**COMPATIBILITY OF MATERIALS EXPOSED TO ISOTHERMAL Pb-Li** – B. A. Pint (Oak Ridge National Laboratory, USA)

## OBJECTIVE

One proposed U.S. test blanket module (TBM) for ITER uses ferritic-martensitic alloys with both eutectic Pb-Li and He coolants at ~475°C. In order for this blanket concept to operate at higher temperatures (~700°C) for a DEMO-type reactor, several Pb-Li compatibility issues need to be addressed. Some of the issues being currently investigated are the use of corrosion resistant alloys and coatings, the transformation of alumina exposed to PbLi and the effect of impurities on dissolution of these materials.

## SUMMARY

Specimens from six Pb-Li capsule experiments exposed for 1000h at 700° or 800°C were further characterized to determine the extent of attack. The $LiAlO_2$ reaction product appeared to spall in some cases, although this may be due to the Pb-Li cleaning process after exposure. The most unusual result was the large Al loss from the coating on Fe-9Cr-2W after 1000h at 700°C in Pb-Li. If this result indicates the rate of Al loss, it has strong implications for the coating lifetime at this temperature. Also, the mass loss from type 316 stainless steel and resulting microstructure were compared for commercial Pb-Li and high purity Pb-Li. The experimental plan is outlined for the next series of 1000h capsule experiments beginning in January 2009.

## PROGRESS AND STATUS

### Introduction

A recent focus of the U.S. fusion energy program has been on developing a proposal for a test blanket module (TBM) for ITER. The dual coolant Pb-Li (DCLL) TBM concept has both He and eutectic Pb-Li coolants and uses ferritic steel as the structural material with a SiC/SiC composite flow channel insert (FCI).[1] The interest in this concept has focused compatibility-related research on Pb-Li. Many materials have poor compatibility with liquid Li,[2] but the activity of Li is very low in Pb-17Li,[3] and this allows a wider range of materials to be considered. However, Pb-Li readily dissolves many conventional alloys above 500°C. While the TBM maximum operating temperature will be <500°C to limit compatibility issues, this blanket concept would be more attractive for a commercial reactor with a higher maximum operating temperature, perhaps >700°C if oxide dispersion strengthened (ODS) ferritic steels[4] were used. However, at these higher temperatures, compatibility is even more of a concern. Therefore, static capsule exposures have been conducted on materials at 700° and 800°C.[5-7] The goal of this series of six capsules was to (1) use Al-containing alloys and coatings to study the transformation of $\alpha$-$Al_2O_3$ to $LiAlO_2$.[8] and (2) determine the effect of switching from high-purity Pb and Li to commercial purity Pb-17Li in the capsule. The previous report[7] included the initial results from these capsules and this report includes additional characterization. The next series of capsule experiments is now being prepared to follow up on these results.

### Experimental Procedure

Static capsule tests were performed using Mo inner capsules and type 304 stainless steel outer capsules to protect the inner capsule from oxidation. Specimens were held inside the Mo capsule by a Mo wire. The specimens were ~1.5 mm thick and 4-5 $cm^2$ in surface area with a 0.3 $\mu$m surface finish. The capsules were loaded with 125g of commercial purity Pb-14.3at.%Li in an argon-filled glove box. The Pb-Li and specimen chemistry along with details of how the specimens were prepared was reported previously.[7] A

summary of conditions and mass change after exposure is given in Table I. To remove residual Pb-Li on the surface after exposure, specimens were soaked in a 1:1:1 mixture of acetic acid, hydrogen peroxide and ethanol for up to 72 h. Post-test surfaces were initially examined using x-ray diffraction (XRD) and secondary electron microscopy (SEM). The specimens that formed a surface oxide were then coated with copper to protect that layer, sectioned and metallographically polished for analysis by electron microprobe analysis (EPMA).

**Results and Discussion**

Table I summarizes the mass change data along with two previous exposures where high purity Pb and Li were used instead of commercial Pb-Li.[5-7] The mass change for 316SS at 700°C was slightly higher in this exposure than in the previous exposure in high purity Pb-Li indicating that the higher O content in commercial Pb-Li did not have a beneficial effect on dissolution. Figure 1 shows polished cross-section of both 316SS specimens exposed at 700°C. A similar Ni-depletion zone was observed in both specimens.

