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

A series of six Pb-Li capsule experiments were conducted at 700° and 800°C for 1,000h using commercial purity Pb-17Li. The use of commercial Pb-Li with a higher O content did not reduce the amount of dissolution observed for type 316 stainless steel (316SS) at 700°C. The amount of dissolution for Fe-9Cr-2W (T92) was similar to 316SS at this temperature. However, when an Al-rich diffusion coating was applied to T92, the specimen mass loss was greatly reduced. The aluminized T92 specimen as well as a FeCrAl specimen formed $LiAlO_2$ on the surface. Exposures of FeCrAl and NiAl specimens at 700° and 800°C, pre-oxidized to form α-Al_2O_3, confirmed the prior observation that alumina transforms to $LiAlO_2$ during exposure to PbLi.

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.[5,6] The use of Al-containing alloys and coatings has been studied as well as the transformation of α-Al_2O_3 to $LiAlO_2$.[7] Six capsule experiments were conducted to further study the behavior in Pb-Li and determine the effect of switching from high-purity Pb and Li to commercial purity Pb-17Li in the capsule.

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 capsules were loaded with 125g of commercial purity Pb-17Li in an argon-filled glove box. The difference between this Pb-Li and the higher purity Pb and Li used in prior work is mainly the interstitial elements: O, C and N, Table I. The specimens were ~1.5 mm thick and 4-5 cm^2 in surface area with a 0.3 µm surface finish. The alloy chemical compositions are given in Table 2. Two specimens were pre-oxidized in dry, flowing O_2 to form an external Al_2O_3 scale under conditions shown in Table 3. One

Table 1. Chemical composition using inductively coupled plasma and combustion analysis of the starting Pb and commercial Pb-Li ingot (in ppma except for Li in atomic%).

	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

Table 2. 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
T92 (9Cr-2W)	87.2	0.1	9.9	0.02	80	5120	2330	87	0.55W, 0.46Mn 0.30Mo,0.32Si
ODS FeCrAl	67.8	0.02	20.0	10.6	7430	340	210	50	0.44Ti,0.23Y 0.04Si, 0.04Mn
PM FeCrAl	65.2	0.1	21.3	9.7	1730	1320	1510	<	1.6Mo,1.1Si,0.15Y 0.07Hf,0.06Zr,0.02Ti
Ni-42.5Al+Hf	<	58.0	<	41.9	40	380	<	<	0.048Hf

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

specimen of T92 was aluminized using chemical vapor deposition (CVD) for 6h at 900°C in a laboratory scale reactor. The process details and resulting coating microstructure are provided elsewhere.[8] These conditions produce a thin ~40µm thick coating with a maximum surface Al content of ~18at.%. Specimen mass was measured before and after exposure on a Mettler-Toledo balance with an accuracy of ±0.04 mg. Exposures were performed in resistively heated box furnaces for 1000 h. To remove residual Pb-Li on the surface, 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).

Results and Discussion

Table 3 summarizes the mass change data for these capsule experiments. In Figure 1, the mass change results are compared to prior work.[5,6] The mass change for 316SS at 700°C was slightly higher in this exposure than in the previous exposure in high purity Pb-Li (-3.79 mg/cm^2). Therefore, the higher O content in the commercial Pb-Li did not have a beneficial effect on dissolution. While Ni is selectively

Table 3. 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
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
Ni-42.5Al+Hf	2h at 1200°C	800°C	- 0.51

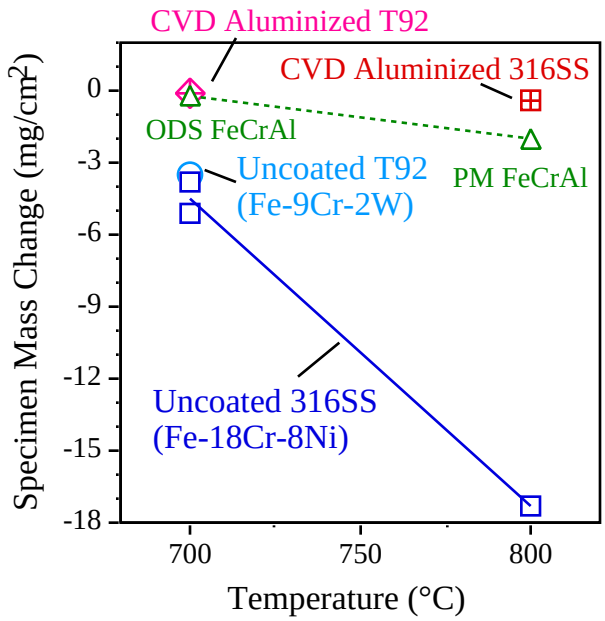

Figure 1. Specimen mass change as a function of exposure temperature in Pb-17Li for 1000h.

