

FURTHER CHARACTERIZATION OF THE TRANSFORMATION OF Al_2O_3 TO LiAlO_2 IN Pb-17Li AT 800°C – B. A. Pint and K. L. More (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 $\sim 475^\circ\text{C}$. In order for this blanket concept to operate at higher temperatures ($\sim 750^\circ\text{C}$) for a DEMO-type reactor, several Pb-Li compatibility issues need to be addressed. One issue is functional coatings such as alumina for corrosion resistance and a tritium permeation barrier.

SUMMARY

In order to study the compatibility of $\text{-Al}_2\text{O}_3$ with Pb-17Li, a FeCrAl substrate was pre-oxidized at 1000°C to thermally grow an external alumina scale. The specimen was then isothermally exposed to Pb-Li for 1000h at 800°C in a Mo capsule. The alumina layer prevented dissolution of the metallic substrate but was found to transform to LiAlO_2 . The current report includes additional XRD and TEM characterization of the external oxide layer before and after exposure to Pb-Li.

PROGRESS AND STATUS

Introduction

A recent focus of the U.S. fusion energy program has been on developing a proposal for a test blanket module (TBM) for ITER. The dual coolant Pb-Li (DCLL) TBM concept has both He and eutectic Pb-Li coolants and uses ferritic steel as the structural material and a SiC/SiC composite flow channel insert (FCI).[1] The interest in this concept has focused compatibility-related research on Pb-Li. Many materials have poor compatibility with liquid Li,[2] but the activity of Li is much lower in Pb-17Li,[3] and this allows a wider range of materials to be considered. However, Pb-Li still readily dissolves many conventional alloys. While the TBM maximum operating temperature will be $<500^\circ\text{C}$, this blanket concept would be more attractive for a commercial reactor with a higher maximum operating temperature, perhaps $>700^\circ\text{C}$ if oxide dispersion strengthened (ODS) ferritic steels[4] were used. However, at these higher temperatures, compatibility is even more of a concern. Therefore, static capsule testing has been conducted on materials at 700° and 800°C . [5,6] In order to study the Pb-Li compatibility and potential for corrosion protection of $\text{-Al}_2\text{O}_3$, one FeCrAl substrate was pre-oxidized at 1000°C to thermally grow an external alumina scale. The specimen was then isothermally exposed to Pb-Li for 1000h at 800°C in a Mo capsule.[6] A previous report characterized the external oxide layer before and after exposure to Pb-Li and found that the $\text{-Al}_2\text{O}_3$ layer transformed to LiAlO_2 . [7,8] The current report includes additional characterization of the oxide layer before and after exposure to Pb-Li at 800°C . [8]

Experimental Procedure

Specimens of ODS FeCrAl (Plansee alloy PM2000, Fe-20at.%Cr-10.6Al-0.7O-0.4Ti-0.2Y) with dimensions of $\sim 15 \times 18 \times 1-1.5\text{mm}$ were polished to a $0.3\mu\text{m}$ finish. Pre-oxidation of both specimens was conducted with a rapid insert to a pre-heated furnace at 1000°C in dry, flowing O_2 for 2h. One specimen was then held with Mo wire in a Mo capsule containing 125g high purity (99.9999%) Pb shot (chemical composition in Table 2) and 0.86g Li to make Pb-17at.%Li. The Mo capsule was loaded in an argon-filled glove box and it was then welded shut to prevent interstitial contamination during the test. The Mo capsule was then sealed inside a type 304 stainless steel capsule and was heated inside a resistively-heated box furnace in air to 800°C for $\sim 1\text{h}$ to allow the Pb and Li to melt. The capsule was then inverted to submerge the specimen in Pb-Li. After 1,000h at 800°C , the system again was inverted to allow the liquid metal to drain away from the specimen. To remove residual Pb-Li on the specimen, it was soaked in a 1:1:1 mixture

of acetic acid, hydrogen peroxide and ethanol for up to 72 h. Both specimens were characterized including x-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) equipped with an energy dispersive spectrometer (EDS). Cross-sectional TEM specimens were prepared using focused ion beam thinning. A W layer was applied to the specimen surface to protect the outer surface of the reaction product.

