FURTHER CHARACTERIZATION OF THE COMPATIBILITY OF Al_2O_3 WITH 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 steels with both eutectic Pb-Li and He coolants at ~475°C. In order for this blanket concept to operate at higher temperatures (~750°C) for a DEMO-type reactor, several Pb-Li compatibility issues need to be addressed. One issue is the viability of functional coatings such as alumina for corrosion resistance and/or as a tritium permeation barrier.

SUMMARY

In order to study the compatibility of α-Al_2O_3 with Pb-17Li, FeCrAl substrates were pre-oxidized at 1000°C to thermally grow an external alumina scale. Prior work showed that a 1,000 h isothermal exposure of these specimens to Pb-Li at 700° or 800°C transformed the α-Al_2O_3 to $LiAlO_2$. In this experiment, the pre-oxidized specimen was isothermally exposed to Pb-Li for 1,000 h at 500°C. Characterization showed that some α-Al_2O_3 remained but cross-section transmission electron microscopy (TEM) showed that the outer (~180 nm) portion of the original α-Al_2O_3 microstructure was disrupted. Further work is needed to determine if Li is present or if a reaction occurred in this outer layer of oxide.

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 that has both He and eutectic Pb-Li coolants.[1] The interest in this concept has focused compatibility-related research on Pb-Li.[2-5] Many materials have poor compatibility with liquid Li,[6] but the activity of Li is much lower in Pb-17Li,[7] and this allows a wider range of materials to be considered. For example, SiC and α-Al_2O_3 readily dissolve in Li, but not in Pb-17Li.[2-6,8] For a reduced activation, ferritic martensitic (FM) steel structural material, an Al-rich coating can inhibit dissolution in Pb-Li by forming an Al-rich oxide layer. This layer can also function as a permeation barrier.[4,5,9,10] While the DCLL maximum operating temperature for an ITER test blanket module (TBM) will be <500°C, this blanket concept would be more attractive for a commercial reactor with a higher maximum operating temperature, perhaps >700°C if oxide dispersion strengthened (ODS) ferritic steels[11] were used. Compatibility is even more of a concern at these higher temperatures. In order to study the Pb-Li compatibility and potential for corrosion protection of α-Al_2O_3 in Pb-Li, a model system was used with ODS FeCrAl substrates pre-oxidized at 1000°C to thermally grow an external alumina scale. Prior work showed that in 1,000 h isothermal Pb-Li exposures at 700° and 800°C, the α-Al_2O_3 layer on ODS FeCrAl specimens fully transformed to $LiAlO_2$.[3,4] As a follow up experiment, a similar pre-oxidized specimen was exposed at 500°C, closer to the current TBM conditions. The results from this experiment are presented in this report.

Experimental Procedure

Specimens of ODS FeCrAl (Plansee alloy PM2000, Fe-20at.%Cr-10.6Al-0.7O-0.4Ti-0.2Y) with dimensions of ~15 x 18 x 1-1.5mm were polished to a 0.3 μm finish. Pre-oxidation was conducted with a rapid insert to a pre-heated furnace at 1000°C in dry, flowing O_2 for 2 h. Isothermal exposures to Pb-Li were conducted for 1,000 h in a Mo capsule containing 125 g of Pb-Li with the specimen suspended by a Mo wire. 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 for ~1 h to allow the Pb-Li to melt. The capsule was then inverted to submerge the specimen in Pb-Li. After 1,000h at the test temperature, 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. The mass change was then measured. A summary of the experimental conditions is given in Table 1. The post-exposure Li content was measured using inductively coupled plasma analysis. After exposure, the specimen was characterized including light microscopy of polished cross-sections, scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS), x-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) with EDS. Cross-sectional TEM specimens were prepared using focused ion beam milling. A C layer followed by a W layer was deposited on the specimen surface to protect the outer surface of the reaction product.

