Kinetics of interfacial reactions in molten U/solid Y_2O_3 system

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Abstract

The reactivity between liquid uranium and polycrystalline yttria substrates of various grain-sizes is studied at 1673 K under high vacuum–low p_{O_2} conditions ($p_{O_2} \approx 10^{-7}$ Pa). At short contact times, uranium oxidation occurs at the metal/oxide interface from oxygen transferred from the yttria substrate which is transformed to an under-stoichiometric state. At long contact times, deoxidation occurring at the uranium free surface predominates and leads to complete elimination of oxidized uranium by a dissolution–evaporation mechanism. © 1998 Elsevier Science B.V.

1. Introduction

In the search for liquid uranium-resistant refractory ceramics, yttrium oxide is interesting because of its greater thermodynamic stability in comparison with UO_2. For example, at 1673 K the standard Gibbs energy of formation for Y_2O_3 is -476 kJ/at g O compared to -398 kJ/at g O for UO_2 [1]. Moreover, interactions between molten uranium and yttrium are very weak as evidenced by the very low solubility of Y in molten U (close to 0.5 at.% at $T = 1700$ K [2]).

Despite these thermodynamic considerations, the formation of reaction products in U/Y_2O_3 system has been previously reported [3,4].

In the present work, the reactivity of liquid U/Y_2O_3 couple is studied at 1673 K as a function of time up to 200 h. The aim of this study is to identify the type of reactions occurring in this system as well as the mechanisms responsible. The effect of these reactions on wetting of yttria by uranium is discussed elsewhere [5,6].

2. Experimental method

The experiments are carried out in a metallic furnace heated by molybdenum resistance under a dynamic vacuum better than 10^{-3} Pa obtained by an oil diffusion pump. In order to decrease the oxygen partial pressure p_{O_2} in the furnace, the specimens are placed in a tantalum isothermal chamber in which the value of oxygen partial pressure, p_{O_2}, was evaluated at $p_{O_2} \approx 10^{-7}$ Pa [6].

Uranium used in this study contains 35 ppm of oxygen and 100 ppm of carbon. Aluminium, chromium, iron and nickel are the most important metallic impurities, with a total content of 30 ppm. Parallelepipedic uranium samples of 5 g are machined before testing.

The Y_2O_3 samples have a thickness of 2 mm and a diameter of 20 mm. The substrate is polished to a roughness of about 1 nm. Yttria substrates of 1 µm grain-size were produced by hot isostatic pressing at 1673 K under 150 MPa for 1 h, using a 99.999% pure powder. A limited number of experiments were performed with substrates of 6 µm grain-size produced by sintering at 2073 K under vacuum for 3 h. Yttria can be under-stoichiometric, Y_2O_{3-x}, due to oxygen vacancies. The maximum value of x at 1673 K, corresponding to Y/Y_2O_3 equilibrium, is about 0.08 [7,8]. The stoichiometry of yttria is roughly indicated by its colour, changing from white to black as the oxygen concentration decreases. HIP substrates are white while sintered yttria is black. Before experiments, the latter substrates are transformed to white by oxidation in air at 1773 K for 2 h. Experiments consist in heating the samples to the experimental temperature (1673 K) at a rate

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Table 1
Results of reaction product thickness for polycrystalline yttria ($d_g = 1$ μm and $d_g = 6$ μm) after contact with liquid U at 1673

Time (hours)	Grain-size of yttria (microns)	Substoichiometric zone in the substrate	Reaction product thickness (microns) UO_2	Reaction product thickness (microns) $(U,Y)O_x$
1	1		2	traces
	6		0.5	traces
3	1		3.5	traces
12.5	1		6.5	traces
50	1		4.4	2.5
	6		7	traces
200	1		-	7

The black color of the substrate means under-stoichiometry.

of 5 K/min, maintaining the sample at this temperature for a certain time (from 1 to 200 h) and then cooling at room temperature at a rate of 50 K/min. After cooling, the reaction product morphology and chemistry are characterized by optical microscopy, microprobe, SEM and X-ray diffraction.

