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Fundamental and applied experimental investigations of corrosion of steel by LBE under controlled conditions: kinetics, chemistry, morphology, and surface preparation: quarterly report

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Fundamental and applied experimental investigations of corrosion of steel by LBE under controlled conditions: kinetics, chemistry, morphology, and surface preparation.

Quarterly Report: Project start - October 2004

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Introduction

This project has four components: (1) the fabrication of a materials test apparatus with unique capabilities, (2) comparative studies of steel corrosion under gas phase conditions comparable to the Lead Bismuth Eutectic (LBE) oxygen control conditions, (3) isotope labeling studies, and (4) collaborative efforts with other workers in the field.

(1) Materials test apparatus

We have made progress in the preparation of a laboratory at UNLV for the collocation of multiple experiments utilizing molten lead alloys. We have pending a review of the final plan for the space renovation, and have started baseline environmental studies for lead activities at UNLV.

We are midway in the process of generating the engineering drawing for the test facility, and have started purchasing the standard parts for the device.

(2) Comparative gas phase studies

We accepted delivery of an Oxygen Control System from KALLA, Germany; a nuclear laboratory in Germany with a large program in lead and LBE technology. Training of students occurred during the delivery and installation, and useful discussions were started with Drs Muller and Weisenburger of KALLA.

We have set up a tube furnace for gas phase studies, and are doing initial characterizations.

(3) Isotope labeling studies

Isotope labeling can be used to measure diffusion of materials under realistic conditions. We plan two methods for the introduction of isotope labels into the steels systems under study.

For oxygen, chemical methods using O^{18} enriched reactants are possible. We have purchased O^{18} enriched water and plan to electropolish our steel samples to introduce a labeled oxide layer than then can be tracked using Secondary Ion Mass Spectroscopy (SIMS).

For iron and chromium we intend to use the ion beam/mass separator located in Prof. Farleys' laboratory. The apparatus has been brought back on line, and we expect test experiments (probably using the O^{18} water) soon.

Contact has been initiated with EMSL laboratory at DOE's Pacific Northwest Laboratory, where we expect to do the SIMS studies.

(4) Collaborative work

A major effort has been underway to aid efforts at LANL and INEL.

We have examined over 30 samples by SEM for LANL on a professional courtesy basis, and have another 19 samples which we have mounted for examination here at UNLV. Those samples include some motivated by our previous studies under the TRP program.

We are collaborating with Dr. Loewen of INEL in the investigation of the effects of silicon on the corrosion of steel by LBE. We have 4 samples of iron with varying amounts of silicon up to about 4% which have been exposed to oxygen controlled LBE in an isothermal test system at INEL.

We have found significant new results – the silicon is found in three different forms in this system. These results are clearest in our Xray Photoelectron Spectrometry (XPS) Sputter Depth Profiles (SDPs) (Appendix).

In the oxide layer at the surface of the iron the silicon is in the form of a silicate – SiO_4-2 (binding energy 102eV in XPS studies). At the bottom of the oxide layer/start of the metal layer the silicon is in the form of silica – SiO_2 (binding energy 103.5eV in XPS). In the metallic iron the silicon is in metallic form (binding energy of 99eV in XPS).

At the bottom of the oxide layer we found both silica and carbide inclusions in the iron grain boundaries. Iron and silica in the grain boundaries indicate significant mobility of silicon and oxygen under the test conditions. Further, we found both lead and lead oxide droplets at the bottom of the oxide layer, indicating failure of the oxide to protect the iron in localized areas. A paper covering this work is expected to be submitted by the end of the year.

Other program activities

Attendance at the AFCI semiannual meeting, September 04.

Publication of a manuscript in Journal of Nuclear Materials July 04

Meetings with LANL staff in September, August, May – sample studies, the formation of a theory/experiment collaboration, and issues with the planned test facilities discussed.

