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

Two sets of capsules experiments exposed for 1000h at 500°-700°C were completed to determine the effect of various factors on the amount of dissolution in Pb-Li. The first set examined the effects of Al-rich coatings and the characterization has been completed. Thin coatings exposed at 700°C showed significant Al loss with different variations: (1) pre-oxidation, (2) O gettering and (3) exposure in pure Pb without Li. Less Al loss was observed after exposure at 600°C. A second series of capsules were recently completed that explored the effect of Fe and Ni impurities on the dissolution rate and dissimilar metal reactions between Fe and SiC at 600°C. Based on only the mass gain data, there is some indication of a dissimilar metal effect in Pb-Li.

PROGRESS AND STATUS

Introduction

The current focus of the U.S.fusion energy materials program is to address issues associated with the dual coolant Pb-Li (DCLL) blanket concept[1] for a test blanket module (TBM) for ITER and enhanced concepts for a DEMO-type fusion reactor. A DCLL blanket 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). Thus, recent U.S. compatibility research has examined compatibility issues with Pb-Li.[2-6] Unlike Li, where many materials (especially oxides) are dissolved or degraded,[7] a wider range of materials are compatible with Pb-Li because of the low Li activity in eutectic Pb-Li.[8] For example, SiC is readily dissolved by Li[9] but not Pb-Li.[3,4] However, because of higher solubilities, Pb-Li readily dissolves many conventional alloys above 500°C. This is not a concern for a DCLL TBM operating at <500°C, however, a DCLL blanket for a commercial reactor would be more attractive with a higher maximum operating temperature, perhaps >600°C if oxide dispersion strengthened (ODS) ferritic steels[10] were used. Even at 550°C, a recent study of Eurofer 97 (Fe-Cr-W) showed a very high mass transfer rate in flowing Pb-Li.[11] Therefore, preliminary Pb-Li compatibility experiments are being conducted at 500°-800°C in order to investigate several concepts before flowing tests are conducted. Two sets of capsule experiments have been completed to investigate (1) the effectiveness of Al-rich coatings to inhibit dissolution, (2) the effect of Fe and Ni impurities on the amount of dissolution and (3) potential dissimilar material effects between Fe and SiC. Characterization has been completed from the first set but only mass change data is available for the second set of capsules.

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. For the dissimilar material experiments, the Mo inner capsule was replaced by a carbon steel capsule or

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

	Li	Fe	Cr	Ni	Mn	Si	Al	Mo	C	O	N	S
Pb	n.d.	<4	<4	<4	<4	<40	<8	<2	<170	1270	<40	<50
PbLi (UCLA)	14.3%	<30	<70	<30	<30	<120	<60	<40	750	4820	180	<50
PbLi (Atlantic)	19.8%	21	<3	<3	<3	18	<6	<2	2510	4730	<12	<100
PbLi (Atlantic)	21.0%	165	<3	<3	<3	17	<6	<2	2760	14460	<12	<100

a CVD SiC container was included inside the Mo capsule. The specimens were ~1.5 mm thick and 4-5 cm^2 in surface area with a 0.3 μm surface finish. Specimens were aluminized in a laboratory scale chemical vapor deposition (CVD) reactor for 6h at 900°C. Chemical and microstructural details of the coating formed under these conditions are given elsewhere.[12] Pre-oxidations were conducted in dry flowing O_2 for 2h at 800° or 1000°C. The Mo and Fe capsules were loaded with 125g of commercial purity Pb-Li in an argon-filled glove box. The Pb-Li used in these experiments was from a different batch (from Atlantic Metals) than the previous batch (received from UCLA) and the chemistry from two different locations is shown in Table I. There was a distinctly higher Li content in the new batch of Pb-Li. In one capsule, only high purity Pb was added, composition in Table I. Additions to the Pb-Li were made as metal powder during loading. After exposure, residual Pb-Li on the specimen surface was removed by soaking 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 2 summarizes the mass change data from the first series of capsules. Several prior runs are included for comparison noting that a different Pb-Li batch was used for those experiments. Figure 1 summarizes the effect of Al (either as a coating or alloy addition) on the mass loss as a function of capsule temperature from this study and prior work[3-6]. Clearly the presence of Al retards dissolution. However, one concern about the relatively thin CVD coatings is the limited Al reservoir in the coating and the significant Al loss from the coating after only 1kh at 700°C.[13] The four capsule exposures of aluminized T92 specimens were conducted to investigate this loss of Al. Figure 2 shows the specimen exposed at