Results and Discussion

Prior reports described the specimen mass change and oxide morphologies and metallographic cross-sections.[5-8] To further clarify the transformation of the external oxide layer from $\text{-Al}_2\text{O}_3$ to LiAlO_2 , Figure 1 shows the XRD results with and without exposure to Pb-Li. The XRD spectra for the unexposed $\text{-Al}_2\text{O}_3$ scale is shown in Figure 1a with peaks matching JCPDS card #83-2080. The peaks are relatively weak for the thin ($<0.5\mu\text{m}$) oxide layer compared to the strong ferritic substrate peak. In Figure 1b, all of the major peaks on the Pb-Li exposed specimen matched with JCPDS card #38-1464 for tetragonal LiAlO_2 . The peaks are stronger in this case because the oxide layer increased in thickness after exposure to Pb-Li.[7]

Because the pre-oxidized $\text{-Al}_2\text{O}_3$ layer was so thin, a TEM cross-section was necessary to examine the microstructure of the reaction product. Figure 2 shows a STEM cross-section along with EDS maps of several minor elements. The STEM annular dark field image shows a thin outer layer and an inner layer with a columnar grain structure, typical of the scale formed on Y-doped FeCrAl.[9] Fine voids (dark in this image) could be observed in the oxide, but generally the layer was dense and adherent. The thin ($\sim 100\mu\text{m}$) outer layer was rich in Cr and Fe, Figures 2b and 2c, typical of the first-formed transient oxide on FeCrAl.[10] However, very little Cr and Fe was detected below this outer layer. Within the $\text{-Al}_2\text{O}_3$ inner layer, some second phase oxide precipitates were observed, rich in Y and/or Ti, Figures 2d and 2e. These elements also were observed to be segregated to the $\text{-Al}_2\text{O}_3$ grain boundaries in the maps.[11-13] Arrows point to the Y- and Ti-rich oxides and grain boundaries, Figures 2d and 2e.

For the oxide layer after exposure to Pb-Li, selected area diffraction (by TEM) was consistent with the lattice spacings of the tetragonal structure of LiAlO_2 . Unfortunately, the LiAlO_2 TEM section was easily damaged by the electron beam. Therefore, more extensive chemical analysis (such as Figure 2 for the $\text{-Al}_2\text{O}_3$ section) was not possible.

Because the temperature of this exposure is higher than expected in most blanket concepts, additional experiments are being planned to study this reaction at lower temperatures. A capsule is currently being assembled to expose a similarly pre-oxidized ODS FeCrAl specimen for 1,000h at 700°C in Pb-Li.

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] J. E. Battles, *Intern. Mater. Rev.* 34 (1989) 1.
- [3] P. Hubberstey, *J. Nucl. Mater.* 247 (1997) 208.
- [4] S. Ukai and M. Fujiwara, *J. Nucl. Mater.* 307 (2002) 749.
- [5] B. A. Pint, J. L. Moser and P. F. Tortorelli, *J. Nucl. Mater.* 367-370 (2007) 1150.
- [6] B. A. Pint, *Fus. Sci. Tech.* 52 (2007) 829.
- [7] B. A. Pint and K. L. More, *DOE/ER-0313/42* (2007) 53.
- [8] B. A. Pint and K. L. More, *J. Nucl. Mater.* in press.
- [9] F. A. Golightly, F. H. Stott and G. C. Wood, *Oxid. Met.*, 10 (1976) 163.
- [10] W. J. Quadackers, A. Elschner, W. Speier and H. Nickel, *Appl. Surf. Sci.*, 52 (1991) 271.
- [11] T. A. Ramanarayanan, M. Raghavan and R. Petkovic-Luton, *J. Electrochem. Soc.* 131 (1984) 923.

