Determination of the Oxidation State of Irradiated Nuclear Fuel Using SIMS

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During the fission of UO₂ nuclear fuel oxygen is set free. Part of the oxygen liberated reacts with the fission products and forms oxides of these elements. The balance dissolves in the fuel matrix increasing its stoichiometry as indicated by the oxygen to metal (O/M) ratio, or is absorbed by the Zircaloy tube which contains the fuel. The O/M ratio is generally acknowledged to be the most important chemical property of UO₂ nuclear fuel during irradiation. This is because the oxygen potential, ΔG(O₂), and the related O/M ratio of the fuel, affect diffusion controlled processes such as grain growth [1], creep [2] and fission gas release [1], the thermal conductivity of the fuel [3] and the chemical state and hence the behaviour of the fission products. The ΔG(O₂) and O/M ratio of the fuel are not constant during irradiation but change with burn-up (time) due to the incorporation of fission products.

Recent work at ITU has revealed that it might be possible to measure the radial variation of the O/M ratio in irradiated UO₂ nuclear fuel using secondary ion mass spectrometry (SIMS). Radial distributions of the 16O⁻ ion intensity, and the 238UO₂⁺/238U⁺ and 238UO⁺/238U⁺ ion intensity ratios were measured in a UO₂ fuel with a pellet burn-up of 65 MWd/kgHM using 133Cs⁺ and 16O⁺ primary ion beams (see Figs.1 and 2). It is assumed that the form of the profiles accurately reflects the radial change in the fuel O/M. Accordingly, they reveal that although no change in the UO₂ stoichiometry occurred in the interior of the fuel, the O/M ratio increased close to the fuel surface before falling noticeably at the periphery. This latter observation is consistent with the view that the Zircaloy cladding acts as an oxygen getter.

To confirm that the 16O⁻ ion intensity profile and the 238UO₂⁺/238U⁺ and 238UO⁺/238U⁺ profiles represent the radial variation in the fuel stoichiometry, ion emission from three samples of un-irradiated polycrystalline UO₂ with stoichiometries of 1.96, 2.01 and 2.15 was studied. It was found that the 16O⁻ ion intensity correlates perfectly with the UO₂ stoichiometry (Fig.3) and that a close relationship exists between the 238UO₂⁺/238U⁺ and 238UO⁺/238U⁺ ion intensity ratios and the UO₂ stoichiometry (Fig. 4). Thus, it is concluded that SIMS can be used to measure the radial variation...
of the O/M ratio in irradiated UO₂ fuel. At present, it does not appear that the ¹⁶O⁻ ion intensity and 
²³⁸UO²⁺/²³⁸U⁺ and ²³⁸UO⁺/²³⁸U⁺ ion intensity ratios measured on unirradiated UO₂ can be applied in a quantitative manner to determine the local stoichiometry of irradiated fuel. The values obtained on irradiated UO₂ fuel are inconsistent with those for unirradiated UO₂. It is assumed that this is mainly because for irradiated fuel the sputtering yield and the ¹⁶O⁻, ²³⁸UO²⁺, ²³⁸UO⁺ and ²³⁸U⁺ ion yields are affected by the presence of fission products and transuranic elements dissolved in the fuel matrix and by radiation damage.

References

Fig.1. Distribution of ¹⁶O⁻ ion intensity across the radius of an irradiated UO₂ nuclear fuel with a burn-up of 65 MWd/kgHM.

Fig.2. Variation of the ion ratios 
²³⁸UO²⁺/²³⁸U⁺ and ²³⁸UO⁺/²³⁸U⁺ across the radius of an irradiated UO₂ nuclear fuel with a burn-up of 65 MWd/kgHM.

Fig.3. ¹⁶O⁻ ion intensity related to the stoichiometry of un-irradiated polycrystalline UO₂.

Fig.4. ²³⁸UO²⁺/²³⁸U⁺ and ²³⁸UO⁺/²³⁸U⁺ ion ratios related to the stoichiometry of un-irradiated polycrystalline UO₂.