COMPATIBILITY OF MATERIALS EXPOSED TO ISOTHERMAL Pb-Li – B. A. Pint and K. A. Unocic (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

The specimens from a recent set of capsule experiments are being characterized. The experiments examined the effect of Fe and Ni impurities on the 700°C dissolution of type 316 stainless steel (316SS) and Fe-9Cr-2W (T92) in Pb-Li. The addition of 1000 ppma Fe or Ni did not appear to significantly change the amount of dissolution or the surface morphology. Also, a series of capsule exposures at 600°C examined possible dissimilar material reactions between Fe and SiC. Based on surface analysis of the capsules, no Fe or Si was transferred. Future characterization will focus on C transfer. A new series of experiments planned for 500-700°C will clarify any dissimilar material interaction in this system.

PROGRESS AND STATUS

Introduction

A 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.[2-7] Compared to Li,[8] a wider range of materials can be compatible with Pb-Li because of the low activity of Li.[9] In particular, SiC readily dissolves in Li, but not Pb-17Li.[3,4,10] However, because of higher Ni and Fe 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[11] were used. Even at 550°C, a recent study of Eurofer 97 (Fe-Cr-W) showed a very high dissolution rate in flowing Pb-Li.[12] Therefore, preliminary Pb-Li compatibility capsule experiments are being conducted at 500°-700°C in order to investigate several concepts before flowing Pb-Li compatibility tests are conducted. Recent capsule experiments have investigated (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 of the first set of coated specimens was presented in the previous report.[13] The initial characterization results from the second set of capsules that addressed the second and third topics is reported here.

Experimental Procedure

Static capsule tests were performed using Mo, carbon steel or SiC inner capsules and type 304 stainless steel outer capsules to protect the inner capsule from oxidation. Because the SiC capsule could not be welded shut, an additional Mo capsule was used in that case. For the steel and Mo capsules, 1 mm diameter Mo wire was used to hold the specimens. For the SiC capsule, a SiC spacer held the specimen at the bottom of the capsule. The specimens were ~1.5 mm thick and 4-5 cm^2 in surface area with a 600

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

grit surface finish. The Fe specimen was unalloyed and the SiC specimen was high-purity from Rohm & Haas and made by chemical vapor deposition. The Mo and Fe capsules were loaded with 125 g 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. Additions of Fe or Ni powder were made during loading. The capsules were welded shut in a glove box to prevent the uptake of impurities during exposure. 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 specimen surfaces were examined using x-ray diffraction (XRD) and secondary electron microscopy (SEM) equipped with energy dispersive x-ray (EDX) analysis. Specimen and capsule surfaces were examined by x-ray photoelectron spectroscopy (XPS). After surface characterization, the specimens were metallographically sectioned and polished and examined by light microscopy.

Results and Discussion

Table 2 summarizes the mass change data from the second capsule series as reported previously.[13] Prior runs using a different batch of Pb-Li are included for comparison. Additions of Fe and Ni were made to simulate Pb-Li contaminated by Fe or Ni from dissolution. The behavior of T92 was examined because in the reported 550°C loop data,[12] the loop is partially made of stainless steel and therefore the Pb-Li in the loop should contain some Ni. However, capsule experiments use nominally uncontaminated Pb-Li. Even a monometallic martensitic steel loop would become saturated with Fe and Cr during operation. The results also are plotted in Figure 1a. Unfortunately, the baseline Pb-Li exposures for T92 and 316SS without a Fe or Ni addition at 700°C (Table 2) was conducted with a different Pb-Li source (Table 1). The

Table 2. Mass change of specimens in second series after 1000h exposures in Pb-Li

