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Oxygen potential measurements in high burnup LWR UO_2 fuel

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Abstract

A miniature solid state galvanic cell was used to measure the oxygen potential $\Delta\overline{G}(O_2)$ of reactor irradiated UO_2 fuel at different burnups in the range of 28 to ≥ 150 GWd d/t M. This very high burnup was achieved in the rim region of a fuel with a cross section average burnup of 75 GWd d/t M. The fuels had different enrichments and therefore different contributions of fission of ^{235}U and ^{239}Pu. The temperature range covered was 900 to 1350 K. None of the fuels showed a significant oxidation. Rather, if allowance is made for the dissolved rare earth fission products and the Pu formed during irradiation, some of the fuels were very slightly substoichiometric and the highest possible degree of oxidation corresponded to $UO_{2.001}$. In general, the $\Delta\overline{G}(O_2)$ at 750°C was about -400 kJ/mol, corresponding to the $\Delta\overline{G}(O_2)$ of the reaction $Mo + O_2 \rightarrow MoO_2$. The implication of these results which are in contrast to commonly assumed ideas that UO_2 fuel oxidizes due to burnup, are discussed and the importance of the fission product Mo and of the zircaloy clad as oxygen buffers is outlined.

1. Introduction

UO_2 fuel is commonly assumed to oxidize with increasing burnup, in particular for Pu fission, since the fission products consume less oxygen than is liberated by fission of (tetravalent) U and Pu. Although two fission products are formed from each U (or Pu) atom, many of the fission products are metals (Mo, Tc, Ru, Rh, and Pd, with particularly high yields for fission of Pu) or rare gases (Kr, Xe) and many of them are trivalent (lanthanides). Also, dissolution of trivalent rare earth ions (and also of Pu) in UO_2 causes the oxygen potential, $\Delta\overline{G}(O_2)$ to increase (to become less negative) at constant oxygen-to-metal, O/M, ratio. Changes in $\Delta\overline{G}(O_2)$ and in oxidation state of the fuel (its O/M ratio) affect many important properties and influence significantly the irradiation behaviour of the fuel; examples are clad inside corrosion, fuel thermal conductivity and hence operating temperatures, diffusion and gas release rates, creep and plasticity of the fuel etc. A knowledge of the development of $\Delta\overline{G}(O_2)$ and of the O/M ratio of the fuel with burnup is therefore of large scientific and technological interest. We had previously developed a miniature solid state galvanic cell to successfully measure $\Delta\overline{G}(O_2)$ of unirradiated and irradiated fast breeder $(U, Pu)O_{2-x}$ fuel up to high burnups of 11 at% [1]. This cell was modified to allow measurements on UO_{2+x}, hence measurements at higher oxygen potentials, thus that a large range of $\Delta\overline{G}(O_2)$ values between about -650 and -150 kJ/mol can now be reliably measured, even for very high burnups up to 200 GWd d/t M in the rim region of UO_2 fuel [2]. Any oxidation of UO_2 due to high burnup would be therefore easily measurable. This cell has been used to obtain the new data reported here.

Experimental work and estimates on fuel oxidation with burnup were made already some 25 years ago. Davies and Ewart [3] reported that ^{235}U thermal fission is slightly oxidizing: (enriched) UO_2 was predicted to oxidize to $UO_{2.004}$ at 10% burnup, whereas thermal fission of ^{239}Pu was reported to cause significant oxidation: MO_2 was precicted to oxidize to $MO_{2.060}$ at 10% burnup (M = U and Pu). Fast fission of Pu was predicted to act similarly ($\Delta O/M = 0.053$ at 10% burnup), as later confirmed for originally substoichiometric fuel $(U, Pu)O_{2-x}$ by Ewart et al. in the laboratories of the author [4].

A more elaborate and sophisticated picture was more recently provided by Kleykamp [5]. Kleykamp allowed for the consequences of the formation of

