O/M-RATIO MEASUREMENT TECHNIQUES

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ABSTRACT

Coulometric titration (CT) is described and shown to be a viable method for measuring O/M-ratios in defected fuels. Radial and longitudinal profiles have been obtained. New methods that have the potential to provide O/M-ratios in small zones (1-30 μm^3, c.f. ~10 mm^3 for CT) are being investigated in order to be able to identify higher oxidation phases at grain boundaries, cracks and interfaces between pellets. With its ability to provide oxidizing as well as reducing atmospheres, CT can be used to make materials in controlled oxygen atmospheres and to compare oxidation rates between different fuel types.

1. INTRODUCTION

Oxidation of fuel through holes in the sheath affects important fuel properties: thermal conductivity and melting point; fission-product diffusion rates; and uranium and oxygen diffusion rates, which enhance grain growth and increase fission-gas release. The objectives of this program were to develop the techniques for reliable measurement of O/M ratio as a function of radial and longitudinal position and apply these techniques to defected fuels. Ultimately, the aim is to determine which parameters control the amount of oxidation in defected fuels. First measurements of O/M-ratios of a defected fuel were given at the 7th International Conference on CANDU Fuel [1].

A companion paper in these Proceedings (Z. He et al. [2]) provides ceramography and O/M-ratio measurements on three defected elements. This paper describes the methods of coulometric titration (CT) for the O/M-ratio measurements, shows additional capabilities of CT, and introduces two new methods for making localized O/M-ratio measurements that are being investigated at AECL.

2. MEASURING O/M-RATIO BY COULOMETRIC TITRATION

Small fuel samples are obtained in a hot cell from specific radial and longitudinal locations in an irradiated fuel sample (see Section 3). The samples are placed individually in the furnace of the CT apparatus (Figure 1). Ar gas containing H_2, e.g., 1300 ppm H_2, is passed over the sample and into a CT cell, which measures how much O_2 is required to convert all the H_2 to H_2O. As the sample is heated to 1000°C, it releases (or absorbs) O_2 which combines with H_2 in the gas flow, causing a decrease in the O_2 required in the CT cell to convert the H_2 to H_2O. This process continues until no further O_2 is released (or absorbed) from the sample. Figure 2 shows the reduction of a sample of U_3O_8 to UO_2. The *titration current* in this figure represents the amount of O_2 needed in the CT cell to exactly convert all the H_2 to H_2O. The total amount of O_2 released from the U_3O_8 is obtained by integration and converted to the change in stoichiometry of the sample during the measurement. If the final O/M-ratio is known, the initial stoichiometry is obtained by adding the change in O/M-ratio to the final value. For fuel samples under these test conditions, the final stoichiometry is taken to be 2.000 since the conditions are reducing, but not so reducing as to make UO_2 become sub-stoichiometric. As another example, Figure 3 shows the results of an O/M-ratio measurement of an actual irradiated fuel sample from a defected fuel element. Assuming that all the oxygen released from the sample during the measurement came from altering the stoichiometry of the UO_2, and not from other phases that might be present, the fuel sample had an initial stoichiometry of $UO_{2.072}$ in this example.

A schematic diagram of the CT cell is shown in Figure 4. The wall of the tube is composed of zirconia (ZrO_2) doped with calcia (CaO). At 700°C this material readily conducts O^{2-} ions. When an electrical voltage is applied via Pt contacts, O^{2-} ions are formed at the outer surface from O_2 in the atmosphere and conduct through the wall where they recombine with other O^{2-} ions and desorb from the cell surface as O_2. In this way, O_2 is passed from the atmosphere through the cell wall and into the flowing gas stream. The amount of O_2 in the gas stream is monitored by separately measuring the electrical voltage between the inner and outer surfaces and this is used to control (by a feedback loop) the current of O_2 into the gas stream so that only enough O_2 is added to exactly convert all H_2 to H_2O.

