

COMPATIBILITY ISSUES FOR A HIGH TEMPERATURE DUAL COOLANT BLANKET – 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 (~750°C) for a DEMO-type reactor, several Pb-Li compatibility issues need to be addressed. A SiC/SiC composite flow channel insert is proposed to reduce the steel dissolution rate (and the magnetohydrodynamic pressure drop). Prior capsule testing examined dense, high-purity SiC in Pb-Li at 800°-1200°C and found detectable levels of Si in the Pb-Li after 2,000h at 1100°C and 1,000h at 1200°C. Current capsule experiments are examining several different SiC/SiC composite materials at 1000°C. Another issue involves Pb-Li transport between the first wall and heat exchanger. Aluminide coatings on type 316 stainless steel and Al-containing alloys capable of forming an external alumina scale have been studied in capsule experiments at 700° and 800°C.

SUMMARY

Compatibility experiments are being conducted to support higher temperature Pb-Li dual coolant concepts. Based on prior work on monolithic SiC at 1100°-1200°C, SiC/SiC specimens were evaluated at 1000°C. The high O content in the commercial PbLi led to oxide layer formation on monolithic SiC specimens and small mass changes for composite materials. Further characterization is needed to determine the degree of interaction observed for the composite specimens. Aluminum-containing alloys and aluminide coatings performed well in PbLi at 800°C compared to uncoated 316SS. Model aluminide coatings made by chemical vapor deposition reduced the dissolution rate for 316SS at 800°C by a factor of 50. The superior compatibility performance of the alloys containing Y and Zr dopants suggests that similar additions may be beneficial for the performance of protective aluminide coatings in this temperature range. Higher resolution characterization of the thin alumina layer is needed to determine the effect of exposure to Pb-Li.

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 and 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 much lower in Pb-17Li,[3] and this allows a wider range of materials to be considered. However, Pb-Li still readily dissolves many conventional alloys. While the TBM maximum operating temperature will be <500°C, this blanket concept would be more attractive for a reactor with a higher maximum operating temperature, perhaps >700°C if oxide dispersion strengthened ferritic steels[4] were used. However, at these higher temperatures, compatibility is even more of a concern. Therefore, static capsule testing is being conducted on SiC/SiC composites and corrosion resistant coatings are being investigated to protect metallic components.

Experimental Procedure

Static capsule tests were performed using dense chemical vapor deposited (CVD) -SiC (99.9995% purity) or Mo inner capsules and type 304 stainless steel or alloy 600 outer capsules to contain the inner capsule and prevent oxidation. When an unsealed CVD SiC inner capsule was used, a welded

intermediate Mo capsule also was included.[5] The specimens were held in the bottom of the CVD SiC crucible with a CVD SiC spacer. For Mo inner capsules, the specimens were hung with Mo wire. The capsules were loaded with either commercial Pb-17Li or high purity (99.9999%) Pb shot and Li in an argon-filled glove box. Specimens were (1) monolithic CVD SiC (3 x 8 x 12mm), (2) sintered NITE[6] SiC matrix material (provided by T. Hinoki at Kyoto Univ.), (3) SiC/SiC composites (3 x 8 x 12mm coupon, Figures 1a and 1b) supplied by B. Riccardi at ENEA, Italy, and ~11 mm OD tube supplied by H. Feinroth at Gamma Engineering, Figures 1c and 1d), (4) type 316 stainless steel (316SS) and (5) Al-containing alloys (Table 1). The alloy specimens were ~1.5mm thick and 4-5cm² in surface area with a 0.3µm surface polish. The Al-containing alloys were pre-oxidized for 2h at 1000°C in dry, flowing O₂ to form an external Al₂O₃ scale. Two specimens of 316SS were CVD aluminized for 4h at 1050°C in a laboratory scale reactor and then immediately annealed for 2h at the same temperature.[7,8] These conditions produce a ~200µm thick coating with and a ~20µm thick Al-rich outer layer, (Fe,Ni)₃Al. One of the coated specimens was pre-oxidized for 2h at 800°C in laboratory air. Specimen mass was measured before and after exposure on a Mettler-Toledo balance with an accuracy of ±0.04mg. Exposures were performed in resistively heated box furnaces for 1000h.