Table 2. Mass change of specimens after 1000h exposures with a Mo capsule.

Specimen	Pre-oxidation	Temperature	Environment	Mass Change (mg/cm^2)
T92	none	600°C	Pb-Li (Atlantic)	- 1.27
T92 + CVD Al	none	600°C	Pb-Li (Atlantic)	- 0.04
*T92	none	700°C	Pb-Li (UCLA)	- 3.47
*T92 + CVD Al	none	700°C	Pb-Li (UCLA)	- 0.09
T92 + CVD Al	2h at 800°C	700°C	Pb-Li (Atlantic)	0.00
T92 + CVD Al	none	700°C	Pb-Li + 0.18%Zr	0.53
T92 + CVD Al	none	700°C	Pb	0.00
ODS FeCrAl	2h at 1000°C	500°C	Pb-Li (Atlantic)	- 0.11
*ODS FeCrAl	2h at 1000°C	700°C	Pb-Li (UCLA)	- 0.06

* Prior work with different Pb-Li chemistry

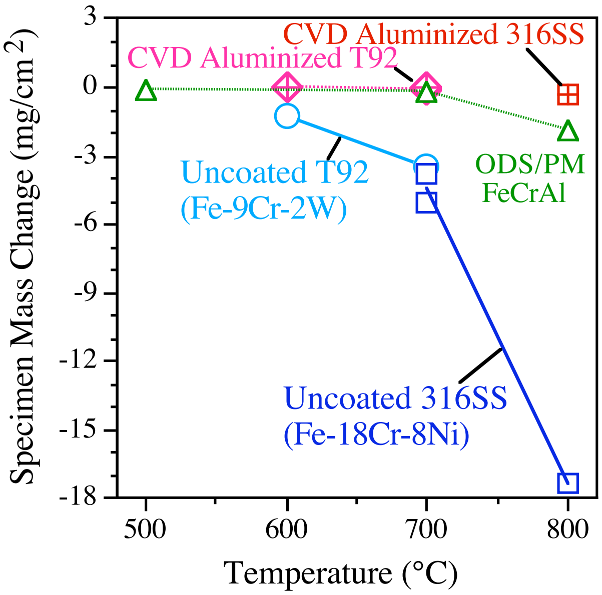

Figure 1. Specimen mass loss as a function of exposure temperature in Pb-Li for 1kh in Mo capsules. Alumina-forming alloys or coatings have much lower mass gains than conventional Fe-base alloys.

600°C. A relatively uniform oxide product was formed. Using XRD, the layer was identified as $LiAlO_2$. Based on the Al profiles in Figure 2b, very little Al was lost during this exposure, likely due to the lower temperature and limited interdiffusion at this temperature.[14]

Figures 3-5 show aluminized T92 specimens under various conditions at 700°C. One hypothesis about the Al loss was that the bare coating rapidly lost Al to the liquid metal before a protective oxide layer was