Appendix: Studies of Iron/Silicon alloys in LBE

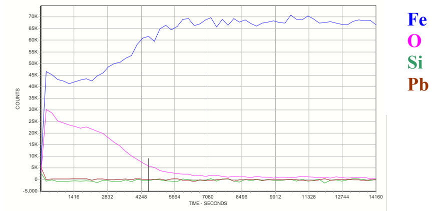
Starting composition of samples

Metal	Concentration (wt%)												
	Fe	Si	P	S	Mo	Cu	Cr	Al	Ti	C	Mn	Ni	Fe
Fe	Bal	0.05	0.007	0.016	0.017	0.03	0.04	0.031	0.002	0.02	0.31	0.03	99.447
Fe-1.24% Si	Bal	**1.24**	0.006	0.001	0.01	0.03	0.09	0.005	0.003	0.01	0.04	0.08	98.485
Fe-2.55% Si	Bal	**2.55**	0.003	0.001	0.1	0.03	0.08	0.003	0.006	0.017	0.12	0.15	96.940
Fe-3.82% Si	Bal	**3.82**	0.022	0.025	-	-	-	-	-	0.011	0.24	-	95.882

Changes of Si conc. at the intersection of bulk and oxide layer

Sample	Si in bulk	Si at the surface of sample (after SDP)	Differences of Si in bulk of samples in sequence		
	(1)	**(2)**	**(3)**	**(1)-(2)**	**(2)/(1)**
Fe 44	0.05	0		0.05	0
Fe 1 44	1.24	0.03	1.19	1.214	0.021
Fe 2 44	2.55	0.09	1.31	2.457	0.0365
Fe 3 44/3 43	3.82	2.43	1.27	1.391	0.6359

XPS/SDP studies

<table>
<tr><td>Sample</td><td>%Fe</td><td>%Si</td><td></td><td colspan="3">Binding Energy (eV)</td></tr>
<tr><td>Fe 44</td><td>100</td><td>0</td><td>Cycle</td><td>Fe</td><td>Si</td><td>O</td></tr>
<tr><td colspan="3" rowspan="8">*Time of sputtering: 5,664 s
~ thickness 3.3984μm


*Oxide layer thickness (by WDS): hard to determine</td><td>2</td><td>710</td><td></td><td>530</td></tr>
<tr><td>13</td><td>710, 707</td><td></td><td>530</td></tr>
<tr><td>15</td><td>710, 707</td><td></td><td>530</td></tr>
<tr><td>17</td><td>707</td><td></td><td>530</td></tr>
<tr><td></td><td></td><td></td><td></td></tr>
<tr><td></td><td></td><td></td><td></td></tr>
<tr><td></td><td></td><td></td><td></td></tr>
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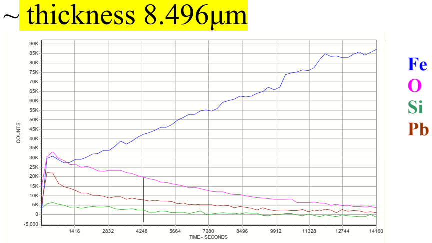
</table>

<table>
<tr><td>Sample</td><td>%Fe</td><td>%Si</td><td></td><td colspan="3">Binding Energy (eV)</td></tr>
<tr><td>Fe 1 44</td><td>99.974</td><td>0.026</td><td>Cycle</td><td>Fe</td><td>Si</td><td>O</td></tr>
<tr><td colspan="3" rowspan="8">*Time of sputtering: 14,160 s
~ thickness 8.496μm


*Oxide layer thickness (by WDS): around 1.2μm</td><td>2</td><td>710</td><td>102</td><td>530</td></tr>
<tr><td>15</td><td>710, 707</td><td>102</td><td>530</td></tr>
<tr><td>27</td><td>707</td><td>102</td><td>530</td></tr>
<tr><td>45</td><td>707</td><td>103, 99</td><td>530</td></tr>
<tr><td></td><td></td><td></td><td></td></tr>
<tr><td></td><td></td><td></td><td></td></tr>
<tr><td></td><td></td><td></td><td></td></tr>
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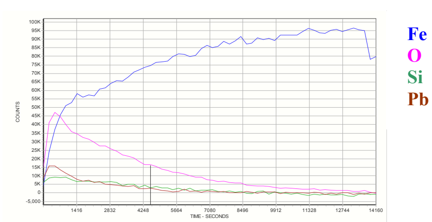
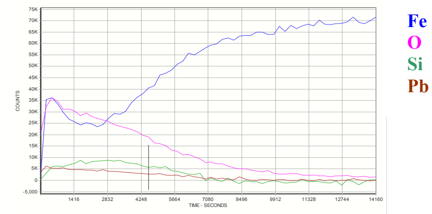
</table>

