

COMPATIBILITY OF CVD SiC WITH Pb-Li AT 800°-1100°C—B. A. Pint, L. D. Chitwood, and J. R. DiStefano (Oak Ridge National Laboratory, USA)

OBJECTIVE

The objective of this task is to assess the long-term, high-temperature compatibility of SiC/SiC composites and Pb-Li. One proposed fusion reactor concept uses SiC/SiC composites with a self-cooled Pb-17Li blanket. One attractive feature of ceramic composites is their high temperature capabilities (1000°C). However, there is no compatibility data above 800°C for this system. As the first step in the evaluation process, monolithic SiC was exposed to Pb-17Li in capsule tests at 800°-1100°C.

SUMMARY

Static Pb-17Li capsule tests were performed on monolithic SiC specimens. To avoid unwanted reactions with Pb-Li, the SiC specimens were contained in 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.

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.) Present assessments of the materials feasibility for these concepts are incomplete because there is little information available on the high temperature compatibility of SiC with Pb-Li at temperatures of 800°C and higher. In a static exposure at 427°C, SiC composites (but not monolithic SiC) dissolved in unalloyed Li.[4,5] However, the activity of Li in Pb-17Li is greatly reduced (1.2×10^{-4} at 500°C)[6] suggesting that compatibility would be better with the eutectic. Previous results at 800°C have shown limited reaction between Pb-17Li and SiC composites.[7,8] Other work has examined the compatibility of SiC and its composites with ceramic breeding materials for He-cooled concepts.[9]

In order to obtain information about SiC compatibility with Pb-17Li at 800°-1100°C, static capsule experiments were conducted with specimens of high-purity CVD SiC. These experiments used high-purity monolithic SiC instead of composites as a first step towards evaluating SiC compatibility to avoid the microstructural and microchemistry complexities of composites and due to the better compatibility found for monolithic material compared to SiC/SiC composites in Li.[4] Capsules were exposed for 1000h at 800°, 1000° and 1100°C.

Experimental Procedure

Proper execution of the experiment is a critical part of this type of test, particularly at the high temperatures of interest. In order to isolate the specimen-liquid metal system and avoid additional contamination of the liquid metal during the test, it is preferable to perform a capsule test in a sealed (i.e. welded) refractory metal inner capsule which is then placed in a secondary, oxidation- resistant outer capsule to prevent the refractory metal capsule from oxidizing during the test. Refractory metals are relatively inert to Li in this

temperature range.[10] This type of capsule experiment has been successfully used in testing ceramics in Li.[11] A Mo inner capsule appears to be inert to Li at temperatures 800°C , and is expected to be compatible with Pb-Li.[12] However, Mo_2C (-77.4kJ/mol) is more stable than SiC (-45.6kJ/mol) at 823°C .[13] Therefore, a Mo capsule could affect the corrosion process, similar to the increased corrosion observed when vanadium alloy capsules were used for AlN samples exposed to Li.[11] (No problems were reported with Mo capsules at 800°C but higher temperatures may be a problem, including the formation of a Pb-Mo-C phase.[8]) Thus, for this experiment, a SiC inner crucible was used to contain the Pb-Li and then this unsealed, but lidded crucible was placed inside a Mo secondary capsule that was sealed by arc welding, Figure 1. The Pb-Li composition was obtained by adding appropriate amounts of 99.999% purity Pb shot and pieces of high purity unalloyed Li (140 ppmw N)[11] to the SiC crucible. To hold the SiC specimen in place at the bottom of the SiC capsule during the test, a SiC holder was used. The lid of the SiC capsule was held closed with a 0.25mm diameter Mo wire fed through the lid of the Mo capsule and welded in place during assembly. The outer oxidation resistant capsule was type 304 stainless steel or type 600 Inconel. The various capsules and crucibles were loaded and sealed in a high-purity argon glove box using gas-tungsten-arc welding. In order to ease specimen removal, at the end of the high temperature exposure the entire assembly was inverted so that the Pb-Li would drain away from the SiC specimen, Figure 1b.