2.1 Preparation of samples of irradiated fuel

Figure 5 shows a schematic diagram of a defected fuel element. In this example, there is a primary defect at one end and a secondary deuteriding defect at the other end. Slices of fuel about 1 cm long, are cut from the element at various longitudinal positions. CT powder samples, 50-150 mg, are drilled from radial locations as shown in Figure 6 with a diamond drill 1.6-2.0 mm diameter. This is done in air. Tests have shown that only very fine powder will oxidize to any appreciable extent in air at room temperature. The texture of irradiated fuel can vary (from very hard to quite friable) and as result the powder produced from drilling also varies. Hard irradiated fuel typically generates a fine powder and testing has shown it can oxidize over an hour to a limit of about 0.01 increase in stoichiometry. The coarser powders do not oxidize to any significant extent.

2.2 Multi-phase systems

In multi-phase systems, such as irradiated fuel or simulated irradiated fuel (SIMFUEL), the amount of oxygen absorbed (or released) can still be measured, but interpretation of the results is more difficult because it is unclear which phase is absorbing (or releasing) at any time. Thus, we can't ultimately separate how much oxygen is absorbed by each phase. Figure 7 shows release from SIMFUEL with two peaks, suggesting release from two different phases, but more precise interpretation is difficult.

3. NEW METHODS FOR O/M-RATIO MEASUREMENT

Figures 8 and 9 show two examples of irradiated fuel where there appears to be a higher oxide phase of uranium oxide present. In Figure 8, there is a ~50 μm wide band of a higher oxide phase on both sides of a pellet interface. In Figure 9, a thin separate phase surrounds the grain boundaries. In both cases, the CT method, which utilizes a drill of diameter ~1800 μm, cannot identify the new phase but only give an average O/M-ratio over a much larger area. Consequently, two new methods are being examined at AECL that may be able to measure O/M-ratio in much smaller regions than CT and be able to identify the new phases. A description of the proposed methods and preliminary results follow.

3.1 X-Ray Diffraction

The principle with this method is to prepare small powdered samples of irradiated fuel from the zone of interest and use X-ray diffraction (XRD) to determine quantitatively the type and amount of each phase present. Figure 10 shows an XRD pattern for a mixture of unirradiated UO_2 and U_4O_9. The two main peaks are at the correct positions for UO_2 and U_4O_9, and the intensities of these peaks can be correlated to the amount of each phase present. The advantage of this method over CT is that smaller samples of powder may be used and phase identification should be possible.

3.2 Electron Probe Wavelength Dispersive X-Ray Analysis (EP WDX)

The hardware for WDX analysis is an optional, commercially available, attachment for scanning electron microscopes. A high energy electron beam impacts a sample and causes the emission of x-rays characteristic of the elements that are present in the sample at the beam position. The elements can be identified quantitatively. The region emitting x-rays is typically about $(1\text{-}3\ \mu m)^3$. New microscopes can utilize lower energy electrons and result in sub-micron sized interrogation zones. This method is currently showing promise on unirradiated specimens, but a newer microscope may be required for irradiated specimens to separate the signal x-rays from background.

3.3 Advanced Mode of CT Operation

By putting a second CT cell in the gas flow *upstream* of the sample furnace, the usefulness of the equipment is greatly increased. This upstream cell can add oxygen to the gas flow and thus provide for the creation of oxidized samples. For example, this setup of the CT apparatus has been used to prepare slightly oxidized samples of UO_2 and $(U, Pu)O_2$ for electrochemistry experiments related to measuring dissolution of fuel into ground water. It is also planned to fabricate hyperstoichiometric UO_2 and $(U,Dy)O_2$ to measure their thermal properties. This CT setup can also be used to compare oxygen absorption into various materials at specified temperatures and oxygen partial pressures. For example, the response of irradiated fuel or SIMFUEL to oxidizing atmospheres can be compared with that for unirradiated fuel. Or, oxygen absorption of $(U,Dy)O_2$ fuel, used to lower void-reactivity, can be compared to that for UO_2 at various temperatures and oxygen pressures. Both the kinetics and the total amount of absorbed oxidation can be compared, if the test conditions of the experiment allow the experiment to be completed in a reasonable length of time. If not, at least some information on the relative rates of absorption is obtained.