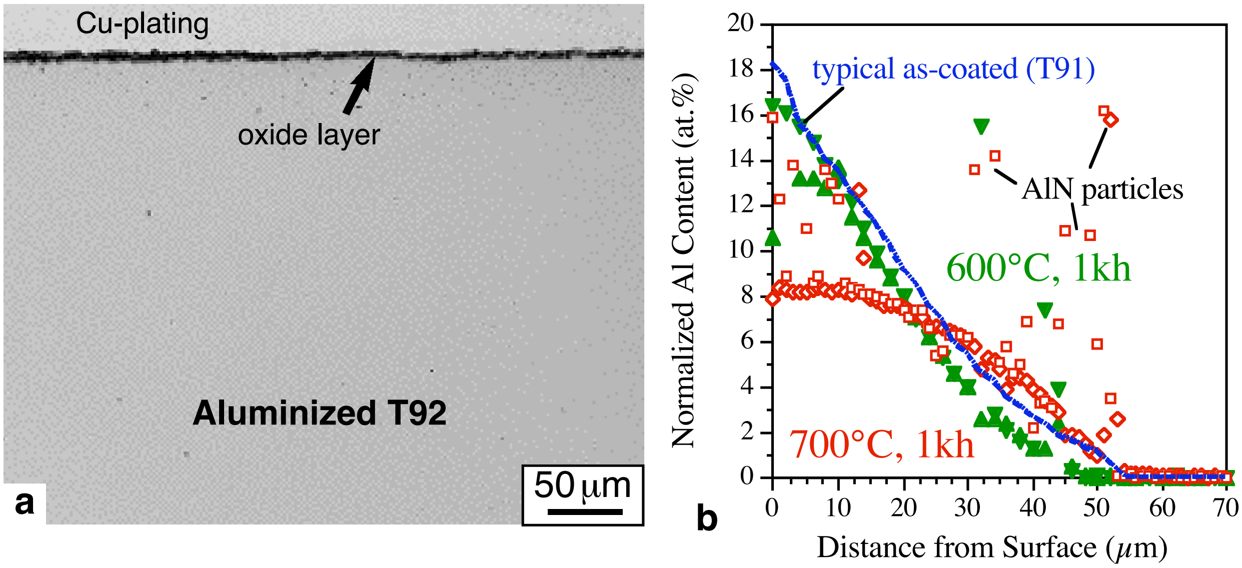

Figure 2. (a) Light microscopy of aluminized T92 polished cross-section after 1kh at 600°C in commercial Pb-Li (b) EPMA composition profiles comparing a typical as-coated Al profile to the Al profile after exposure at 700°C and 600°C.