Figure 2 shows a polished cross-section of uncoated T92 after exposure at 700°C. In general, the W and Mo were not depleted near the surface. In areas that showed obvious metal loss, such as in Figure 2a, there was Cr depletion. However, Cr depletion was not observed in all locations as shown in the second Cr profile in Figure 2b.

Figure 3 shows the surface of the aluminized T92 specimen that showed only minimal mass loss, Table I, presumably due to the formation of a protective oxide layer, that was identified by XRD as $LiAlO_2$.[7] Figure 4 shows a polished cross-section of the same specimen. The rougher areas in Figure 3 are typical of the as-deposited coating where the outer layer is not completely uniform, see Figure 4b. However, there are some smoother areas (arrow in Figure 3), which appear to be where the oxide has spalled. Figure 4a shows a region with a relatively thick oxide layer including some oxide protrusions or pits. The region analyzed in Figure 4b showed very little oxide on the surface, Figure 4c. The arrow in Figure 4b indicates a pit where an oxide protrusion may have been located, such as those seen in Figure 4a. As is typical of these coatings,[9] N from the substrate reacts with the Al to form acicular AlN particles at the coating-substrate interface, Figure 4d. Figure 4e shows Cr-rich precipitates in the substrate and lower half of the coating that are likely carbides.

Aluminum profiles from two locations on the exposed coating are shown in Figure 5. For comparison, the Al profile from a typical coating made by this process on alloy T91 (Fe-9Cr-1Mo) also is shown.[10] As expected, little interdiffusion occurred during the exposure.[11] However, a large fraction of the coating Al reservoir appears to have been depleted during the exposure. It is not clear if the depletion is due to

Table 1. Mass change of specimens after 1000h exposures in Pb-17Li with a Mo capsule.

| Specimen | Pre-oxidation | Temperature | Mass Change ($mg/cm^2$) |
|---|---|---|---|
| 316SS | none | 700°C | - 5.06 |
| 316SS | none | 700°C | - 3.79 (high purity Pb and Li) |
| T92 | none | 700°C | - 3.47 |
| T92 + CVD Al | none | 700°C | - 0.09 |
| PM FeCrAl | none | 800°C | - 1.93 |
| ODS FeCrAl | 2h at 1000°C | 700°C | - 0.06 |
| ODS FeCrAl | none | 700°C | - 0.20 (high purity Pb and Li) |
| Ni-42.5Al+Hf | 2h at 1200°C | 800°C | - 0.51 |

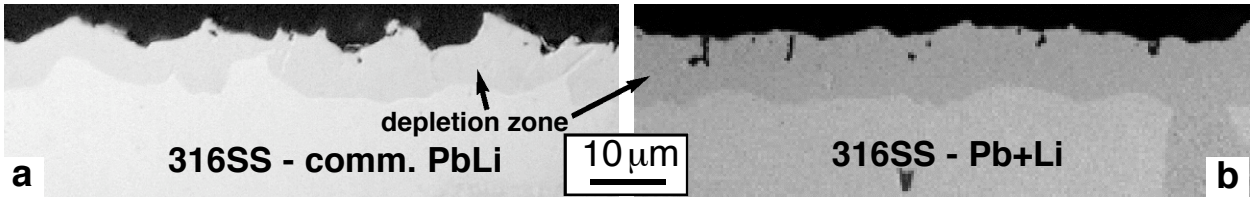



Figure 1. Light microscopy of polished cross-section of type 316 stainless steel after 1000h at 700°C (a) commercial purity Pb-Li and (b) high purity Pb-Li.

dissolution or oxide formation. Except for selected areas where the oxide was extremely thick, no significant metal loss appears to have occurred, otherwise the tail of the Al profile would not match the as-deposited profile. Further analysis is required to determine if this depletion could be due to only oxide formation or also include some oxide dissolution. Prior work on aluminized Fe-Cr steel showed similar penetration attack of a 100$\mu$m thick coating on EUROFER 97 with a peak Al content of ~60 at.% after exposure for 6292 h at 480°C in flowing Pb-Li.[12] In that case, the oxide was assumed to be $Al_2O_3$ and the starting coating was not characterized to determine the amount of Al lost from the coating during exposure. If Al depletion is a concern, one solution is to increase the Al content in the coating. An example is shown in Figure 5 where the Al activity was increased during the deposition process to increase the amount of Al in a T91 substrate. However, minimizing the amount of Al in the first wall may be desired.

