Task 23

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

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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.

Thus, for long term reliability of the structures, it is necessary to provide some protection of the steel surface from corrosion, without affecting the bulk properties of the steel. One such technique that has been well investigated is the use of oxygen control at the surface of the steel, which maintains a coating of oxide layer that protects the steel surface. The protective layer forms due to the higher affinities of the steel alloying components to oxygen compared to lead and bismuth. However, once a continuous film of oxide is formed, a competing process takes place; the oxide layer interacts with the LBE causing reduction of the oxide layer at higher temperatures. It is thus critical to maintain an optimum flow of oxygen at the LBE/steel interface, which is made challenging by the non-uniform temperature distribution in the transmutation systems. In addition, while the oxygen control technique works effectively at lower temperatures, it is not appropriate for higher operational temperatures (500-600^{o}C), which is becoming increasingly important. Thus, it is necessary to develop alternative techniques for corrosion protection of steel that will perform reliably at elevated temperatures and under thermal cycling in LBE.

RESEARCH OBJECTIVES AND METHODS

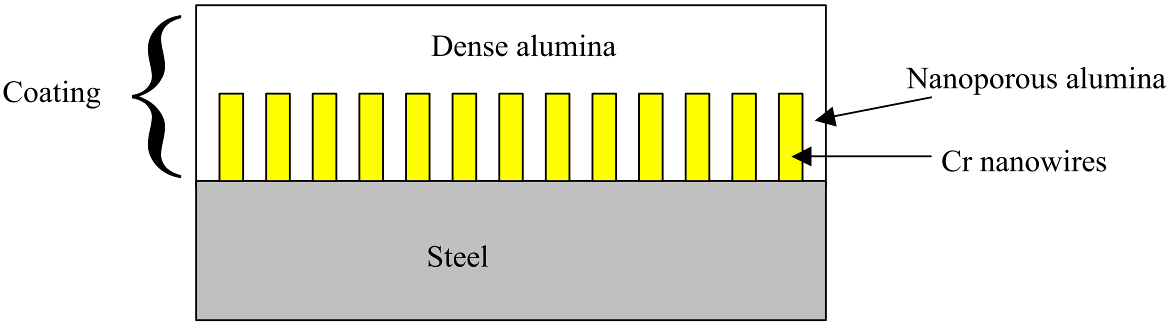
The objective of this project is to develop a novel nanostructure based coating technology that will provide significantly improved corrosion resistance for steel in LBE at elevated temperatures (500-600^{o}C), as well as provide long-term reliability under thermal cycling. The nanostructure based coatings 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. The innovation of this project is the use of a nanoporous alumina layer for the coating, which is mechanically flexible and can expand and contract with the underneath steel surface. As a result, the mechanical integrity of the coating is preserved under thermal cycling. 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. The nanostructure based coatings developed in this project will significantly enhance the long-term reliability of steel structures in LBE at elevated temperatures and under thermal cycling.

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

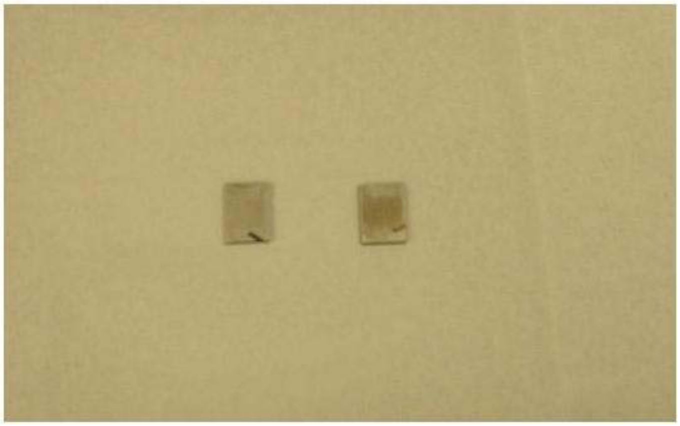
Phase I will develop the fabrication technology for the coatings on steel, and study their structural integrity at elevated temperatures and under thermal cycling.