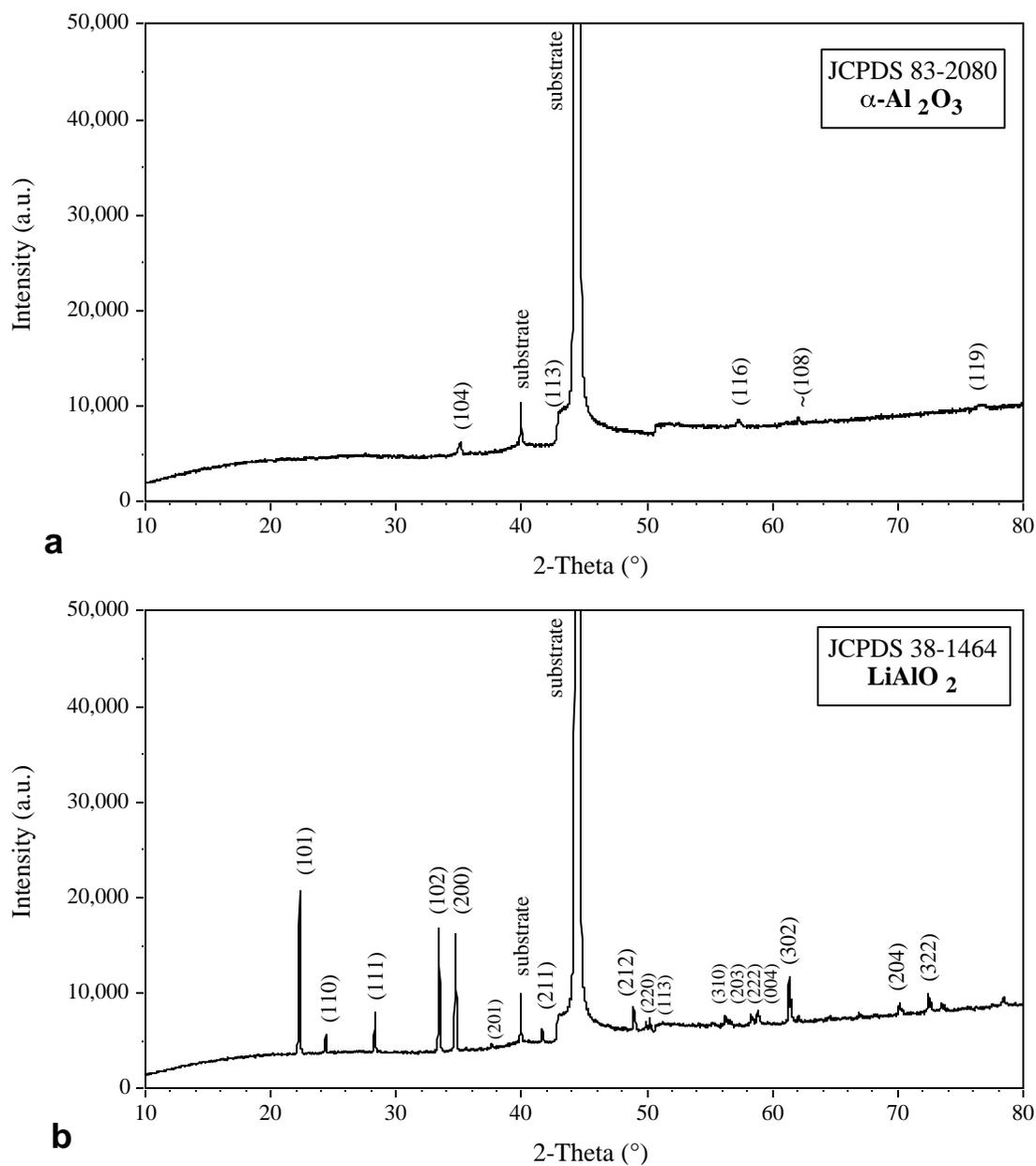


Figure 1. X-ray diffraction from ODS FeCrAl (a) after pre-oxidation for 2h at 1000°C and (b) after pre-oxidation and subsequent exposure for 1000h at 800°C in Pb-Li.

[12] K. Przybylski, A. J. Garratt-Reed, B. A. Pint, E. P. Katz and G. J. Yurek, J. Electrochem.Soc. 134 (1987) 3207.

[13] B. A. Pint, Oxid. Met. 45 (1996) 1.