Figure 6 shows the surface of PM FeCrAl (Kanthal alloy APMT [13]) after exposure at 800°C. This material is a candidate tubing alloy for construction of a high-temperature loop. This specimen was not pre-oxidized before exposure which may explain the mass loss and the non-uniform attack, similar to the pits observed for aluminized T92. Some of the mass loss could be due to oxide spallation which was evident in some areas with bare metal exposed, Figure 6b. The morphology of the $LiAlO_2$ layer (identified by XRD [7]), Figure 6c, was very similar to that observed on NiAl+Hf and ODS FeCrAl after exposure at 800°C, although both of those specimens were pre-oxidized before exposure. The pits were evident in the

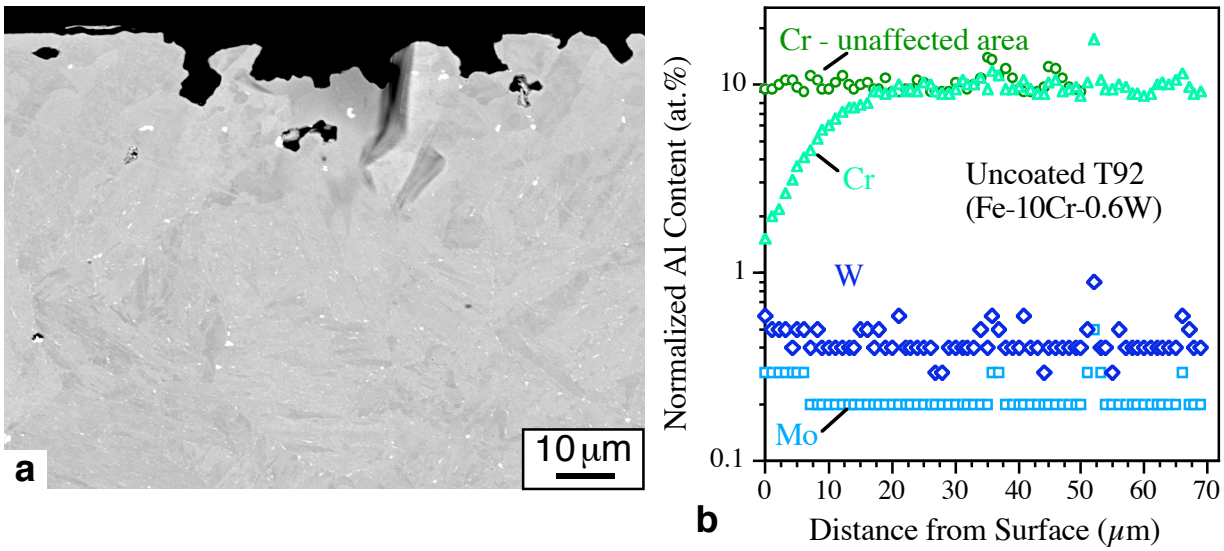



Figure 2. (a) SEM image of T92 polished cross-section after 1,000h at 700°C in commercial Pb-Li. (b) EPMA composition profiles showing no W or Mo depletion and only Cr depletion in regions where there was clear metal loss such as (a). In unaffected areas where there was no obvious metal loss, no Cr loss was detected.

