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The effect of rare-earth fission products on the rate of U_3O_8 formation on UO_2

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Abstract

The rate of U_3O_8 formation on the surface of flat neodymium-doped UO_2 disks was measured by X-ray diffraction and the kinetic data were fitted to a two-dimensional nucleation-and-growth model. The results indicate that neodymium doping in the UO_2 tends to inhibit U_3O_8 formation. A quantitative relationship between the activation energy for U_3O_8 formation and the neodymium content of the UO_2 has been derived from the kinetic data. Our data are consistent with recent results obtained for the oxidation of used LWR fuel, which suggests that fission products in solid solution are likely the cause of U_3O_8 inhibition observed for used fuel. © 1998 Elsevier Science B.V.

1. Introduction

In many countries, dry air storage is gaining acceptance for the intermediate storage of used nuclear fuel after several years of cooling under water and before final disposal in a geological repository [1]. One limitation of dry storage is the potential oxidation of fuel in the small number of elements that become defected in the reactor. In particular, the oxidation of UO_2 to U_3O_8 produces a 36% increase in volume of the fuel matrix, which can lead to splitting of the sheath and fuel spalling [2–4]. This can complicate subsequent handling and disposal of the fuel. Therefore, it is important to understand UO_2 fuel oxidation in sufficient detail to define appropriate allowable conditions (such as time and temperature) for the safe handling and storage of used fuel.

It is widely known that UO_2 oxidation proceeds by two stages [5–8]:

$$UO_2 \rightarrow U_3O_7/U_4O_9 \rightarrow U_3O_8. \quad (1)$$

The formation of U_3O_7/U_4O_9 [1] displays parabolic kinetic behaviour because this first stage of oxidation is controlled by the rate of oxygen diffusion through a discrete layer of the oxide product [11,12]. In contrast, the formation of U_3O_8 displays sigmoidal reaction kinetics [2,13,14] consistent with a nucleation-and-growth mechanism [15].

The effect of dopants on the UO_2 oxidation process has been studied for many years [16–21] because of the development of mixed-oxide and burnable-poison fuels in the nuclear industry and because dopants can influence the UO_2 sintering process. Moreover, significant amounts of fission products are present as a solid solution in used fuel [22]. In particular, the effect of rare-earth (RE) dopants on the oxidation of UO_2 has been studied extensively [18,23,24] because the RE are major fission products and

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[1] The nature of the product of the first stage of UO_2 oxidation varies depending on the oxidation conditions and the type of fuel. At low temperatures, spent light-water reactor (LWR) fuel, or UO_2 with high dopant levels oxidizes to a cubic U_4O_{9+y} phase, whereas unirradiated UO_2 oxidizes to tetragonal U_3O_7 (see Refs. [9,10]). For simplicity, we use the unqualified terms U_3O_7/U_4O_9 or U_3O_7 to refer to the product of the first stage of UO_2 oxidation.

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because of their use as burnable poisons [25]. Wilson et al. [18] noted increasing resistance to oxidation with increasing amounts of M_2O_3 (M = Y, La) in solid solution with UO_2 when oxidized in air in the range 1375 to 1750°C. Thomas et al. [10] compared the oxidation at lower temperatures (< 600°C) of pure UO_2 with doped materials containing 4 and 8 wt% Gd_2O_3 as well as 0.4 wt% NbO_2, using thermal analysis and X-ray diffraction (XRD). They found that with each type of material the eventual product of oxidation was U_3O_8 but that increasing dopant levels raised the threshold for U_3O_8 formation in terms of both temperature and weight gain. Oxidation experiments performed on doped UO_2 show that it commonly retains the fluorite-type structure to higher temperatures and for longer times, than the undoped material [10,17,21].