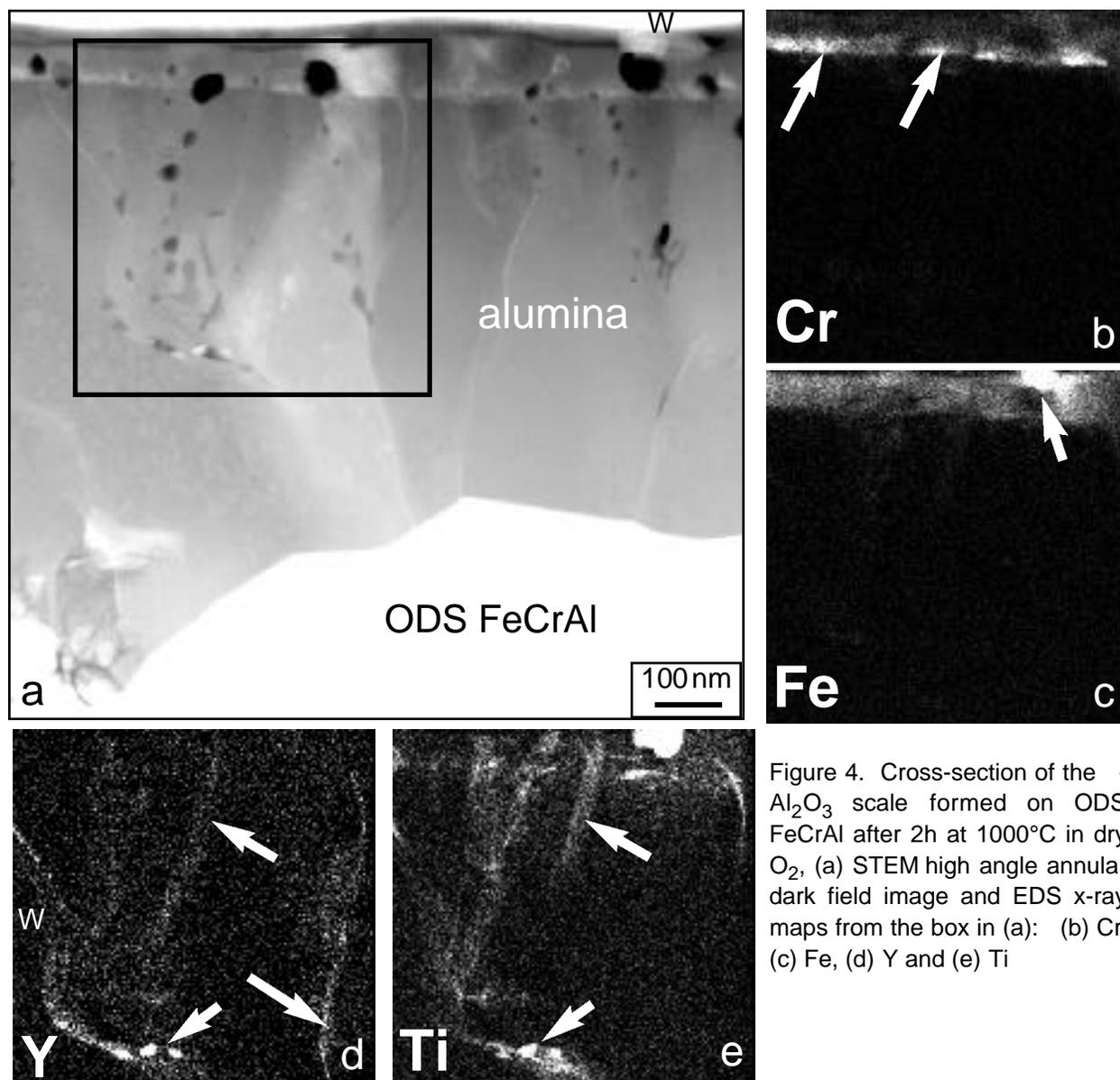


Figure 4. Cross-section of the Al_2O_3 scale formed on ODS FeCrAl after 2h at 1000°C in dry O_2 , (a) STEM high angle annular dark field image and EDS x-ray maps from the box in (a): (b) Cr, (c) Fe, (d) Y and (e) Ti