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

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TRP Task 23
Project Title:

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AFCI Research Area: **Transmutation Sciences Technology**

Abstract:
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.*

Work Proposed for Funding Year 2004-2005, Goals, and Expected Results:
Year 1 of the project will develop the coating technology and evaluate the structural integrity of the coatings at elevated temperatures and under thermal cycling. The project goals and expected results for Year 1 are to (i) develop the technology to create thick nanoporous alumina layers on HT-9 and EP-823 steel, (ii) deposit Cr nanowires inside the alumina pores, (iii) create capping layers of alumina on the Cr nanowires, and (iv) evaluation of the structural integrity of the coatings at elevated temperatures and under thermal recycling.

Funding Requested:

Funding Year:	**2004-2005**	**2005-2006**	**2006-2007**
Total (K$)	128	111	112

PROPOSAL NARRATIVE

Background and Rationale

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 [1]. 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 [2]. 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 [2]. 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.

The use of an anti-corrosion coating layer on steel surface is a promising means to provide corrosion protection at elevated temperatures (> 500^{o}C). In fact, preliminary investigations have successfully demonstrated the feasibility of such coatings: alumina-coated steel immersed in molten lead at a constant temperature of 520^{o}C have shown significantly improved surface stability [3]. For transmutation applications, however, there is also an additional requirement: it is necessary for the coating layer to be able to withstand thermal cycling and continue to provide effective passivation of the steel surface. This is made difficult by the fact that most anti-corrosion coating materials are thermally mismatched to steel. As an example, alumina (Al_2O_3), which is widely used as an anti-corrosive coating, has a thermal expansion coefficient of $8x10^{-6}$ /K whereas for HT9 steel it is $11.44x10^{-6}$ /K [1]. Such mismatch poses a significant problem for coating survivability under thermal cycling.

In this project, we propose to develop a nanostructure based coating technology that will address the above issues. The innovativeness of the proposed structure is in the use of a *nanoporous* layer of coating, which eliminates the thermal mismatch problem at the coating/steel interface. A schematic cross-section of the proposed system is shown in Figure 1. The anti-corrosion coating layer consists of a thick layer of nanoporous alumina with the pores filled in with nanowires of an oxidizing metal such as Cr, followed by a thick layer of *dense* alumina. Each layer (nanoporous alumina, Cr nanowires, and dense alumina) will be between 40 – 100 microns thick. The nanoporous nature of the bottom alumina layer (in which the Cr nanowires are embedded) makes the anti-corrosion coating mechanically flexible, allowing it to expand and contract with the underneath steel surface, *thus preserving its mechanical integrity under thermal cycling*. In fact, thermal barrier coatings based on nanostructures have been shown to significantly improve wear resistance [4]. The anti-corrosion coating provides protection at two levels. The top layer of dense alumina provides the first layer of protection; dense alumina is a robust anti-corrosion material and is widely used for corrosion protection at higher temperatures. The Cr serves two purposes: (i) it acts as a solid filler material for the pores in the nanoporous alumina thus enhancing its mechanical and chemical integrity, and, (ii) provides a second layer of defense against corrosion by providing a replenishable source of Cr (for the formation of protective layers of Chromium oxide), in case the alumina layer is compromised. *The proposed coating system thus provides multiple layers of protection against corrosion, contributing to the long-term structural reliability of steel in transmutation systems.* In addition, multiple stacked layers of structures shown in Figure 1 can be created on the steel surface for further protection against corrosion.

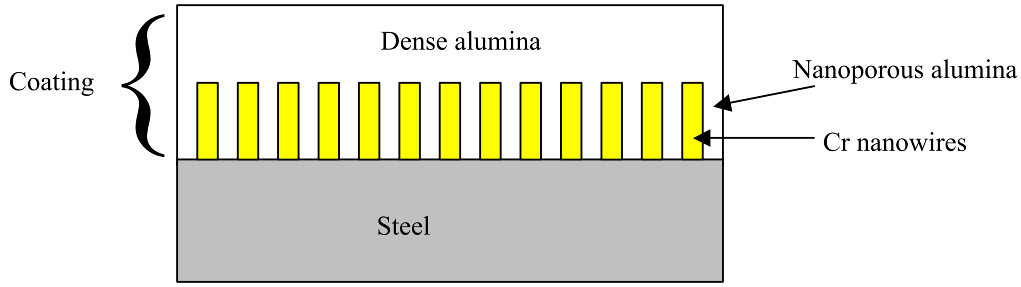

Figure 1. Schematic cross-section of the proposed nanostructure based anti-corrosion coating. The nanoporous nature of the bottom alumina layer allows it to expand and contract with the steel surface thus preserving the mechanical integrity of the coating under thermal cycling. The dense alumina layer, which is a robust anti-corrosion material, 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 against corrosion by supplying a replenishable source of chromium (for the formation of a protective layer of chromium oxide) 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.