To remove residual Pb-Li after exposure, the specimens were soaked in a mixture of acetic acid, hydrogen peroxide and ethanol for 24-72h. The composition of the Pb-Li after testing was determined by inductively coupled plasma analysis and combustion analysis. Post-test surfaces were examined using Auger electron spectroscopy (AES) and secondary electron microscopy (SEM). Cross-sections of the metal specimens were examined using electron probe microanalysis (EPMA).

Results and Discussion

SiC/SiC compatibility with Pb-Li. Prior work on CVD SiC specimens in Pb-Li showed dissolution (detectable Si levels in the PbLi after exposure) after 2,000h at 1100°C and 1,000h at 1200°C.[9,10] No dissolution was detected after 5,000h at 800°C. Therefore, the present testing was performed at 1000°C

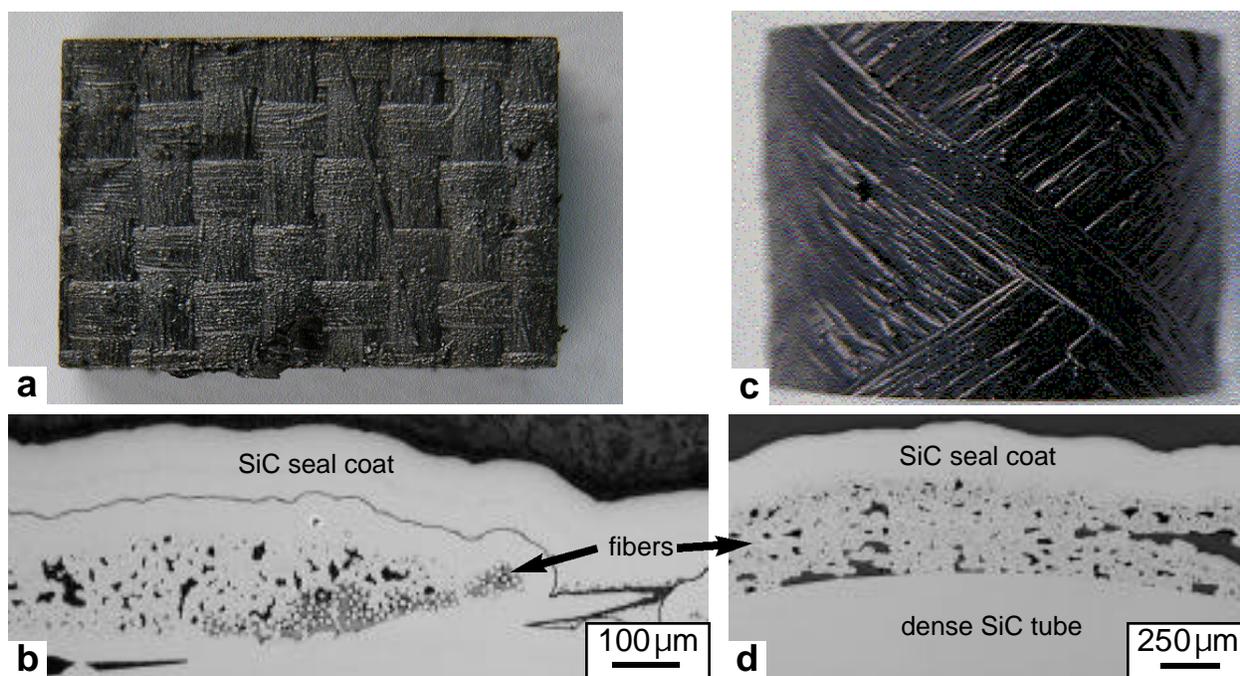


Figure 1. Photographs (a,c) of the SiC/SiC specimens and (b,d) polished sections showing the dense SiC seal coat on the surface of both composites. (a,b) coupon supplied by E.U. and (c,d) U.S. supplied tube.

Table 1. Alloy chemical compositions (atomic% or ppma) determined by inductively coupled plasma analysis and combustion analysis.