4. SUMMARY

In summary, coulometric titration is a viable method for measuring O/M-ratios in defected fuels. Radial and longitudinal profiles can be obtained. New methods that have the potential to provide O/M-ratios in small zones (1-30 μm^3, c.f. ~10 mm^3 for CT) are being investigated in order to be able to identify higher oxidation phases at grain boundaries, cracks and interfaces between pellets. With its ability to provide oxidizing as well as reducing atmospheres, coulometric titration can be used to make materials in controlled oxygen atmospheres and to compare oxidation rates between different fuel types.

5. REFERENCES

1. R.A. Verrall and J.F. Mouris, "Capability for Measurement of O/U Ratios in As-Discharged Defected CANDU Fuel", Proceedings of the 7th CANDU Fuel Conference, Vol. 2, published by the Canadian Nuclear Society, ed. B.J. Lewis, p3A-1 (2002).
2. Z. He, R.A. Verrall, J.F. Mouris and C. Buchanan, "Characterization of Fuel Pellet Oxidation in Defected Fuel Elements Using O/M Measurements and Optical Microscopy", these proceedings.

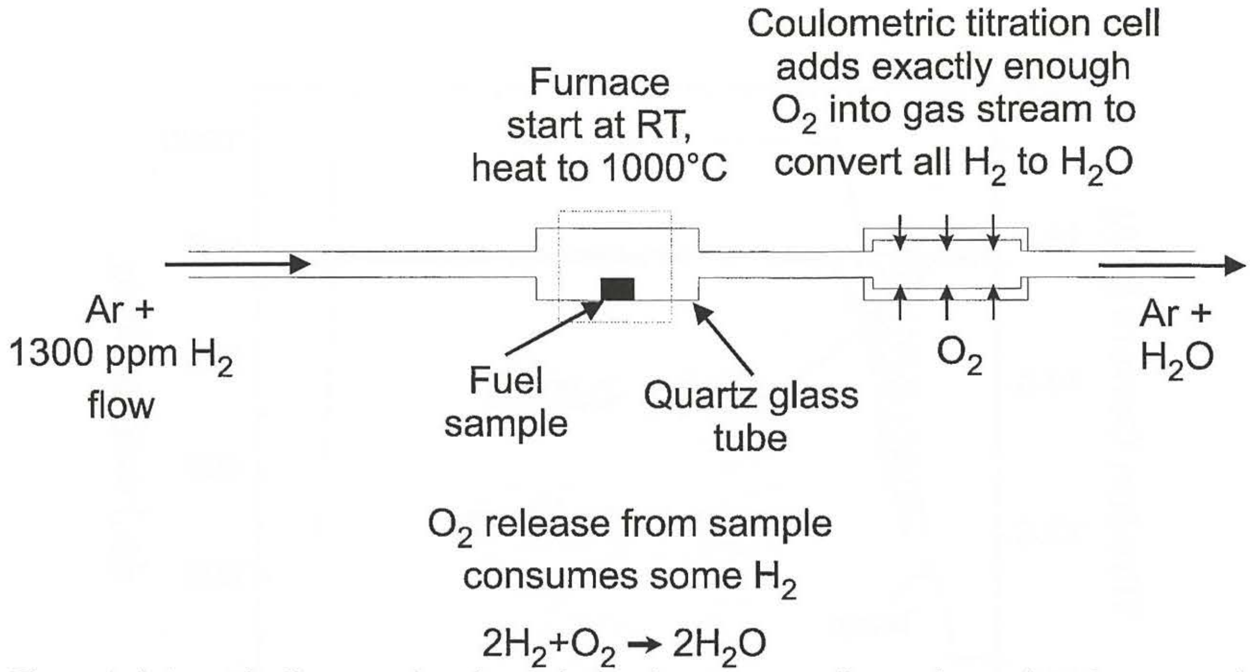

Figure 1. Schematic diagram of coulometric titration apparatus. In an advanced mode, a second coulometric titration is placed in the flow stream upstream of the furnace to facilitate adding oxygen to the gas flow.