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

Phase III will use the data from Phases I and



Schematic cross-section of the proposed nanostructure based coating. The nanoporous nature of the bottom alumina layer allows it to expand and contract with the steel surface thus preserving the mechanical integrity of the coating under thermal cycling. The dense alumina layer, provides the first layer of protection against corrosion. The Cr nanowires, in addition to enhancing the structural and chemical integrity of the nanoporous alumina, provides a second layer of protection in case the alumina layer is compromised. Stacked multiple layers of the coating structure can be created on steel surface to provide increased protection against corrosion.



Photograph of two anodized samples showing the porous alumina on steel.

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.

The following are the specific goals this year for the project:

- To develop the technology to create thick nanoporous alumina layers on HT-9 and EP-823 steel.
- To electrochemically deposit Cr nanowires inside the alumina pores.
- To develop the technology to create thick dense alumina layer on top of the Cr nanowires.
- To investigate the structural integrity of the coatings at elevated temperatures and under thermal recycling.

RESEARCH ACCOMPLISHMENTS

A specialized sample holder was developed for the anodization of alumina on steel. In addition, it was determined that oxalic acid was the most appropriate acid for the anodization of these structures. The steel samples obtained from LANL were first cut into a number of pieces, each measuring 11mm x 8mm x 1.6mm, to allow multiple experiments.

The steel samples were cleaned and a thin layer of titanium (10 nm thick) was deposited on the surface of the steel followed by deposition of a thick layer of 99.999% aluminum (1 um thick) using e-beam evaporation. The Ti layer was deposited for improved adhesion of aluminum on steel; direct deposition of aluminum on steel showed poor adhesion. The samples were then anodized in 0.3M Oxalic acid solution maintained at 15^{o}C using a constant current density of 20mA/cm^2. Visual inspection of the samples (shown in the figure above) also confirmed the formation of the porous alumina layer. The samples were then coated with a thin layer of gold and characterized by SEM imaging. However, the surface of the sample was found to be very rough, which made high resolution imaging very difficult.

ACADEMIC YEAR HIGHLIGHTS

- Adhesion properties of thin film nanoporous alumina templates" was submitted by to the *J. Vacuum Science & Technology* (in review).
- "Nanostructure Based Corrosion-Barrier Coatings on Steel for Transmutation Applications," was presented at the ANS Student Conference, April 2005, Columbus, OH (*received 2nd best paper award*).
- "Template based Nanofabrication: Mechanical Characterization of Film-substrate Interface" was presented at the 3rd International Conference on Experimental Mechanics, Singapore, Nov. 29-Dec. 1, 2004.
- "Nanostructure based Composite Material Coatings on Steel" by B. Das and P. Singaraju was presented at the Int. Conf. Adv. Composite Mat (ICRACM-2004), Varanasi, Dec. 17-19, 2004.

An important requirement for this project is good adhesion of the coating film on the substrate under thermal cycling. Towards this goal, the samples were subjected to thermal cycling to 300^{o}C and 400^{o}C. Visual inspection of the samples showed the appearance of thermally cycled samples was the same as the uncycled (room temperature) samples. Also, a preliminary scratch test using a pin showed the alumina coating to have good adhesion to steel after thermal cycling.

FUTURE WORK

The next phase of the project will focus on (i) appropriate sample preparation to enable SEM imaging, (ii) thermal cycling to higher temperatures, (iii) deposition of Cr nanowires, (iv) formation of dense top alumina layer, and (v) characterization of the nanoporous coatings. While in the earlier alumina coatings the presence of nanopores could be confirmed, the samples were difficult to image due to surface roughness. To overcome this problem, nanoporous alumina coatings will be fabricated on polished steel surface. The steel samples will be polished mechanically as well as electrochemically followed by the deposition of aluminum. The nanoporous coatings on steel substrates will be subjected to elevated temperature thermal cycling, up to 500^{o}C and 600^{o}C. As before, the adhesion properties of the nanoporous alumina films will be evaluated using scratch tests.

Cr will be deposited inside the alumina nanopores electrochemically to form the Cr nanowires. Next, a dense layer of alumina will be formed on the surface through the hydration technique. If the hydration technique proves to be inadequate to form a sufficiently thick dense alumina layer, sputtering technique will be used to form such layers. The coating layers will be characterized next using scratch tests under different thermal cycling conditions.

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