Material	Fe	Ni	Cr	Al	O	C	N	S	Other
316SS	65.1	8.9	19.9	0.02	490	3360	2380	68	1.94Si, 1.67Mn, 1.38Mo, 0.21Cu
ODS FeCrAl	67.8	0.02	20.0	10.6	7430	340	210	50	0.44Ti, 0.23Y, 0.04Si, 0.04Mn
Fe-28Al-2Cr+Zr	70.0	<	2.0	27.9	70	400	<	46	0.026Zr, 0.005Hf
Ni-42.5Al	<	57.3	<	42.6	40	380	<	<	<

< indicates below the detectability limit of <0.01% or <0.001% for interstitials

on SiC/SiC composites. This temperature is much higher than would be used for a DCLL FCI but SiC/SiC composites also are being evaluated for structural materials in higher temperature concepts.[11] The specimens were exposed in individual CVD SiC crucibles to avoid cross contamination. These exposures were recently completed so only initial characterization results are currently available.

Unlike the previous tests on CVD SiC where high purity Pb and Li were heated together in the capsule test, commercially prepared Pb-17Li was used for these tests. The major difference was higher N, C and especially O contents in the starting commercial material, Table 2. (Based on the high Li-O affinity and prior results, the high O content likely suppressed the measured Li in the commercial PbLi.) Initially, one specimen of CVD SiC was exposed. Prior work with high purity Pb and Li at 800°-1200°C typically showed mass changes of ± 0.01 mg/cm². [9, 10] With commercial Pb-Li, the mass gain was much higher at 1,000°C (Figure 2). Wetting of the specimens by Pb-Li did not occur after exposure at 800°C[12] but did occur in this case. Some residual PbLi was removed during cleaning, ~150 mg. Because the CVD SiC is fully dense, there is little opportunity for liquid metal penetration and there was no evidence of such in the prior work. Thus, the likely explanation for the mass gain is the formation of a surface oxide layer. For comparison, the mass gain for a CVD SiC specimen isothermally exposed for 1,000h at 1000°C in laboratory air also is shown in Figure 2. The mass gain for the sintered SiC NITE matrix sample was

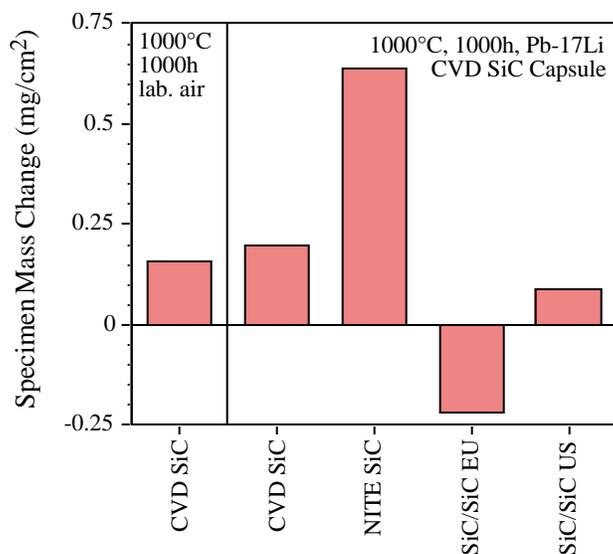


Figure 2. Specimen mass change for SiC and SiC/SiC composite specimens after 1,000h at 1000°C in commercial Pb-17Li.

Table 2. Chemical composition using inductively coupled plasma and combustion analysis of the starting Pb, commercial Pb-Li ingot and the Pb-Li after capsule exposures at 800°C for 1000h (in ppma except for Li in atomic%).