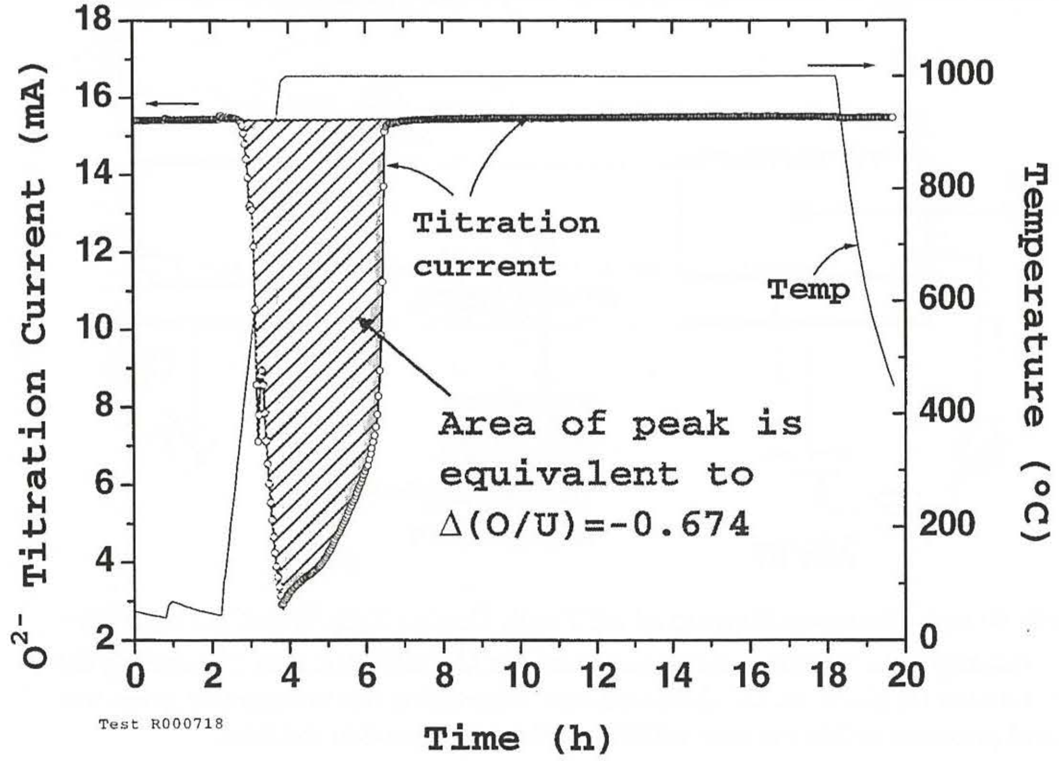

Figure 2. Reduction of U_3O_8 to UO_2. The measured Δ(O/U) was 0.674, which is only 1% off the expected value of 0.667.

