![CAMECA Science & Metrology Solutions]

EPMA Applications to Nuclear Science: Investigating Absorber Rod Oxidation

Assessing the use of hafnium as absorber material in control rods

Investigating new materials and devices for improved protection of the vessel from the neutron flux in Light Water Reactors (LWR), French nuclear engineers are currently considering the introduction of uncladded hafnium absorber rods at the periphery of the reactor core. The French Radioprotection and Nuclear Safety Institute (IRSN) and the Karlsruhe Institute of Technology (KIT) conducted a joint study to evaluate the oxidation behavior of hafnium in accidental situations. Indeed, at high temperatures relevant to severe accidents (above 700° C), water steam will interact with the hafnium in the rod, leading to a critical energy release that could damage the reactor core.

The experiment

In order to simulate the oxidation conditions in steam, rod hafnium specimens were heated at temperatures ranging from 700-1400°C over several hours, both in a horizontal furnace coupled with a quadrupole mass spectrometer to measure the composition of the off-gas mixture and in a thermogravimetric analyzer. After oxidation, a dense and adherent oxide film can be observed at the surface of the rod sample using optical microscopy, with thickness increasing with temperature but remaining thin for all tested conditions (<35 µm). These results demonstrate the excellent resistance of the hafnium rods as they did not undergo breakaway oxidation.

The importance of oxygen quantification

For good understanding of the rod oxidation processes, oxygen concentration variations in the metal below the oxide layer must be accurately quantified. The EPMA profile [Figure 1] reveals oxygen diffusion in the metal down to approximately 200 µm.

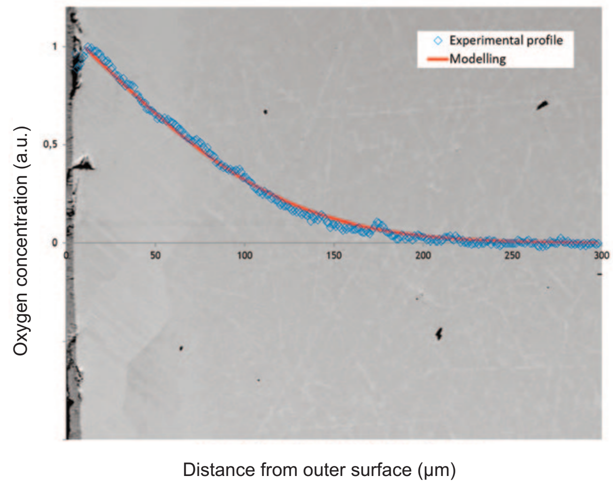
The diffusion coefficient of oxygen in hafnium is estimated at each temperature by fitting the experimental oxygen profiles. Results are in agreement with published data in air or oxygen up to 1200°C and give additional results up to 1400°C.

Comparison of the diffusion coefficient of oxygen in hafnium and Zircaloy-4 shows that they are of the same order of magnitude. However, the oxidation rate of hafnium is much lower than the Zircaloy-4 oxidation rate in the same temperature range. Moreover, the residual strength of oxidized Hf claddings was sufficient to prevent the cladding fragmentation during quenching, confirming Hf as an adequate element to be implemented as an absorber in LWRs.

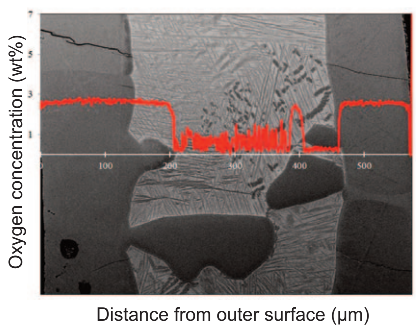
Instrumentation

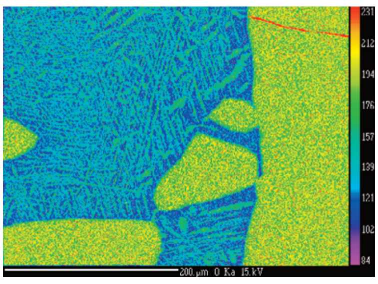
CAMECA EPMA is a tool of choice for performing quantitative analysis of light elements such as oxygen. Indeed, Wavelength Dispersive Spectrometers (WDS) offer better sensitivity and spectral resolution than Energy Dispersive Spectrometers. The high sensitivity CAMECA WDS ensure excellent detection limits and quantitative analysis from sub-micron areas providing precise and accurate compositional information.