Research Objectives:

The overall objective of this project is to develop a nanostructure based coating technology for steel that will provide effective corrosion protection in LBE at higher temperatures (500 - 600^{o}C), and provide long-term reliability under thermal cycling. Working with our DOE collaborator, the stainless steel alloys HT-9 and EP-823 have been 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 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.

Project Goals: The following are the specific goals for Year 1 of this project:

- Develop the technology to create thick nanoporous alumina layers on HT-9 and EP-823 steel.

- Electrochemically deposit Cr nanowires inside the alumina pores.

- Develop the technology to create thick dense alumina layer on top of the Cr nanowires.

- Investigate the structural integrity of the coatings at elevated temperatures and under thermal recycling.

Technical Impact:

The successful completion of this project will develop a coating technology for HT-9 and EP-823 steel that will provide effective corrosion protection in LBE at elevated temperatures (500 - 600^{o}C), and provide long-term reliability under thermal cycling. The coatings can also provide increased reliability at lower operational temperatures by acting in conjunction with the oxygen control technique. Such coatings are expected to significantly contribute to the long-term reliability of HT-9 and EP-823 steels used in transmutation systems.

Research Approach / Scientific Investigation Plan:

Fabrication Procedure:
The nanoporous alumina, that is at the foundation of the proposed coating technology, is formed by the anodization (or electrolytic oxidation) of metallic aluminum into porous alumina. This is a natural self-organized process that does not require any lithographic tools. When aluminum is anodized in a suitable acidic electrolyte under controlled conditions, it oxidizes to form a hydrated aluminum oxide (alumina) containing a two dimensional hexagonal array of cylindrical pores as schematically shown in Figure 2. The pore diameter and the inter-pore spacing depend on electrolyte pH, temperature, the anodization current density and aluminum microstructure (grain size). The anodization parameters can be precisely controlled to form pore diameters between 4 nm and 100s of nm and pores can be 10s of microns deep. Anodized aluminum has been investigated during the last fifty years due to its central role in providing a corrosion resistant coating for aluminum [5]. Within the last fifteen years, the nanometer scale pores in porous alumina fabricated on *bulk* aluminum substrates have also been used to synthesize various metals and semiconductor material [6]. While the use of bulk aluminum substrate demonstrates the basic fabricational concepts, for any useful application of this method, it is necessary to create the nanoporous alumina layer on non-aluminum substrates. To address this, we have developed the technology to create nanoporous alumina films on a variety of substrates including silicon, silicon dioxide, glass and ceramic [7]. We have also successfully used such nanoporous alumina films to synthesize a variety of metal and semiconductor nanowires [7]; Figure 3 shows such CdS nanostructures created on a silicon substrate.

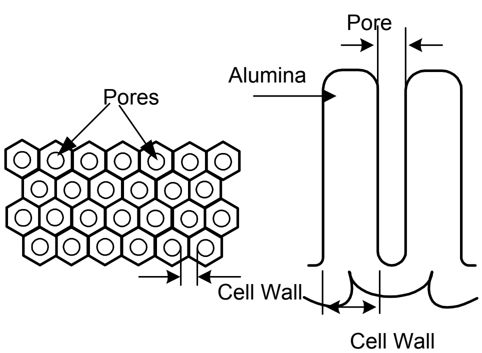

Figure 2: Schematic top and cross -sectional views of hexagonal array of pores formed in anodized alumina.

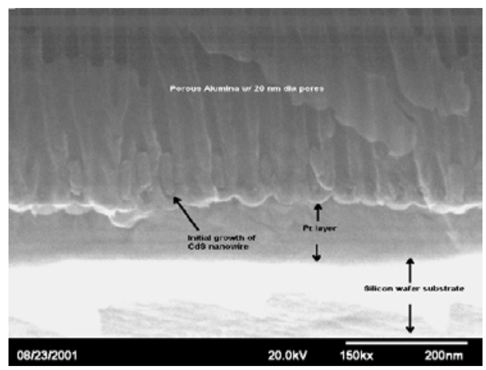

Figure 3: CdS nnowires formed in the pores of anodized alumina on a silicon substrate (Das, [7]).