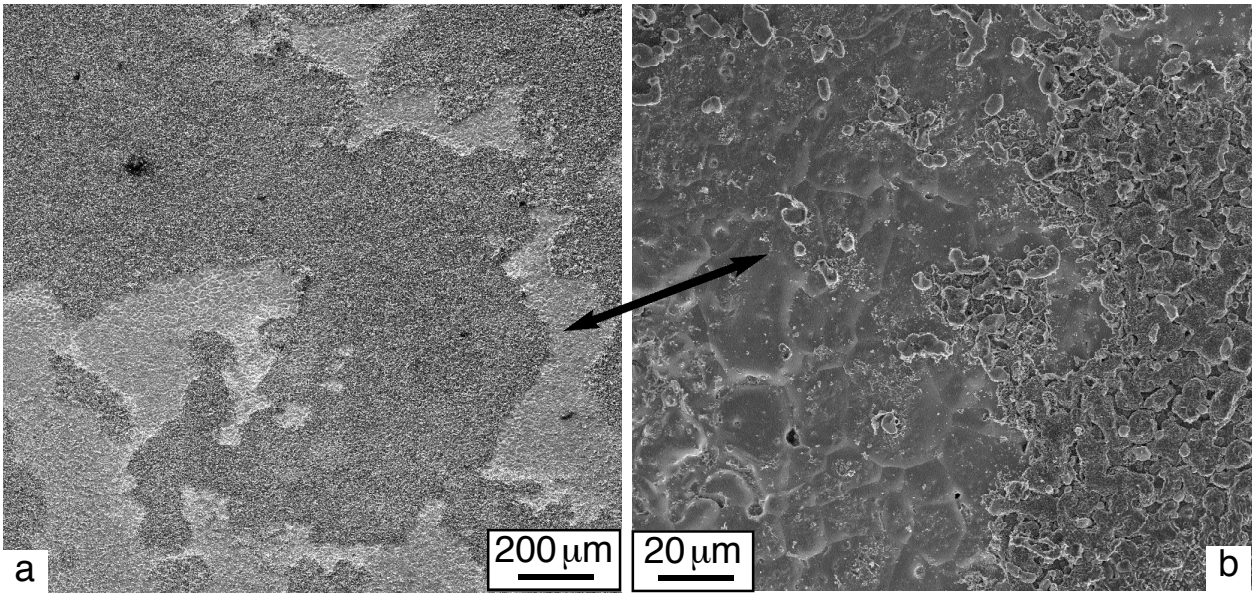
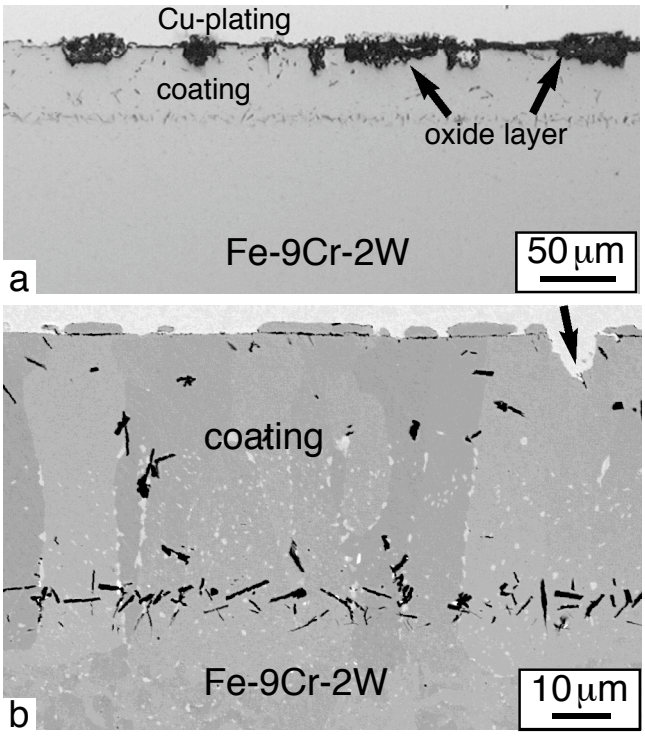



Figure 3. SEM plan view images of the reaction product on aluminized T92 after exposure to Pb-17Li at 700°C for 1,000h. Higher magnification in (b) shows smoother areas



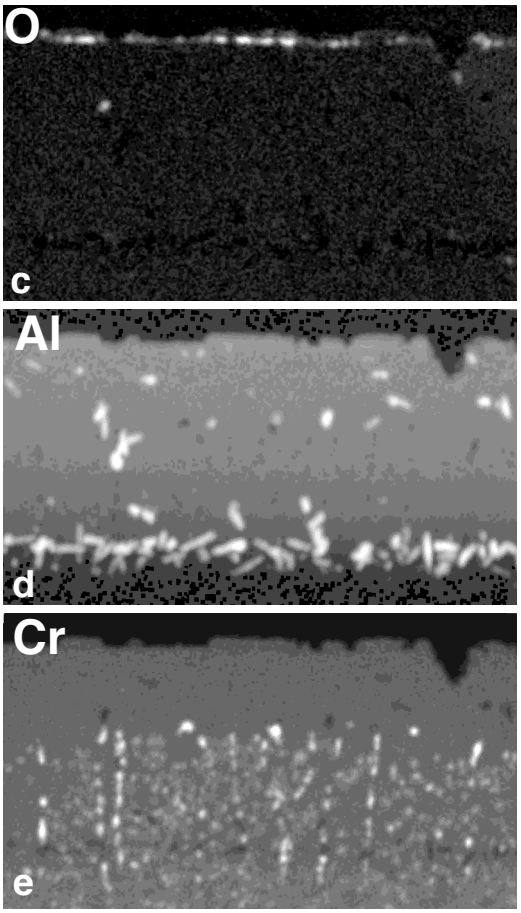




Figure 4. Polished cross-section of aluminized T92 after exposure to PbLi for 1kh at 700°C. (a) light microscopy, (b) secondary electron image, and EPMA maps of the same region in (b) are shown in (c) O, (d) Al and (e) Cr.