removed from stainless steel in Pb-Li, the mass loss for uncoated T92 (only 0.1%Ni) also was relatively high at 700°C. As expected, the thin Al-rich coating significantly reduced the mass loss for T92 at 700°C, similar to the previous results for ODS FeCrAl at 700°C and aluminized 316SS at 800°C, Figure 1.

Bare (i.e. no pre-oxidation) FeCrAl made by a powder metallurgy (PM) process (Kanthal alloy APMT) showed some mass loss at 800°C, higher than ODS FeCrAl (Plansee alloy PM2000) at 700°C. However, the mass loss was an order of magnitude less than the mass loss previously observed for uncoated 316SS at 800°C, Figure 1. The Al in PM FeCrAl formed a protective surface oxide that limited dissolution. As a result, this commercial tube alloy is a prime candidate for a metallic loop.

Finally, the pre-oxidized Hf-containing NiAl was exposed for two reasons. The first was to compare the result to NiAl without Hf that was exposed after a similar pre-oxidation.[5] The large mass loss for that specimen (-2.72 mg/cm^2) was attributed to poor adhesion of the pre-formed α-Al_2O_3 layer. The addition of Hf is known to improve alumina scale adhesion,[9] a similar effect as Y in the FeCrAl alloys, Table I. The lower mass loss for the Hf-containing NiAl specimen was attributed to better adhesion of the pre-formed alumina layer, however, as shown in Figure 2, the oxide was removed at the specimen edges after exposure. Dissolution of the metal where the oxide was removed likely explains the mass loss for this alloy. However, the pre-formed oxide layer did reduce the dissolution since this Ni-base material showed a lower mass loss than the Fe-base PM FeCrAl specimen, Table 3.

The second reason for the NiAl+Hf exposure was to confirm the earlier observation that pre-formed α-Al_2O_3 transforms to $LiAlO_2$ when exposed to Pb-Li.[7] All of the Al-containing specimens in this series were analyzed by XRD and all showed $LiAlO_2$ diffraction peaks and no α-Al_2O_3 peaks. This observation confirmed the earlier result for ODS FeCrAl at 800°C for a Ni-base alloy and on the same alloy at a lower temperature, 700°C. The surface oxide morphologies on ODS FeCrAl and NiAl+Hf before and after exposure are shown in Figure 3. Similar to the prior characterization,[6,7] the oxide grain size significantly increased due to the transformation on both specimens. The pre-formed oxide on NiAl+Hf showed the

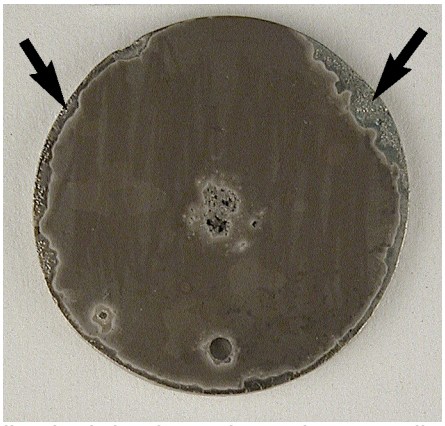

Figure 2. Photograph of pre-oxidized NiAl+Hf specimen (1.55cm diameter) after exposure to Pb-Li at 800°C for 1000h. The arrows show where the oxide was missing after exposure. There is a casting defect in the center of the disk and a hole at the bottom where the specimen was held with a Mo wire.