Test	Li	Fe	Cr	Ni	Mn	Si	Al	Mo	C	O	N	S
Starting Pb	n.d.	<4	<4	<4	<4	<40	<8	<2	<170	1270	<40	<50
Comm. PbLi	14.3%	<30	<70	<30	<30	<120	<60	<40	750	4820	180	<50
316SS	16.5%	<30	<30	270	<30	<120	<60	<20	480	2040	<40	<50
316SS+Al	17.6%	<30	<30	<30	<30	<120	<60	<20	590	1370	<40	<50
316SS+Al/O	17.5%	<30	<30	<30	<30	<120	<60	<20	730	2100	<40	<50
FeCrAl	17.3%	<30	<30	<30	<30	<120	<60	90	460	5280	<40	<50
Fe ₃ Al	16.3%	<30	<30	<30	<30	<120	<60	<20	540	1230	<40	<50
NiAl	16.7%	<30	<30	150	<30	<120	<60	<20	520	2640	<40	<50

significantly higher than the CVD SiC specimen. This may be due to reaction with the Al-Y-Si oxide sintering aid.[6]

The mass gains for the two SiC/SiC composite specimens after cleaning are shown in Figure 2. Because of the possibility of liquid metal becoming entrapped in the composite during exposure, the net mass change may be a combination of oxidation (mass gain), dissolution (mass loss) and mass gain due to entrapped metal. The mass changes should not be used to compare the relative behavior of these materials. Significant differences in behavior can be attributed to a dense SiC seal coat on the composites (Figures 1c and 1d) which may prevent interaction of the fibers and fiber interfaces with PbLi. Both the EU and US SiC/SiC specimens were seal coated on the outer surfaces but the fibers were exposed on the cut sides. Complete characterization of the PbLi chemistry and composite microstructure is needed to fully evaluate the differences between these materials.

Using AES, the initial post-exposure characterization of the reaction products on the CVD SiC specimens has been performed. The oxide formed during oxidation in air at 1000°C was uniform across the specimen and ~6.5 μm thick. In contrast, the oxide formed in PbLi at 1000°C was not uniform in thickness. In some areas the oxide was only 0.1 μm thick. In other areas, oxide nodules containing Fe and Si were observed. The source of Fe is not apparent. No Pb or Li was detected in the surface oxide.

In order to test the experimental procedure, a CVD SiC specimen also was exposed in a Mo capsule instead of a CVD SiC capsule. The mass gain was almost identical. The oxidation of the specimens in the commercial PbLi may have obscured any difference between the tests. Future work with commercial PbLi may require purification of the PbLi or gettering during the capsule test.

Corrosion Resistant Coatings in Pb-Li. Because of the low activity of Li in Pb-17Li, alloys or coatings that form an adherent external Al₂O₃ scale should be resistant to dissolution in Pb-Li.[13] This has been confirmed at fairly modest temperatures.[14,15] Similar aluminide coatings also are being evaluated as tritium permeation barriers.[16] To assess the potential performance of aluminide coatings or alumina-forming alloys at higher temperatures, some baseline compatibility data are being examined using static capsule testing. The first experiments were conducted on model materials (Table 1). A Fe₃Al composition was selected as being similar to aluminide coatings formed on Fe-base alloys[7,8] and a Ni-42Al composition is similar to the composition of a CVD aluminide coating on a Ni-base alloy.[17] In addition, an ODS FeCrAl (Plansee alloy PM2000) was tested as this alloy could be used without a coating. Based on positive results for these model materials at 700°C,[9,10] the model materials as well as CVD aluminide coatings on 316SS substrates were tested at 800°C for 1,000h using high purity Pb and Li.

Table 3. Mass change of specimens after 1000h at 800°C in Pb-17Li with a Mo capsule

Specimen	Pre-oxidation	Mass Change	
		(mg)	(mg/cm ²)
316SS	none	-79.51	-17.30
316SS + CVD Al	none	- 1.55	- 0.34
316SS + CVD Al	2h at 800°C	- 1.93	- 0.43
ODS FeCrAl	2h at 1000°C	+ 1.58	+ 0.24
Fe-28Al-2Cr+Zr	2h at 1000°C	- 1.55	- 0.37
Ni-42.5Al	2h at 1000°C	-12.12	- 2.72

