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Task 23

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

B.J. Das

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 °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 was to develop a novel nanostructure based coating technology that will provide significantly improved corrosion resistance for steel in LBE at elevated temperatures (500-600 °C), as well as provide long-term reliability under thermal cycling. The nanostructure based coatings consisted 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.

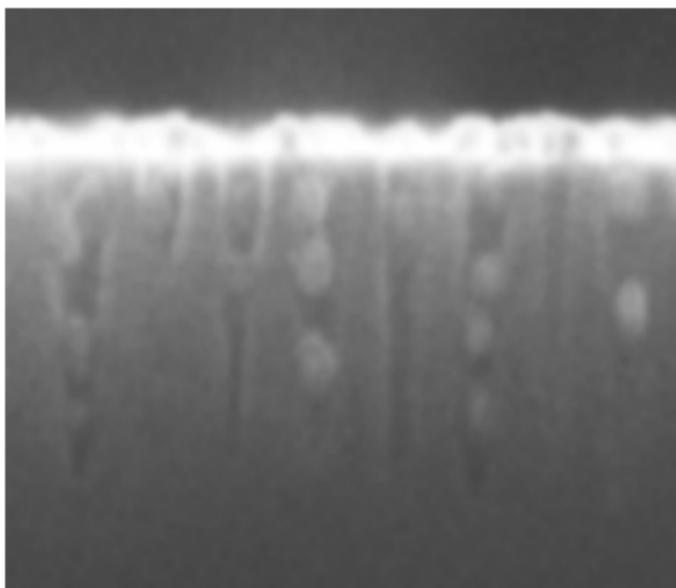
The innovation of this project was the use of a nanoporous alumina layer for the coating, which is mechanically flexible and can expand and contract with the underneath steel surface. As a result, the mechanical integrity of the coating is preserved under thermal cycling. In addition to their usefulness 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 national laboratory 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 was achieved in three phases; each phase will be carried out over a one-year period.

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

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

Phase III used the data from Phases I and II to develop an



Cross-sectional image of electro-phoretically deposited nanoparticles inside nanoporous alumina.

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 were used for increased resistance to corrosion.

During Year 3 of the project (2006-2007), extensive investigation was carried out on the deposition of longer and improved quality metal nanowires inside the pores using a new technique as well as the establishment of the experimental setup for characterization of the coatings.

RESEARCH ACCOMPLISHMENTS

As reported previously, during Phases I and II of the project, a significant problem was encountered with the synthesis of Cr nanowires inside the alumina pores, the uniformity of coverage was very poor. As a result, alternative metals to form nanowires were looked into and nickel was selected primarily due to its established electrochemical synthesis procedure.

A number of recipes were investigated for their suitability for synthesis inside nanoscale pores, and the process parameters were experimentally optimized for the synthesis of nanowires. The deposition of the Ni nanowire was performed in a two-electrode arrangement with a mixture of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and H_3BO_3 as the source of Ni. The wires were deposited at a potential difference of 1 V between the anode and the cathode and at ambient temperatures. The Ni nanowire samples were characterized by Field Emission Scanning Electron Microscopy (SEM), which showed excellent uniformity and coverage. However, while Ni can provide very good structural integrity to the porous alumina, one potential problem is its higher dissolution rate in LBE.

In addition, it was noted that the heights of the Ni nanowires were limited, and even with extended deposition times, the heights were limited to a few tenths of a micron. This limited height was believed to be arising due to the dynamics of fluid flow inside the nanoporous alumina.

To address the above issues, two different approaches were taken, A systematic study was continued during the past year to improve the deposition uniformity of the Cr nanowires, and some improvement was achieved. The uniformity of coverage showed improvement and experimental optimization of process parameters was continued for further improvement of the coverage uniformity. In addition, a new and promising approach was initiated for the deposition of metal nanowires inside the nanoporous alumina as described below.

During the third year, a new technique was initiated and investigated for the deposition of metal nanowires inside the nanoporous alumina. This technique involves the electro-phoretic deposition of nanoparticles inside the pores followed by recrystallization into nanowires. The major advantage of this technique is that the chemistry of nanoparticle synthesis is separated from the formation of nanowires, as a result it has the potential to eliminate the limitations encountered in nanowire synthesis. Nanowire deposition inside the alumina pores is made challenging by the nanoscale fluid flow and chemical reactions inside the nanoscale volume of nanoporous alumina pores. In this new technique, nanoparticles of the desired metal are first synthesized by an established technique in an emulsion form, which are then incorporated inside the nanoporous alumina pores. Since nanoparticles are relatively less complex to incorporate inside pores, it provides an excellent means for the synthesis of nanowires of good uniformity and desired heights. The nanoparticles can be synthesized using an established technique such as sol gel technique. The nanoparticles can be then annealed to form the nanowires or sonication can be used during electro-phoretic incorporation to form the nanowires.

Deposition of Cr nanowires on steel substrates will be achieved by using the following procedure. A new batch of steel samples will be coated with metallic aluminum which will be anodized using constant current anodization. Since it is not possible to obtain cross-sectional images of the structures on steel samples, the voltage-time characteristics will be measured to monitor the quality of the anodized alumina structures. A typical voltage-time characteristic obtained during the anodization of aluminum on steel samples, when compared to data from silicon samples, confirms the good quality of the nanoporous alumina. Cr nanoparticles will be synthesized using the sol-gel technique and will be then electro-phoretically incorporated inside the nanoporous alumina. Sonication will be used during deposition to fuse the nanoparticles to form nanowires. A sonication apparatus was obtained for this purpose. This will be followed by the deposition of a thick film of dense alumina, the process technology for which has already been developed during the previous phase of the research.

TASK 23 PROFILE

Start Date: July 2004

Completion Date: November 2007

Conference Proceedings:

B. Das, "Nonlithographic Nanoscale Devices," invited paper, International Conference on MEMS and Semiconductor Nanotechnology, Kharagpur, India, December, 2006.

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