Considerable evidence suggests that used fuel displays oxidation resistance, similar to that shown by doped UO_2. It has been reported that the induction time (t_i) for U_3O_8 powder formation shows a positive correlation with burnup [26,27] although there is considerable scatter in the data. Similarly, Gilbert et al. [28] reported that unirradiated UO_2, or used fuel with a burnup below 15 MW d/kg U, oxidizes to U_3O_8 more readily than used fuel with a burnup greater than 15 MW d/kg U. Choi et al. [29] studied the oxidation behaviour of simulated high-burnup nuclear fuel, i.e. SIMFUEL [30], and reported that the resistance to U_3O_8 formation increased with burnup. There is not, however, unanimous agreement that burnup (or doping) is associated with increased oxidative resistance. Bennett et al. [31,32] oxidized advanced gas-cooled reactor (AGR) used-fuel fragments in air and found that t_i is somewhat shorter for used fuel than unirradiated UO_2. They also reported that there is no relationship between t_i and the extent of burnup in the range 11.7 to 26.7 MW d/kg U. It is difficult to rationalize the difference between oxidation behaviour reported by Bennett et al. [31,32] and others [26–29]; the differences are perhaps due to fuel microstructure.

The enhanced stability (relative to pure UO_2) of the fluorite-type phase in doped UO_2 or used fuel is thus generally well established, although there is not universal agreement on this point. However, the relationship between RE content and oxidation resistance has not yet been examined quantitatively. We have thus measured the kinetics of U_3O_8 formation for a series of UO_2 samples with a range of neodymium contents. The results are compared with data obtained with used fuel, and applications to the safe dry air storage of used nuclear fuel are discussed.

2. Experimental

2.1. Sample preparation and oxidation

Sintered pellets (12 mm diameter) of $(U_{1-x}Nd_x)O_2$ ($x = 0.01$, 0.02 or 0.03) were prepared by mixing finely divided Nd_2O_3 and UO_2 powders, cold pressing, and then sintering in a hydrogen (10%)/nitrogen atmosphere at 1650°C for 2 h. The homogeneity of this material was confirmed by scanning electron microscopy/energy dispersive X-ray spectroscopy. The oxidation behaviour of neodymium-doped UO_2 was compared with that of undoped CANDU® [2] fuel pellets.

For each sample, disks about 2 mm thick were cut from the cylindrical pellet using a low-speed diamond saw. One surface of each disk was then polished manually using 400-grit abrasive paper. Previous work with UO_2 has shown that the rate of formation of U_3O_8 is more reproducible on a surface with a 400-grit finish than on more highly polished surfaces, where U_3O_8 nucleates preferentially at cracks and other flaws [33]. After polishing, the disks were cleaned with ethanol and then distilled water prior to oxidation. The samples were then oxidized in unlimited laboratory air in a convection oven with temperature control accurate to within 2°C. At selected intervals, each sample was cooled to room temperature and the XRD pattern was recorded. Samples were then returned to the oven, and the heat treatment (at the same temperature) was continued. The heat–cool–analyze cycle was continued until there was visible evidence of U_3O_8 powder formation on the sample surface. At such time, the experiments were terminated, because powder formation and spalling negate the XRD data. Surface oxidation of doped UO_2 samples generally only proceeded to 10–20% before the samples crumbled. Air-oxidation experiments were performed at 200, 225, 250, 260, 275, 300 and 325°C. Oxidation times varied with temperature and were in the range 1 to 5000 h.

2.2. Collection and quantitative treatment of the XRD data

The XRD data were collected using a Rigaku Rotaflex diffractometer equipped with a 12 kW rotating-anode Cu Kα source and a diffracted-beam monochromator. The diffractometer scanning rate was 10° (2θ)/min for qualitative peak identification and 1° (2θ)/min for the acquisition of integrated intensities for specific peaks.

