Development of Self-Healing Zirconium-Silicide Coatings for Improved Performance of Zirconium-Alloy Fuel Cladding

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ABSTRACT:

During operation in a Light Water Reactors (LWR), zirconium-alloy fuel claddings develop a reasonably thick oxide layer due to reaction with water which limits heat transfer. This reaction also results in the production of hydrogen which forms hydrides in the cladding and causes brittleness. Under high temperature accident conditions, zirconium-alloy fuel claddings exhibit profuse exothermic oxidation accompanied by release of hydrogen gas due to reaction with water/steam. This research focuses on the development of self-healing zirconium-silicide coatings on the surface of zirconium-alloy cladding material to mitigate oxidation under both normal and high temperature accident conditions.

Transition metal silicides such as zirconium-silicide are known for their outstanding high temperature oxidation resistance due the formation of a dense layer of silica (SiO_2) on the surface which exhibits a self-limiting parabolic growth behavior. The Zr-Si phase diagram shows the formation of many intermetallic compounds of different Zr/Si ratios. Furthermore, both Zr and Si readily form their respective oxides at high temperatures and depending on the stoichiometry of the Zr-silicide, surface layers of ZrO_2 or SiO_2 or even $ZrSiO_4$ may form. Assuming that ZrO_2 were to form above Zr-silicide, the zirconium activity in the silicide will be reduced, favoring the oxidation of silicon to SiO_2 under the ZrO_2 layer. This inner layer of SiO_2 can serve as the barrier layer to oxygen and moisture transport in addition to ZrO_2 and the glassy properties of SiO_2 at elevated temperatures can accommodate stresses from crystallographic transformations of the outer ZrO_2 layer and incipiently seal any cracks that may form. Thus, in a high temperature oxidizing environment multiple intermetallic compound layers can form with ZrO_2 or SiO_2 sandwiched layers, in effect evolving naturally into a compositionally and functionally graded multilayered system that is expected to provide the necessary protection under accident conditions.

Zirconium-silicide coating deposition methods to be investigated include magnetron sputtering, spray cating technologies, and fused slurry methods. Corrosion testing will be performed in prototypical steam and water environments as well as under loss of coolant accident conditions (LOCA). In addition, to corrosion work, ion irradiation studies will be undertaken on both as-deposited zirconium-silicide coatings and coated samples after corrosion tests. These studies are intended to provide information on the radiation stability of zirconium-silicides in terms of physical defect morphologies and compositional redistribution, as well mixing of interfaces due to irradiation. To more fundamentally understand the transport of oxygen in the oxide layers that form in Zr-silicide coatings complementary molecular dynamics and temperature accelerated dynamics modeling will be performed. Additionally, these modeling efforts will be aimed at investigating the effects stresses and grain boundaries in these oxide layers, on oxygen transport through the oxide layers which in effect dictates the kinetics of oxidation.