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(U, Pu, RE)O_2 phases (RE = rare earths), the formation of (U, Pu)Pd_2 precipitates, the oxidation of Mo, the formation of phases such as Cs_2MoO_4, compound formation of alkali metals with chalkogen fission products and with U and Pu as well as oxygen gettering at the clad. Based on these considerations, Kleykamp [5] predicted that the average increase in O/M ratio due to Pu-fission is just half as large as the above value of Ewart and Davies. For LWR UO_2 fuel, he predicted an increase of 0.0013 in O/M per at% burnup, i.e. a composition of $UO_{2.0065}$ at 5 at% burnup of originally stoichiometric UO_2. However, for fuel operating at high power, and hence at high temperatures, his careful X-ray microanalysis of fuel and Zircaloy clad showed that the fuel remains essentially stoichiometric, since for these conditions, the clad getters oxygen by forming a reaction layer. Kleykamp analyzed this layer in a high power fuel rod of 4.3 at% burnup: it consisted of a Cs–Zr–O phase and ZrO_2 or α-Zr(O) layers, causing a constant O/M ratio of 2.000 + (0.001 to 0.005) over the fuel radius. This getter effect would be expected to be reduced at low power (colder) fuel. Despite this available knowledge, UO_2 fuel is still sometimes reported to show significant oxidation, based on indirect observations like presence of needle-shaped features (assumed to be U_4O_9) or lattice parameter, a_0, measurements (a_0 depends on Pu content, content of dissolved REs, degree of radiation damage, and and is thus not a well-suited indicator of the O/U ratio). Values as high as $UO_{2.2}$ were, for instance, claimed for a UO_2 fuel of 4.3 at% burnup [6].

In todays UO_2 LWR fuel at high burnup, about equal amounts of fission products are due to thermal fission of U and of Pu. The most direct quantity of interest for the chemistry of fuel, clad and fission products is the oxygen potential, $\Delta\overline{G}(O_2)$. This quantity was frequently measured for unirradiated UO_2 and UO_{2+x} and it was also frequently modelled as a function of O/U ratio (e.g. Refs. [2,7–10]. These measurements yielded the well-known S-shaped curve with a large increase in $\Delta\overline{G}(O_2)$ at the stoichiometric composition (from about −500 to −300 kJ/mol at 1000 K). Reliable data have also been published for UO_2 containing trivalent rare earths (Gd, Nd, Pr, La, Y) or elements that can be reduced to the trivalent state (Ce, Pu) (e.g. Refs. [2,10]). Replacement of U^{4+} by RE^{3+} (or Ce^{3+} or Pu^{3+}) ions requires either introduction of oxygen vacancies, or an increase in the oxidation state (valence) of some of the remaining U ions. This causes the $\Delta\overline{G}(O_2)$ to increase (to become less negative). This is understood in modelling activities (e.g. Ref. [11]), and is also confirmed by measurements on simulated burnup fuel or SIMFUEL (e.g. Refs. [12,13]).

As a consequence, the $\Delta\overline{G}(O_2)$ is more negative for stoichiometric UO_2 than for stoichiometric (U, RE)O_2 or stoichiometric SIMFUEL at a constant temperature. Or, equivalently, at constant temperature (e.g. 1000°C) and constant $\Delta\overline{G}(O_2)$ (e.g. −246 kJ/mol), the O/M ratios for UO_2, 3 at% and 6 at% SIMFUEL are 2.0025, 2.001 and 2.0005, respectively [2,13]. (Note, that 1 at% burnup corresponds to 9.4 GWd d/t M). The exact relation between $\Delta\overline{G}(O_2)$ and O/M ratio for irradiated LWR UO_2 is not known. The present work provides some more experimental $\Delta\overline{G}(O_2)$ values for high burnup UO_2 fuel, and parallel work on SIMFUEL [13,14] will provide further insights into the above relation between $\Delta\overline{G}(O_2)$ and O/M ratio for fission product-containing UO_2.

2. Experimental techniques and investigated fuels

The modified miniaturized galvanic cell based on the system {Pt/sample (irradiated UO_2)/ThO_2–Y_2O_3 electrolyte/reference (Fe/FeO)/Pt} is shown in Fig. 1 and was described previously in its first form [1] and its modified version [2]. The latter was used for the present measurements. The main features of the fuels used are summarized in Table 1. The burnup range was 29 to about 200 GW d/t M; this latter high value was reached in the rim-region of a fuel of 75 GW d/t M cross section average burnup [2]. The rim region of this fuel was much thicker than the frequently reported 150 to 200 μm. A very detailed structural analysis with scanning and transmission electron microscopy [15] and a modelling treatment of the rim structure formation

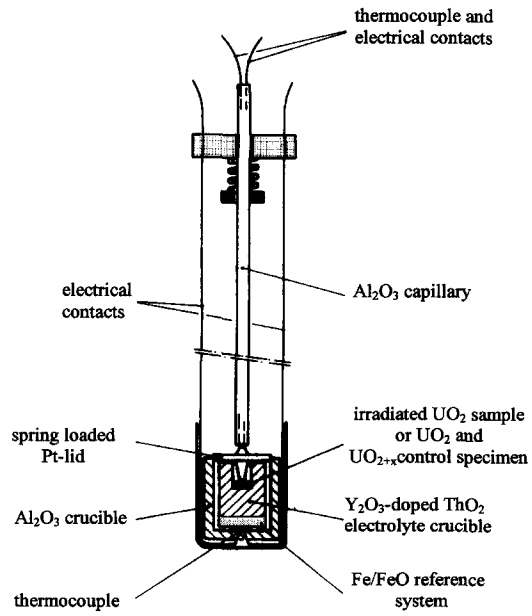

Fig. 1. Scheme of the miniature solid state galvanic cell to measure emf-values, and thus oxygen potentials, of high burnup UO_2.