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

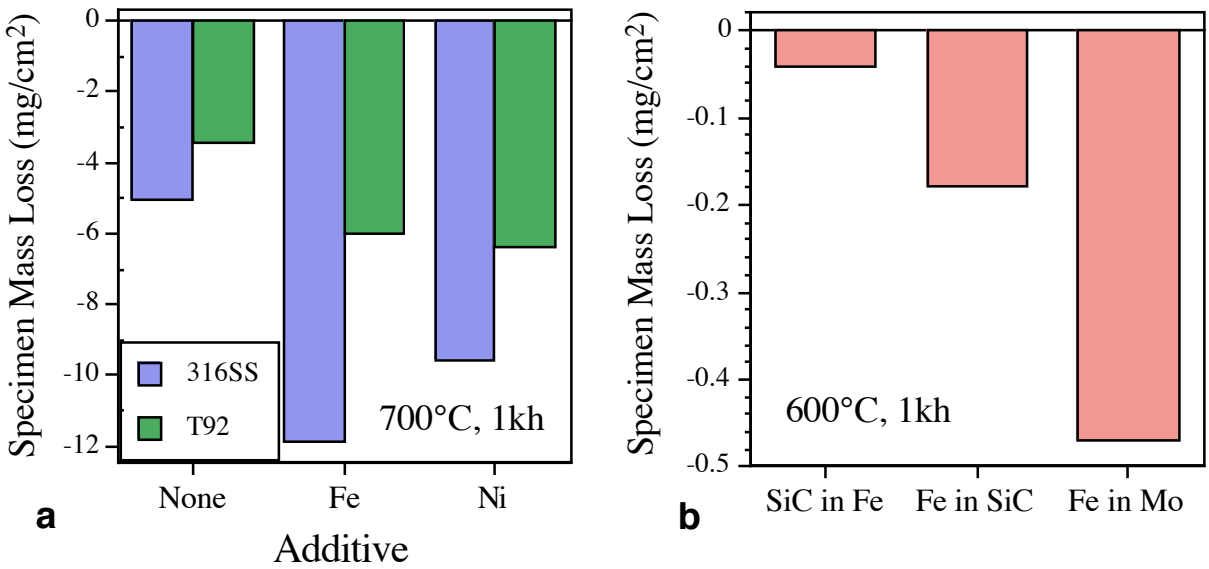

Figure 1. Mass loss results from the second series of capsule experiments.(a) the effect of Fe and Ni additions on the mass lass after 1kh at 700°C and (b) the dissimilar material effect between SiC and Fe after 1kh at 600°C.

difference in Pb-Li chemistry appears to have significantly affected the mass loss and a reliable comparison is not possible with the current data set. Generally, the dissolution was higher for 316SS compared to T92, as expected. Compared to the Fe addition, the Ni addition slightly 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 dissolution. In contrast, the Ni addition had little effect on the mass loss for T92.

Figure 2 shows examples of the surface morphologies of 316SS and T92 after exposure to Pb-Li. On the 316SS surface, remnants of a Mo-rich phase in the steel could be observed, Figure 2a. No difference in surface morphology was noted between the Fe and Ni additions. Figure 2b shows the morphology of the T92 specimen exposed with additional Fe in the Pb-Li. Some areas were observed to have relatively little dissolution, which is likely due to the inhibiting affect of the native oxide on the specimens.[12] The T92 specimen exposed with a Ni addition had a similar surface morphology. Figures 3 and 4 show cross-sections of the T92 and 316SS specimens, respectively. Again, little difference was noted between the Fe and Ni additions. In Figure 4, the Ni-depleted ferritic surface layer can be observed and is similar in depth in both specimens. The ferritic layer also was detected by XRD. The amount of depletion in each case will be quantified using electron microprobe analysis (EPMA).

Figure 1b summarizes the dissimilar material experiments conducted at 600°C. The 0.04 mg/cm^2 mass loss for SiC was higher than observed at 1000°-1200°C using SiC capsules.[3,4] A small amount of residual Li and C contamination was found on the SiC specimen surface by XPS but otherwise no significant degradation was apparent after exposure. The difference in mass loss compared to prior work at higher temperatures could be due to the higher Li content in this experiment, 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 between the SiC capsule wall and the Fe specimen. No transfer would be expected in the Mo capsule, where only Fe dissolution is expected. A similar transfer could have occurred between the SiC specimen and the mild steel capsule wall in the first experiment resulting in a