3. Results

The results obtained at 1673 K are given in Table 1. The change in stoichiometry of the substrate indicated by its colour, white for stoichiometric to black for understoichiometric, are also given schematically. The thickness of reaction products is measured at the interface far from the triple line (Fig. 1). Two reaction products were identified by X-ray diffraction: the U dioxide UO_2 and a $UO_2-Y_2O_3$ solid solution [9] denoted $(U,Y)O_x$. Its compo-

sition was found by microprobe analysis to be close to $U_{0.6}Y_{0.4}O_{2.1}$. Like UO_2, the structure of $(U,Y)O_x$ is fcc with $a = 0.536$ nm against a value $a = 0.5496$ nm for UO_2 [6].

From the results of Table 1, it appears that a qualitative change is produced between 12.5 and 50 h. For $t \leq 12.5$ h the reaction product at the interface is UO_2. Its thickness, measured by S.E.M., increases rapidly with time. X-ray diffraction shows the presence of $(U,Y)O_x$ as well but only in traces. Between $t = 12.5$ h and $t = 50$ h, the total thickness of reaction product zone did not seem to vary. However, a significant part of the UO_2 was transformed into $(U,Y)O_x$. At $t = 50$ h, from chemical analysis of the solidified drop, the mole fraction of oxygen in uranium was found to be $X_O = 1.2 \times 10^{-3}$. At $t = 200$ h, all the UO_2 layer was transformed into $(U,Y)O_x$. In this case, from chemical analysis of the solidified drop, the mole fraction of yttrium dissolved in uranium was found to be $X_Y = 2.4 \times 10^{-4}$. The substrate, all white at the beginning of the experiment, becomes black close to the metal/yttria interface. For $t \leq 12.5$ h, only part of the substrate is black.

However, the black area increases with time and, at $t = 50$ h and $t = 200$ h, all the yttria substrate is uniformly black. Attempts to measure the stoichiometric parameter x of Y_2O_{3-x} of black yttria by microprobe analysis were unsuccessful due to the lack of precision of oxygen concentration measurement.

During cooling, the differences in the linear expansion coefficients between the metallic drop and the ceramic substrate lead to systematic fracture partly at the interface and partly in the substrate (mixed fracture) (Fig. 1).

When the grain-size of yttria increases, the uranium oxidation rate at the interface decreases strongly for the short duration experiment ($t = 1$ h). However, no difference in the thickness of reaction products exists between the two grain-size substrates at $t = 50$ h.

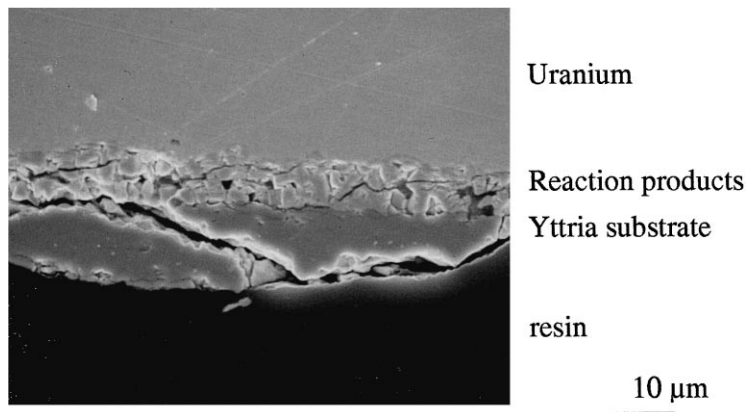Fig. 1. Cross-section of the drop/substrate interface (SEM) ($t = 200$ h, $T = 1673$ K, $d_g = 1$ μm). During cooling, thermomechanical stress led to cracks partly at the interface and partly in the substrate.

Finally, when the temperature increases by 100 K for yttria with $d_g = 1$ μm, no reaction products were visible at the interface after 50 h. However, the roughness of this interface is high (several microns) compared with the initial roughness of only a few nanometers. During cooling, the drop detached from the substrate by a cohesive fracture (Fig. 2). From chemical analysis, the mole fraction of oxygen dissolved in uranium was found to be $X_O \approx 10^{-4}$ which is lower by a factor 10 than the value measured when UO_2 was present at the interface

4. Discussion

During isothermal holding at 1673 K, two opposite reactions occur in the U/Y_2O_3/vapour system. The first is uranium oxidation, the second uranium deoxidation.