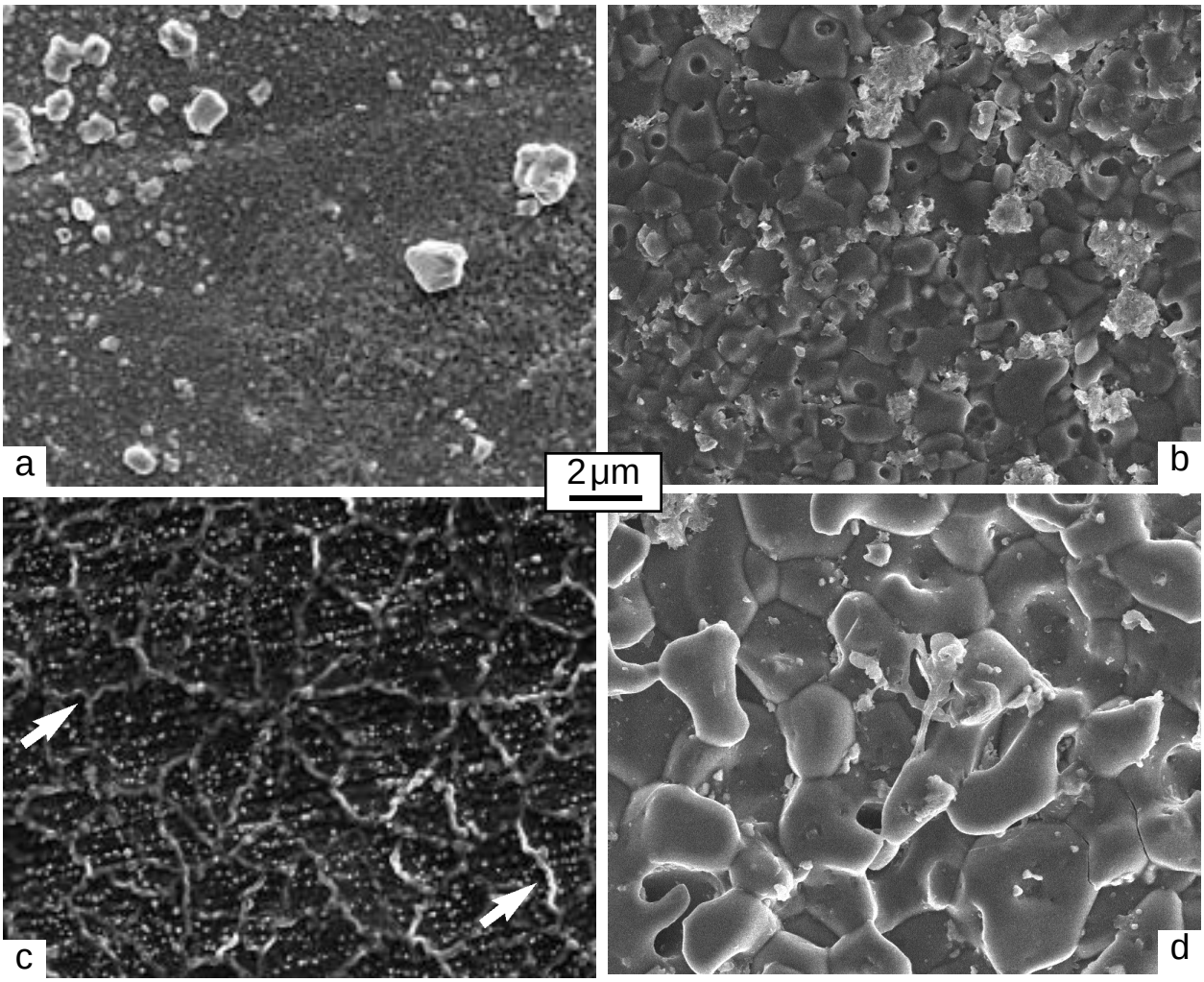

Figure 3. SEM plan view images of the reaction product before (a,c) and after (b,d) exposure to Pb-17Li at 700°C for 1,000h on ODS FeCrAl (a,b) and Hf-doped NiAl (c,d).

typical ridge structure (arrows in Figure 3c).[10] That structure was gone after exposure, Figure 3d. Further characterization of these specimens is in progress. After surface characterization is complete, the specimens will be metallographically sectioned to examine the oxide thickness, degree of alloy depletion and thickness of the coating layer.

To further study the effect of Pb-Li on oxides, the quartz ampoule that was filled with Pb-Li for exposure at 800°C is now being reexamined.[11] The quartz ampoule was used to determine if Si dissolved into Pb-Li as part of the evaluation of quartz as a potential loop material. Examining pieces of quartz by x-ray photoelectron spectroscopy (XPS) has indicated that a Li-Si-O likely formed on the surface and possibly Li carbonate. However, more work is needed to examine crystalline Li silicate standards in XPS to clarify which phases formed.

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