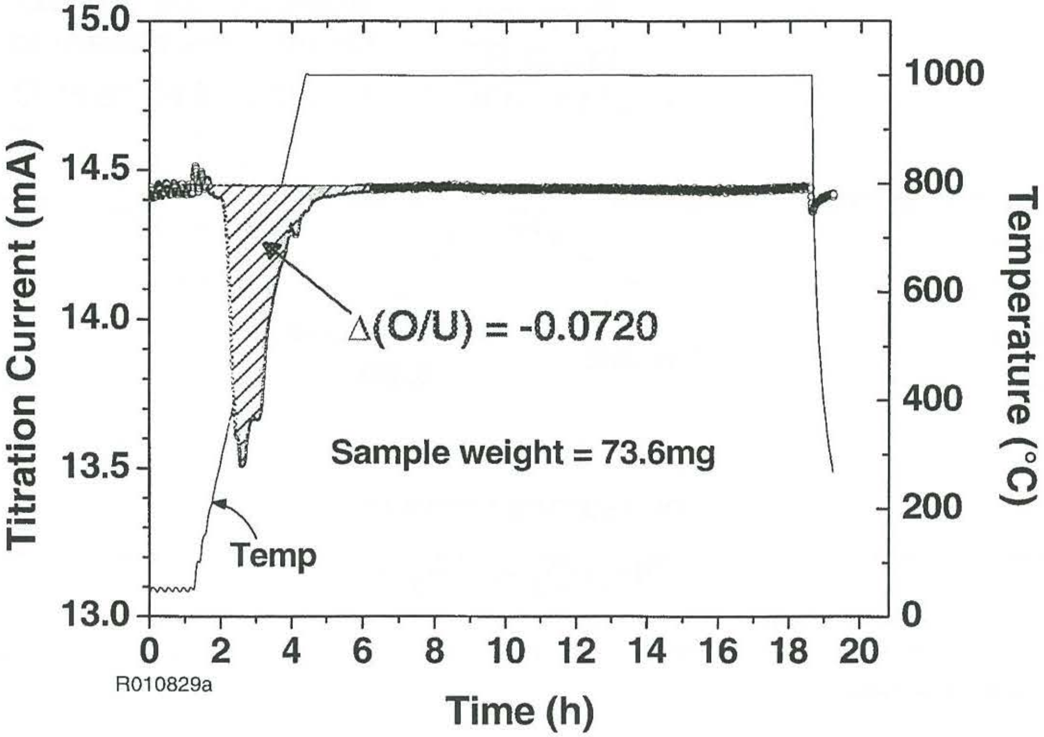

Figure 3. Reduction of an irradiated sample of UO_2 from a defected fuel element.

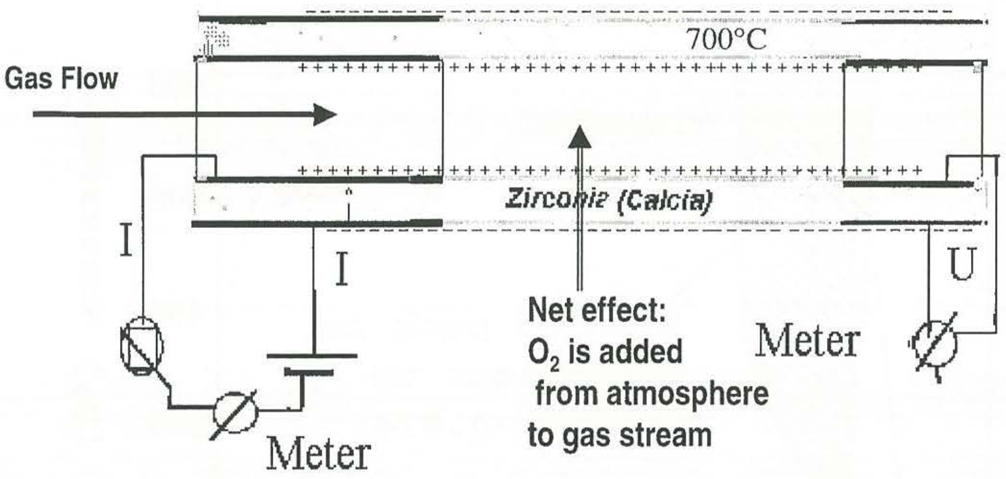

Figure 4. Rough schematic diagram of a CT cell. Doping ZrO_2 with CaO increases the O^{2-} vacancy concentration, thus enhancing the O^{2-} diffusion rate. Measuring the electric current (I) gives the O^{2-} diffusion rate. Measuring the voltage (U) gives the O_2 partial pressure inside the tube relative to the value outside the tube.