Results and Discussion

Table 1 summarizes the conditions of the three exposures conducted to date and the resulting specimen mass change. Unfortunately, the Li content in the experiments has not been consistent. This issue is being addressed for the final experiment in this series to be conducted at 600°C. The mass changes were all relatively low compared to Fe-base alloys without Al (e.g. Fe-9Cr or Fe-18Cr-10Ni). The higher mass loss after exposure at 500°C could be related to the higher Li content in this experiment, Table 1.

To characterize the surface oxide after exposure to Pb-Li at 500°C, the specimen was first examined using XRD and plan-view SEM. Figure 1 shows the XRD results. Peaks were present for α-Al_2O_3 but were far less distinct than before exposure to Pb-Li.[3] Figure 2a shows the surface morphology. Nodules rich in Ti were present on the surface and Fe and Cr peaks were present in the EDS spectra along with Al and O. If present, Li would not be detected by EDS. The specimen was then sectioned for further examination. Figure 2b shows the polished cross-section. At this magnification, the oxide appears very similar to that after pre-oxidation at 1000°C with no clear changes. However, because the oxide is <1 μm in thickness, it is not possible to characterize the microstructure without a TEM section as was done for a specimen that received only the pre-oxidation.[3]

Figure 3 shows the TEM cross-section of the oxide after exposure to Pb-Li. Before exposure, the thermally-grown α-Al_2O_3 had a mainly columnar structure with an outer ~100 nm layer of equiaxed oxide grains rich in Fe and Cr.[3] After Pb-Li exposure at 500°C, only the inner half of the remaining oxide appears to retain the original columnar structure. Voids (arrows) are present on some of the oxide grain boundaries. This is not uncommon in thermally-grown α-Al_2O_3 .[3,12] There is no indication of an outer equiaxed layer. The outer half of the oxide, ~180 nm, does not appear to have a distinct grain structure. Maps using EDS showed the oxide consisted primarily of Al and O with some enrichment of Ti in the metal adjacent to the oxide. Maps at higher magnification are needed to determine if Y and Ti ions remain segregated to the oxide grain boundaries after exposure.[3,13,14] The specimen also will be examined using Auger electron spectroscopy to determine if Li is present in the oxide. It appears that some reaction

Table 1. Summary of Pb-Li experiments conducted on pre-oxidized ODS FeCrAl.

Temperature	Pb-Li source	Li (post-test) (at.%)	Mass Change (mg/cm^2)	Phases (XRD)
500°C	Atlantic (ORNL)	27.3	-0.11	Al_2O_3
600°C	(currently being assembled)			
700°C	Atlantic (UCLA)	13.2	-0.06	$LiAlO_2$
800°C	Mixed Pb and Li	17.3	+0.24	$LiAlO_2$

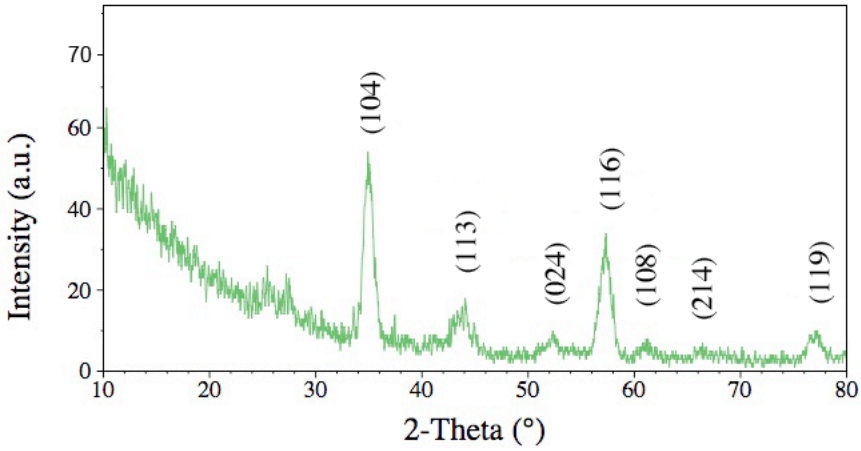

Figure 1. X-ray diffraction from ODS FeCrAl after pre-oxidation for 2h at 1000°C followed by 1 kh in Pb-Li at 500°C. The α-Al_2O_3 peaks are noted.