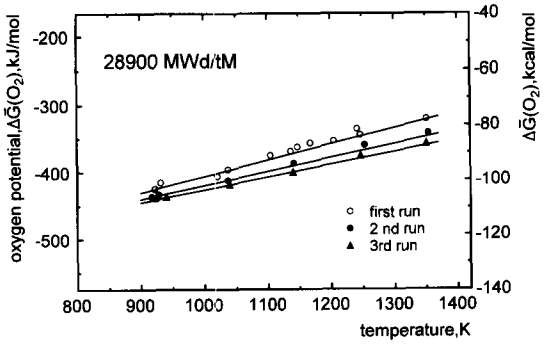

Fig. 2. Oxygen potential measurements of UO_2 fuel at 28900 MW d/t M burnup as a function of temperature.

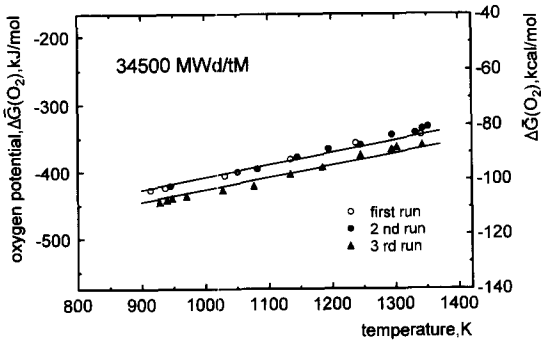

Fig. 3. Oxygen potential measurements of UO_2 fuel at 34500 MW d/t M burnup as a function of temperature.

[16] of this fuel are given separately. Small pieces of these fuels of a few mg weight were introduced into the cell and repeatedly measured in the temperature range of about 900 to 1350 K. These repeated measurements (called first, second or third run in Figs. 2–4) consisted in going up and down in temperature on 3 different days. Between the different measurements with the high burnup UO_2, measurements with unirradiated UO_2 or UO_{2+x} with known O/U ratio were made to test the cell and to guarantee absence of errors due to radiation damage, or other possible reasons.

Table 1
Some details of the investigated fuels

Fuel	Initial enrichment (%)	Burnup (GWd/tM)	Inner surface clad oxidation
1	6.85	28.9	very thin, no gap closure
2	5.0	34.5	very thin, no gap closure
3	8.25	58	up to 10 μm, only local patches
4a	1.46	75	15 to 20 μm
4b	1.46	up to 200 RIM area of fuel 4a	

3. Results with irradiated fuel

Figs. 2 to 4 show the results for the fuels with 28.9, 34.5 and 58 GWd d/t M burnup. All pieces originated from about mid-radial positions. A small decrease in $\Delta\overline{G}(O_2)$ by about 15 to 30 kJ/mol was observed for the lower two burnups for repeated runs. In contrast, the fuel of 58 GW d/t M burnup showed practically identical results for one fuel piece and for repeated runs and a small increase in $\Delta\overline{G}(O_2)$ for repeated runs for the second piece. This fuel yielded the lowest $\Delta\overline{G}(O_2)$ values, and for this reason and to confirm the results on the first fuel piece, two pieces were measured. A possible explanation of the low values may be the power-time history of the fuel. This fuel experienced an unusual power history, with a high rating in the first cycle, a low rating in the second cycle and a high rating again in the third cycle.