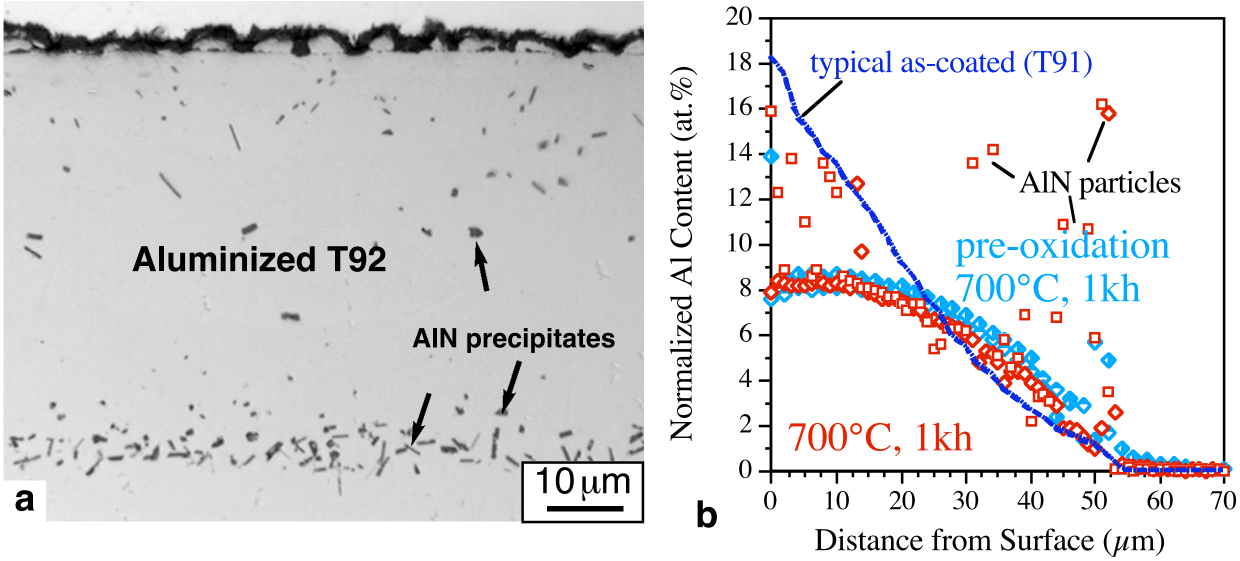

Figure 3. (a) Light microscopy of aluminized and pre-oxidized T92 polished cross-section after 1kh at 700°C in commercial Pb-Li (b) EPMA composition profiles comparing a typical as-coated Al profile to the Al profile after exposure at 700°C with and without pre-oxidation.

formed. Figure 3 shows results for the aluminized T92 specimen that was pre-oxidized for 2h at 800°C prior to exposure. The oxide was also identified by very distinct $LiAlO_2$ XRD peaks, consistent with prior results for pre-oxidized ODS FeCrAl at 700° and 800°C.[5,6] No penetrations of the coating were observed and no mass loss was detected, Table 2, suggesting the pre-oxidized coating was more protective. However, a similar Al depletion was observed as occurred without pre-oxidation, Figure 3b. Some Al was consumed during pre-oxidation but the amount of loss is higher than would be expected from

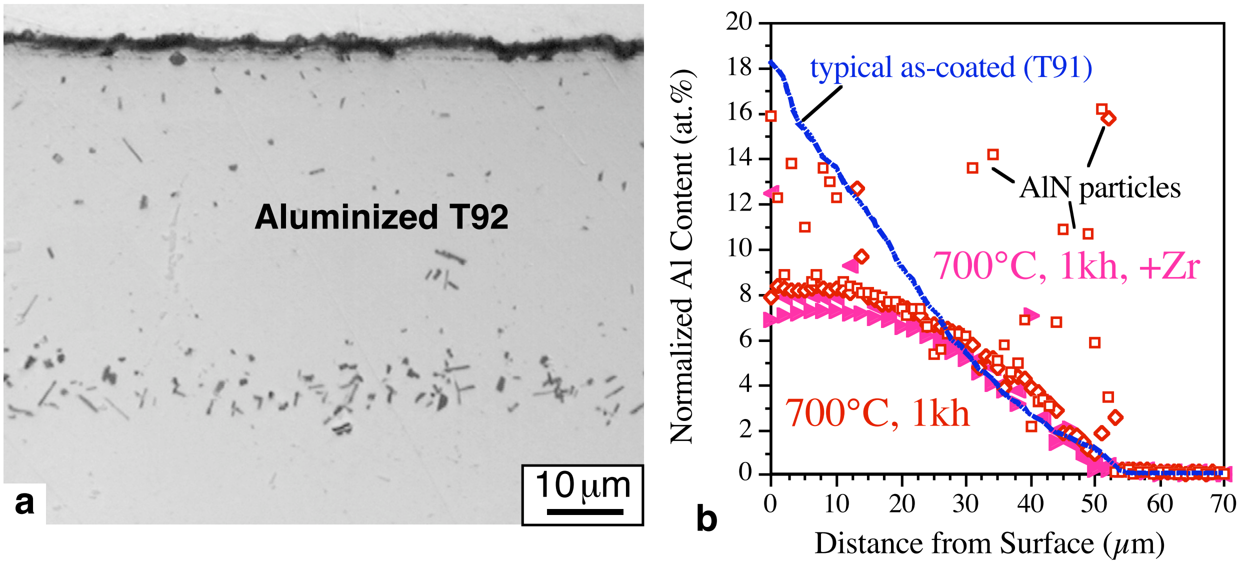

Figure 4. (a) Light microscopy of aluminized T92 polished cross-section after 1kh at 700°C in commercial Pb-Li + Zr (b) EPMA composition profiles comparing a typical as-coated Al profile to the Al profile after exposure at 700°C with and without a Zr addition.