The progress of U_3O_8 formation was followed by monitoring XRD peak intensities, using the procedure developed by Choi et al. [29]. Thus the fraction of the surface oxidized to U_3O_8 was determined for each sample by measuring the integrated intensity of the overlapping [200] and [130] peaks for U_3O_8 ($2\theta \simeq 26.0°$ with Cu Kα radiation) and the [111] feature for U_3O_7/U_4O_9 ($2\theta \simeq 28.5°$). These intensities were termed $I_{U_3O_8}$ and $I_{U_3O_7}$, respectively. From these intensities, the fraction, F, of the surface oxidized to U_3O_8 will be given by [29]

$$F = \frac{I_{U_3O_8}}{I_{U_3O_8} + \alpha I_{U_3O_7}}, \tag{2}$$

[2] CANDU® is a registered trademark of Atomic Energy of Canada.

where the empirical factor (α) accounts for the different absolute XRD intensities and mass absorption coefficients of U_3O_8 and U_3O_7. Previously published results have shown that α is 0.450 ± 0.033 [29].

The XRD analysis depth in our samples is approximately 1 μm for the selected XRD peaks [9,29]. The formation of U_3O_8 on the surface of the 12 mm disks can thus be considered equivalent to a two-dimensional nucleation-and-growth reaction mechanism. Recently, McEachern et al. [34] showed that such two-dimensional reaction kinetics can be modelled by

$$F(t) = 1 - \exp\left\{ -\frac{\pi\kappa t^3}{3} + \frac{\pi^2\kappa^2 t^6}{180} - \frac{11\pi^3\kappa^3 t^9}{45\,360} + \frac{5\pi^4\kappa^4 t^{12}}{399\,168} \right\} \quad (3)$$

where F is the fraction of the surface oxidized, t is the time and κ is an effective rate constant, defined by

$$\kappa = K_g^2 K_n, \quad (4)$$

where K_n ($s^{-1}\ m^{-2}$) is the rate of nucleation per unit area and K_g ($m\ s^{-1}$) is the rate of linear growth of the circular nuclei.

3. Results and discussion

For each sample, $I_{U_3O_8}$ and $I_{U_3O_7}$ were measured from the XRD data and the fraction of the sample surface converted to U_3O_8 was calculated by use of Eq. (2). Each experimental run yielded a series of F values obtained at various times during the course of the reaction. The value of the rate constant, κ, was then calculated for each temperature and dopant concentration by minimizing the sum of the squares of deviations between calculated and experimental values of F according to Eq. (3). The results are displayed in Table 1. Typical agreement between the experimental data and the curves obtained by fitting these data to Eq. (3) is displayed in Fig. 1.

An Arrhenius plot for the composite rate constant κ is displayed in Fig. 2. Data for 325°C are not included in Fig. 2 because they deviate from linearity; other workers have reported similar observations above 300°C [2,35–37]. The reasons for such non-linearity are not well known. It may be due to experimental difficulties associated with the relatively short reaction times, or to a change in oxidation mechanism around 300 to 350°C [2,35–37]. The Arrhenius expression was calculated (200 to 300°C) for each neodymium concentration shown in Fig. 2. The results were as follows [3]:

$$0\ \text{at.\%}\ \ln(\kappa) = -\frac{5.81 \times 10^4}{T\ (\text{K})} + 95.88, \quad (5)$$

$$1\ \text{at.\%}\ \ln(\kappa) = -\frac{6.32 \times 10^4}{T\ (\text{K})} + 104.66, \quad (6)$$

$$2\ \text{at.\%}\ \ln(\kappa) = -\frac{6.54 \times 10^4}{T\ (\text{K})} + 107.70, \quad (7)$$

$$3\ \text{at.\%}\ \ln(\kappa) = -\frac{6.40 \times 10^4}{T\ (\text{K})} + 105.04. \quad (8)$$