4.1. U oxidation at the U/Y_2O_3 interface: oxygen flow

Oxidation of uranium at the interface may be due to oxygen provided by yttria, leading to an increase in x in Y_2O_{3-x}, as well as to oxygen provided by the furnace atmosphere. The maximum thickness of UO_2 formed by oxygen of the furnace may be evaluated by calculating the oxygen flow, $\emptyset_O$, arriving on the free surface of the substrate, according to the molecular flow equation [10]:

$$\emptyset_O = (\sum \alpha_i a_i p_i)/(2 M_i RT)^{1/2}, \qquad (1)$$

in which p_i is the equilibrium partial pressure of the vaporising molecule i, α_i is the vaporisation coefficient ($\alpha_i \leq 1$), a_i, the number of oxygen atoms in the molecule, M_i, the molar mass of the molecule, and R the ideal gas constant.

In our case, the expression for the oxygen flow is

$$\emptyset_O^f = 2 \alpha_{O_2} p_{O_2}^f / (2 M_{O_2} RT) 1/2, \qquad (2)$$

where $p_{O_2}^f$ is the oxygen partial pressure in the furnace.

Taking $\alpha_{O_2} = 1$, the maximum value of impinging oxygen flow is calculated:

$$\emptyset_O^f \text{ (in mol m}^{-2} \text{ s}^{-1}) = 3.8 \times 10^{-2} p_{O_2}^f \text{ (in Pa)}.$$

Then, the maximum thickness of UO_2 layer which can be produced from furnace oxygen is written:

$$e_{UO_2}^{max} = \left(M_{UO_2} \emptyset_O^f \Omega_s / 2 \Omega_i \rho_{UO_2} \right) t = 3 \times 10^3 p_{O_2}^f t, \qquad (3)$$

where Ω_s is the area of substrate surface collecting oxygen (equal to the area of a 20 mm diameter substrate), Ω_i is the area of the drop/substrate interface (10 mm in diameter) and ρ_{UO_2} is the mass volume of UO_2 ($\approx 11 \times 10^3$ kg m^{-3}). The thickness e_{UO_2} is in microns when $p_{O_2}^f$ is in Pa and t in hours. Taking $p_{O_2}^f = 10^{-7}$ Pa and $t = 1$ h, we find $e_{UO_2}^{max} = 3 \times 10^{-4}$ μm which is negligible compared with the experimental value observed at $t = 1$ h (Table 1). Clearly, in such low p_{O_2} atmospheres, oxidation of uranium at the interface is mainly due to the oxygen provided by the substrate. This conclusion is valid for all combinations of parameters t and $p_{O_2}^f$ for which $e_{UO_2}^{max}$ is less than a 'measurable' value of thickness, say 10^{-1} μm. Conversely, for long durations and/or high $p_{O_2}^f$ values, it may be expected that the furnace oxygen would contribute to interfacial oxidation of uranium. Indeed, as is described elsewhere, experiments performed with $t = 50$ h and $p_{O_2}^f = 10^{-4}$ Pa led to $e_{UO_2} \approx 20$ μm, significantly more than the 7 μm obtained for the same time at $p_{O_2} = 10^{-7}$ Pa (Table 1) [6].

In low p_{O_2} atmosphere, stoichiometric yttria provides oxygen to uranium, becoming itself sub-stoichiometric. This is consistent with the observation that yttria becomes black near the interface and that the black area progresses, until all the substrate becomes black. At this point, the oxygen of the substrate available for uranium oxidation is completely consumed and consequently, the growth of UO_2 layer is stopped. It is reasonable to assume that the value of x in Y_2O_{3-x} corresponds to the p_{O_2} value fixed
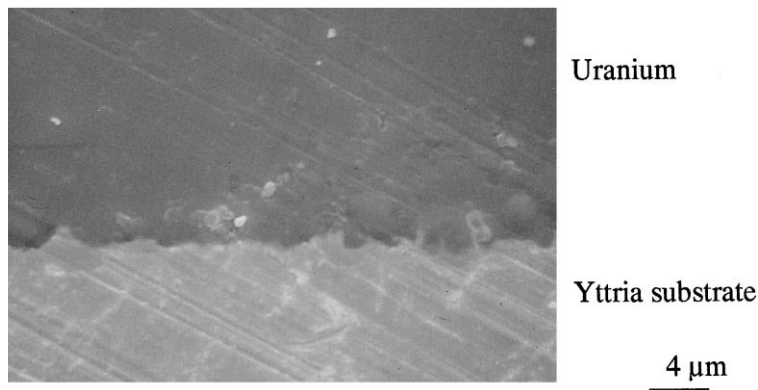

