

COMPATIBILITY ISSUES FOR Pb-Li SYSTEMS – B. A. Pint, P. F. Tortorelli, and J. L. Moser (Oak Ridge National Laboratory)

OBJECTIVE

The objective of this task is to assess the long-term, high-temperature compatibility of various materials with Pb-Li. One proposed fusion reactor concept uses SiC/SiC composites with a self-cooled Pb-17Li blanket. Another concept uses a SiC/SiC flow channel insert with a dual coolant of He and Pb-Li at ~800°C. This concept also requires tubing material to carry the Pb-Li between the first wall and the heat exchanger. As a first step in the evaluation process, monolithic SiC and potential tubing and coating materials are being exposed to Pb-17Li in capsule tests at 700°-1200°C.

SUMMARY

Several long-term capsule tests with high-purity SiC specimens have recently been completed. The specimen mass showed little change after various times at 800°, 1100° and 1200°C. After 2,000h at 1100°C, a low level of Si was detected in the Pb-17Li after the test. A number of Al-containing alloys were screened for 1000h at 700°C in PbLi in order to confirm the role of Al in protecting Fe- or Ni-base alloys against dissolution. The dissolution rates for 316SS were significantly higher than those for the Al-containing alloys, including Ni-42.5at.%Al, which showed the lowest mass loss in the test.

PROGRESS AND STATUS

Introduction

Among the proposed fusion reactor concepts, silicon carbide composites are a structural material option that is thought to allow the highest reactor operating temperature (1000°-1100°C) and thus the highest operating efficiency.[1,2] Both the TAURO and ARIES-AT proposals have Pb-17at.%Li self-cooled blankets which are attractive because the Pb-17Li acts as coolant, neutron multiplier and tritium breeder.[3] (The eutectic Pb-Li composition was chosen because it has a low melting point of 235°C.) Another concept uses SiC/SiC composite flow channel inserts with a dual coolant blanket based on ARIES-ST.[4] The insert serves as an electrical and thermal insulator between Pb-Li at 800°C and He-cooled ferritic steels. This concept also requires corrosion resistant tubing to carry the Pb-Li between the first wall and the heat exchanger. Contact of Fe-base, or particularly Ni-base, alloys with flowing Pb-Li at this temperature would result in unacceptably high dissolution rates[5-7]. While refractory metals are one option to transport Pb-Li outside the first wall[8], fabrication and durability of Nb or Mo tubing could be an issue. An alternative is to consider corrosion resistant coatings for conventional Fe- or Ni-base alloys that would have sufficient strength to operate at 700°C. Since the activity of Li in Pb-17Li is greatly reduced (1.2×10^{-4} at 500°C)[9], both thermodynamic calculations[10] and experimental results[11] suggest that aluminide coatings (or Al containing alloys) could be protective, but little experimental work has been performed above 450°-600°C. Present assessments of the materials feasibility for both of these strategies are incomplete because there is little information available on the high temperature compatibility with Pb-Li at temperatures of 700°C and higher.

To complement prior work on SiC,[12-14] an initial series of static Pb-17Li capsule tests were performed on high-purity (99.9995%) chemical vapor deposited (CVD) -SiC specimens and the experimental procedure and results are detailed elsewhere.[15,16] (These experiments used monolithic SiC specimens instead of composites as a first step towards evaluating SiC compatibility to avoid the microstructural and microchemistry complexities of composites) To avoid unwanted reactions of the capsule with Pb-Li, the SiC specimens were contained in CVD SiC capsules. After 1000h at 800°C, no wetting was observed between Pb-Li and SiC and therefore no chemical attack would be expected. At 1100°C, there was

evidence of only limited wetting after 1000h. After cleaning the specimens, no mass change was measurable at either temperature suggesting that SiC is compatible with static Pb-17Li to at least 1100°C. In both cases, no Si was detected in the Pb-Li after the test.[17] To follow up on these results, longer experiments were initiated at 800° and 1100°C and a 1000h test was conducted at 1200°C. Capsule tests also were initiated at 700°C to evaluate the role of Al in protecting Fe- and Ni-base alloys.