The high purity (99.9995%) CVD -SiC specimens were manufactured by Rohm and Haas Company Advanced Materials (Woburn, MA) and had dimensions of $3 \times 8 \times 12 \text{ mm}$ and a density of 3.21g/cm^3 . Specimen mass was measured before and after exposure on a Mettler-Toledo balance with an accuracy of $\pm 0.02\text{mg}$. The sealed capsules were exposed in laboratory air for 1000h at 800° , 1000° and 1100°C in resistively heated box furnaces with a thermocouple positioned near the capsule. After exposure, cleaning

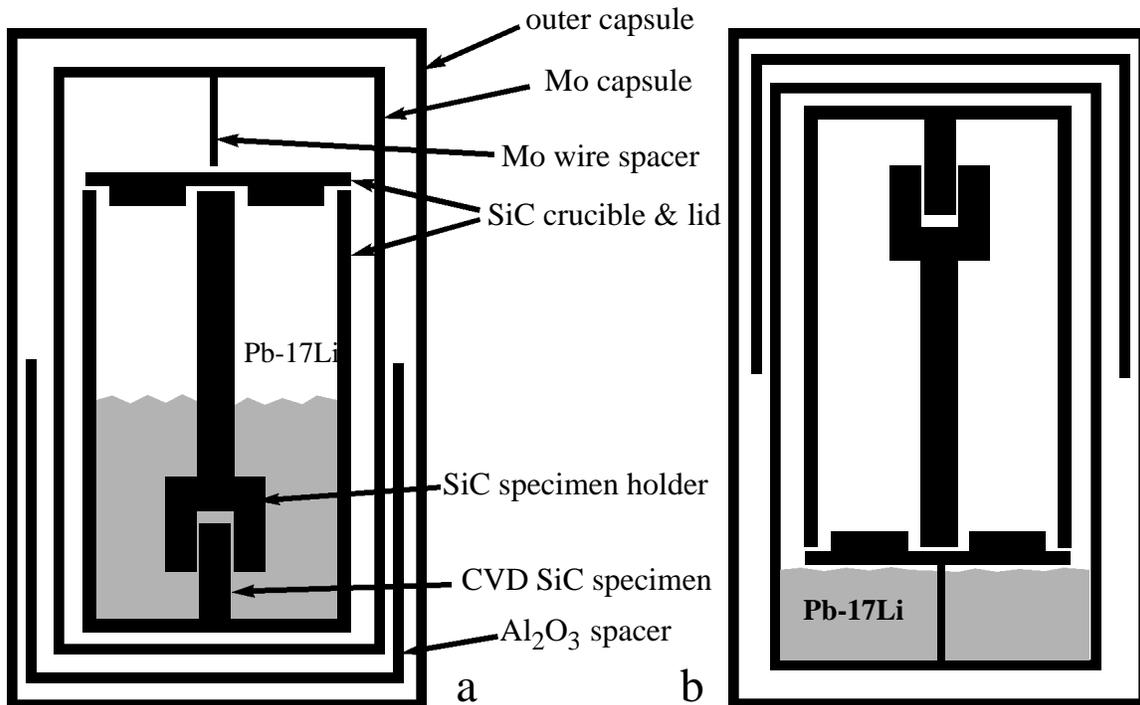


Figure 1. Schematic of the capsule test (a) during loading and at temperature and (b) after test. The outer capsule is stainless steel or a Ni-base Inconel alloy. The secondary capsule is Mo and the inner capsule and specimen holder are SiC. The capsule is inverted at the end of the test to allow the Pb-Li to flow away from the SiC specimen and crucible. An alumina spacer was used at 1100°C .

of the specimen was a significant issue. Various techniques have been suggested in the literature, including a mixture of acetic acid, hydrogen peroxide and ethanol;[14] just acetic acid and hydrogen peroxide;[5] stoichiometric amounts of nitric acid;[12] and immersion in low temperature liquid Li followed by Li removal in alcohol or water.[15] The first method was used in this study with the specimen immersed for 24h. After exposure, specimens were characterized by Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS).

