6.2 COMPATIBILITY OF MATERIALS EXPOSED TO ISOTHERMAL Pb-Li – B. A. Pint, K. A. Unocic and S. J. Pawel (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 metal temperatures (up to 700°C) for a DEMO-type reactor, several Pb-Li compatibility issues need to be addressed. Some of the issues currently being investigated are the compatibility of dispersion strengthened Fe-Cr alloys compared to conventional wrought material, the performance of Al-rich coatings to inhibit corrosion and dissimilar material interaction between SiC and ferritic steel. Planning is under way to transition the compatibility testing from isothermal capsules to thermal convection loops.

SUMMARY

Isothermal capsule experiments were completed on coated and uncoated Grade 92 (9Cr-2W) specimens for 5,000 h in Pb-Li to determine the long-term stability of the coating at 600° and 700°C. Thin ~50µm Al-rich diffusion coatings showed similar low mass changes at both temperatures. However, extensive Al loss was observed after 5,000h at 700°C. In contrast, a thicker diffusion coating where intermetallic aluminide phases formed showed a mass loss after 5,000h at 700°C due to partial spallation of the aluminide coating outer layer. Characterization of the 5,000h specimens is still in progress. These results indicate that (1) Al-rich coatings greatly reduce dissolution at 700°C in Pb-Li but do not prevent it and (2) the effectiveness of coating strategies to improve compatibility are limited. In order to further evaluate the coating concept and wrought and oxide dispersion strengthened (ODS) FeCrAl alloys, plans are being made to build a Pb-Li thermal convection loop of Fe-9Cr or FeCrAl tubing.

PROGRESS AND STATUS

Introduction

A current focus of the U.S. fusion 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-17 at.%Li coolants and uses reduced activation ferritic-martensitic (FM) steel as the structural material with a SiC/SiC composite flow channel insert (FCI). Thus, recent U.S. compatibility research has examined issues with Pb-Li.[2-9] Compared to Li,[10] a wider range of materials can be compatible with Pb-Li because of the low activity of Li.[11] In particular, SiC readily dissolves in Li, but not Pb-17Li.[2,4,12] However, like Pb, Pb-Li dissolves Fe, Cr and especially Ni from many conventional alloys above 500°C.[13,14] This is not a concern for a DCLL TBM operating at <500°C. However, a DCLL blanket for a commercial DEMO-type reactor would be more attractive with a higher maximum operating temperature, perhaps >600°C if ODS ferritic steels [15-18] 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.[14] Therefore, preliminary Pb-Li compatibility capsule experiments are being conducted at 500°-800°C in order to investigate several concepts before flowing Pb-Li compatibility tests are conducted. The final coating capsule tests have been completed with 5,000h exposures at 600° and 700°C and the initial characterization of those specimens is reported. The next phase of this compatibility evaluation is to build a thermal convection loop where both Al-rich coatings and FeCrAl alloys can be evaluated at 550°C and higher Pb-Li temperatures.

Experimental Procedure

Static capsule tests were performed using Mo inner capsules and type 304 stainless steel (SS) outer capsules to protect the inner capsule from oxidation. The uncoated specimens were ~1.5 mm thick and 4-5 cm^2 in surface area with a 600 grit surface finish and were held with 1 mm diameter Mo wire. (Mo can be considered to be essentially inert under these conditions.) For coated specimens, the coupons were polished to a 0.3 µm alumina finish and cleaned ultrasonically in acetone and alcohol. Aluminizing was performed in a laboratory-scale chemical vapor deposition (CVD) reactor consisting of an inductively heated alumina tube with flowing H_2 carrying the $AlCl_x$ vapor. The reactor has been described in detail elsewhere.[19] The thinner coatings were deposited during 6h at 900°C and the thicker coating was deposited under the same conditions but with Al/Cr powder in the reactor to increase the Al activity.[6,19,20] The capsules were loaded with 125g of Pb-Li in an Ar-filled glove box. The Pb-Li was melted and cast at ORNL and had Li contents of 15.6-16.5 at%. The Mo and SS capsules were welded shut to prevent the uptake of impurities during the isothermal 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. Mass change was measured with a Mettler-Toledo balance with an accuracy of 0.01 mg/cm^2. Post-test specimen surfaces were examined using x-ray diffraction (XRD) and secondary electron microscopy (SEM) equipped with energy dispersive x-ray (EDX) analysis. After surface characterization, the specimens were metallographically sectioned and polished and examined by light microscopy and electron microprobe analysis (EPMA) equipped with wavelength dispersive x-ray analysis.