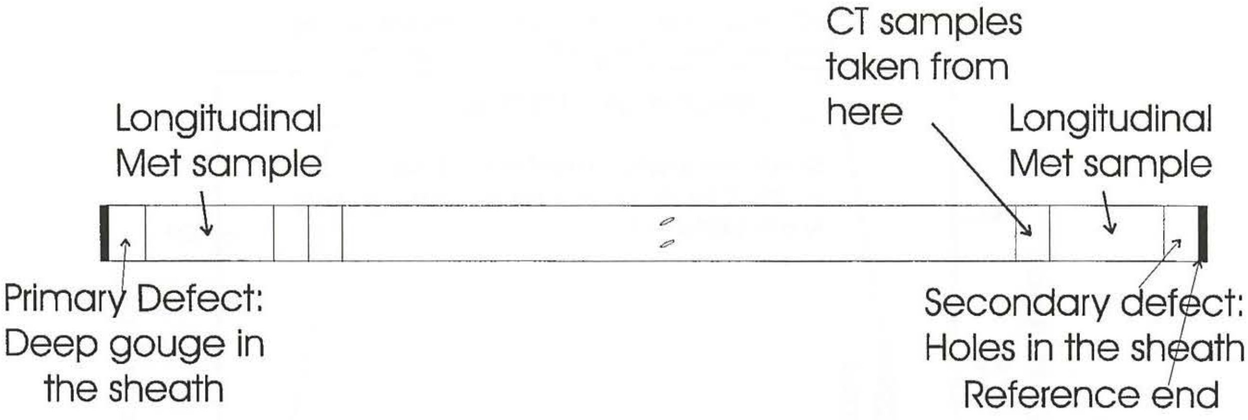

Figure 5. Schematic diagram of a defected fuel element, showing typical longitudinal locations of slices for samples for O/M-ratio measurements. The element centre is another typical location. Also shown are typical locations from which metallographic samples are taken.

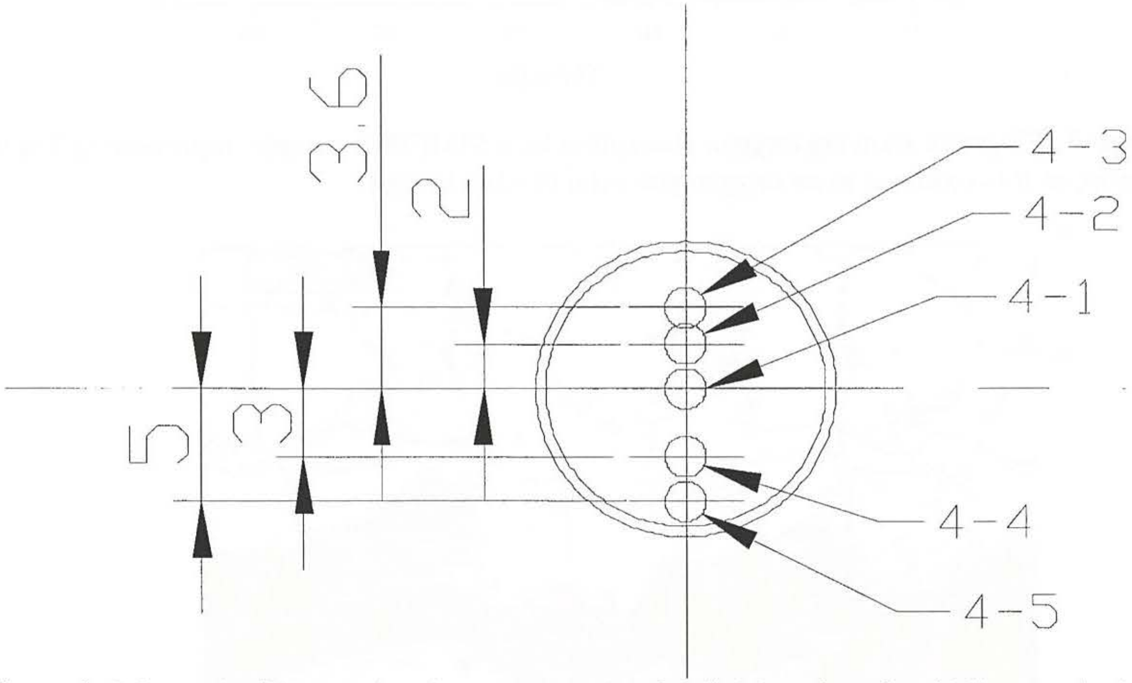

Figure 6. Schematic diagram showing an example of radial locations for drilling to obtain samples for O/M-ratio analysis. Numbers on the right are sample numbers and numbers on the left are distances in units of millimetres from the pellet centre.