<table>
<tr><td>Sample</td><td>%Fe</td><td>%Si</td><td></td><td colspan="3">Binding Energy (eV)</td></tr>
<tr><td>Fe 2 44</td><td>99.420</td><td>0.093</td><td>Cycle</td><td>Fe</td><td>Si</td><td>O</td></tr>
<tr><td colspan="3" rowspan="10">*Time of sputtering: 11,532 s
~ thickness 6.9192μm


*Oxide layer thickness (by WDS): around 1.2μm</td><td>2</td><td>710</td><td>102</td><td>530</td></tr>
<tr><td>5</td><td>710</td><td>102</td><td>531</td></tr>
<tr><td>8</td><td>710, 707</td><td>103</td><td>531</td></tr>
<tr><td>12</td><td>710, 707</td><td>103</td><td>532, 531</td></tr>
<tr><td>16</td><td>707</td><td>103</td><td>532, 531</td></tr>
<tr><td>20</td><td>707</td><td>103</td><td>533,531</td></tr>
<tr><td>21</td><td>707</td><td>103</td><td>533,531</td></tr>
<tr><td>26</td><td>707</td><td>103</td><td>533, 531</td></tr>
<tr><td>30</td><td>707</td><td>103.5, 99</td><td>533, 531</td></tr>
<tr><td>40</td><td>707</td><td>103, 99</td><td>533</td></tr>
</table>

<table>
<tr><td>Sample</td><td>%Fe</td><td>%Si</td><td></td><td colspan="3">Binding Energy (eV)</td></tr>
<tr><td>Fe 3 44</td><td>97.571</td><td>2.429</td><td>Cycle</td><td>Fe</td><td>Si</td><td>O</td></tr>
<tr><td colspan="3" rowspan="8">*Time of sputtering : 14,160 s
~ thickness 8.496µm


*Oxide layer thickness (by **WDS**): 1.5µm</td><td>2</td><td>710</td><td>102</td><td>531</td></tr>
<tr><td>8</td><td>710</td><td>103</td><td>531</td></tr>
<tr><td>11</td><td>710, 707</td><td>103</td><td>**531**, 533</td></tr>
<tr><td>16</td><td>710,707</td><td>103</td><td>**533**, 531</td></tr>
<tr><td>19</td><td>707</td><td>103</td><td>**533**, 531</td></tr>
<tr><td>26</td><td>707</td><td>**103**, 99</td><td>**533**, 531</td></tr>
<tr><td>45</td><td>707</td><td>99</td><td>**533**, 531</td></tr>
<tr><td></td><td></td><td></td><td></td></tr>
</table>

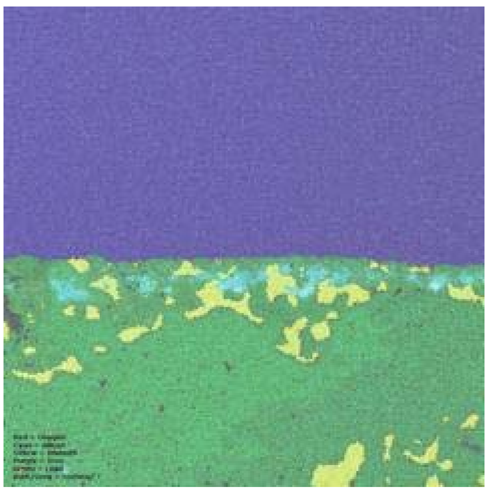
<table>
<tr><td>Sample</td><td>%Fe</td><td>%Si</td><td></td><td colspan="3">Binding Energy (eV)</td></tr>
<tr><td>Fe 3 43</td><td>97.298</td><td>2.702</td><td>Cycle</td><td>Fe</td><td>Si</td><td>O</td></tr>
<tr><td colspan="3" rowspan="8">*Time of sputtering : 14,160 s
~ thickness 8.496µm

