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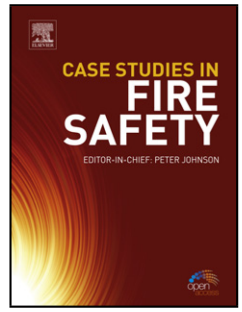

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Chemical state and atomic scale environment of nickel in the corrosion layer of irradiated Zircaloy-2 at a burn-up around 45 MWd/kg

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Highlight

- *Atomic-scale microstructural changes in the Ni-containg SPP and solute Ni present in the corrosion layer of an irradiated Zircaloy-2 cladding have been studied.*
- *The chemical state and quantitative Ni speciation in the oxide layer have been obtained by synchrotron X-ray light experiments, and compared with DFT calculations.*
- *The Ni-bearing SPP in the oxide layer are neither fully dissolved nor entirely oxidized, whereas solute nickel is present ina divalent state adjacent to oxygen vacancies.*
- *The role of Ni on the hydrogen ingress behavior in Zircaloy-2 is discussed.*

ABSTRACT
Zircaloy-2 is used as fuel cladding in commercial boiling water reactors (BWR). A limiting factor for fuel longevity is the waterside corrosion of the cladding during in-service reactor operation and associated hydrogen pickup to the alloy. It is well known that the alloying elements (such as Cr, Fe, Ni etc.) including intermetallic precipitates (also termed as SPP) distribution influences both the oxidation process and hydrogen uptake evolution in this material. This paper reports an experimental investigation on the atomic scale microstructure of nickel-containing intermetallic particles with an emphasis on the oxidation and nickel-dissolution of SPP, and a combined experimental and computational study of solute nickel located in the corroded zirconium oxide microstructure. An irradiated cladding sample, taken from a BWR fuel rod, was prepared for the analysis using electron probe microanalysis (EPMA) and synchrotron-based micro-beam X-ray techniques (µXRF, µXRD and µXAS). The results show that the Ni-bearing SPP in the oxide layer are neither fully dissolved nor entirely oxidized at the given burn-up of the sample investigated. Conversely, all solute nickel present in the corroded layer is mostly oxidized and has an apparent homogeneous Ni^{2+} distribution. By analyzing the µXAS spectra measured at the Ni absorption edge, we have obtained quantitative structural information about both irradiated SPP and the Ni coordination environment in the corrosion layer. There exists strong structural disorder in intermetallic Ni-bearing SPP as also evidenced by µXRD study. The basic structure away from SPP in the oxide area is composed of oxidized nickel atoms adjacent to oxygen vacancies. Finally, first-principles density functional theory (DFT) calculations have been used to discern the nickel speciation in zirconium oxide microstructure that is complementary to the multitude of experimental information. From this joint theoretical and experimental approach, significant insights into the structural specificity of Ni^{2+} ions in monoclinic ZrO_2, electronic factors governing the electron transport processes in the corrosion layer, and the apparent influence of nickel on the hydrogen ingress behavior in Zircaloy-2 are obtained.

KEYWORDS: *Zircaloy-2, Secondary phase precipitates, Oxidation and irradiation effects, Synchrotron radiation.*

1. Introduction

Zircaloy-2 is a zirconium-based alloy, extensively being used as fuel cladding and for coolant channels in boiling water reactors [1,2]. For its long-term applications and in-reactor performance, some of the main limiting factors are oxidation and