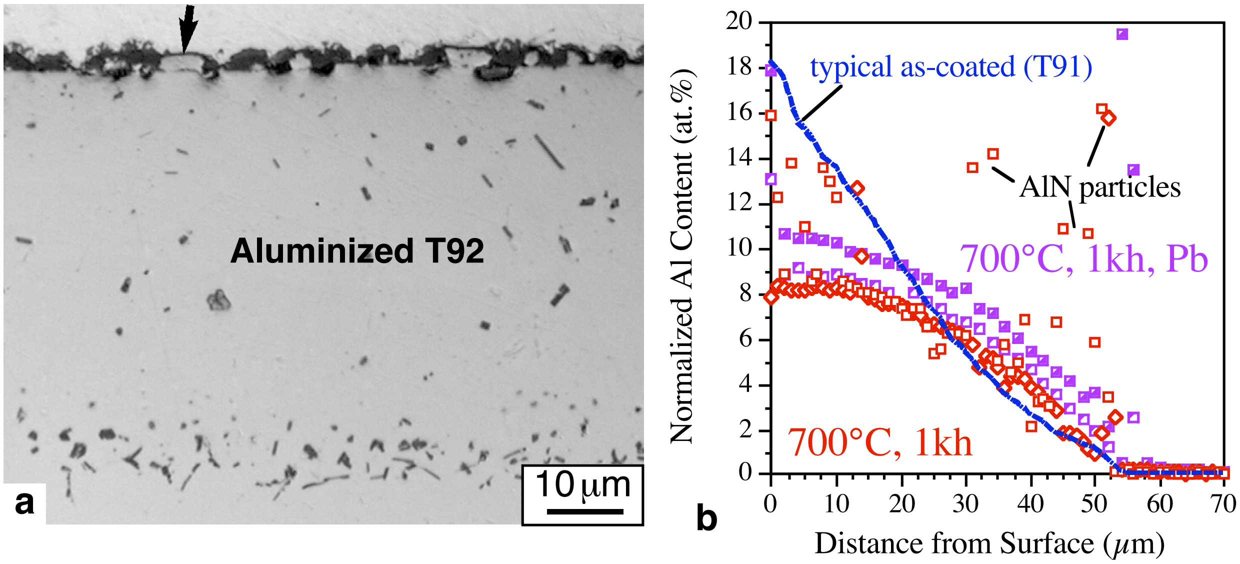

Figure 5. (a) Light microscopy of aluminized T92 polished cross-section after 1kh at 700°C in high purity Pb (b) EPMA composition profiles comparing a typical as-coated Al profile to the Al profile after exposure to Pb and Pb-Li at 700°C. Arrow in (a) shows thin oxide where spallation may have occurred.

the pre-oxidation step. Figure 4 shows the results from the capsule test where 1g of Zr was added to getter O in the Pb-Li. Gettering O could potentially increase the time to form a protective oxide layer. The cross-section appears very similar as Figure 3, the oxide formed was $LiAlO_2$ and the Al loss was slightly higher than the profile without Zr. Finally, Figure 5 shows the aluminized T92 specimen exposed to high purity Pb. The polished corss-section appears similar to the others. However, the outer layer appears rougher and some oxide spallation was evident in SEM examination of the specimen in plan view. The arrow in Figure 5a indicates an area where the oxide is thinner and may have spalled. Without Li present, the oxide was not $LiAlO_2$ but also was not clearly α-Al_2O_3 by XRD. Further characterization is needed of the mixed oxide from this specimen.