The mass change results after exposure and cleaning are shown in Table 3. The selective removal of Ni (e.g. see Ref. 18) produced a very high mass loss from the uncoated type 316SS specimen. Aluminized type 316SS substrates showed much lower mass gains, Table 3. Figure 3 summarizes the observations for 316SS at 700° and 800°C in Pb-17Li and shows the improvement due to aluminizing. However, pre-oxidation of the coating for 2h at 800°C did not result in a decrease in the amount of dissolution. Similar low mass changes were observed for the ODS FeCrAl and Fe₃Al specimens, Figures 4a and 4b. The Fe₃Al specimen had one ~3mm diameter region of bare metal (arrow in Figure 4b) which may explain the mass loss. The NiAl specimen (Figure 4c) showed a more substantial loss (>50%) of the oxide layer after exposure and a larger mass loss, Table 3. One obvious reason for the oxide spallation is the lack of reactive element (e.g. Y or Zr) in this material compared to the other alumina-formers, Table 1. These dopants promote alumina scale adhesion.[19]

All of these specimens have been examined in plan-view by SEM and in cross-section using EPMA. No Pb was detected in any of the cross-sections. The post-test Pb-Li chemistry is shown in Table 2. The depleted surface layer on uncoated 316SS was similar to that observed at 700° with lower levels of Ni, Mn and Si and increased Mo content, Figure 5. However, the layer thickness increased from ~6µm at 700°C to ~20µm at 800°C and the Cr depletion was not as severe as observed at 700°C.[9] Dissolved Ni was detected in the PbLi chemistry, Table 2.

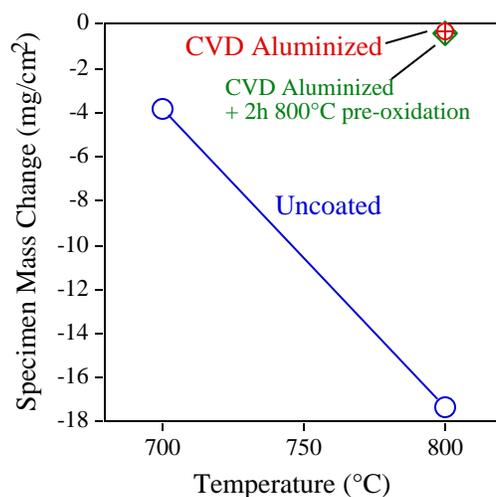


Figure 3. Specimen mass loss after 1,000h in Pb-17Li as a function of temperature for uncoated and coated type 316 stainless steel.

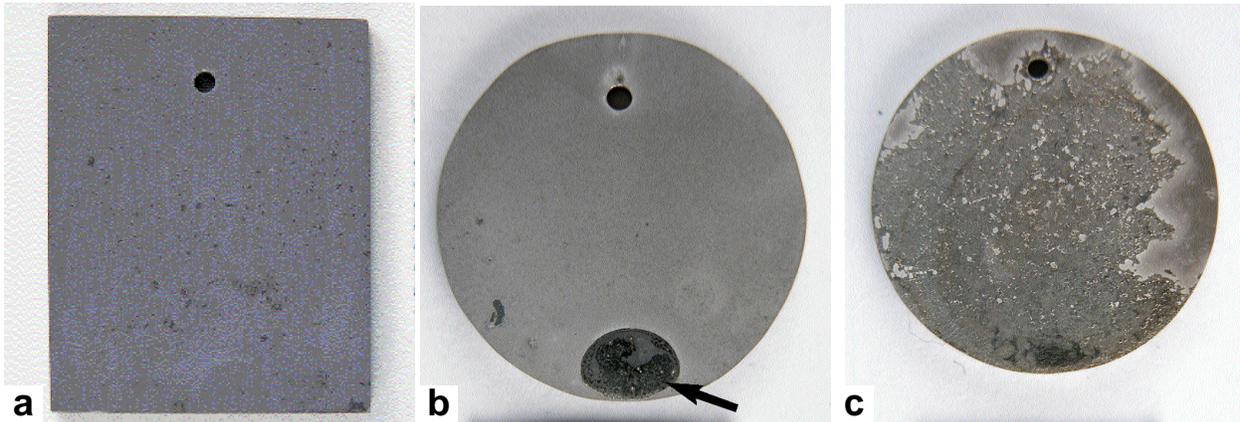


Figure 4. Photographs after exposure for 1000h at 800°C in PbLi (a) ODS FeCrAl, (b) Fe-28Al-2Cr+Zr and (c) NiAl.