Uranium

Yttria substrate

4 μm

Fig. 2. Cross-section of the drop/substrate interface (SEM) ($t = 50$ h, $T = 1773$ K, $d_g = 1$ μm). Interface is rough, but no reaction products are seen.
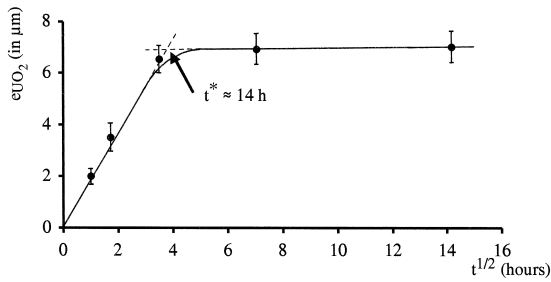
Fig. 3. Total thickness of reaction products plotted versus square root of time for $d_g = 1$ μm and $T = 1673$ K.

at the interface by U/UO_{2-z} equilibrium, i.e., $p_{O_2} \approx 1.4 \times 10^{-20}$ Pa at 1673 K [1]. This assumption is confirmed by the fact that the measured value of the mole fraction of oxygen dissolved in uranium was $X_O = 1.2 \times 10^{-3}$ in good agreement with the value $X_O = 1.3 \times 10^{-3}$ given for the U/UO_{2-z} system at the same temperature in Ref. [11]. Moreover, Gardie and Bordier [4] measured the p_{O_2} value in a liquid uranium/Y_2O_3/vapour system by mass spectroscopy and found values which are very close to those of U/UO_{2-z} equilibrium.

Once all the UO_2 layer has been transformed to solid solution $(U,Y)O_x$, the partial pressure of oxygen at the interface is equal to the value corresponding to the three-phase equilibrium between molten U, solid solution $(U,Y)O_x$ and Y_2O_3 saturated in UO_2. This value, which is evaluated in Appendix A, is $p_{O_2} \approx 10^{-23}$ Pa.

4.2. U oxidation at the U/Y_2O_3 interface: the rate limiting process

When the total thickness of interfacial reaction products is plotted as a function of square root of time, a quasi linear variation is obtained for $0 \le t \le t* = 14$ h, followed by a plateau (Fig. 3). The linear part of the curve indicates that growth of UO_2 is controlled by diffusion.

Two diffusion mechanisms are possible, either diffusion through the growing UO_2 layer or diffusion of oxygen from stoichiometric Y_2O_3 (white areas) to the interface through an increasingly thick layer of under-stoichiometric yttria (black area). Two observations argue for the second hypothesis. First, the oxidation rate is higher near the triple line where the oxygen diffusion field in the substrate is much larger than at the interface far from the triple line. Secondly, for times $t < t*$, the oxidation rate depends significantly on grain-size of the substrate. Indeed at $t = 1$ h, when the grain-size is increased by a factor 6, e_{UO_2} decreases by a factor 4 (Table 1). Such results suggest not only that UO_2 growth is controlled by diffusion of oxygen in the Y_2O_3 substrate, but also that this diffusion occurs preferentially at the yttria grain boundaries. Diffusion in

the polycrystalline yttria can be described using an effective diffusion coefficient, D_{eff}, given by

$$D_{eff} = (1 - F)D_L + FD_{GB}$$

with F the volumic fraction of grain boundaries, $F = 2\delta/d_g$; δ the grain-boundary width (taken as 1 nm [12,13]; D_L and D_{GB} the lattice and grain-boundary diffusion coefficients respectively.

