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"Study of secondary hydriding at high temperature in zirconium based nuclear fuel cladding tubes by coupling information from neutron radiography/tomography, electron probe micro analysis, micro elastic recoil detection analysis and laser induced breakdown spectroscopy microprobe

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HIGHLIGHTS

- More than 50% of the gaseous hydrogen produced by the inner clad oxidation absorbed and trapped into prior-β layer.
- High hydrogen and oxygen local concentrations, up to 3000–4000 wt. ppm and 1.0–1.2 wt.% respectively, within the β phase.
- Enhanced oxygen diffusion into hydrogen enriched prior-β layer, with locally thinner α(O) and thicker prior-β layers.
- Post-quenching hardening of the prior-β structure mainly related to the (local) oxygen concentration.
- The results are very reproducible.

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ABSTRACT

This paper gives an overview of a multi-scale experimental study of the secondary hydriding phenomena that can occur in nuclear fuel cladding materials exposed to steam at high temperature (HT) after having burst (loss-of-coolant accident conditions). By coupling information from several facilities, including neutron radiography/tomography, electron probe micro analysis, micro elastic recoil detection analysis and micro laser induced breakdown spectroscopy, it was possible to map quantitatively, at different scales, the distribution of oxygen and hydrogen within M5™[1] clad segments having experienced ballooning and burst at HT followed by steam oxidation at 1100 and 1200 °C and final direct water quenching down to room temperature. The results were very reproducible and it was confirmed that internal oxidation and secondary hydriding at HT of a cladding after burst can lead to strong axial and azimuthal gradients of hydrogen and oxygen concentrations, reaching 3000–4000 wt ppm and 1.0–1.2 wt% respectively within the β phase layer for the investigated conditions. Consistent with thermodynamic and kinetics considerations, oxygen diffusion into the prior-β layer was enhanced in the regions highly enriched in hydrogen, where the α(O) phase layer is thinner and the prior-β layer thicker.

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[1] M5 is a trademark of AREVA NP registered in the USA and in other countries.

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μ-LIBS
Post-quenching prior-β hardening

Finally the induced post-quenching hardening of the prior-β layer was mainly related to the local oxygen enrichment. Hardening directly induced by hydrogen was much less significant.

1. Introduction

Since the early works of Chung & Kassner [1] and Uetsuka [2], secondary hydriding of nuclear fuel claddings in light water reactors has been a matter of concern for both nominal/incidental conditions (in case of leaking fuels for example [3,4]) and hypothetical accidental conditions, due to the embrittlement effect of hydrogen. In particular, it has been shown that a fast and substantial secondary hydriding of the cladding can occur under loss-of-coolant (LOCA) conditions, during exposure to steam at high temperature (HT) after ballooning and burst. These last fifteen years, numerous "semi-integral" LOCA tests have been performed in particular at ANL (Argonne National Laboratory) [5,6] and JAERI/JAEA (Japan Atomic Energy Agency) [7–10] but also in some other institutes [61,62] on both non-irradiated and irradiated materials. Such thermal-mechanical tests consist in a sequence of ballooning and burst under internal pressure, oxidation under steam at HT and finally cooling and water-quenching of the clad. These tests have shown that:

- Hydrogen pick-up peaks, due to secondary hydriding, ranging from ~1000 wt ppm up to 3000–4000 wt ppm can be observed at a few centimeters from the burst location;
- The inner pre-existing zirconium oxide formed during in-service conditions does not prevent secondary hydriding by oxidation at HT of the inner surface of the cladding after burst.

Secondary hydriding is due to steam ingress through the burst opening into the gap between the nuclear fuel pellets and the clad inner surface. Steam starvation is promoted inside this gap, where the oxygen partial pressure progressively decreases (due to oxidation of the clad inner surface) and the hydrogen partial pressure increases while moving away from the burst opening. Massive hydrogen uptake can occur locally through the clad inner surface due to the high hydrogen partial pressure (H_2/H_2O) within the gap [11] and/or to the formation on thin porous/non-protective oxide at the clad inner surface [1]. As a β-stabilizer, hydrogen mainly concentrates into the inner β phase layer, which is then embrittled [28,55,60].