A possible reason for the small decrease in $\Delta\overline{G}(O_2)$ in the second and third run for the two fuels of 28.9 and 34.5 GW d/t M burnup could be a certain rearrangement, precipitation or compound formation of some fission products during the first anneal. A quantitative description of such a possible process is not the aim of this paper. An alternative possibility is a small surface oxidation of the fuel pieces between preparation of the pieces in the hot cells and the emf measurements in the laboratory. In such a case which we have frequently experienced in previous work on (substoichiometric) $(U, Pu)O_{2-x}$, the thin slightly oxidized surface layer determines the oxygen potential measured in the first run. At the highest temperatures of this run, oxygen diffusion is fast enough to evenly distribute this very small amount of oxygen in the fuel piece, without any measurable change in the total

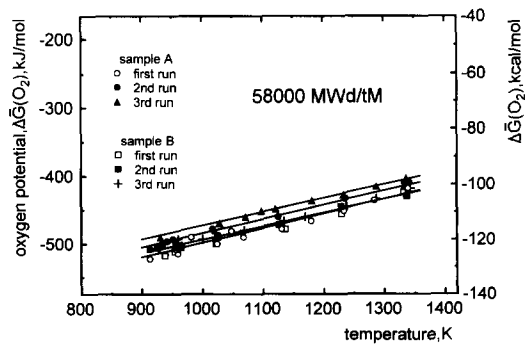

Fig. 4. Oxygen potential measurements of UO_2 fuel at 58000 MW d/t M burnup as a function of temperature. Two different pieces (samples A and B) were used.

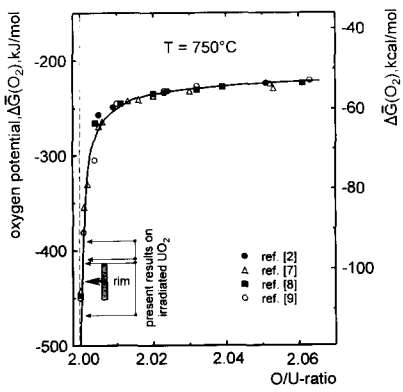

Fig. 5. Oxygen potential data for unirradiated UO_{2+x} at 750°C [2,7–9]. The present data and those of Ref. [2] for irradiated UO_2 are indicated by arrows.

O/U ratio. However, in this case the lines for runs 1 to 3 should not be parallel, but rather the first run should have a smaller slope and the lines should intersect at the highest temperature, as found for $(U, Pu)O_{2-x}$ with slight surface oxidation.

For the present purpose, these small changes are of little importance. The main point is that all values measured are very low. This is shown in Fig. 5 where arrows indicate the $\Delta\overline{G}(O_2)$ values at 750°C for these three fuels and for the fuel with the highest burnup (centre and rim region, i.e. ~ 75 and ~ 200 GWd/tM burnup) [2]. Shown is also the increase in oxygen potential with x in unirradiated UO_{2+x} at 750°C.

Fig. 6, finally, shows a summary of $\Delta\overline{G}(O_2)$ measurements on irradiated oxide fuels. An important increase with burnup had been observed in our previous work with originally substoichiometric $(U_{0.8}Pu_{0.2})O_{2-x}$ fast breeder fuel [1], and a less pronounced increase is seen in Fig. 6 at low burnup for UO_2 LWR fuel. The important point is that all data points are at or below the value for Mo oxidation, hence the reaction $Mo + O_2 \rightarrow MoO_2$.

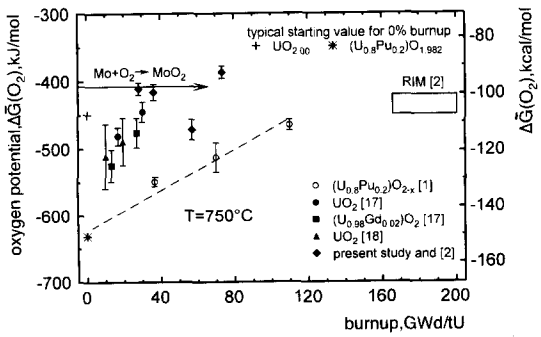

Fig. 6. Burnup dependence of the oxygen potential at 750°C for different irradiated oxide fuels (UO_2, $(U, Gd)O_2$ and $(U, Pu)O_2$). The threshold of Mo oxidation ($Mo + O_2 \rightarrow MoO_2$) is also shown. The square labelled RIM shows the results obtained with 3 fuel pieces from the RIM region of the fuel with the highest burnup [2].