Results and Discussion

Figure 1 shows the mass change for the coated and uncoated Gr.92 specimens reported previously with the most recent results after 5,000h isothermal exposures at 600° and 700°C. The specimens with a ~50µm CVD coating showed low mass changes at both temperatures after 5,000h. The uncoated specimens at both temperatures showed a reduced rate of mass loss compared to the previous 1,000h exposures. This may be due to Pb-Li becoming saturated with the dissolving Fe and Cr at longer times. The rate of dissolution in a capsule test should drop as the liquid becomes saturated, reaching zero at

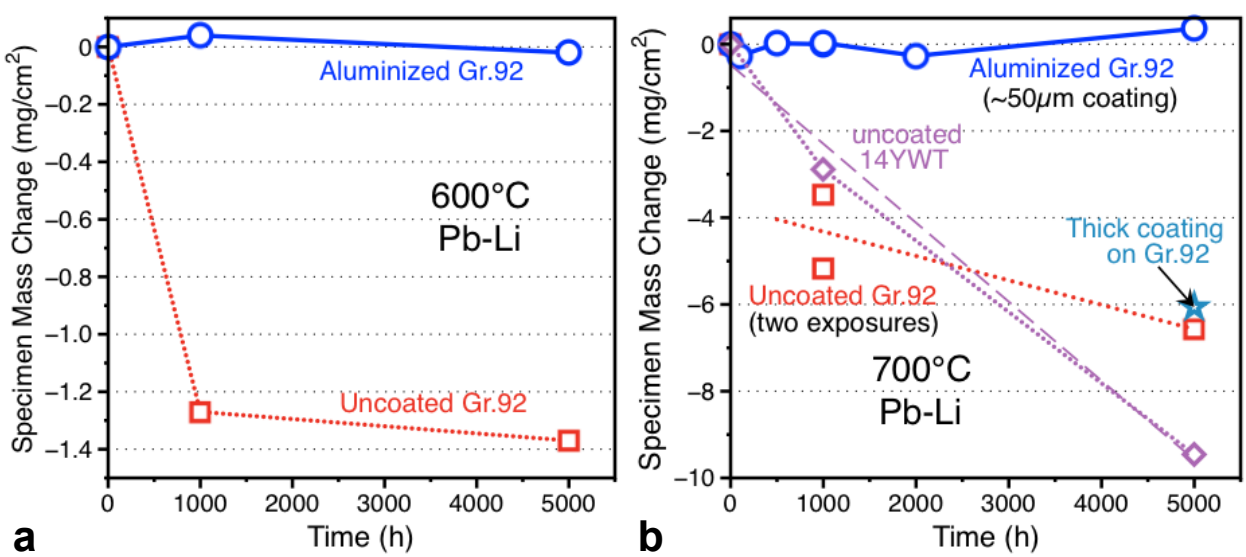

Figure 1. Specimen mass change as a function of exposure time in Pb-Li at (a) 600°C and (b) 700°C.

saturation (which is temperature dependent). This is a primary limitation of an isothermal capsule experiment and loop testing with a thermal gradient is needed to verify the Pb-Li compatibility.