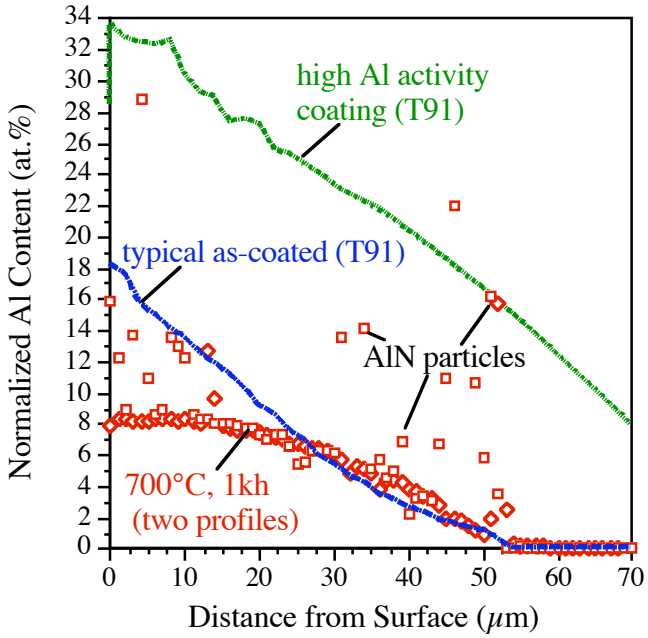



Figure 5. Normalized Al content by microprobe analysis as a function of depth for a typical as-deposited coating on Fe-9Cr-1Mo substrate and coating on Fe-9Cr-2W after exposure for 1kh at 700°C in PbLi. Profile for a coating with a higher Al activity also is shown for comparison.