4. Discussion

The present work extends a previous study [2] on the development of the oxygen potential $\Delta\overline{G}(O_2)$ in LWR fuel with increasing burnup, up to very high burnup values. The oxygen potential $\Delta\overline{G}(O_2)$ (relative partial molar free energy) defines the oxygen partial pressure $p(O_2)$ above the oxide, via the relation

$$\Delta\overline{G}(O_2) = RT \ln p(O_2).$$

It is the quantity needed to predict the chemical behaviour of fission products and the chemical interaction between fuel and clad. It is also the quantity needed to deduce the O/M ratio which in turn is decisive for the defect structure and for diffusion-related processes such as grain growth, creep, fission gas release etc. The technique used here, i.e. emf measurements with a solid-state galvanic cell, gives direct values at the temperatures of interest, i.e. temperatures within those of the operating conditions of LWR fuel. Direct gravimetric determinations of O/M are difficult to perform in a hot cell, and they are difficult to interpret because fission products change their chemical state during oxidation and/or reduction treatments as well, in addition to the changes in the valence state of uranium. Lattice parameters depend on many factors, as stated in Section 3, and are thus not recommended to determine O/M ratios in high burnup fuel.

The fuels studied were selected on basis of their burnups and their enrichments. They thus had very different contributions of Pu fission to the total burnup. In contrast to still existing ideas about fission oxidizing the fuel, in particular for Pu fission, none of the fuels investigated here showed any significant oxidation, not even in the rim zone with an extreme burnup of up to 200 000 MW d/t M. As shown in Fig. 5, the $\Delta\overline{G}(O_2)$ values measured for high burnup fuel correspond to those of stoichiometric UO_2 or very slightly oxidized (unirradiated) UO_{2+x} with $x \leq 0.001$. As explained in Section 3 and in more detail in Ref. [2], the oxygen potential at constant O/M ratio increases due to dissolved Pu and rare earths, which grow in with increasing burnup. Or, expressed otherwise, for a constant $\Delta\overline{G}(O_2)$ and a constant temperature, high burnup fuel has a lower O/M ratio than unirradiated UO_2. The present $\Delta\overline{G}(O_2)$ values for irradiated fuels thus do not only show the absence of oxidation, but rather indicate a very slight substoi-

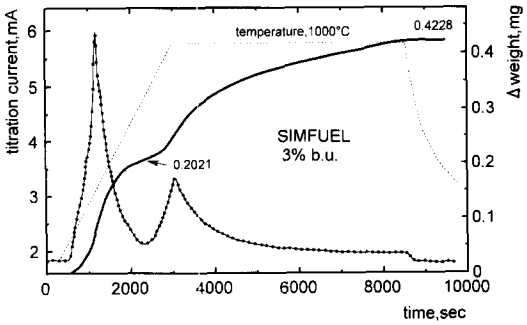

Fig. 7. Oxidation of 3% burnup SIMFUEL, measured by coulometric titration [13], during a linear temperature increase to 1000°C followed by a hold at 1000°C. The first peak represents oxidation of Mo, before UO_2 oxidizes [19].

chiometry of the order of O/M = 1.995 for the highest burnup (200 GW d/t M).

Any conclusive treatment of the development of O/M ratio with burnup must include a realistic description of the chemical state and of the mobility of the fission products in the temperature gradient of the operating fuel. Also, chemical reactions occurring on the inner surface of the clad must be known and included, hence the chemical state of the Zr in the cladding must be properly modelled. The decisive fission product in the fuel is Mo, as indicated in Fig. 6. Mo can be present in the well known five-metal particles, or it can be present as oxide (e.g. [5]). Recent work on SIMFUEL has indeed shown, that Mo oxidizes before the UO_2 matrix does (see Fig. 7). We thus can conclude that oxygen buffering by the oxidation of Mo, aided by the formation of the interaction layer between clad and fuel, causes the oxygen potential to increase only in the first irradiation period and then to remain quasi-constant (at e.g. about −400 kJ/mol at 750°C). At such an oxygen potential, and depending on the kinetics, Cs-zirconates, -uranates and -molybdates can form besides MoO_2, ZrO_2, CsI, Cs_2Te, etc. (e.g. Ref. [20]).

Ongoing work on SIMFUEL and on the interaction layer between fuel and clad, together with more modelling on fission product chemistry will help to better define the exact O/M ratio at high burnup.

5. Conclusions and summary

The present study shows that none of the investigated UO_2 fuels oxidized due to burnup, though some fuel had predominantly Pu fission. Even in the RIM region which underwent grain subdivision and reached extremely high burnups up to 200 000 MW d/t M, the fuel is still not oxidized. Actually, it is slightly substoichiometric. These results can be explained by buffering by the fission product Mo and by the Zr clad.

The implications are manifold. We can conclude that, e.g.,

- the needles sometimes observed in (intact) irradiated fuels are not U_4O_9,
- the kinetics of matter transport are not enhanced due to excess oxygen in the matrix,
- the technologically important RIM structure is formed not because of Pu-fission and oxidation of the fuel matrix, but due to the inherent properties of the UO_2 lattice.

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