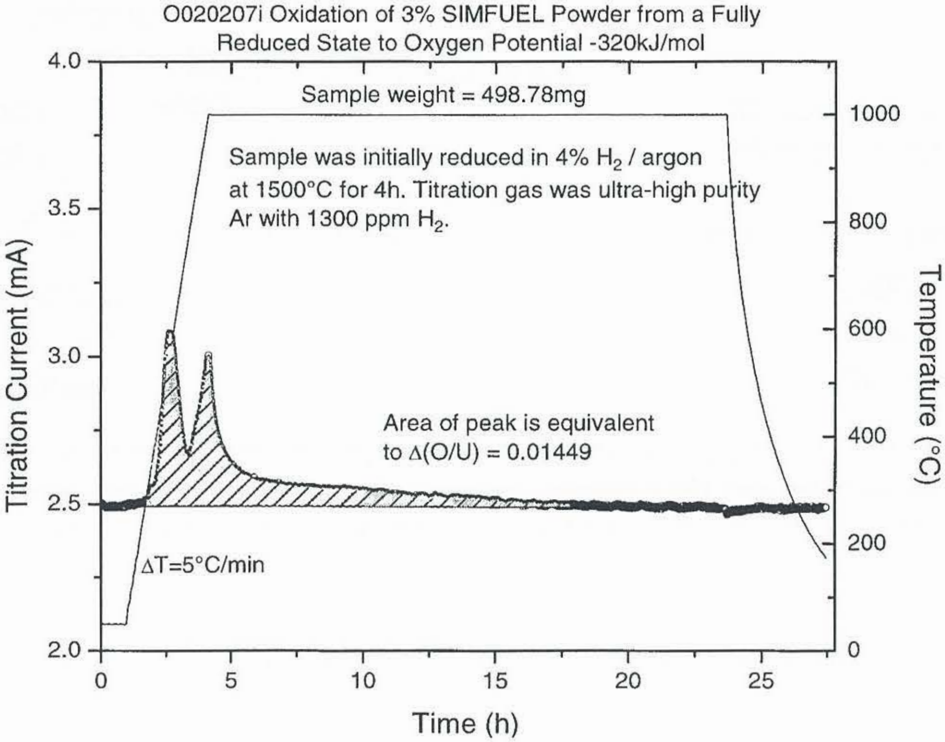

Figure 7. CT graph showing oxygen absorption by a SIMFUEL sample, representing 3 at.% burnup, as it is oxidized to an oxygen potential of -320 kJ/mol.

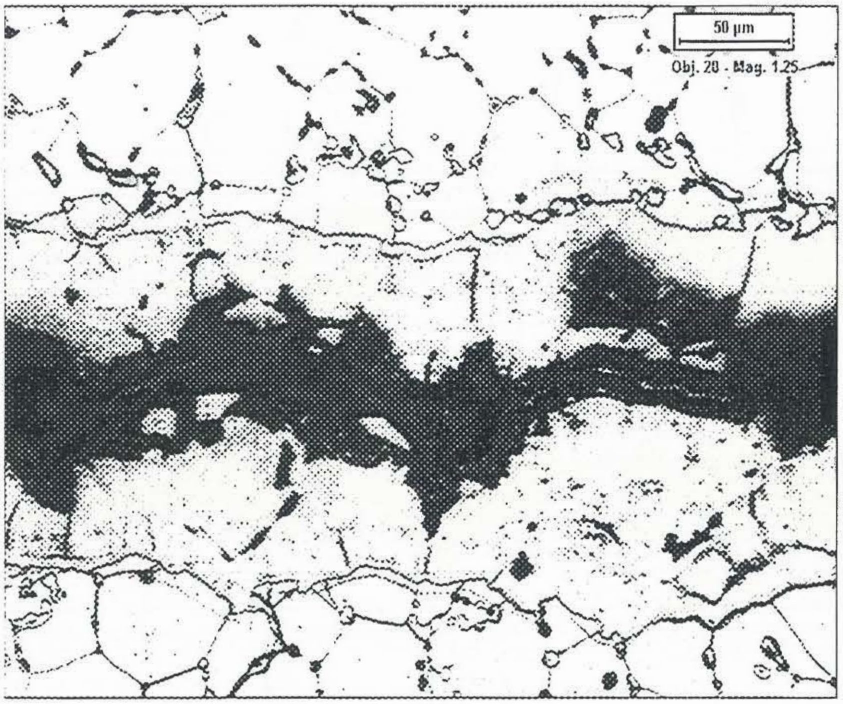

Figure 8. Sample of a defected irradiated fuel element near a pellet-to-pellet interface, showing apparent existence of a higher oxide phase near the interface.