Even if the hydrogen concentrations achieved locally are high, the precipitation of hydrides, if any, is generally very difficult to observe by conventional Optical Microscopy (OM) or Scanning Electron Microscopy (SEM) within the Post-Quenching (PQ) prior-β microstructure, after incursion at HT. Then, for most of the tests mentioned above, the PQ hydrogen concentrations were generally measured by using a destructive melt extraction method, on small rings extracted at various axial positions from burst opening. In consequence, the reported peak hydrogen concentration values, measured at certain axial locations along the tested clad segments, are generally averaged values over the tube circumference. Nevertheless, ANL performed a few PQ hydrogen analyses on circumferential portions of rings extracted at arbitrary axial locations along cladding specimens having experienced "semi-integral" LOCA tests: significant azimuthal gradients of hydrogen concentration were sometimes observed.

More recently, using their QUENCH facility, the Karlsruhe Institute of Technology (KIT) performed some LOCA bundle tests on unirradiated specimens. Secondary hydriding was observed near the burst locations of the tested clad segments [12,13]. To characterize the secondary hydriding which occurred within most of the tested rods, M. Grosse et al. have extensively used Neutron Radiography (NR) [14–18]. From these measurements, non-destructive 3D semi-quantitative mapping of hydrogen was achieved. It was observed that, in most cases, secondary hydriding at HT is characterized by the formation of non-axisymmetric highly hydrogenated bands away from the burst location. This confirms that conventional destructive hydrogen analysis by melt extraction performed on ring samples machined at different axial locations along the cladding having experienced a LOCA transient is not sufficient to have a complete view of the hydrogen spatial distribution within the tested claddings.

However, due to their intrinsic spatial resolution, the different techniques mentioned above (including NR analysis) do not allow to quantify hydrogen partitioning through the cladding wall thickness, i.e., between the different phases/layers of the tested clad segments. Due to the HT oxidation and the subsequent on-cooling $\beta \rightarrow \alpha$ phase transformation, complex oxygen, hydrogen and chemical alloying partitioning occurs down to the micrometer scale [39]. Such phenomena induce prior-β heterogeneous microstructure, which can be viewed as "micro-composite" materials [40]. Thus, multi-scale chemical analysis quantification - mainly of oxygen and hydrogen - is necessary to be able to understand more in depth the metallurgical evolution of the clad and, in a second step, to correlate with its actual local thermal-mechanical properties (hardness, residual strength and ductility…). For that purpose, with the aim of obtaining more insights into the HT secondary hydriding phenomena, the present work was done in order to:

- Generate, in a reproducible manner, secondary hydriding in nuclear fuel cladding specimens, by oxidation in steam at HT after ballooning and burst;
- Quantify the resultant hydrogen and oxygen spatial distributions at different scales, from the centimeter down to the micrometer scale;
- Correlate the oxygen and hydrogen local concentrations with the local hardening of the prior-β phase.

Various advanced facilities located at CEA-Saclay in France have been used: Neutron Radiography/Tomography (NR), Electron Probe Micro Analysis (EPMA), Micro Elastic Recoil Detection Analysis (μ-ERDA) and Laser Induced Breakdown Spectroscopy Microprobe (μ-LIBS). The main results and learnings from this multi-experimental work are illustrated and discussed in this paper. Additionally, it is expected that the present data should be of interest for further modeling of secondary hydriding phenomena, as, for example, recently done by Vehschunov & Shestak [19] and Grosse [20].

2. Experimental procedures

2.1. Materials and thermal-mechanical tests (secondary hydriding)

Fully recrystallized M5™ [21] cladding tube segments from AREVA NP have been used. Their nominal outer diameter and thickness were about 9.5 and 0.57 mm, respectively. These