The final specimen from this series was pre-oxidized ODS FeCrAl exposed at 500°C. Prior work had shown that the α-Al_2O_3 layer formed after 2h at 1000°C transformed to $LiAlO_2$ after exposure to Pb-Li at 700° or 800°C.[5,6] However, after 1kh at 500°C, $LiAlO_2$ peaks were not evident. Figure 6 shows the uniform oxide product. Additional TEM characterization is needed to identify the oxide phases and microstructure after this exposure.

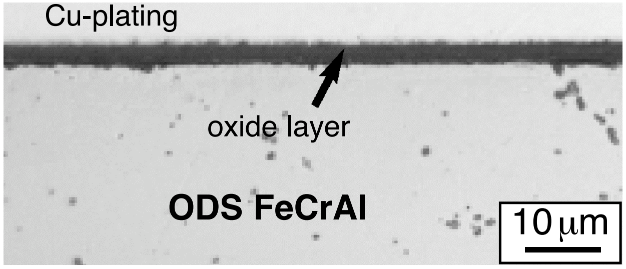

Figure 6. Light microscopy of pre-oxidized ODS FeCrAl (PM2000) polished cross-section after 1kh at 500°C in commercial Pb-Li.

Table 3. Mass change of specimens in second series after 1000h exposures in Pb-17Li

Specimen	Capsule	Temperature	Addition	Mass Change (mg/cm^2)
*316SS	Mo	700°C	none (UCLA)	- 5.06
316SS	Mo	700°C	1000ppma Fe	-11.89
316SS	Mo	700°C	1000ppma Ni	- 9.60
*T92	Mo	700°C	Pb-Li (UCLA)	- 3.47
T92	Mo	700°C	1000ppma Fe	- 6.02
T92	Mo	700°C	1000ppma Ni	- 6.41
CVD SiC	Fe	600°C	none (Atlantic)	- 0.04
Fe	SiC	600°C	none (Atlantic)	- 0.18
Fe	Mo	600°C	none (Atlantic)	- 0.47

* Prior work with different Pb-Li chemistry

A second series of capsules were recently completed and the mass change data after exposure is shown in Table 3. Additions of Fe and Ni were added to simulate Pb-Li contaminated by Fe from dissolution or Ni from stainless steel. The effect of Ni on T92 was investigated for the case of the stainless steel loop described in Ref. 11 which plugged at 550°C. Unfortunately, the change in Pb-Li source (Table 1) appears to have had a significant effect on the mass loss so the baseline Pb-Li exposures for T92 and 316SS without the Fe or Ni addition at 700°C is not a reliable baseline for comparison. Figure 7a summarizes the mass loss data for these exposures. In each case, the dissolution was higher for 316SS compared to T92. Compared to the Fe addition, the Ni addition reduced the mass loss for 316SS, which is expected since Ni is selectively removed from 316SS. By increasing Ni in the Pb-Li, the liquid is closer to saturation which should decrease the amount of mass loss. In contrast, the Ni addition had little effect on the mass loss for T92. Figure 7b summarizes the dissimilar material experiments conducted at 600°C. The 0.04mg/cm^2 mass loss for SiC was higher than observed at 1000°-1200°C using SiC capsules.[3,4] Further