Figure 1:
Experimental oxygen profile in hafnium (red line) and EPMA measured profile (blue points) after steam oxidation.



Optimizing fuel cladding tubes





The WDS at the heart of CAMECA's EPMA deliver highly reproducible quantitative analyses of challenging light species.

In another IRSN nuclear science study, CAMECA EPMA was used to measure the oxygen concentration across Zircaloy cladding tubes, revealing diffusion accross the α *Zr* phase.

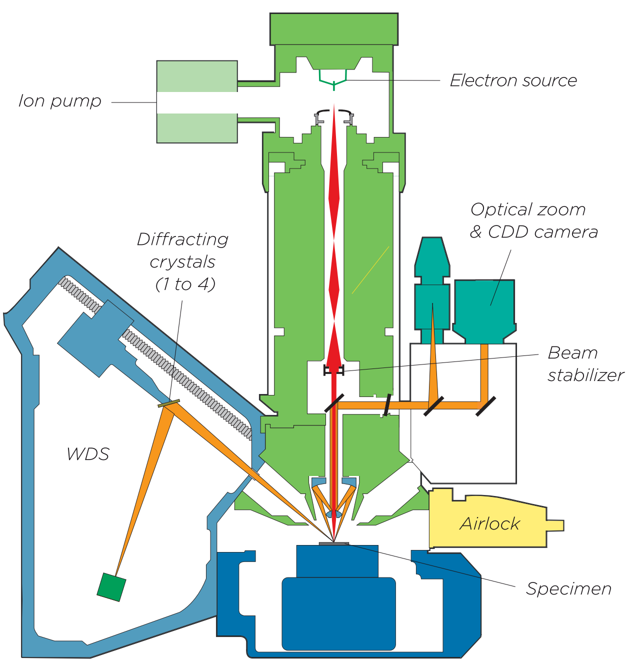
Top: BSE image with oxygen concentration profile.

Bottom: oxygen X-ray map, acquisition conditions: 15 kV/40 nA.

S. Guilbert-Banti et al. Influence of H on H solubility in Zircaloy-4, Journal of Nuclear Materials 469 (2016)

Adapted from S. Guilbert-Banti et al. Hafnium oxidation at high temperature in steam. Journal of Nuclear Materials 550 (2021)

The technology behind



Electron Probe Microanalysis (EPMA)

EPMA works by bombarding a micro-volume of a sample with a focused electron beam (typical energy = 5-30 keV) and collecting the X-ray photons thereby emitted by the various elemental species. The wavelengths of these X-rays being characteristic of the emitting species, the sample composition can be easily identified and quantified by recording WDS spectra (Wavelength Dispersive Spectroscopy). Owing to the internal properties of WDS, the general sensitivity, analysis of light elements and interpretation of qualitative spectra are all superior with EPMA than with standard SEM/EDS systems.

EPMA remains one of the most precise and accurate microanalytical technique. It is a non-destructive, qualitative and quantitative method of elemental analysis of micron-sized volumes at the surface of materials, with sensitivity at the level of ppm. Routine quantification to 1% reproducibility is obtained over several days.

SX Five tactis

Since pioneering Electron Probe MicroAnalysis in the 1950's CAMECA has released several generations of microprobes, all with a proven valuable track record for analytical performance and reliability. The new SXFive-TACTIS builds on this legacy to deliver enhanced imaging and quantitative analysis performance in a user-friendly environment. Key features include:

- New touch-screen interface for unprecedented ease-of-use
- Additional BSE detector for enhanced imaging especially at low voltage
- Fully integrated EDS hyper-mapping module for ultra fast quantitative analysis
- Remote control, including SEM image (experiments can be run from a phone)
- Dual beginner/expert interface allowing multi-user facilities to take full advantage of one single tool.

For more information please visit our web page: www.cameca.com/products/epma/sxfive-tactis

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