Results

The capsule exposed for 1000h at 800°C was opened and disassembled in the argon glove box, Figure 2. Surprisingly, all of the SiC parts and the specimen were almost clean of liquid metal which had drained into the Mo capsule and solidified after the capsule was inverted (Figure 1b). The clean crucible, holder and specimen suggest that Pb-Li did not wet SiC under these conditions. (For capsule exposures in Li, the ceramic specimens and capsule remain covered with a layer of Li after exposures at 400°-800°C.[11]) No change in the specimen appearance was observed after cleaning; although a small amount of powdery black residue was left on the specimen surface. No change in the specimen mass was measurable and the original shiny surface finish was still visible. The specimen was analyzed by XPS and weak Pb and Li signals were detected on the surface but only a layer of C was detected by AES.

During exposure at 1000°C, the capsule system failed causing catastrophic oxidation of the stainless steel and Mo capsules and oxidizing the Pb-Li as well as the SiC parts. The problem was likely caused by a solid state reaction between the stainless steel outer capsule and the Mo secondary capsule. To avoid this problem at 1100°C, an Inconel outer capsule was used and an alumina spacer was included between the Mo and Inconel capsules, Figure 1. The 1000°C test is being repeated.

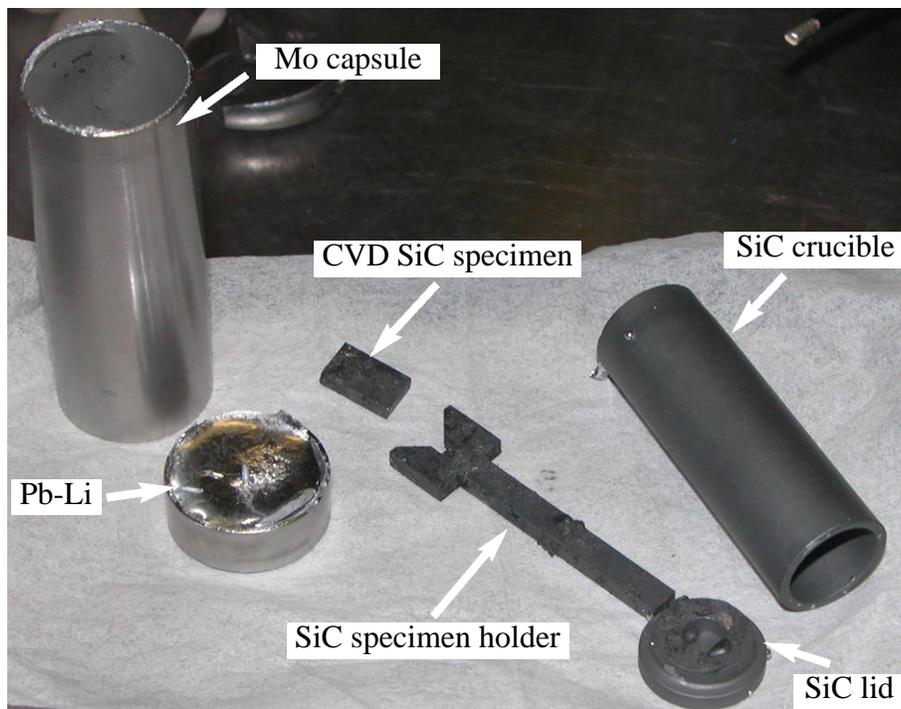


Figure 2. Photograph of the components inside the glove box immediately after disassembly of the 1000h, 800°C capsule test. Note that all of the components came out clean because the Pb-Li did not wet SiC at this temperature.