The activation energy was calculated for each of the Arrhenius expressions (Eqs. (5)–(8)) which exclude the 325°C data. The result obtained for each neodymium composition is given in Table 2 and a plot of the activation energy as a function of neodymium concentration is given in Fig. 3. The uncertainty in the reported activation energies is taken to be 10 kJ mol^{-1} (90% confidence interval) based on a similar analysis reported earlier [34]. The data in Fig. 3 can be fitted approximately to a linear relationship between the activation energy for U_3O_8 formation and neodymium content of the doped UO_2:

$$E_{act} = 166\ \text{kJ mol}^{-1} + 5.46x, \quad (9)$$

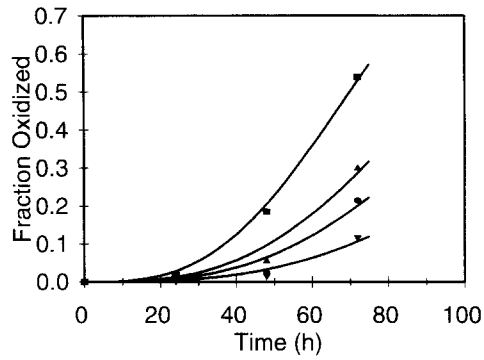

Fig. 1. Fraction of the sample surface oxidized to U_3O_8 for UO_2 disks doped with 0.0 (■), 1.0 (▲), 2.0 (●) or 3.0 (▼) at.% neodymium when heated at 250°C in air.

Table 1
Experimental values of the composite rate constant, κ (h^{-3}) for various temperatures and neodymium concentrations

Temperature (°C)	Neodymium concentration (at.%)			
	0.0	1.0	2.0	3.0
200	2.1×10^{-12}	2.0×10^{-13}	4.9×10^{-14}	7.3×10^{-14}
225	4.1×10^{-10}	4.3×10^{-11}	1.1×10^{-11}	1.5×10^{-11}
250	8.2×10^{-7}	8.8×10^{-7}	5.8×10^{-7}	2.9×10^{-7}
260	8.3×10^{-7}	2.3×10^{-7}	4.4×10^{-8}	3.5×10^{-8}
275	9.2×10^{-5}	7.0×10^{-5}	2.8×10^{-5}	2.6×10^{-5}
300	2.0×10^{-3}	5.5×10^{-4}	3.7×10^{-4}	3.2×10^{-4}
325	6.1×10^{-3}	4.4×10^{-3}	1.3×10^{-3}	7.7×10^{-4}

[3] Throughout this report the term at.% refers to the fraction of the total metal content on an oxygen-free basis.

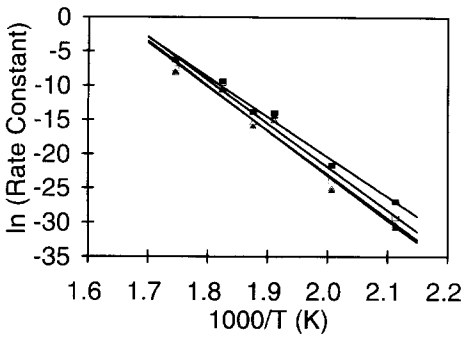

Fig. 2. Arrhenius plot for the composite rate constant κ for U_3O_8 formation for UO_2 doped with 0.0 (■), 1.0 (□), 2.0 (▲) or 3.0 (△) at.% neodymium.

where x is the neodymium concentration of the (U, Nd)O_2 in at.%. The dependence of E_{act} on x is not statistically significant at the 95% confidence level. The effect of neodymium on the *rate* of oxidation, however, is genuine (Table 1).

Direct comparison between our data and that obtained for used fuel is difficult because the composition and structure of used fuel are quite variable. However, a rough comparison between used-fuel data and our results is instructive. Gilbert et al. [26] found a positive correlation between burnup and the (normalized) powder induction time. Examination of their Fig. 1 reveals that the time required for U_3O_8 powder formation around 250°C is an order of magnitude greater for used fuel with a burnup of 25 to 30 MWd/kg U (~ 2.9 at.%) [4] than for pure UO_2. Similarly, Choi et al. [29] found that the time required for U_3O_8 powder formation at 250°C is an order of magnitude longer for SIMFUEL with a simulated burnup of ~ 4.9 at.% than for pure UO_2 (based on eq. 11 of Ref. [29]).