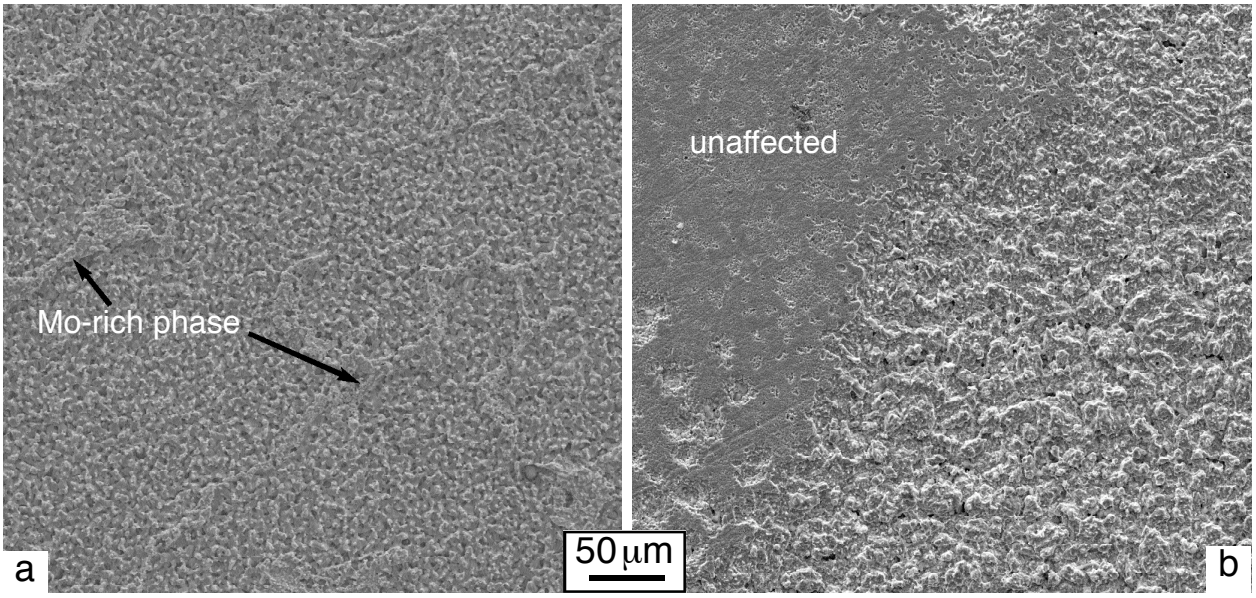

Figure 2. SEM plan view images of the surface of specimens after exposure to Pb-Li at 700°C for 1,000h (a) 316SS with 1000 ppma Ni addition and (b) T92 with 1000 ppma Fe addition.

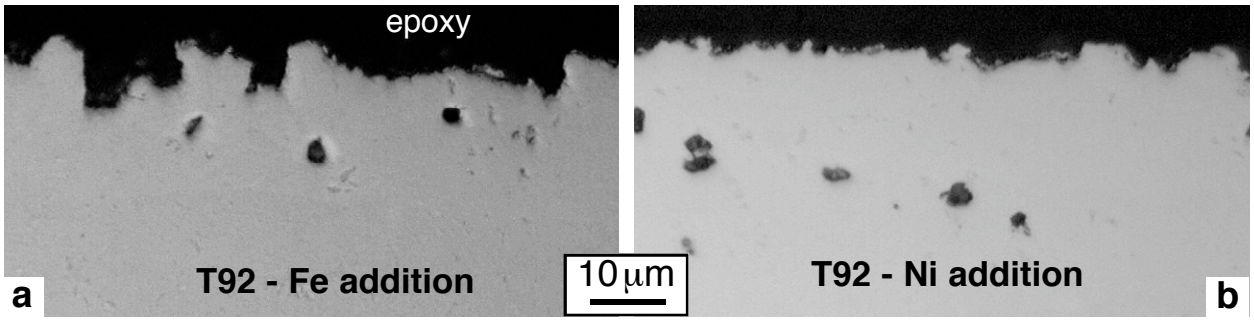

Figure 3. Light microscopy of polished cross-section of T92 after 1000h at 700°C (a) Pb-Li with 1000ppma Fe addition and (b) Pb-Li with 1000ppma Ni addition.