When the capsule exposed for 1000h at 1100°C was opened in the glove box, the SiC parts had a similar appearance as those exposed at 800°C. In this case, the Mo capsule was more brittle and shattered during opening as did the SiC crucible, Figure 3. The Pb-Li drained away from the specimen leaving only a few small patches of metal on the specimen and holder. Before cleaning, the specimen mass had increased by 18mg. However, after 24h in the cleaning solution, there was no measurable change in specimen mass from the original mass. Again there was a black residue on the surface, but the original surface finish could be seen. Further characterization is being performed on this specimen.

Discussion

In agreement with previous static-type experiments, no degradation was noted by exposing SiC in Pb-17Li at 800°C.[7,8] The indication of no wetting at this temperature is important because a lack of wetting precludes any chemical attack.[16] Some limited wetting may have occurred at 1100°C. However, only a few thin patches of metal were left on the specimen after the test and the crucible and holder were relatively free of metal. Observations with stainless steel and mercury indicate that there can be an extended incubation period to develop wetting.[16] Therefore, wetting observations may be dependent on the exposure time. A direct assessment of wetting behavior in this system including the temperature where wetting begins could provide important information about the upper temperature limit for compatibility between SiC and Pb-17Li. However, the high temperatures, high vapor pressure of Li and other experimental difficulties with wetting experiments[17] make this a difficult experiment to perform.

More complete characterization of the SiC specimens is being conducted. Also, the chemistry of the Pb-Li after the tests is being determined. Additional experiments will be performed on monolithic SiC and SiC composites in order to determine the compatibility of fibers and, especially, the fiber-matrix interface which can be susceptible to enhanced corrosion.[18,19] However, it is anticipated that a dense CVD SiC seal coat will cover the outer layer of any SiC composite components.

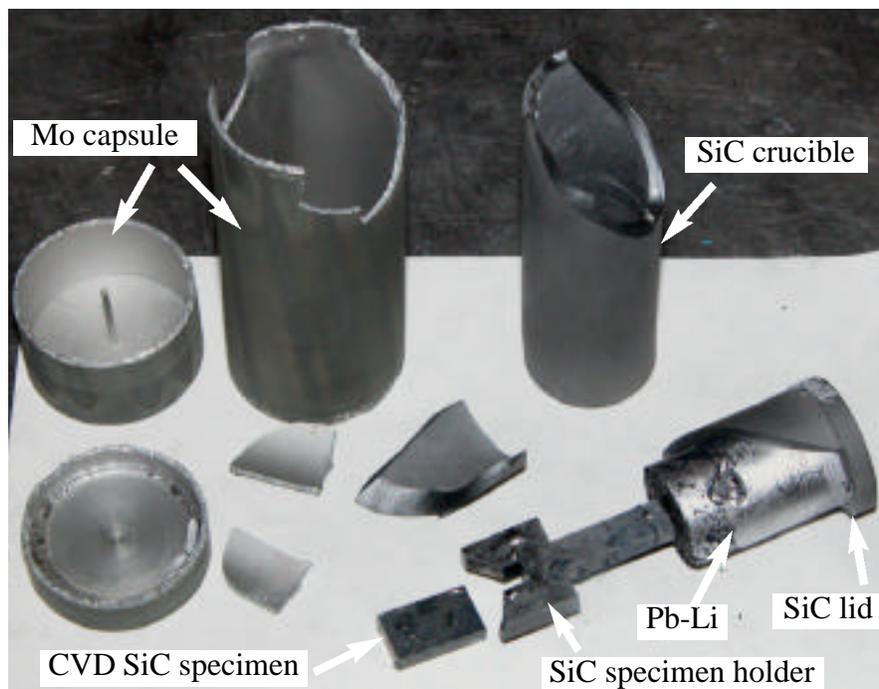


Figure 3. Photograph of the components inside the glove box immediately after disassembly of the 1000h, 1100°C capsule test. The Mo and SiC crucibles broke during disassembly.

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