Figures 6a and 6b show the aluminized coating after exposure. As predicted, the total coating thickness was $\sim 200\mu\text{m}$ with a $\sim 20\mu\text{m}$ outer layer, shown in Figure 6b. This layer was enriched in Ni and Al, Figure 4. However, in some regions the Ni content was much lower (dashed line in Figure 7) which may be due to local dissolution.

Figure 6c shows a cross-section of the NiAl specimen. No Ni depletion was detected in the metal, but in areas without an oxide layer, there appeared to be recession of the metal (arrow). Figure 6d shows the alumina scale formed on ODS FeCrAl, which was similar to that formed on Fe_3Al . The thin alumina scale was difficult to characterize but, in plan-view (Figure 8b), appeared to have a much larger grain size than was observed after a 2h pre-oxidation (Figure 8a). The grains are the size expected after exposures at $\sim 1300^\circ\text{C}$, [20] suggesting accelerated grain growth during the Pb-Li exposure at 800°C. Larger grains are

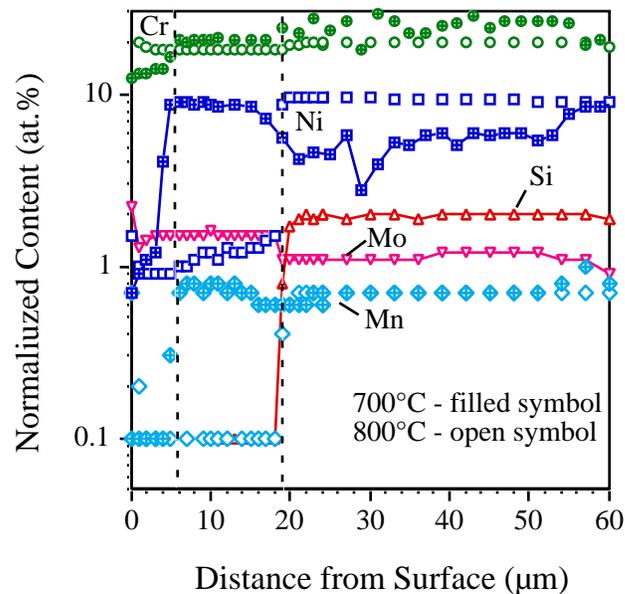


Figure 5. Composition line profiles of a polished cross-section of 316SS after exposure in Pb-17Li for 1,000h at 700°C (filled symbols) and 800°C (open symbols). The depletion zone increases with exposure temperature.