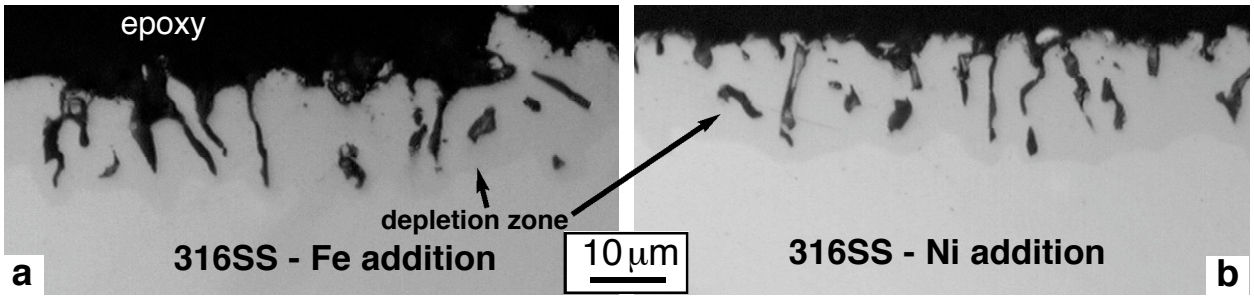

Figure 4. Light microscopy of polished cross-section of type 316 stainless steel after 1000h at 700°C (a) Pb-Li with 1000ppma Fe addition and (b) Pb-Li with 1000ppma Ni addition.

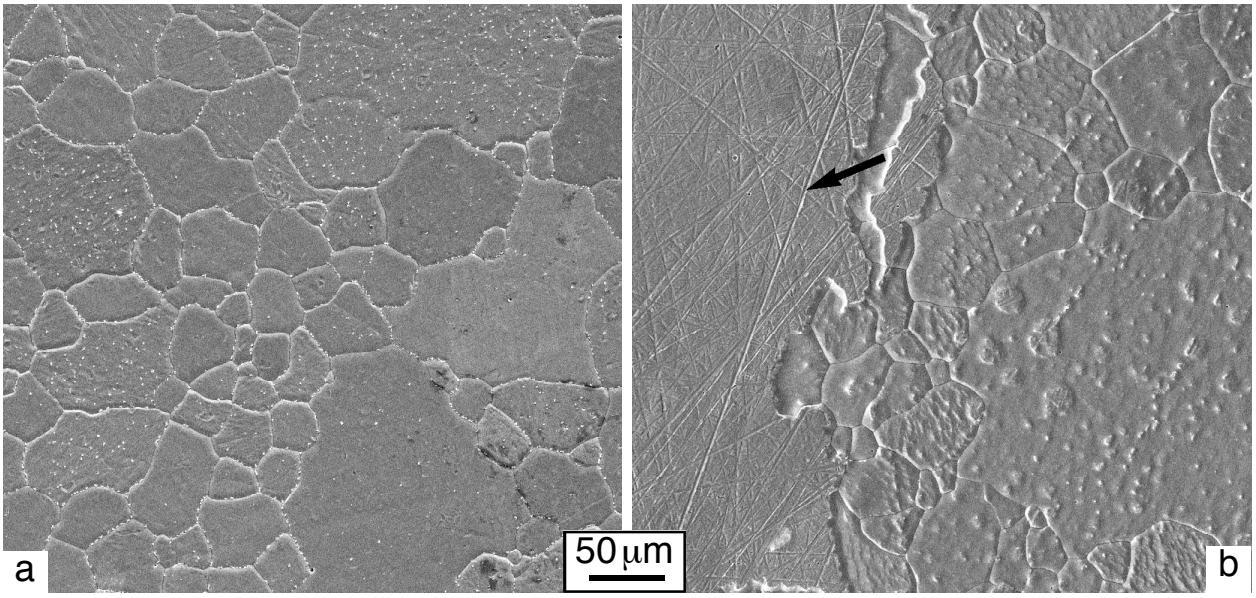

Figure 5. SEM plan view images of the surface of Fe specimens after exposure to Pb-Li at 600°C for 1,000h (a) SiC capsule and (b) Mo capsule.

