

## Spectroscopic studies of Pb corrosion of reactor materials

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### Introduction

The lead and lead-bismuth eutectic (Pb/LBE) is foreseen as a spallation target and coolant in advanced nuclear reactors due to its favorable physical, chemical, thermodynamic and neutronic properties. However, it is well known that steels are severely corroded by Pb/LBE if they are exposed directly at medium to high temperatures. New corrosion-tolerant materials and coatings must be developed to replace structural steel so the operating temperatures of these systems can be increased.[1-2]

In this study, x-ray absorption spectroscopy (XAS) has been used to characterize the surface corrosion of structural materials and potential coatings by lead at temperatures up to 1000°C. The methods developed here appear to be generally useful for future *in-situ* studies at elevated temperatures.

### Methods and Materials

Initial *ex-situ* experiments were conducted on 316L stainless steel, molybdenum metal, and single crystal spinel ( $MgAl_2O_4$ ). The samples were placed in a furnace under an Ar gas flow downstream from Pb pellets, heated to 1000°C for 50 hours, and packed in Ar gas for storage and transportation. For *in-situ* experiments, a specially designed tube furnace insert with Kapton windows permits the introduction of x-rays along the tube axis and the measurement of fluorescence at 90°. The *in-situ* sample was made from a molybdenum rod machined to present a 15° angle to the incident x-rays and coated with a ~3-6  $\mu m$  layer of Pb by thermal evaporation (Mo/Pb). The sample was heated sequentially to 400, 500, 700, 750, 800, 850, and 900°C under flowing Ar gas with intermediate cool-downs to room temperature for the XAS measurements. Fluorescence spectra and XAFS scans were taken using the 19-element Ge detector at the MRCAT 10-ID beam line at the Advanced Photon Source (APS).

### Results

Fig.1 shows that the 316L was severely corroded; the Mo sample exhibited some reddening, but retained a smooth surface, unlike the 316L sample; and the spinel showed virtually no evidence of Pb contamination. Pb fluorescence spectra of the three samples confirm significant surface contamination of the Mo and 316L samples while the spinel shows very little residual Pb on the surface.



316L stainless Molybdenum Spinel

Fig.1. Material surfaces after 50 hours of exposure to Pb at 1000°C in flowing Ar gas.

The *in-situ* Pb fluorescence measurements on the Mo/Pb sample indicate that the Pb film largely remains on the surface at all temperatures. The integrated intensity of the Pb fluorescence peak shows only a small reduction as a function of processing temperature.

The radial distribution functions obtained from the Mo edge XAFS data after each heating step, show that the Mo surface remains largely metallic but with an additional short-range order forming with high temperature processing. Each data set was fit using a pure Mo metal model (in the range  $1.6\text{\AA} < R < 5.6\text{\AA}$ ) and this fit was subtracted to obtain a qualitative measure of the change in the low-R intensity as a function of processing temperature. Fig. 2 shows the residual  $k^3\chi(R)$  for selected temperatures. The low-R peaks exhibit a systematic growth in intensity to a maximum at 750°C but disappear at higher temperatures.

### Discussion

*Ex-situ* studies confirm that 316L stainless steel is heavily corroded by lead vapor at high temperatures. Even when care is taken to limit its exposure with the use of an inert argon atmosphere, residual oxygen impurities remain and attack the substrate. While molybdenum was contaminated by the lead at 700°C and higher, *in-situ* experiments indicate that there may be a self-limiting mechanism present. The spinel proved to be virtually impervious to lead attack. Molybdenum and spinel are, therefore, excellent candidate coatings for 316L stainless steel to prevent Pb corrosion.

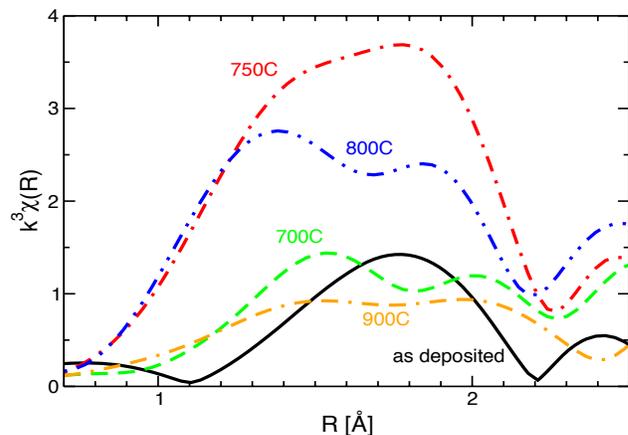


Fig.2. Residual  $k^3\chi(R)$  after removing Mo metal fit for samples treated at different temperatures: as deposited (—); 700°C (---); 750°C (- · -); 800°C (· · ·) and 900°C (- - -).

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### References

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