Results

CVD SiC Specimens. Three new capsule experiments with CVD SiC inner capsules and specimens have recently been completed. After the capsule was opened, the specimens were cleaned with a mixture of acetic acid, hydrogen peroxide and ethanol for 24-72h. The mass changes for these experiments are shown in Table 1 along with the results from the prior experiments. In most cases, the slight mass gains and losses are not statistically significant. The exception is the mass gain for the specimen after 5,000h at 800°C. This specimen will be examined more carefully for possible penetrations or surface reactions. (For the previous two specimens (1000h at 800° and 1100°C), only a layer of C and some residual native oxide was detected by Auger electron spectroscopy. Small amounts of Pb and Li were detected on the specimen surfaces using x-ray photoelectron spectroscopy (XPS).) At the higher temperatures, more wetting of the Pb-Li was observed, as expected. The breakdown of a native SiO₂ surface layer at longer times and higher temperatures may be responsible. Prior work indicated that extended incubation periods were needed to develop wetting between stainless steel and mercury.[18]

At present, only the Pb-Li from the 2,000h/1100°C capsule has been analyzed and these results are shown in Table 2 along with the prior results. (The variation in Li may be an experimental error. It is magnified by the conversion from mass%.) For the most recent experiment, 185ppma Si was detected in the Pb-Li. This is still significantly less Si than was detected by microprobe analysis (350ppmw) after an 800°C exposure by Kleykamp.[13] However, the C content did not increase compared to the shorter test. The other major impurities detected were O and N with low levels of some metals, Table 2. These results suggest that monolithic, high-purity SiC is compatible with Pb-17Li to at least 1200°C in a static environment. More interaction may be expected with SiC-base fibers or the fiber-matrix interface. However, it is anticipated that a dense CVD SiC seal coat will cover the outer layer of any SiC composite components. To study the compatibility of SiC/SiC composites, specimens were recently fabricated by B. Riccardi (ENEA, Italy) and sent to ORNL for capsule exposures.

Metallic Specimens. Few Al-containing alloys have good strength at 700°-800°C except for oxide dispersion strengthened (ODS) FeCrAl. Thus, aluminide coatings may be needed for higher strength conventional alloys. One concern about coatings on Ni-base alloys or even 300-series stainless steels (e.g. type 316, Fe-20at%Cr-10%Ni) is that the outer coating will contain some Ni-rich aluminide[19] and Ni preferentially dissolves in Pb-Li. Another concern was the method for conducting the capsule test. Traditionally, the capsule was made from the same material as the specimen to eliminate the possibility of dissimilar metal interaction.[20] However, it would be difficult to aluminize an entire capsule. Therefore, a standard capsule material might be useful.

Table 1. Mass change of CVD SiC specimens after exposure in Pb-17Li

Temperature	Time	Mass Change	
		(mg)	(mg/cm ²)
800°C	1,000h	-0.02 ±0.04	-0.01 ±0.01
	5,000h	+0.10	+0.03
1100°C	1,000h	-0.02	-0.01
	2,000h	+0.02	+0.01
1200°C	1,000h	+0.04	+0.01

Table 2. Chemical composition using inductively coupled plasma and combustion analysis of the starting Pb and the Pb-Li after capsule exposures at the indicated temperatures for 1000h (in ppma except for Li in atomic%)[12]

Test	Li	Si	C	O	N	Al	Cr	Fe	Mo	Ni	Y
Starting	n.d.	<40	<170	1270	<40	<8	<4	<4	<2	<4	<2
1000h exposure											
800°C	17.49%	<30	1850	4090	100	6	<3	6	<2	<3	<2
1100°C	16.27%	<30	1160	3550	90	<6	<3	6	<2	<3	<2
2000h exposure											
1100°C	15.99%	185	1025	7890	200	<60	<30	<30	<20	<30	<20

A series of experiments was designed to begin assessing some of these issues. Specimens of type 316 stainless steel (Table 3) were exposed for 1000h at 700°C to Pb-17Li in three different capsule materials, type 316, low carbon steel and Mo. Also, several Al-containing alloys, Fe₃Al, NiAl and ODS FeCrAl (Plansee alloy PM2000) were exposed under the same conditions using Mo capsules. (The aluminides were selected as representative of the CVD coating composition and ODS FeCrAl was selected because it could potentially be used as a tube material without coating.) The 1.5mm thick specimens had a surface area of 4-5cm² and all were polished to a 600grit SiC finish prior to exposure and were not pre-oxidized. The same high purity Pb and Li materials was used as in the previously described experiments, Table 2, and the same cleaning procedure was used.