According to the above equation the contribution of grain boundaries to total diffusion depends on the values of ratio D_{GB}/D_L and $F = 2\delta/d_g$. Although F is a small number, (F is 3×10^{-4} for $d_g = 6$ μm and 2×10^{-3} for $d_g = 1$ μm), the value of D_{GB}/D_L is often so high (10^5,[13]) that the lattice contribution to diffusion may be small and even negligible. In the latter case, the e_{UO_2} thickness would vary according to $d_g^{1/2}$. Such a dependence predicts that when the grain size of the substrate increases from $d_g = 1$ μm to $d_g = 6$ μm, e_{UO_2} would decrease from 2 μm to 0.8 μm which agrees well with the experimental value of 0.5 μm.

4.3. U deoxidation

At $t > t* \approx 14$ h, the total thickness does not change but UO_2 is gradually replaced by the solid solution $(U,Y)O_x$. Actually, as the molar volume of $(U,Y)O_x$ is very close to that of UO_2 (the ratio of unit cell volumes being 0.93), the formation of $(U,Y)O_x$, with formula $U_{0.6}Y_{0.4}O_{2.1}$, corresponds to a net decrease in the number of moles, n_U^{ox}, of oxidized uranium at the interface. When this number is calculated and plotted as a function of time (Fig. 4), it is seen that after an initial increase, n_U^{ox} passes through a maximum and then decreases towards 0. By extrapolation of this curve, it is found that the interface layer would completely disappear after about 500 h. Such a result was obtained after only 50 h by increasing temperature from 1673 to 1773 K (Fig. 2).

The general condition for uranium deoxidation is

$$\emptyset_O^e > \emptyset_O^d + \emptyset_O^f,$$

where $\emptyset_O^e$ is the oxygen evaporation flow, $\emptyset_O^d$ is the flow of oxygen arriving at the interface provided by the sub-
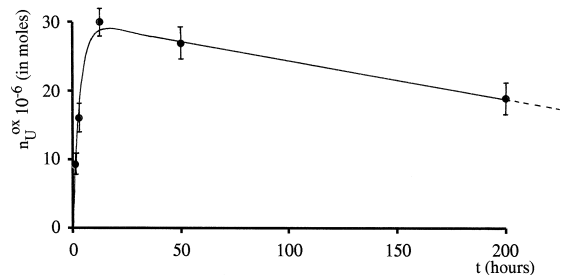

Fig. 4. Number of moles of oxidized uranium at the interface versus time. This number passes through a maximum for $t \approx t*$ and then decreases towards zero.
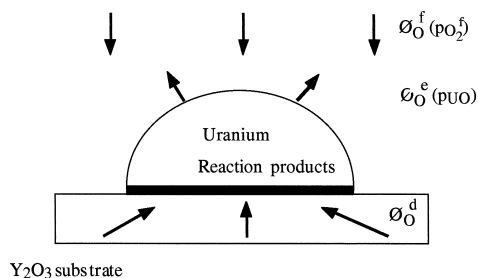
Fig. 5. Definition of the different oxygen flows in the liquid uranium/interfacial reaction products/yttria system.

strate, and $\varnothing_O^f$ is the oxygen flow from the furnace atmosphere impinging on the drop surface (Fig. 5).

For $t < t*$, the term $\varnothing_O^d$ predominates, then $\varnothing_O^d > \varnothing_O^e$ and oxidation occurs. For $t > t*$, no more oxygen is available in the substrate for U oxidation, then $\varnothing_O^d \approx 0$ and the condition for deoxidation of the drops becomes $\varnothing_O^e > \varnothing_O^f \cdot \varnothing_O^f$ is roughly proportional to p_{O_2} in the furnace, equal to 10^{-7} Pa. For evaluating $\varnothing_O^e$, it is noted that as long as a U-oxide layer is present at the U/Y_2O_3 interface, deoxidation can occur by dissolution of this layer into the molten U, diffusion of dissolved oxygen from the interface to the drop surface and evaporation of oxygen from the free surface. As it was found by a mass spectroscopy investigation the oxygen containing molecule in the $U_{(l)}$/$Y_2O_{3(s)}$ system with the highest partial pressure at 1673 K is the U-monoxide [4,14]. Thus, the overall deoxidation reaction can be written as