Based on the results obtained by Gilbert et al. [26] and Choi et al. [29], we conclude that the rate of U_3O_8 formation on unirradiated UO_2 will be an order of magnitude faster than for used fuel with a burnup between 2.9 and 4.9 at.%. Taking the average of these two results, we assume that (to a first approximation) the rate of oxidation for UO_2 will be an order of magnitude faster than for used fuel with a burnup of ~ 3.9 at.%. The rare-earth content of used fuel with a burnup of 3.9 at.% is ~ 1.8 at.% [22]. To compare the data for used fuel and SIMFUEL with our results, one can calculate from Eqs. (5) and (7) that at 250°C the rate constant, κ is 2.28×10^{-7} h^{-3} for UO_2 and 2.42×10^{-8} h^{-3} for UO_2 doped with 2.0 at.% Nd. Using these values of κ one can estimate (Eq. (3)) that oxidation for 100 h at 250°C will result in F values of 0.212 for UO_2 and 0.025 for UO_2 doped with 2.0 at.% Nd. Thus the same 'order-of-magnitude' decrease in reactivity

[4] 1 at.% burnup is equivalent to ~ 9.46 MWd/kg U.

Table 2
Activation energy for the formation of U_3O_8 on the surface of UO_2 disks doped with various concentrations of neodymium

Neodymium concentration (at.%)	E_{act} (kJ mol^{-1})
0.0	161.1
1.0	175.3
2.0	181.3
3.0	177.3

is observed for UO_2 doped with 2 at.% neodymium as for used fuel with a fission-product rare-earth content of ~ 1.8 at.%. Our analysis is clearly only approximate, but it seems reasonable to conclude that used fuel is less prone to air oxidation than unirradiated UO_2 because of rare-earth (and other) fission products present in solid solution in the used fuel.

The lower rate of oxidation for rare-earth doped UO_2 relative to that of the pure material is consistent with results obtained by Thomas et al. [10] for UO_2 doped with gadolinium or with niobium. Our data are also consistent with results reported by Choi et al. [29], who examined the air oxidation of SIMFUEL. Neither SIMFUEL nor rare-earth-doped UO_2 replicate the fission-gas bubble formation and other microstructural details of used fuels. Thus our results do not support the suggestion of Gilbert et al. [28] that increased oxygen grain boundary diffusion rates in used fuel may be responsible for the observed slower rate of U_3O_8 formation in this material than in UO_2.

4. Conclusions

X-ray powder diffraction was used to quantify the rate of U_3O_8 formation on the surface of neodymium-doped UO_2 disks oxidized in air. The kinetic data were fitted to a two-dimensional nucleation-and-growth model, published earlier, and the results were used to develop a quantitative relationship between the U_3O_8-formation rate constant, κ, and the neodymium content of the (U, Nd)O_2.

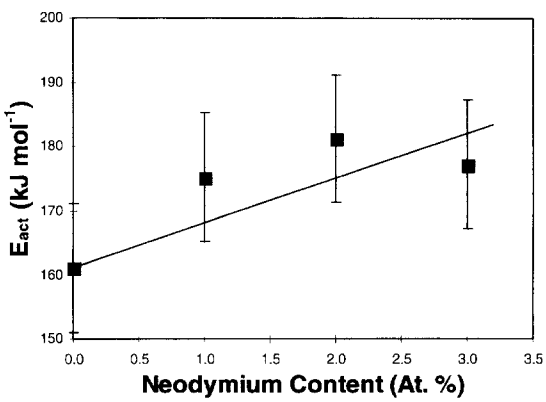

Fig. 3. Activation energy for the formation of U_3O_8 on the surface of UO_2 disks doped with various amounts of neodymium.

Our data show that increased neodymium content of doped UO_2 results in longer U_3O_8 powder-formation times, which is consistent with results obtained for used LWR fuel and SIMFUEL. It thus appears that high-burnup used fuel is more resistant to U_3O_8 formation than low-burnup used fuel, and that this is due, at least in part, to rare-earth (and other) fission products present in solid solution in the used fuel.

Our results indicate that unirradiated UO_2 data can be used judiciously for conservative calculations of rates of U_3O_8 formation on used fuels under dry storage conditions.

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