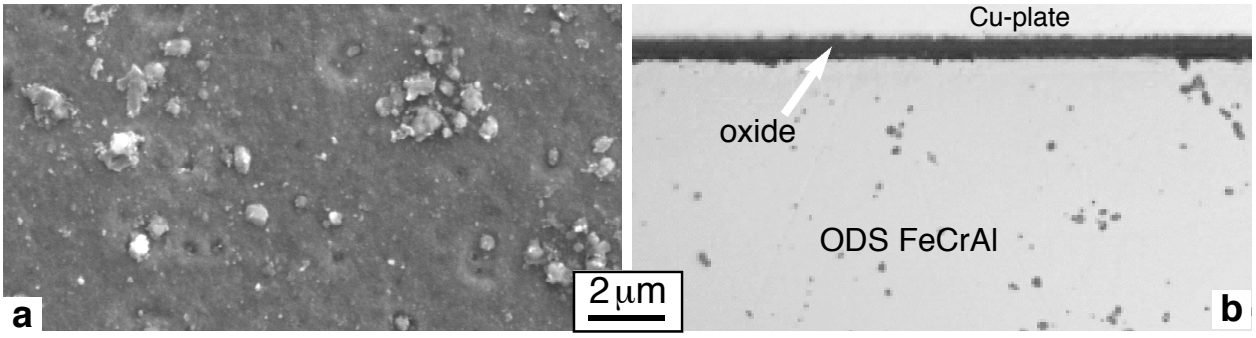

Figure 2. ODS FeCrAl after pre-oxidation followed by exposure to Pb-Li at 500°C for 1kh (a) SEM plan-view image and (b) light microscopy of polished cross-section with protective Cu plating layer.

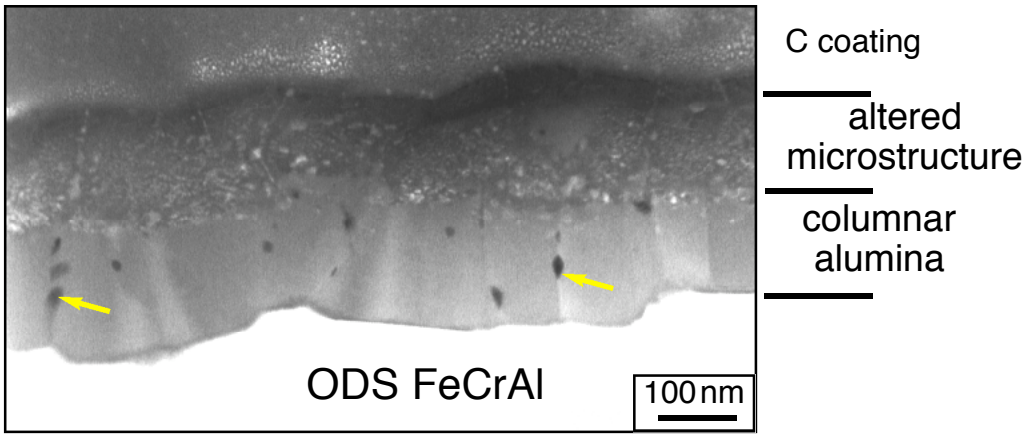

Figure 3. STEM high angle annular dark field image of the surface oxide on ODS FeCrAl after pre-oxidation and subsequent exposure to Pb-Li for 1 kh at 500°C. It appears that the microstructure of the outer portion of the α-Al_2O_3 layer adjacent to the Pb-Li has been disrupted possibly due to a reaction. Voids in the inner, columnar-grained layer are marked by arrows.

or disruption of the alumina microstructure occurred but, based on the XRD data, the oxide was not transformed to $LiAlO_2$ at 500°C.

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