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Development of Nanostructure Based Corrosion-Barrier Coatings on Steel for Transmutation Applications

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Task 23

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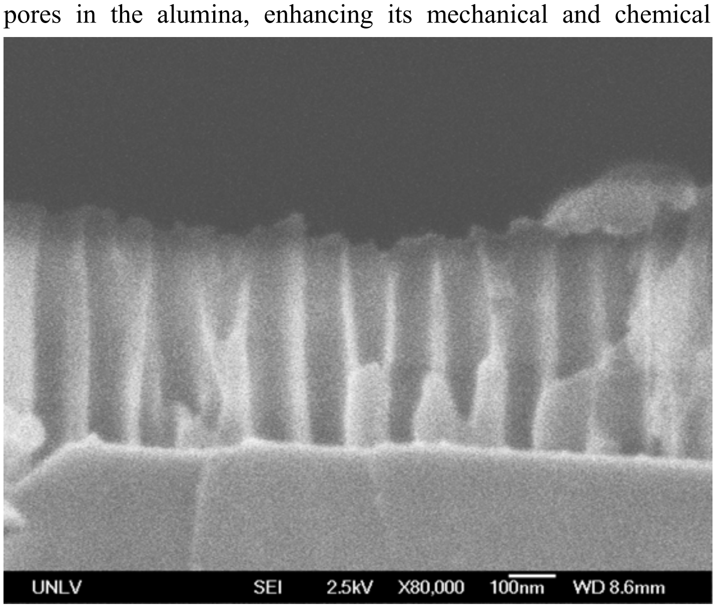
BACKGROUND

Advanced transmutation systems require structural materials that are able to withstand high neutron fluxes, high thermal cycling, and high resistance to chemical corrosion. The current candidate materials for such structures are ferritic and ferritic-martensitic steels due to their strong resistance to swelling, good microstructural stability under irradiation, and the retention of adequate ductility at typical reactor operating temperatures.

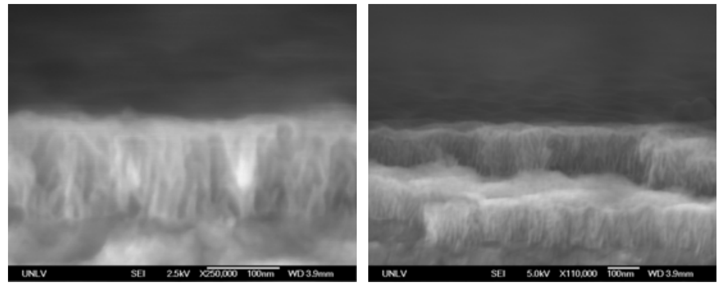
In parallel, lead bismuth eutectic (LBE) has emerged as a potential spallation target material for efficient production of neutrons, as well as a coolant in the accelerator system. While LBE has excellent properties as a nuclear coolant, it is also highly corrosive to stainless steel. The corrosion is due to relatively high solubilities of the base and major alloying components of steel, such as Ni, Fe, Cr, etc. in LBE at elevated temperatures. Without some protection, the steel structures rapidly corrode in LBE through dissolution and leaching of these materials.

RESEARCH OBJECTIVES AND METHODS

The objective of this project is to develop a novel nanostructure based coating technology that will provide significantly improved corrosion resistance for steel in LBE at elevated temperatures (500-600^{o}C), as well as provide long-term reliability under thermal cycling. The nanostructure based coatings will consist of a layer of nanoporous alumina with the pores filled with an oxidizing metal such as Cr, followed by a capping layer of alumina. Alumina, which is a robust anti-corrosion material, provides corrosion resistance at elevated temperatures. The Cr serves two purposes: (1) it acts as a solid filler material for the pores in the alumina, enhancing its mechanical and chemical integrity, and (2) it acts as a second layer of defense against corrosion by providing a replenishable source of Cr (for the formation of a Chromium oxide protective layer) in case the alumina layer is compromised. In addition to their usefulness at higher temperatures, the proposed coatings can also provide increased reliability at lower temperatures by complementing the oxygen control technique.



Cross-sectional FESEM image of Cr nanowires inside a porous alumina template showing non-uniform distribution of nanowires.



Cross-sectional FESEM images of Ni nanowires electrochemically deposited inside nanoporous alumina for different time lengths.

Working with LANL collaborators, the stainless steel alloys HT-9 and EP-823 were chosen as the candidate materials for investigation. The project objective will be achieved in three phases; each phase will be carried out over a one-year period.

Phase I will develop the fabrication technology for the coatings on steel, and study their structural integrity at elevated temperatures and under thermal cycling.

Phase II will perform corrosion studies of the structures in LBE at elevated temperatures.

Phase III will use the data from Phases I and II to develop an optimized coating technology for improved structural integrity under thermal cycling, and improved corrosion resistance in LBE at elevated temperatures. If necessary, multiple layers of such coating structures will be used for increased resistance to corrosion.