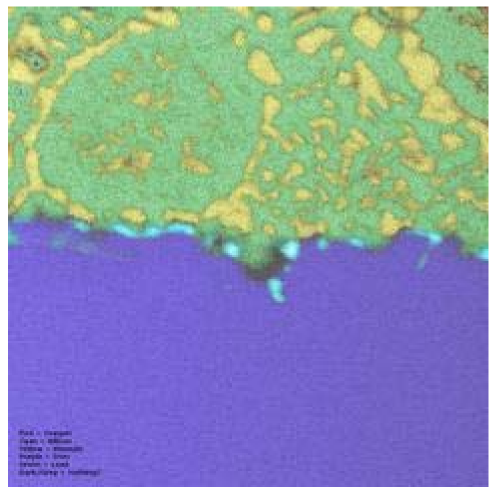

*Oxide layer thickness (by **WDS**): 1.5µm</td><td>2</td><td>710</td><td>102</td><td>530.5</td></tr>
<tr><td>8</td><td>710,707</td><td>**103**, 99</td><td>531</td></tr>
<tr><td>13</td><td>710, 707</td><td>**103**, 99</td><td>**531**, 533</td></tr>
<tr><td>18</td><td>710,**707**</td><td>**103**, 99</td><td>**531**, 533</td></tr>
<tr><td>24</td><td>707</td><td>**103**, 99</td><td>531,533</td></tr>
<tr><td>33</td><td>707</td><td>103, 99</td><td>531,533</td></tr>
<tr><td>52</td><td>707</td><td>103, **99**</td><td>531,**533**</td></tr>
<tr><td></td><td></td><td></td><td></td></tr>
</table>

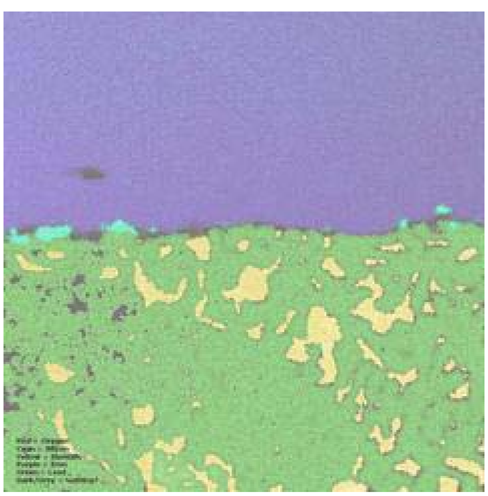
WDS Maps of Fe-Si samples

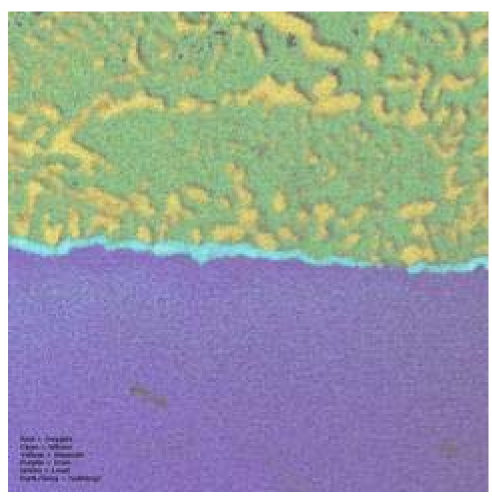
Legend:
Oxygen
Silicon
Bismuth
Iron
Lead
Dark/Grey = (no signal)

All maps are 68 µm per side.
(Click on images for full-size view)


Fe-44


Fe1-44


Fe2-44


Fe3-44

Notes:

-Fe 44: Oxide layer has been dissolved into LBE. (???)

-Fe 144 and Fe 244: The oxide layer is at the surface of the bulk as a barrier to stop LBE intrusion into the bulk. However, we can see that the Si is not enough to make a full barrier. Hence, in this case LBE still can attack the bulk to some extent.

-Fe 344: Si now is concentrated enough to make a nearly full barrier to protect the bulk from corrosion by LBE.

- There are other interesting features of Fe244 and Fe344 WDS spectrum: Underneath of oxide layer we can clearly see the Si-depleted zone. Especially, with Fe 344, underneath of Si-depleted zone we have Si-enriched zone and Si-depleted zone consequently.