Surface studies of Corrosion of Stainless Steel by Lead Bismuth Eutectic

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Surface studies of Corrosion of Stainless Steel by Lead Bismuth Eutectic

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Acknowledgements

Collaborators:

- Ning Li and Los Alamos National Laboratory
- Advanced Light Source at LBNL

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Fig. 1 – Ingestion radio-toxicity of 1 ton of spent nuclear fuel. With a separation efficiency of 99.9% of the long-lived by-products from the waste, followed by transmutation, reference radio-toxicity levels can be reached within 700 years.
Why is Lead Bismuth Eutectic Important?

- Changing national security stances have led to reexamination of nuclear waste reprocessing
- Dangerous actinides can be separated and transmuted into safer products, creating a waste form dangerous for only hundreds of years, in addition to the production (up to 1/3 of the original fission energy) of useful energy (see Fig. 1)
- Non-moderating coolants or spallation targets for production of fast neutrons is required for transmutation
- Russian experience with LBE coolants in their nuclear submarine fleet makes LBE an attractive possible transmutation coolant technology
- Corrosion of steel by LBE is an important sticking point in the utilization of LBE
316 and 316L – Overview

• Our samples are derived from samples processed by IPPE (Russia) (see below). We focused initially on the 316 and 316L samples.

• SEM investigations show that the initial and corroded samples have significant levels of surface imperfections and roughness.

• EDX measurements show that 316 and 316L start with equivalent near surface compositions, but after corrosion 316 is Fe enhanced, whereas 316L was Cr enhanced.

• The corrosion layer in the 316 sample was found to be ~10 microns thick, and the corrosion layer in the 316L sample was less than a micron thick.
SEM Images of 316 Stainless Steel

SEM analysis of the surface of the unexposed 316 sample reveals the fresh steel surface without exposure to LBE.

The surface of the exposed, corroded 316 steel sample is drastically different when viewed at the same magnification as the above image.
316 steel tube

(unexposed)

(exposed, T = 550°C, t = 3000hr)
SEM Images of 316L Stainless Steel

SEM analysis of the surface of the unexposed 316L sample reveals the fresh steel surface without exposure to LBE.

The surface of the exposed, corroded 316L steel sample is drastically different when viewed at the same magnification as the above image.
316L steel tube

(unexposed)

(exposed, $T = 550^\circ C$, $t = 3000\text{hr}$)
X-ray Photoelectron/Sputter Depth Profiles

- XPS (X-ray Photoelectron Spectrometry) measures atomic composition and oxidation state of the top few atom layers of a sample.

- Sputter depth profiling uses an energetic ion beam to remove material in a controlled fashion to allow analyses to occur at varying depths into the sample.

- We find that the 316 sample had a layer of iron oxide formed above a chromium oxide layer.

- 316L retains the chromium oxide layer on the surface, as found in the initial samples, with a possible increase in chromium oxide thickness.
X-ray Photoelectron Spectrometry

Sputter Depth Profiling

5kV Ar ion sputtering

X-rays

XPS electrons

5kV Ar ion sputtering
XPS Depth Profile of 316L Stainless Steel Exposed to LBE for 3000 hours at 550 Degrees C (Non-Rotating)

Key
- C 1s Peak for 316L Exposed Stainless Steel
- O 1s Peak for 316L Exposed Stainless Steel
- Fe2p Peak for 316L Exposed Stainless Steel
- Ni2p Peak for 316L Exposed Stainless Steel
- Cr2p Peak for 316L Exposed Stainless Steel
- Mo2p Peak for 316L Exposed Stainless Steel
- Si2p Peak for 316L Exposed Stainless Steel (not normalized – please ignore)

Note the chromium oxide layer is intact even after 3000 hours (brown and purple lines)
XPS Depth Profile of 316 Stainless Steel Exposed to LBE for 1000 hours at 550 Degrees C (Rotating)

Key
- Dark brown line: O1s Peak for 316 Exposed Stainless Steel
- Dark blue line: Fe 2p Peak for 316 Exposed Stainless Steel
- Green line: Ni 2p Peak for 316 Exposed Stainless Steel
- Light blue line: Cr 2p Peak for 316 Exposed Stainless Steel

Note enhancement of Fe & O at surface (purple and black lines) and depletion of Cr (blue line)
XPS Depth Profile of 316L Stainless Steel Exposed to LBE for 1000 hours at 550 Degrees C (Non-Rotating)

Note that initial chromium oxide layer is preserved (blue & black lines) over the metal surface. A small amount of surface iron oxide is seen (purple and black lines).
XPS Depth Profile of 316 Stainless Steel Exposed to LBE for 3000 hours at 550 Degrees C (Rotating)

Note formation of iron oxide layer at surface (green and purple lines) above chromium oxide layer (brown and purple lines)
Conclusions

• Corrosion of steel by LBE seems to have strong dependence on surface and near surface structure

• In particular:

  • **Annealed** 316 oxide: ~ 10 microns thickness, iron oxide surface depleted in chromium

  • **Cold rolled** 316L oxide: ~ 1 microns thickness, native protective chromium oxide preserved

  • Other alloys (D-9, HT-9) show complementary trends (same surface -> same corrosion trend)

• Evidence of migration during corrosion process

  • Metals moving from bulk to surface – where is the iron oxide layer coming from (on top of the buried chromium oxide layer)?
Future Work - Experimental

- Examine corrosion processes from different surface preparations, steel compositions
- Start collaborations to prepare samples suggested by our and others work
- Other characterizations of the samples, including:
  - Micro-Raman spectroscopy depth profiling using sputter milled surfaces
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ИТОГО: 616,94

Главный инженер лаб. 119

Н.С. Скворцов
Future Work - Mechanisms

• Discussions with colleagues led to the discovery of earlier work on 304 stainless suggesting that cold worked surfaces, with the smaller grain sizes associated, had thicker and more stable protective chromium oxide layers.

• We have a selection of samples clustered around the composition of 316 – we can look at the effects of surface preparation with the 316, 316L, and D-9 samples.

• Comparison of the D-9 with the similarly polished HT-9 will examine the effects of composition.
Bibliography