Mass changes from the initial capsule experiments are shown in Table 4 and the chemical analysis for the Pb-Li after test are shown in Table 5. The lowest mass loss for a 316SS specimen was in the 316SS capsule. This can be understood based on the fundamental flux equation governing dissolution in a liquid metal like Pb-Li:

$$J_i = k (C_i^S - C_i) \quad [1]$$

where J_i is the flux of species i into (positive) or from (negative) the liquid metal, C_i^S is the solubility of i in the Pb-Li and C_i is the instantaneous concentration of i in the liquid. In a capsule experiment, dissolution continues until the liquid metal is saturated, i.e. $C_i^S = C_i$. Therefore, with a 316SS capsule, the predominant dissolution of Ni and Cr would reach saturation quickly due to the large surface area of the capsule itself (relative to the specimen). This correlates well with the high levels of Ni, Mn and Cr observed in the Pb-Li from this capsule, Table 5. In contrast, with a Fe or Mo capsule all of the Ni and Cr needed to reach saturation would come from the 316SS specimen. Thus the higher mass losses for these tests are expected. However, the measured mass change also may be affected by dissimilar metal transfer to the specimen surface or to the capsule wall. In general, Mo was not detected in the Pb-Li after these tests so this is not expected to be a problem. Additional characterization of the specimens and capsule material

Table 3. 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

Table 4. Mass change of specimens after 1000h at 700°C in Pb-17Li

Specimen	Capsule	Mass Change	
		(mg)	(mg/cm ²)
316SS	316SS	-3.1	-0.67
316SS	Fe	-26.2	-5.72
316SS	Mo	-17.4	-3.79
ODS FeCrAl	Mo	-1.4	-0.20
Fe-28Al-2Cr+Zr	Mo	-1.0	-0.25
Ni-42.5Al	Mo	-0.4	-0.09

will help to determine the extent of any such interactions.

All of the Al-containing materials showed relatively low specimen mass losses despite the use of Mo capsules. Based on thermodynamic calculations[10], it is likely that the addition of Al results in the formation of a protective Al₂O₃ layer by gettering O from the Pb-Li. (The higher levels of O and N in the Pb-Li after exposure may reflect contamination during specimen collection or handling after the test, Table 5.) Initial characterization by scanning electron microscopy equipped with energy dispersive x-ray analysis confirmed that Al-rich oxide layers are present. In view of the high solubility of Ni in Pb-Li, it was surprising that the specimen of NiAl showed the lowest mass loss, Table 4. However, this material had the highest Al content (Table 3) and possibly was able to form a protective alumina layer more easily than the other materials. The high level of Fe in the Pb-Li from this capsule is unexplained. Additional characterization of these specimens is underway. The next series of capsule experiments will examine CVD-coated 316 and pre-oxidized Al-containing alloys.

For both liquid metal systems, future work will eventually need to include flowing liquid metal experiments with a temperature gradient. Static capsule experiments can only be expected to produce a limited picture of the compatibility issue where saturation of one or more of the dissolving components can inhibit further reaction, Eqn. 1. However, the observation of little or no detectable Si in the Pb-Li and low mass losses for the Al-containing materials are promising results for candidate materials in the Pb-Li system.

Table 5. Chemical composition using inductively coupled plasma and combustion analysis of the starting Pb and the Pb-Li after capsule exposures at the indicated temperatures for 1000h (in ppma except for Li in atomic%)

Test	Li	Fe	Cr	Ni	Mn	Si	Al	Mo	C	O	N	S
Starting	n.d.	<4	<4	<4	<4	<40	<8	<2	<170	1270	<40	<50
316SS (SS)	16.4%	60	160	740	380	<60	<60	<20	1420	4810	160	320
316SS (FS)	17.3%	30	<30	90	30	<60	<60	<20	970	3346	40	110
316SS (Mo)	17.4%	<30	<30	90	<30	<60	<60	<20	1590	7440	60	903
FeCrAl (Mo)	17.9%	30	<30	<60	<30	<60	<60	<20	1260	4140	90	370
Fe ₃ Al (Mo)	16.5%	<30	<30	<60	<30	<60	<60	<20	1520	14860	320	110
NiAl (Mo)	18.2%	840	<30	30	<30	<60	<60	20	1200	10310	370	1100

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