Project Plan:

The project objectives will be achieved through successful accomplishments of the following project tasks:

Task 1 . *Develop the technology to create thick nanoporous alumina layers on HT-9 and EP-823 steel.*

This task is divided into the following sub-tasks:

- **Fabrication of a dedicated anodization apparatus for the anodization of aluminum films on large steel substrates**

  Since our current research using nanoporous alumina primarily focus on electronic and photonic devices, our present anodization apparatus is set up for small circular substrates that are approximately 0.1 mm thick. For this project, we will develop a dedicated anodization apparatus that will handle larger and thicker substrates. Anodization is performed in a simple wet chemistry apparatus that is relatively easy to fabricate and we have significant experience in designing and implementing them [8]-[9]. During apparatus design, we will consult our DOE collaborator to identify substrate dimensions.

- **Deposition of aluminum metal on HT-9 and EP-823 steel substrates**

The steel substrates will be obtained from our DOE collaborator. The substrates will be cleaned, following which a thick film of aluminum metal will be deposited on them. Aluminum can be deposited using a variety of techniques including Hot-Dip process, Wire-arcing, Plasma thermal spraying and Sputtering. For this project we will investigate Hot-Dip process and Sputtering techniques due to the superior material quality obtained by these techniques. For the Hot-Dip technique, the samples will be sent to a commercial vendor, who will perform the coatings; such commercial services are readily available. Sputtering technique is a high vacuum technique (and hence more expensive), that provides very high quality aluminum films, in terms of purity and grain size. These films will be used to investigate the effects of the aluminum quality on the integrity of the coating. Sputtered aluminum films will be deposited at the National Nanofabrication Facility at University of California at Santa Barbara, where the PI has an ongoing account. The aluminum film thickness will be determined in consultation with our DOE collaborator, however, the final alumina layer will be at least 120 microns thick.

- **Anodization of aluminum films to create nanoporous alumina on steel substrates**

The aluminum films will be anodized in a sulfuric acid solution under constant current conditions. As a standard procedure, the electrolyte will be cooled to about $2^{o}C$ to minimize pore size variation. Porous alumina with three different pore dimensions (between 10 nm and 50 nm) will be created to investigate the effect of pore size on mechanical integrity. During anodization, the potential-time characteristics will be monitored to determine the endpoint in order to avoid oxidation of the steel surface. If necessary, a thin barrier metal such as platinum will be applied between the steel and the aluminum to prevent oxidation; we often put a 20 nm thick platinum layer on silicon substrates to prevent oxidation of the silicon (Figure 3).

Task 2 . *Electrochemically deposit Cr nanowires inside the alumina pores.*

Electrochemical deposition of Cr is an established industrial process, which we also have extensive experience in. The Cr will be deposited from a solution of chromium salt in our electrochemical cell.

Task 3 . *Fabricate dense alumina layer*

The dense alumina layer on top of the Cr nanowires will be created using a hydrolyzing step. In this process, the substrate is immersed in boiling deionized water for a specific time period, which grows the alumina layer from the sides on the top. We have significant experience in creating such dense layers [10], and will determine the optimum hydrolyzing time for the desired alumina layer thickness.

Task 4. *Investigate the structural integrity of the coatings at elevated temperatures and under thermal cycling.*

The nanostructure based coatings will be extensively characterized for their microstructural and mechanical properties at room temperature as well as at elevated temperatures and under thermal cycling. Polished microsections and fracture surfaces will be prepared for microscopy analysis. The microstructures of the coating will be determined by optical microscopes, Scanning Electron Microscopes and Transmission Electron Microscopes. Investigations will be made of pores, lamellae boundaries and microcracks, and their total distribution on the coatings will be characterized by image analysis. Since the propagation of micro cracks is a potential candidate for coating delamination, particular attention will be paid to it. Mechanical properties of the coatings will be studied by microhardness measurements and adhesion scratch tests. Microhardness testing will be performed from the coating cross-section using a microhardness tester. The adhesion scratch test will be performed by drawing a loaded stylus across a coated surface under an increasing normal load until some well-defined failure occurs at the critical load. The critical failure events and changes in the failure mechanisms can be identified from relative values of the vertical and horizontal forces. The samples will be subjected to thermal testing during which the surface temperature will be varied cyclically between approximately room temperature and 600 ºC. The thermally cycled coatings will be investigated for microstructural and mechanical properties as described above.