Figure 2 shows polished cross-sections of the specimens exposed for 5,000h at 600° and 700°C with and without a ~50µm CVD coating. The uncoated specimens have a non-uniform surface and the roughness increased with exposure temperature. What appears to be oxide at the surface may be remnants from the cleaning process or partially due to poor adhesion of the Cu-plating. The coated specimens show a typical coating microstructure.[5,21] Especially at the coating-substrate interface, acicular AlN precipitates form due to reaction between Al in the coating and N (0.06 wt.%, 0.23 at.%) in the steel. The concentration of AlN particles marks the original coating-substrate interface in Figure 2d and, to a lesser extent, for the lower temperature exposure in Figure 2b. At both temperatures, a thin surface oxide is present which was identified as $LiAlO_2$ by XRD. In some cases, there are areas where the oxide appeared to be spalled, which may have occurred during cleaning but also could reflect poor adhesion of this oxide layer. For the coated specimen exposure at 700°C, this specimen is the fifth in a time series of specimens.[7] Figure 3 shows Al profiles from this specimen compared to the nominal as-coated composition (shaded area) and the shorter exposures at 700°C. It is obvious that the Al content continues to drop in the coating with increasing exposure time. It is also evident that the Al loss (area under the shaded curve) cannot be explained by back diffusion into the Grade 92 substrate or the small quantity of AlN precipitates. It appears that Al is slowly being lost into the Pb-Li suggesting that the $LiAlO_2$ surface layer is not a perfect barrier to dissolution. More likely the rate limiting dissolution step is now Al being lost from the $LiAlO_2$ layer and being replaced by Al from the substrate. A longer exposure would likely expend the Al reservoir in the coating.

A thicker coating (i.e. larger Al reservoir) was applied to one Grade 92 specimen. Surprisingly, this specimen showed a mass loss of -6.1 mg/cm^2 after 5,000h at 700°C, Figure 1b, a similar mass loss as the uncoated specimen. The reason for the mass loss appears to be coating spallation. For higher Al

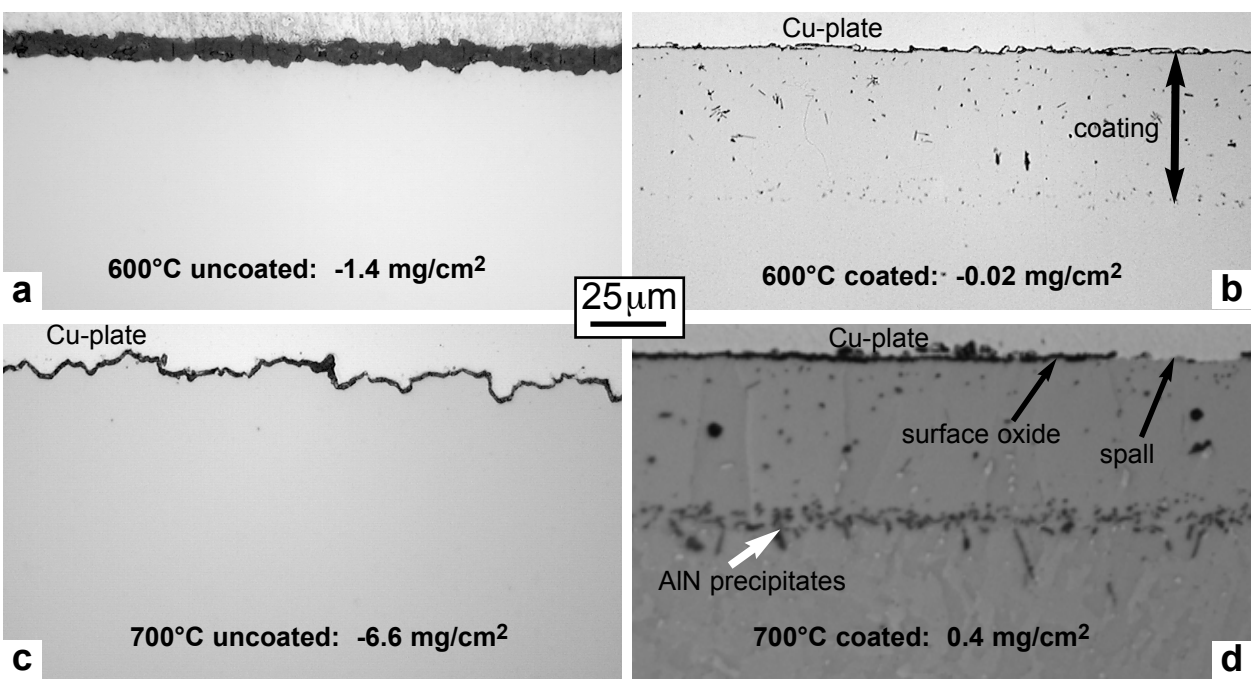

Figure 2. Light microscopy of Grade 92 specimens exposed to Pb-Li for 5,000h (a) uncoated 600°C, (b) coated 600°C (c) uncoated 700°C and (d) coated 700°C.