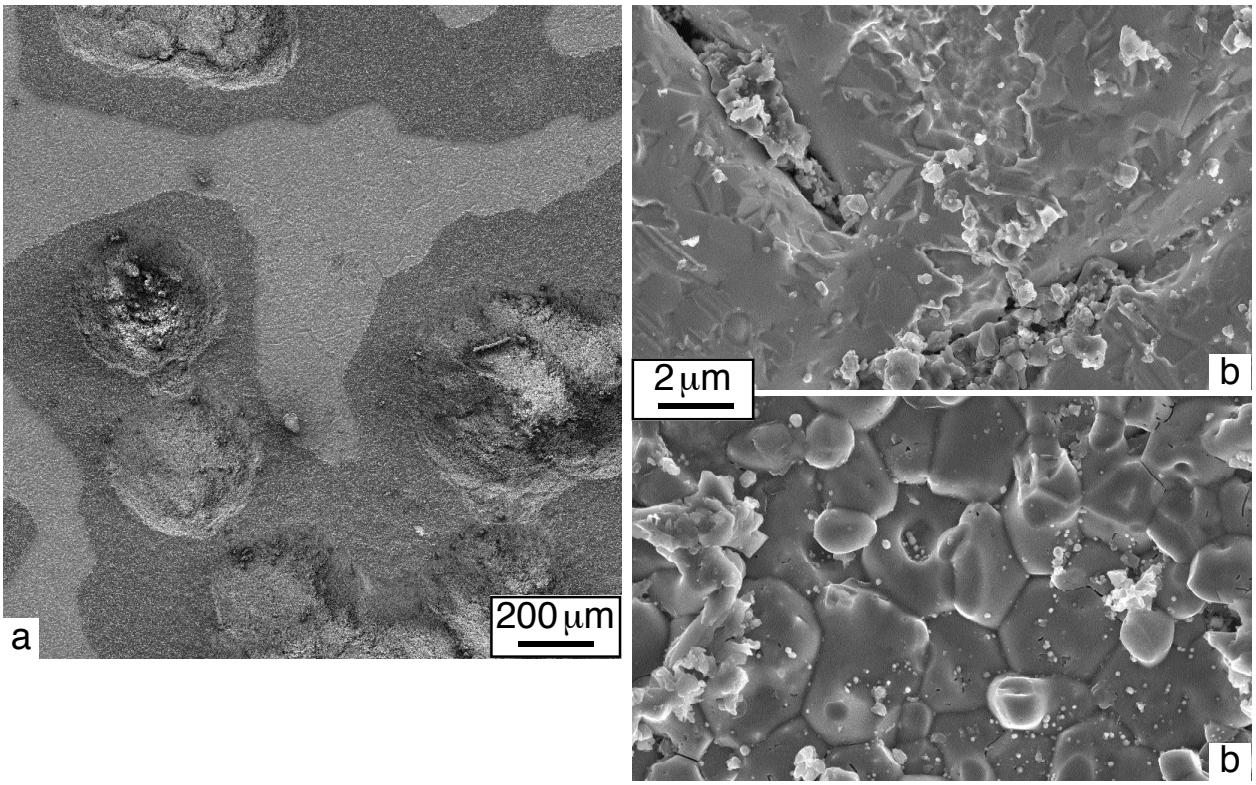



Figure 6. SEM plan view images of the reaction product on PM FeCrAl after exposure to Pb-17Li at 800°C for 1,000h, higher magnification in (b) shows bare metal revealed by spallation and in (c) the morphology of the $LiAlO_2$ surface layer.

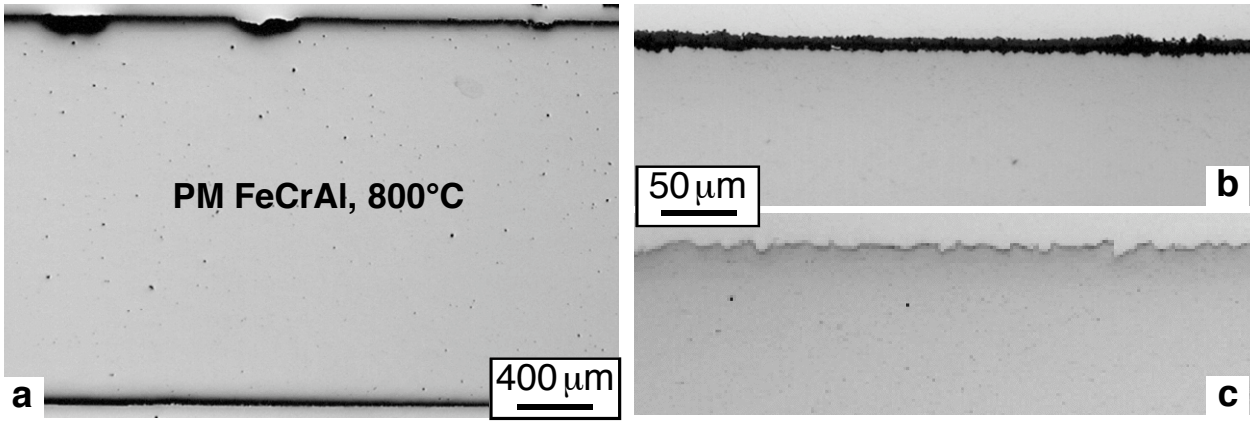



Figure 7. Light microscopy of polished cross-section of PM FeCrAl exposed for 1,000h at 800°C to commercial purity Pb-Li, (b,c) are higher magnification showing areas with and without surface oxide.

polished cross-section, Figure 7a. At higher magnification, some areas showed a uniform surface oxide, Figure 7b, whereas in other areas the $LiAlO_2$ layer had spalled. The cross-section was examined by EPMA but no composition gradients were observed beneath the surface, including Al.

Finally, Figure 8 shows the oxide layer remaining on the pre-oxidized specimens, NiAl+Hf and ODS FeCrAl (Plansee alloy PM2000) exposed at 800° and 700°C, respectively. Both specimens initially had a layer of $\alpha$-$Al_2O_3$ on surface before exposure. After exposure, both oxide layers had transformed to $LiAlO_2$.[7] As this has already been studied by TEM for ODS FeCrAl exposed at 800°C,[8] further characterization of these specimens does not appear to be necessary. For ODS FeCrAl, a prior Pb-Li exposure at 700°C showed a slightly higher mass loss when the specimen was not pre-oxidized, Table I. This result suggests that pre-oxidation reduces dissolution. However, the previous exposure also used high purity Pb and Li which may have altered the result.

