference is: "An x-ray absorption spectroscopy study of Mo oxidation in Pb at elevated temperatures", S. Liu, D. Olive, J. Terry and C.U. Segre, *J. Nucl. Mat.* **392**, 259-263 (2009).

Jeff Terry and Shanshan Liu attended the ATR user meeting at Idaho National Laboratory, where it was announced that MRCAT, through IIT, will be accepting proposals from the Nuclear Energy community for experiments to be done at MRCAT in advance of construction of NRRCAT. We expect to have 18 shifts available for these experiments in the 2009-3 run beginning in October 2009.