mass loss. Figure 5 shows the surface of the Fe specimens in each experiment. The grain boundaries in the specimen are highlighted because they were selectively attacked, creating a groove (Fig. 6a) with faceting (arrow in Fig. 6a) seen at high temperature. The small bright particles seen in Figure 5 and 6a

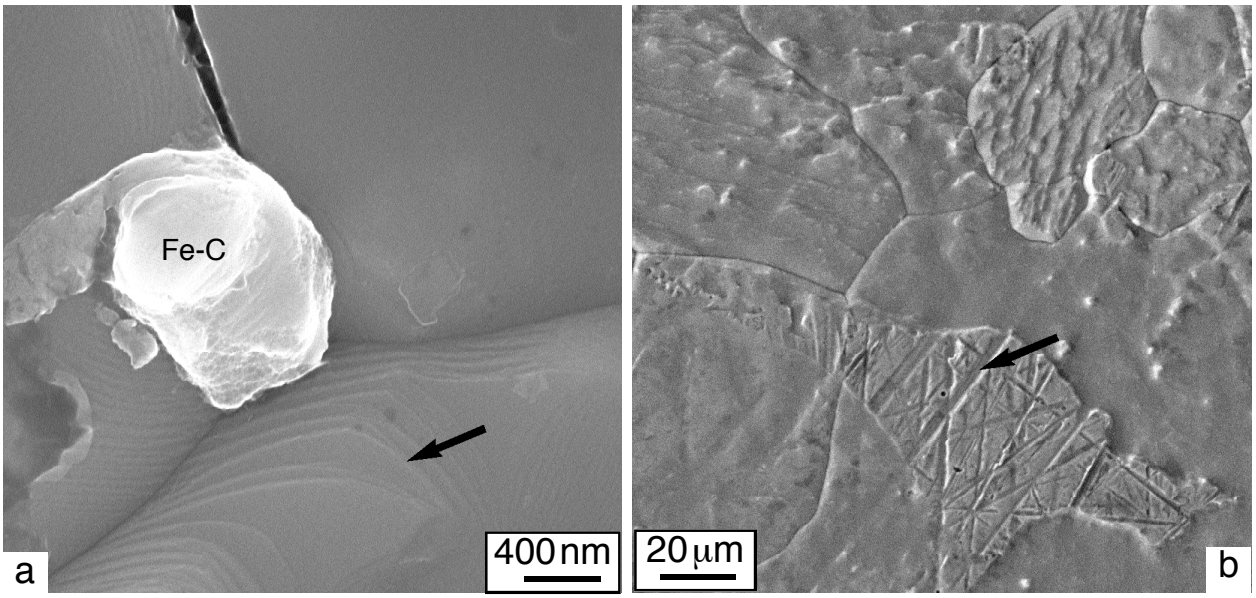

Figure 6. SEM plan view images of the surface of Fe specimens after exposure to Pb-Li at 600°C for 1,000h (a) SiC capsule, showing Fe-C particle and faceting at a triple point and (b) Mo capsule, where the arrow marks a grain with unusual features, also seen in Figure 5b at lower magnification.

had a C peak using EDX analysis. However, they could not be conclusively identified and were found for both types of capsule. For the specimen exposed in the Mo capsule, some grains appear to have scratches on them. However, at higher magnification, there may be some orientation related phase formation, arrows in Figures 5b and 6b. Cross-section of these specimens showed little difference with no obvious phase formation (e.g. carbides) or degradation. More surface characterization is needed for these specimens to further understand these surface features.

The steel and SiC capsules also were examined by XPS after exposure. There was no indication of Fe deposition on the SiC capsule or Si deposition on the mild steel capsule. Therefore, if mass transfer is occurring in this system, C is the primary element of interest and further characterization will focus on determining any difference in C content in the Fe specimens.

Based on the results of these dissimilar material experiments, a more complete test matrix will be conducted at 500°-700°C with Fe and SiC specimens and SiC and mild steel capsules. The results from these capsule experiments should more conclusively determine if any mass transfer is occurring in this system and the effect of temperature on the mass transfer.

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