To follow up on these results, a new series of capsule experiments is being assembled for exposure beginning in January 2009, Table 2. The performance of uncoated and aluminized T92 will be examined at 600°C to determine the protective behavior of the coating and measure the Al loss from the coating after exposure. Additional aluminized T92 specimens will be exposed at 700°C in order to examine (1) the effect of pre-oxidation on coating behavior and (2) the effect of O content in the Pb-Li on oxide formation. In order to reduce the O content of the Pb-Li, ~1g of Zr chips will be added to the capsule. A lower O content may inhibit the surface oxide layer from forming. The effect of Li on the surface product will be studied in the last two capsule experiments. Aluminized T92 will be exposed to unalloyed Pb with no Li addition in order to study the phase of the reaction product. Pre-oxidized ODS FeCrAl will be exposed at 500°C to see if the transformation of $\alpha$-$Al_2O_3$ to $LiAlO_2$ occurs at 500°C.

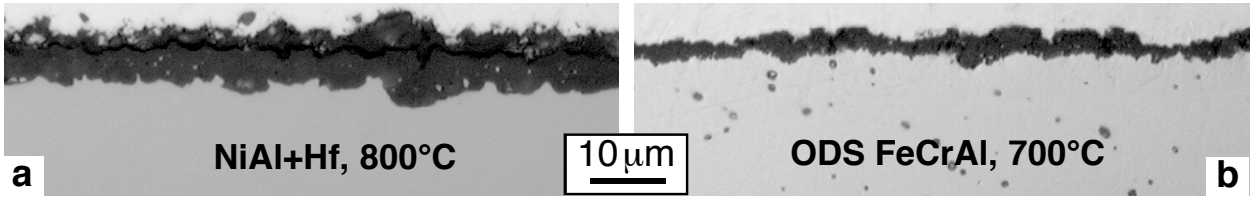



Figure 8. Light microscopy of polished cross-section of pre-oxidized specimens exposed for 1,000h to commercial purity Pb-Li, (a) Ni-42Al+Hf at 800°C and (b) ODS FeCrAl at 700°C.

Table 2. Experiment plan for next series of 1000 h Mo capsules begun in January 2009

| Specimen | Pre-oxidation | Temperature | Purpose |
|---|---|---|---|
| T92 | none | 600°C | Baseline data |
| Aluminized T92 | none | 600°C | Effect of coating at 600°C |
| Aluminized T92 | none | 700°C | Add Zr, create low O PbLi |
| Aluminized T92 | 2h at 800°C | 700°C | Determine effect of pre-oxidation |
| Aluminized T92 | none | 700°C | Expose to unalloyed Pb |
| ODS FeCrAl | 2h at 1000°C | 500°C | Check oxide transformation at 500°C |

**References**


[1] M. Abdou, D. Sze, C. Wong, M. Sawan, A. Ying, N. B. Morley and S. Malang, Fus. Sci. Tech., 47 (2005) 475.
[2] J. E. Battles, Intern. Mater. Rev. 34 (1989) 1.
[3] P. Hubberstey, J. Nucl. Mater. 247 (1997) 208.
[4] S. Ukai and M. Fujiwara, J. Nucl. Mater. 307 (2002) 749.
[5] B. A. Pint, J. L. Moser and P. F. Tortorelli, J. Nucl. Mater. 367-370 (2007) 1150.
[6] B. A. Pint, Fus. Sci. Tech. 52 (2007) 829.
[7] B. A. Pint, DOE/ER-0313/44 (2008) 67.
[8] B. A. Pint and K. L. More, J. Nucl. Mater. 376 (2008) 108.
[9] Y. Zhang, B. A. Pint, K. M. Cooley and J. A. Haynes, Surf. Coat. Tech. 200 (2005) 1231
[10] Y. Zhang, B. A. Pint, K. M. Cooley and J. A. Haynes, Surf. Coat. Tech. 202 (2008) 3839.
[11] Y. Zhang, A. P. Liu and B. A. Pint, Mater. Corr. 58 (2007) 751.
[12] J. Konys, W. Krauss, Z. Voss and O. Wedemeyer, J. Nucl. Mater., 367-370 (2007) 1144.
[13] B. Jönsson, R. Berglund, J. Magnusson, P. Henning and M. Hättestrand, Mater. Sci. Forum, 461-464 (2004) 455.