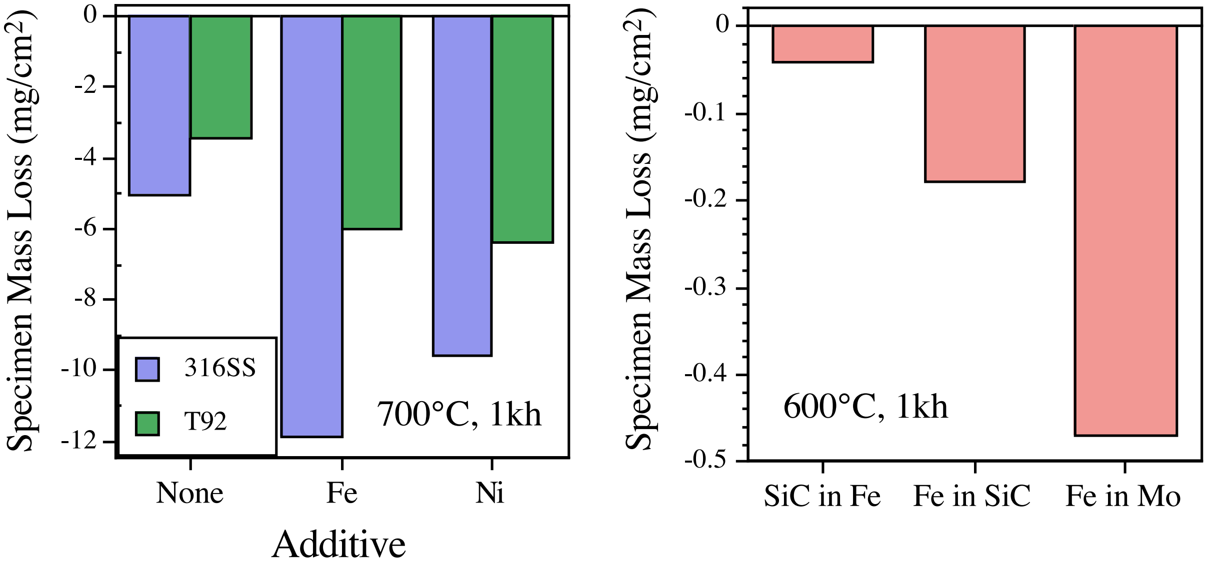

Figure 7. Mass loss results from the second series of capsule experiments exposed for 1kh in Pb-Li, (a) the effect of Fe and Ni additions on the mass loss of 316SS and T92 at 700°C and (b) the dissimilar material effect between Fe and SiC at 600°C.

characterization is needed to determine the extent and uniformity of attack. The mass loss also could be due to the new Pb-Li source, perhaps due to the higher Li content of this Pb-Li, Table 1. For the Fe specimens, the mass loss was lower in the SiC capsule compared to the Mo capsule. A potential C transfer could have occurred in both Fe/SiC capsules because of the higher stability of Fe carbides compared to SiC. Characterization of the Fe specimen should determine if any C transfer occurred.

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] B. A. Pint J. L. Moser and P. F. Tortorelli, Fus. Eng. Des. 81 (2006) 901.
[3] B. A. Pint, J. L. Moser and P. F. Tortorelli, J. Nucl. Mater. 367-370 (2007) 1150.
[4] B. A. Pint, Fus. Sci. Tech. 52 (2007) 829.
[5] B. A. Pint and K. L. More, J. Nucl. Mater. 376 (2008) 108.
[6] B. A. Pint, Mater. Sci. Forum, 595-598 (2008) 549.
[7] J. E. Battles, Intern. Mater. Rev. 34 (1989) 1.
[8] P. Hubberstey, J. Nucl. Mater. 247 (1997) 208.
[9] T. Yoneoka, S. Tanaka and T. Terai, Mater. Trans. 42 (2001) 1019.
[10] S. Ukai and M. Fujiwara, J. Nucl. Mater. 307 (2002) 749.
[11] J. Konys, W. Krauss, J. Novotny, H. Steiner, Z. Voss and O. Wedemeyer, J. Nucl. Mater. 386-88 (2009) 678.
[12] Y. Zhang, B. A. Pint, K. M. Cooley and J. A. Haynes, Surf. Coat. Tech. 202 (2008) 3839.
[13] B. A. Pint, DOE/ER-0313/45 (2008) 61.
[14] Y. Zhang, A. P. Liu and B. A. Pint, Mater. Corr. 58 (2007) 751.