Expected Technical Results for Year One:

- Development of a fabrication technology for the creation of thick nanoporous alumina layers on HT-9 and EP-823 steels.
- Development of a fabrication technique to create Cr nanowires embedded in nanoporous alumina on HT-9 and EP-823 steels.
- Development of a fabrication technique for the creation of dense alumina layers on top of Cr nanowires.
- Characterization data for nanostructure based coatings on HT-9 and EP-823 steel at elevated temperatures and under thermal cycling as a function of alumina pore diameter.

Capabilities at UNLV and National Laboratories:

The fabrication and characterization of the nanostructure based coatings will be carried out at UNLV Nanotechnology Laboratory (Das), UNLV Materials Performance Laboratory (O'Toole), LANL Materials Science Laboratory (Maloy) and the National Nanotechnology User Facility at UCSB. The PI has an established agreement with UNLV Materials Performance Laboratory for thermal testing of the coatings. The capabilities at UNLV include fabrication and characterization equipment such as electron-beam evaporation, sputtering, anodization apparatus, electrodeposition systems, furnaces, precision electronic balances, precision saw, variable speed grinder/polisher, X-ray diffraction system, scanning electron microscopes, transmission electron microscope, constant load testing fixtures, high temperature heat treatment furnaces and adhesion scratch test system. The National Nanotechnology User facility at UCSB is a fully equipped fabrication facility, where the PI has an established account. The equipment to be used at UCSB is a large area sputtering system with a deposition rate of 300-400 nm/min. The facility at LANL that are important for this project include equipment for mechanical tests including creep, dynamic tests, fatigue, fracture, high pressure, indentation, nano-indentation and thermal cycling.

The LANL investigator (S. Maloy) is the AFCI Fuels & Materials Project Leader, and brings extensive knowledge and expertise related to structural behavior of steel in radiation environments. The UNLV investigator (B. Das) has over fifteen years of experience in fabrication and characterization of nanoscale materials and devices including metallization, anodization, SEM, etc. *One of his current projects involves the creation of metal nanowires in alumina templates created on plastic substrates, which involves mechanical characterization of porous alumina coatings on plastic.* The experience and equipment from this project will be of significant help in the successful characterization of the proposed coating structures.

<u>Equipment Requested for TRP User Labs</u>:

1. Anodization apparatus for thick and large area steel samples: this equipment will be constructed and housed in UNLV's Nanotechnology Laboratory. The equipment will consist of (i) an electrochemical cell (to be constructed), (ii) a HP power supply, (iii) data acquisition system consisting of a HP voltmeter, National Instruments Data Acquisition card, Lab View software and a PC.

Project Timeline with Milestones and Deliverables:

<u>Timeline Narrative</u>:

This project is planned to cover three years, beginning in Fall 2004. During the first year, the fabrication technology for the coatings on steel will be developed. This will include the fabrication of a dedicated anodization apparatus, which will allow anodization of thick and large area steel samples. During equipment construction, the steel samples will be obtained, cleaned and coated with aluminum. These samples will then be anodized in the new apparatus. Following this, Cr will be electrochemically deposited inside the alumina pores, followed by the creation of the thick layer of dense alumina. The coatings will be next extensively characterized for mechanical and microstructural properties under thermal cycling. During Year 2, extensive corrosion studies of the coatings in LBE will be carried out at elevated temperatures. The LBE loop at UNLV will be used for this purpose. Corrosion studies will include (i) electron probe microanalysis, (ii) MicroRaman characterization, (iii) X-ray Diffraction, (iv) X-ray Photoelectron Spectroscopy (XPS), and (v) microbalance measurements for the elemental, chemical and mass characterization related to corrosion. The necessary equipment for such measurements are currently available at UNLV. During Year 3, the results from previous year will be used to develop the optimum technology for maximum corrosion prevention in LBE, as well as for mechanical integrity under thermal cycling. This may include the creation of multiple stacked layers of the coatings investigated in the previous two years.

Timeline, Major Milestones and Deliverables for Year One

TASKS	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul
1. Create nanoporous alumina												
-- Apparatus construction												
-- Aluminum Deposition												
-- Form nanoporous alumina												
2. Deposit Cr nanowires												
3. Create alumina capping												
4. Characterize coatings												
Reporting Requirements												
Travel for LANL meetings												

Quarterly report   Final report

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