During Year 2 of the project (2005-2006), extensive investigation was carried out on the deposition of metal nanowires inside the pores as well as the deposition of the top dense layer of alumina. The following are the specific goals this year for the project:

- To develop the technology to deposit metal nanowires inside nanoporous alumina layers on HT-9 and EP-823 steel.
- To develop the technology to create thick dense alumina layer on metal nanowires created on steel substrates.

RESEARCH ACCOMPLISHMENTS

During Phase I of the project, a significant problem was encountered with uniformity of Cr nanowires synthesized inside the alumina pores. A systematic study was carried out to improve the

ACADEMIC YEAR HIGHLIGHTS

- "Nanostructure based Corrosion-Barrier Coatings on Steel" was submitted to the *J. Nuclear Materials* (in review).

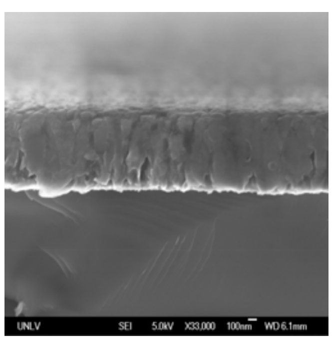
deposition uniformity; however no significant improvement could be achieved. This was a puzzling situation since a well established recipe for the deposition of Cr was used. The only explanation for the observed non-uniformity is the restricted space inside the nanopores that may not be amenable to the Cr synthesis chemistry.

As a solution to the above problem, alternative metals were looked at to form the nanowires. The purpose of the metal nanowires is to provide structural integrity to the nanoporous alumina, as well as a second defense mechanism against corrosion by oxidizing in case the top alumina layer is compromised. Nickel was selected due to its established electrochemical synthesis procedure and deposition of Ni nanowires was achieved.

In addition to the direct electrochemical deposition technique, another approach was initiated to deposit Ni inside the nanopores. This technique involves the electro-phoretic deposition of Ni nanoparticles inside the pores. A primary advantage of this technique is the improved flexibility of the Ni nanowires (consisting of nanoparticles) with thermal cycling.

Once the process parameters for the deposition of Ni nanowires were optimized, the deposition technique was transferred to steel samples. Deposition of Ni nanowires on steel substrates was achieved by using the following procedure. A new batch of steel samples were coated with metallic aluminum which were first anodized using constant current anodization. The voltage across the cathode and anode was monitored to monitor the anodization process. Since it is difficult to obtain cross-sectional images of samples created on steel samples, the filling of the nanoporous alumina pores with Ni had to be confirmed from the current-time characteristics. Based on comparison of such data with that from nanowires deposited on a silicon substrate, the Ni nanopillars deposited in the nanopores on a steel substrate are expected to have similar features as on silicon substrates.

The thick layer of dense alumina on top of the Ni nanowires provides the first layer of defense against corrosion for the steel substrates. After investigating the various techniques to deposit alumina, sputter deposition was identified as the appropriate technique for depositing thick layers of insulators. However, the insulating nature of alumina makes it a difficult task to deposit by sputtering technique. To address this problem, a pulsed DC sputtering technique was used, which is a relatively new technique for the deposition of insulators. An alumina sputter target of the appropriate dimensions was obtained for this purpose and an extensive preliminary testing was carried out to optimize the deposition process. Such preliminary experiments were carried out on silicon substrates since it allows cross-sectional imaging of the samples. The deposition rate for alumina was determined from a series of such cross-sectional images. The experimentally obtained deposition rate was used to deposit a 3 micron layer thick dense alumina layer on top of the Ni nanowires. The samples are currently being tested for thermal recycling. Effort is also continuing to deposit thicker layers of alumina, preferably up to 10 microns.



A typical cross-sectional image of dense alumina deposited on a silicon substrate by pulsed DC sputtering. Charging of the insulator prevented from getting SEM images of thicker alumina layers

FUTURE WORK

The next phase of the project will focus on:

- extensive thermal cycling characterization of the coating layers on HT-9 and EP-823 steel at elevated temperatures,
- experimentally optimize coating parameters for maximum adhesion for thermal cycling,
- investigate and develop the deposition technique for Cr nanowires inside the alumina pores,
- evaluate the structural integrity of the coatings with Cr at elevated temperatures and under thermal cycling, and
- characterization of the coating layers in LBE.

A programmable furnace will be acquired and a specialized sample holder fabricated to perform automated thermal cycling of the coatings developed on steel samples. The samples will then be characterized by SEM and also scratch tests to evaluate the structural integrity and adhesion properties of the coatings for thermal cycling at different temperatures. The process technology will be developed for the deposition of Cr inside the alumina nanopores electrochemically to form the Cr nanowires. The nanoporous coatings on steel substrates will be subjected to elevated temperature thermal cycling, up to 500°C and 600°C. As before, the adhesion properties of the nanoporous alumina films will be evaluated using scratch tests.

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