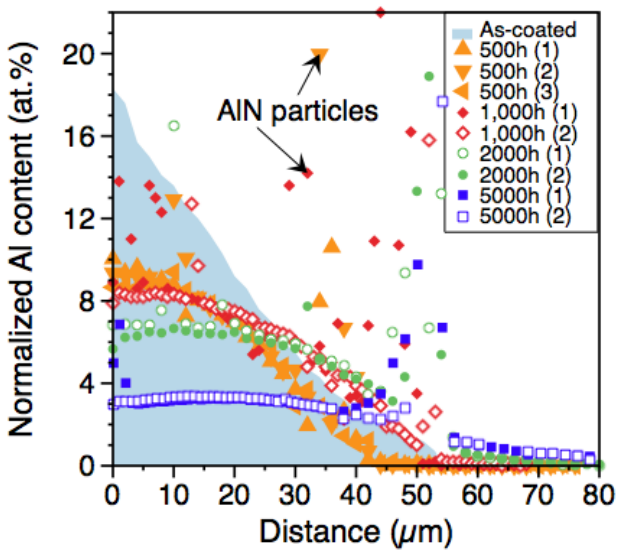

Figure 3. Normalized Al content by EPMA as a function of depth for coated Gr.92 specimens after exposure for 500-5,000h at 700°C in Pb-Li. A typical as-coated Al profile is shown in shaded area.

contents, intermetallic (Fe-Al) phases begin to form and an inner and outer layer is evident, Figure 4a. (Note that the magnifications in Figures 2 and 4 are different.) The outer layer likely grew by outward diffusion of Fe while the inner layer by inward Al diffusion.[19] In some locations, the outer layer was absent (e.g. Figure 4b), a likely explanation for the large mass loss. In addition to the AlN precipitates, this coating apparently contains a large number of voids, some filled or partially filled with oxide. The composition has not been evaluated but these voids are likely Kirkendall-type, formed due to the loss of Al during exposure. One advantage of the thinner coating is that the Fe(Al) coating phase has a similar coefficient of thermal expansion (CTE) as the substrate.[21] However, the intermetallic phases (particularly Fe_3Al and FeAl) all have significantly higher CTEs, thus thermal strains due to the CTE differential may have caused spallation. In Figure 4a, there also appears to be oxide formed at the interface between the inner and outer coating layers. This has been observed during steam and wet air oxidation of similar coatings and was attributed to cracking or other imperfections in the outer coating

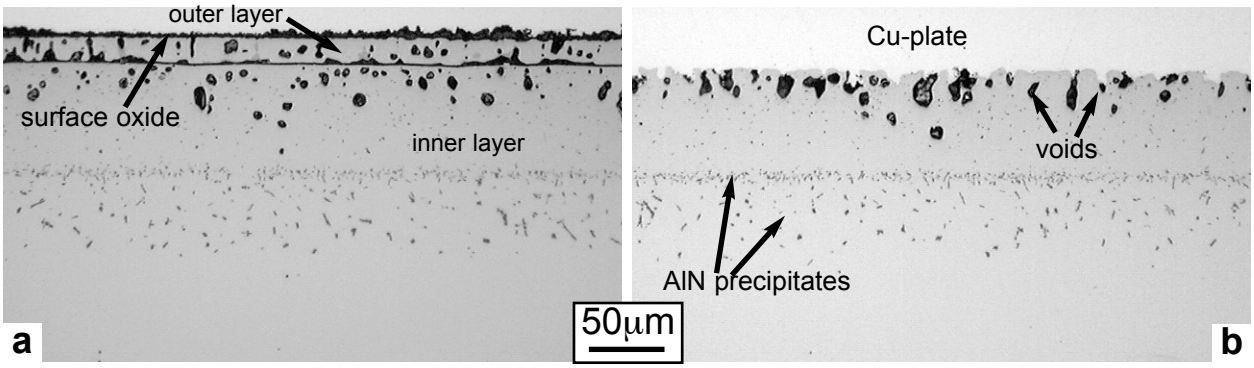

Figure 4. Light microscopy of high-Al content coating on Grade 92 specimen exposed to Pb-Li for 5,000h at 700°C. In (b), the outer coating layer has been lost during exposure.