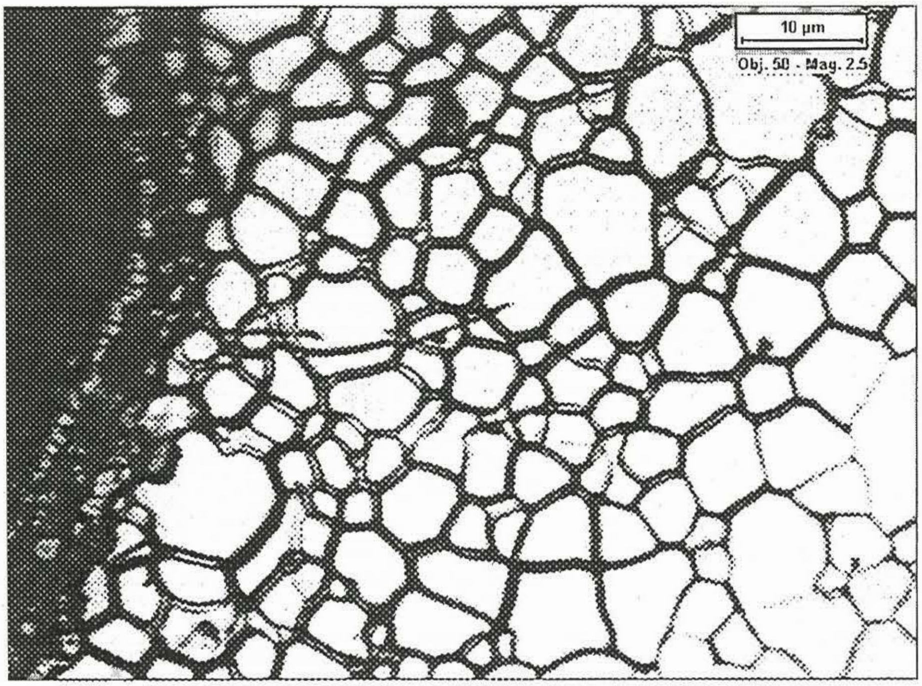

Figure 9. Sample of a defected fuel element showing an apparent higher oxide phase along the grain boundaries.

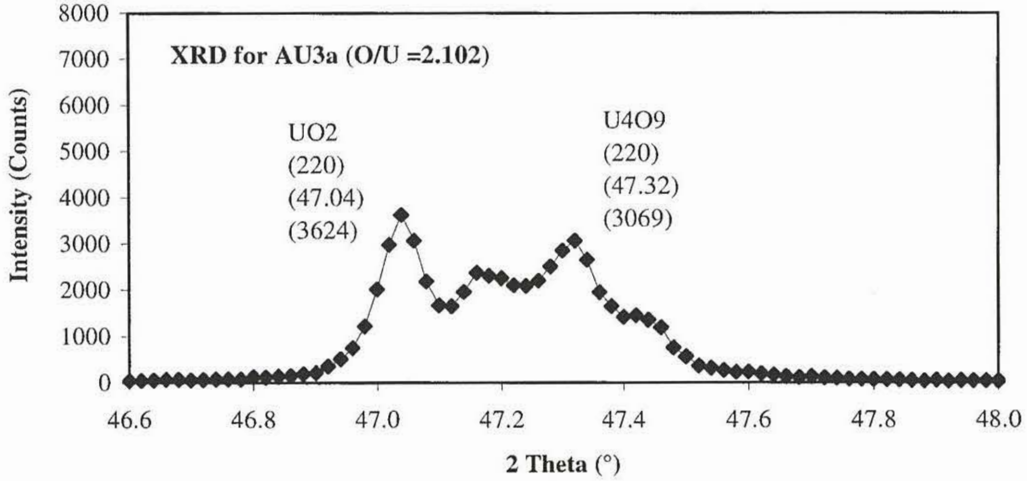

Figure 10. XRD pattern of a mixture of unirradiated UO_2 and U_4O_9. The two main peaks are the 220 reflections from the two phases. Positions and intensities are indicated on figure.