$$UO_{2(s)} + U_{(l)} \rightarrow 2UO_{(g)}. \tag{4}$$

Consequently, the evaporation flow of oxygen $\varnothing_O^e$ is proportional to p_{UO}. The value of p_{UO}, fixed by the monovariant equilibrium reaction (5), is 1.5×10^{-4} Pa. This is much higher than the value of $p_{O_2}^f = 10^{-7}$ Pa, meaning that deoxidation of uranium does occur. Note that a similar monovariant equilibrium involving $Al_2O_{3(s)}$, $Al_{(l)}$ and $Al_2O_{(g)}$ phases was used in Ref. [10] to explain deoxidation of liquid aluminum drops under high vacuum. Similarly deoxidation of AuSi droplets was explained by means of a monovariant equilibrium involving $SiO_{2(s)}$, silicon dissolved in molten Au and $SiO_{(g)}$ [15].

Table 2
Comparison between calculated and experimental values of deoxidation times at two temperatures

Temperature (K)	p_{UO} (Pa)	t_{min}^e (calculated) (h)	t^e (experimental) (h)
1673	1.5×10^{-4}	80	(500)
1773	10^{-3}	12	< 50

The value of 500 h was obtained by extrapolation of n_U^{ox} versus time curve, Fig. 4.

By introducing the equilibrium value of p_{UO} in expression (1), the evaporation flow of oxygen can be calculated taking $\alpha_{UO} = 1$. Then, the minimum time, t^e, needed to dissolve and evaporate a 7 μm thick layer of UO_2 is calculated (Table 2) (in this semi-quantitative calculation, no difference will be made between UO_2 and $(U,Y)O_x$). At 1673 K, this time is 80 h. From the results of Table 2, it is seen that the calculated values of t_{min}^e predict rather well the net acceleration of U-deoxidation due to an increase in temperature.

5. Conclusion

In the molten U/Y_2O_3 system under a high vacuum–low p_{O_2} atmosphere, two types of reaction occur:

Oxidation of uranium at the interface from oxygen provided by stoichiometric yttria which is transformed to under-stoichiometric yttria. This reaction predominates for short contact times as long as oxygen for U-oxidation is available in the yttria. The rate of reaction is controlled by diffusion of oxygen at yttria grain boundaries. For this reason, the oxidation reaction rate is sensitive to the grain size of the yttria substrate. The UO_2 layer, formed initially at the interface, is gradually transformed into a UO_2–Y_2O_3 solid solution.

Deoxidation of uranium, occurring by a dissolution–evaporation mechanism. This process is effective for long contact times and leads to complete elimination of any reaction products from the U/Y_2O_3 interface. During the above reactions and because of them the partial pressure of oxygen in the vicinity of the U/Y_2O_3 interface decreases gradually from 10^{-7} Pa to 10^{-23} Pa. This has a considerable effect on the wetting and the adhesion energy of uranium on yttria, as discussed elsewhere [16].

Appendix A

The value of p_{O_2} for the equilibrium of three phases, molten U–$(U,Y)O_x$–Y_2O_3 saturated in UO_2, can be calculated from the experimental values of the mole fraction X_Y* of Y dissolved in molten U in equilibrium with $(U,Y)O_x$ and Y_2O_3. At 1673 K, we measured $X_Y* = 2.4 \times 10^{-4}$.

For high dilutions, the activity coefficient of Y in U is nearly constant (Henry's law), thus the activity a_Y* is $2.4 \times 10^{-4}/4.3 \times 10^{-3} = 0.056$, where 4.3×10^{-3} is the mole fraction of Y in molten U in equilibrium with pure solid yttrium [2].

For the reaction

$$Y_2O_{3(s)} \rightarrow 2(Y) + 3/2O_{2(g)} \tag{5}$$
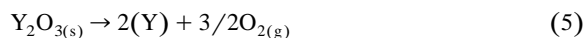
(where the parentheses mean that yttrium is dissolved in U), the equilibrium constant is written

$$K = \left(a_Y *^2 p_{O_2}^{3/2} \right) / a_{Y_2O_3}.$$

K is calculated from standard Gibbs free energy data of Ref. [1]. Then, taking $a_{Y_2O_3} \approx 1$ and $a_Y * = 0.056$, we find $p_{O_2} = 9 \times 10^{-24}$ Pa.

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