allowing ingress of oxygen to this interface.[21] The combination of oxidation and void formation at the interface may have sufficiently weakened the interface between the inner and outer layer to cause the observed spallation. Based on this result, pursuing coatings with a larger Al reservoir does not appear to be a promising strategy. For the highest temperature compatibility, an Al containing alloy appears to be a more promising strategy for a structural alloy with long term Pb-Li compatibility.

Regarding construction of a Pb-Li thermal convection loop, Kanthal APMT (FeCrAl) tubing [22] has been purchased. At this time, a supplier has not yet been identified for 9Cr steel tubing because of the small (~50m) quantity of tubing required. A supplier is being identified for the needed Pb-Li. The first loop should be ready for operation in late 2013, targeting operation of 550°C peak temperature for 1000h with a temperature gradient of approximately 100°C. A similar harp shaped loop was designed and operated at ORNL in 2007 with V-4Cr-4Ti tubing and flowing Li.[23]

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, Fus. Sci. Tech. 52 (2007) 829.
[3] B. A. Pint and K. L. More, J. Nucl. Mater. 376 (2008) 108.
[4] B. A. Pint, Mater. Sci. Forum 595-598 (2008) 549.
[5] B. A. Pint, J. Nucl. Mater. 417 (2011) 1195.
[6] B. A. Pint, L. R. Walker and K. A. Unocic, Mater. High Temp. 29 (2012) 129.
[7] B. A. Pint and K. A. Unocic, J. Nucl. Mater. in press.
[8] B. A. Pint and K. A. Unocic, DOE/ER-0313/50 (2011) 115.
[9] B. A. Pint and K. A. Unocic, DOE/ER-0313/51 (2011) 73.
[10] J. E. Battles, Intern. Mater. Rev. 34 (1989) 1.
[11] P. Hubberstey, J. Nucl. Mater. 247 (1997) 208.
[12] T. Yoneoka, S. Tanaka and T. Terai, Mater. Trans. 42 (2001) 1019.
[13] O. K. Chopra, D. L. Smith, P. F. Tortorelli, J. H. DeVan and D. K. Sze, Fusion Technol., 8 (1985) 1956.
[14] J. Konys, W. Krauss, J. Novotny, H. Steiner, Z. Voss and O. Wedemeyer, J. Nucl. Mater. 386-88 (2009) 678.
[15] S. Ukai and M. Fujiwara, J. Nucl. Mater. 307 (2002) 749.
[16] G. R. Romanowski, L. L. Snead, R. L. Klueh, D. T. Hoelzer, J. Nucl. Mater., 283-287 (2000) 642.
[17] R. L. Klueh, J. P Shingledecker, R. W. Swindeman, D. T. Hoelzer, J. Nucl. Mater. 341 (2005) 103.
[18] D. A. McClintock, M. A. Sokolov, D. T. Hoelzer and R. K. Nanstad, J. Nucl. Mater., 392 (2009) 353.
[19] Y. Zhang, B. A. Pint, K. M. Cooley and J. A. Haynes, Surf. Coat. Technol. 202 (2008) 3839.
[20] A. Rouaix-Vande Put and B. A. Pint, Surf. Coat. Technol. 206 (2012) 5036.
[21] B. A. Pint and Y. Zhang, Mater. Corros. 62 (2011) 549.
[22] B. Jönsson, R. Berglund, J. Magnusson, P. Henning and M. Hättestrand, Mater. Sci. Forum, 461-464 (2004) 455.
[23] B. A. Pint, S. J. Pawel, M. Howell, J. L. Moser, G. Garner, M. Santella, P. F. Tortorelli, F. W. Wiffen and J. R. Distefano, J. Nucl. Mater. 386-388 (2009) 712.