

Characterization of HT-9 Ferritic-Martensitic Steels Oxidized in Lead Bismuth Eutectic

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INTRODUCTION

The Lead-Cooled Fast Reactor (LFR) design is one of the advanced systems currently under consideration for the Generation IV initiative. Because of its low melting point, low chemical reactivity, high boiling point, good gamma shielding, and high transparency to neutrons, lead bismuth eutectic (LBE) is an considered an ideal candidate for cooling these fast reactors. In order to use LBE as a coolant, however, the corrosion of the materials which will be in contact with it must be understood and controlled. To do this, we must study and characterize the growth mechanisms of the oxide layers on these materials in hopes of modeling them and eventually improving their characteristics. Using a combination of techniques, the oxide layers formed on three ferritic-martensitic HT-9 steel samples corroded in LBE are analyzed.

CORROSION TESTING

HT-9 samples from Timken Company were corroded in LBE with 10^{-6} wt% oxygen concentration, flowing at 2 m/s. Two of the samples were held in flowing LBE for 4 weeks at 500°C in the Delta Loop at Los Alamos National Laboratory (LANL). The other sample was held in flowing LBE for 18 weeks at 550°C at the Institute of Physics and Power Engineering (IPPE) loop in Russia.

OXIDE LAYER CHARACTERIZATION

Cross sectional samples of the oxide layers formed during LBE corrosion were examined at the Advanced Photon Source at Argonne National Laboratory using microbeam synchrotron radiation. The microbeam has a footprint on the sample of 0.2 micron x 2 micron, and enables the user to collect both diffraction and fluorescence signals simultaneously. The high brilliance of the synchrotron source enables the precise detection of diffraction signals from small volume fraction phases that can not be detected with classical x-ray diffraction. In addition the fluorescence signals allow us to precisely determine chemical composition. Thus, high-quality structural (x-ray diffraction) and elemental (x-ray spectroscopy) information can be obtained at very high

spatial resolution along the sample's oxide layer. Complementary images were also taken using a Scanning Electron Microscope (SEM).

RESULTS

The sample held for 18 weeks at the higher temperature has a thick oxide which contains several distinct sublayers. An SEM image of the 18-week 550°C IPPE loop sample, given in Figure 1(a), shows several oxide layers that formed during LBE corrosion. The chemical composition variation in these layers (from the fluorescence signal) is shown in Figure 1(c). Figure 1(b) shows the main phases observed in each layer from indexing the diffraction patterns.

The samples held in LBE for only 4 weeks at 500°C exhibit thinner oxide layers which contain sublayers similar to those in the sample held for 18 weeks.

In the metal layer of the 18 week IPPE loop sample only bcc iron peaks are observed. Following this, the inner oxide layer begins. This inner layer is highly porous, probably due to iron migration out of it into the outer oxide layer. In the metal-inner layer interface a chromium-rich band is observed (Fig 1(c)) which meanders to follow the original grain boundaries of the metal [1]. The diffraction patterns from this region show peaks associated with the Cr_2O_3 phase as well as some Fe_3O_4 (magnetite) and small concentrations of bcc iron from the original metal. The Cr_2O_3 phase eventually gives way to form FeCr_2O_4 as the chromium concentration drops off. Once the Cr_2O_3 phase has tailed off, the remainder of the inner oxide shows strong diffracted intensities of peaks associated with Fe_3O_4 as well as FeCr_2O_4 .

In the outer oxide layer, large columnar grains are observed except at the interface with the inner oxide layer where they are smaller and more equiaxed [1]. The diffraction patterns show peaks associated with Fe_3O_4 . EDS shows some small lead and bismuth deposits from the coolant distributed throughout, and higher concentrations of this are often associated with intergranular cracking.

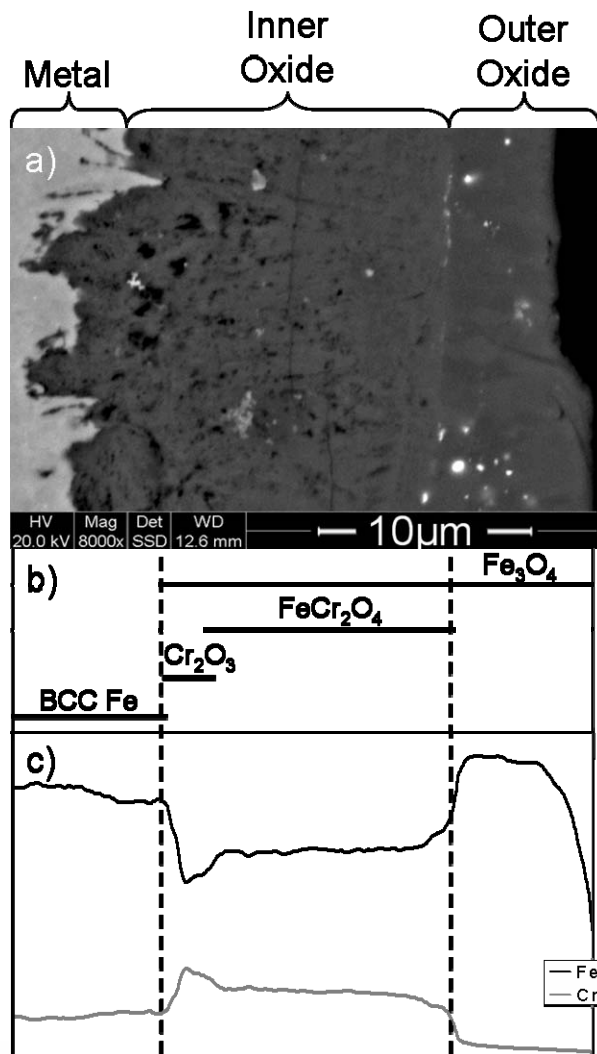


Fig. 1. a) SEM image of HT-9 corroded for 18 weeks in 550°C LBE. Layers are labeled on top and correlate to those shown using dashed lines below. b) Simplified x-ray diffraction results for each of the oxide layers. c) Fluorescence data showing iron and chromium concentrations throughout the oxide layers.

CONCLUSIONS

The structures seen in the HT-9 samples are all layered and suggest an evolution similar to that proposed in Hosemann, et al. [2] in which it is believed that the inner oxide was once part of the original metal and the outer oxide grew outward from it. These layers develop as iron diffuses outward from the metal while oxygen diffuses inwards to create chromium-rich (iron-depleted) porous regions closer to the metal, and iron-rich (chromium-depleted) areas further from the metal.

Lead and bismuth seen only in the outer layer and in higher concentrations near cracks indicates that the LBE coolant is likely getting in via intergranular cracks.

Another possibility is that the coolant is trapped on the surface of the oxide during corrosion, and the oxide grows around it.

Comparison of these results to those from HT-9 oxidized at lower temperatures for shorter times should give more insight to the evolution of these oxides and continue to aid in building a cohesive model of their growth.

REFERENCES

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2. P. Hosemann, M. Hawley, D. Koury, J.G. Swadener, J. Welch, A.L. Johnson, G. Mori and N. Li. "Characterization of oxide layers grown on D9 austenitic stainless steel in lead bismuth eutectic" *Journal of Nuclear Materials*, (In Press) (2008).