TRANSFORMATIONS AND CRACKS IN ZIRCONIA FILMS LEADING TO OXIDATION OF ZIRCALOY

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INTRODUCTION.

Oxidation is the source of major degradation process of Zircaloy fuel cladding used in nuclear power plants. Cladding is the outer layer of the fuel rods, standing between the coolant and the nuclear fuel. It is made of a corrosion-resistant material with low absorption cross section for thermal neutrons, usually Zircaloy. Despite the unquestionable presence of the tetragonal phase and its transformation to the monoclinic phase of the ZrO_2 scale grown on Zircaloy, it is still unclear what promotes breakaway oxidation.

MATERIALS AND METHODS.

Oxidation kinetics measurements, Raman spectroscopy, atomic force microscopy and optical microscopy were used to shed new light on surface chemistry and internal stress evolution during Zircaloy nuclear fuel cladding oxidation at high temperatures.

RESULTS AND DISCUSSION.

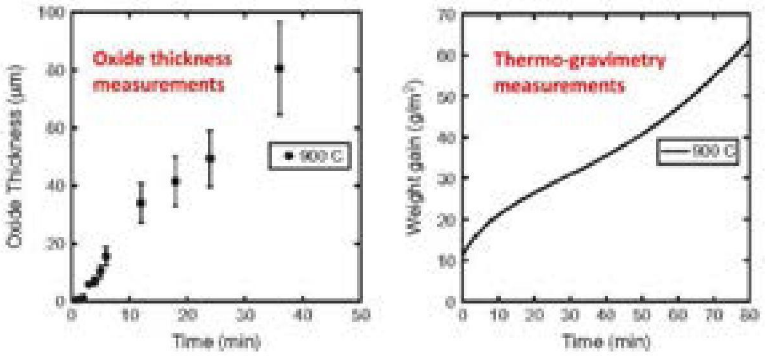

Figure 1. *Air-oxidation kinetics of Zircaloy-4 at 900 C.*

The results of this work suggest that breakaway oxidation of Zircaloy is caused by the change of circumferential stress sign from compressive to tensile, which triggers catastrophic cracks to propagate from the oxide free surface toward the oxide–metal interface. The stress sign changes at a critical oxide thickness, which depends on the circumferential stress at the interface (Fig. 2 and Fig. 3). This biaxial interfacial stress is promoted by a lattice expansion stress that accompanies the tetragonal to monoclinic crystal phase transition. In contrast with current research in the literature, this allotropic transformation is suggested to be beneficial, not detrimental, because it contributes to retard the thresholds for the change of circumferential stress sign, and thus breakaway oxidation. The tetragonal phase was revealed to localize at the interface and adopt the shape of prismatic isosceles triangles detected at early stages of oxidation. These growth morphologies are consistent with a cationic oxidation mechanism. Upon phase transition, the monoclinic variant quickly dominates the oxide scale above the interfacial regions and forces the overall oxidation to proceed by an anionic diffusion mechanism. The results of Raman spectroscopy compared well with those of atomic force microscopy (Fig. 4).

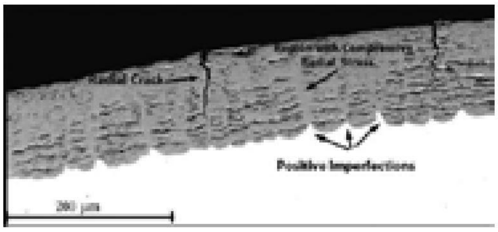

Figure 2. *Cross-sectional SEM image of Zircaloy-4 oxidised in air for 147 days at 470 C.*

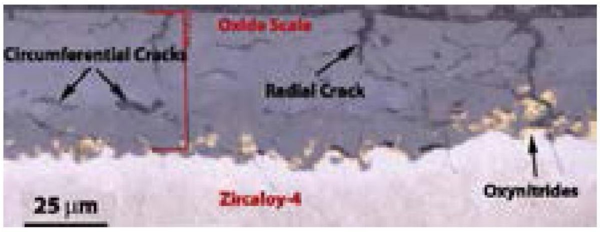

Figure 3. *Micrograph of Zircaloy-4 oxidised for 30 min at 900 C.*

CONCLUSION.

This work was aimed to identify the root cause of breakaway oxidation of Zircaloy and the origin of Zircaloy cladding failure. Circumferential compressive stress is highly promoted by tetragonal to monoclinic phase transition. Therefore, this transformation is rather beneficial as it will increase the time to attain critical oxide thickness (at which the stress changes from compressive to tensile), and thus retards breakaway oxidation.

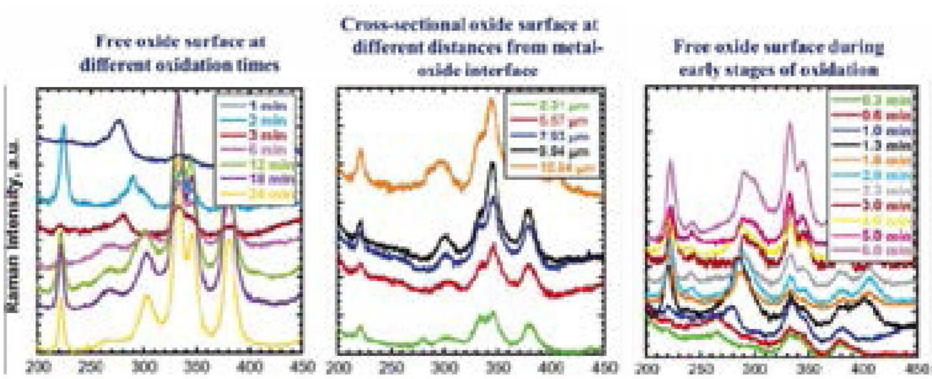

Figure 4. *Raman spectroscopy of the Zircaloy-4 film.*

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