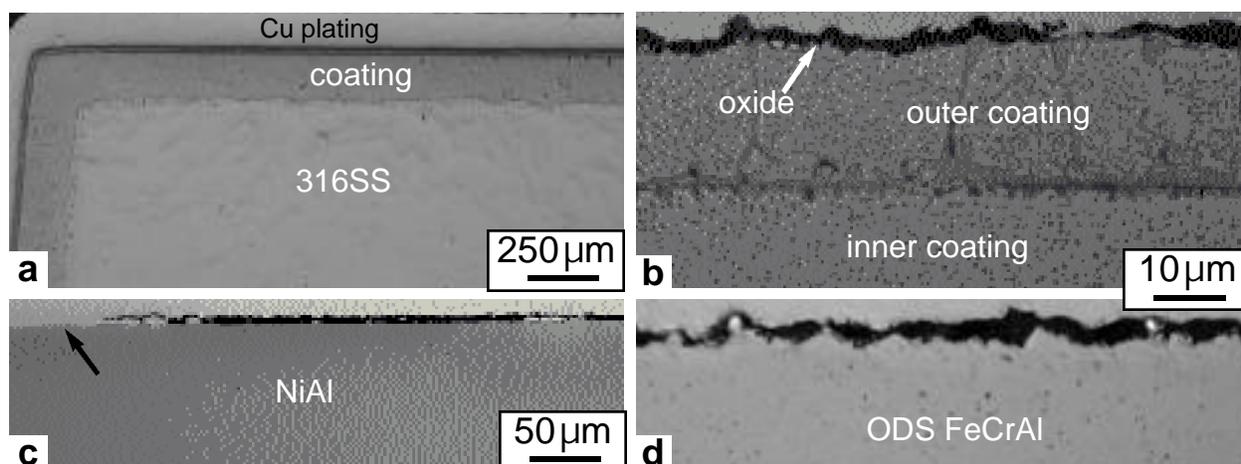


Figure 6. Light microscopy images of specimens after 1000h at 800°C in Pb-Li. (a) Aluminized 316SS, and pre-oxidized (b) aluminized 316SS, (c) NiAl and (d) ODS FeCrAl. Arrow in (c) shows missing oxide layer.

sometimes associated with the formation of a Fe-rich surface oxide. Further characterization is needed. Prior work on alumina layers exposed to Pb-Li concluded that the oxide was degraded during exposure.[21]

An important future step in this work will be to conduct experiments in flowing Pb-Li with a temperature gradient. Static capsule experiments can only produce limited compatibility information because saturation of one or more dissolving components can inhibit further reaction.

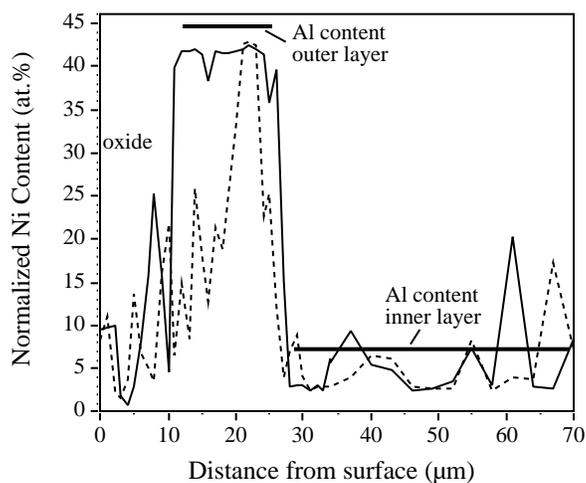


Figure 7. Nickel profiles from aluminized 316SS. The outer layer is rich in Ni and Al but in some regions (dashed line) this outer layer has been depleted.

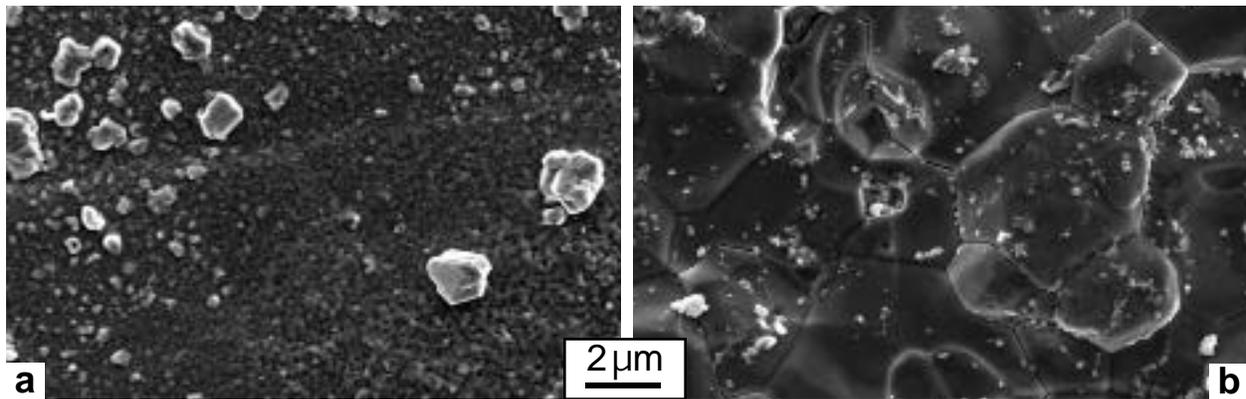


Figure 8. SEM secondary electron plan-view image of the oxide on ODS FeCrAl (a) after oxidation for 2h at 1000°C and (b) after oxidation and exposure to PbLi at 800°C.

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