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APPLICATION OF SECONDARY ION MASS SPECTROMETRY
TO THE STUDY OF A
CORROSION PROCESS--OXIDATION OF URANIUM BY WATER

S. S. Cristy

J. B. Condon

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S. S. Cristy
J. B. Condon

Instrumentation and Characterization Department

Y-12 Development Division

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# Application of SIMS to the Study of a Corrosion Process--Oxidation of Uranium by Water

S. S. Cristy and J. B. Condon

Oak Ridge Y-12 Plant, Martin Marietta Energy Systems Inc.
Oak Ridge, Tennessee 37831, USA

Corrosion of metals is an extremely important field with great economic and engineering implications at the Oak Ridge Y-12 Plant. To effectively combat corrosion, one must understand the processes occurring. This paper shows the utility of Secondary Ion Mass Spectrometry (SIMS) data for elucidating the processes occurring in one particular corrosion process--the oxidation of uranium by water--and for validating a theoretical model.

Although much has been written about the oxidation of uranium by water[1-2], before these SIMS studies the mode of diffusion, the role of hydrogen, the location of the rate limiting step, and the locus of inhibition by oxygen were unknown. Some of this work has been previously reported[3-5].

High-purity uranium, $\gamma$ quenched from 825°C and then annealed at 625° was used. The surfaces were polished with 0.25$\mu$m diamond in ethanol. Exposures to isotopically-altered reactants or natural abundance-reactants were made in selected sequences in an ultra-high vacuum (UHV) system equipped with a constant temperature bath. Depth profiles were followed using an Applied Research Laboratories (ARL) Ion Microprobe Mass Analyzer (IMMA). Typically a 5nA, $N_2^+$ ion beam, focused to 4$\mu$m and rastered over an area 31 by 39$\mu$m was used for sputtering. The secondary ion current was electronically apertured.

As reported at the SIMS II conference[3], a simple alternation of exposures to $^{18}OH_2$ and $^{16}OH_2$ shows that the water adsorbed last produces the oxide nearest the metal and thus the oxygen (in some form) is diffusing to the oxide/metal interface to react. Multiple exposure experiments with five alternating layers showed that the oxygen species migration left the permanent oxide lattice positions essentially unaffected by this passage (Figure 1). The slope of the $^{16}O^-$ signal between the first and second layers was the same as between the third and fourth layers. Therefore, the slopes between layers are due to the final usage or precipitation of the migrating species and not to interdiffusion in the oxide lattice, and the diffusion mode is interstitial rather than vacancy.

In earlier studies[1], the rate controlling step was assumed to be the diffusion of water through fine capillaries to the oxide surface. The profiles in Figure 2 demonstrate that the rate controlling step for the reaction is not the diffusion of reactant; as in a final 5 minute exposure to $^{16}OD_2$ after two exposures totalling 24 hours, oxide equivalent to 86 minutes of exposure or 6% of the total oxide is exchanged. Thus the diffusion rate of reactant far exceeds the oxidation rate. Rapid changes in oxide isotopic composition as a function of third exposure times from 0 to 10 minutes were found. At 10 minutes, essentially the maximum exchange is reached.
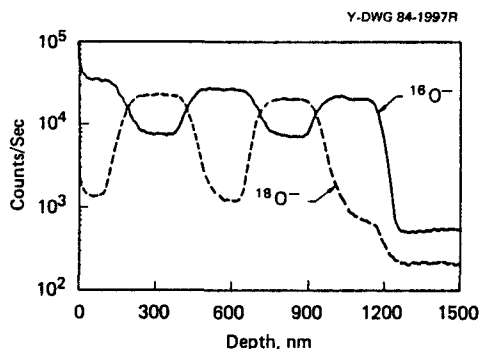
Figure 1. Depth profile on uranium sample exposed to $^{16}OH_2$, $^{18}OH_2$, $^{16}OH_2$, $^{18}OH_2$, $^{16}OH_2$ for 6h each (80°C, 0.6kPa)
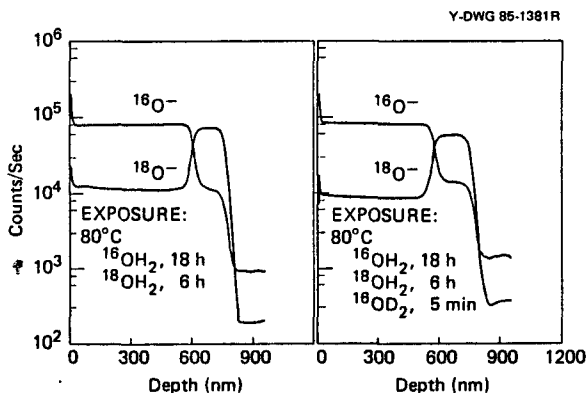
Figure 2. Depth profiles illustrating rapidity of diffusion in water formed uranium oxide

$OH^-$ has been postulated as the diffusing species in the water oxidation of uranium[1] and the formation of uranium hydride is suspected as accountable for the higher oxidation rates observed with water compared to pure oxygen[1,6]. Indeed hydrogen gas is evolved in the reaction and the presence of hydride in the oxide has been confirmed[1,7]. To test the role of hydrogen, uranium was exposed to $^{18}OH_2$ followed by $^{16}OD_2$. The deuterium profile was found to mimic the coprecipitant oxide $^{16}O$, but no evidence for a hydride intermediate of finite lifetime was found. However, the deuterium substitution did reduce the oxidation rate, implying a role for hydrogen in the mechanism. The deuterium concentration left in the oxide was found to be approximately 2 to 3% atomic and was incorporated as a stable portion since no exchange was observed when additional exposures to $OH_2$ were made.

The model adopted for the water oxidation of uranium is derived from a model successfully applied to the hydriding of uranium[4,8,9]. In this model, OH in some form is transported rapidly through the oxide to the oxide/metal interface. The rate of the reaction then depends on the rate of hydriding to cause spalling or breaking up of uranium metal which is known to occur when 1.4 to 3% of the uranium is hydrided[9]. The oxidation then occurs rapidly with the microscopically divided uranium. The mathematics of the model provides two equations which can be used to check its validity. The first (1) predicts the rate of reaction:

$$V = \left[-kC°/\ln U\right](D/akU)^{1/2}, \tag{1}$$

where V is the velocity of the moving front, k is a combination of rate constants, C° is the solubility for hydrogen in the metal, U is the metal concentration at the transformation boundary (spall front), D is the diffusion coefficient for hydrogen in the metal, and a is the stoichiometric ratio for the reaction. A comparison of the calculated rates and data compiled by RITCHIE[10], COLMENARES[11], and HOPKINSON[12] is shown in Figure 3. The second (2) predicts the product profile:

$$d \ln P/dx = U\left[akU/D\right]^{1/2}, \tag{2}$$

where P is the product concentration and x is the location of the transformation boundary. The isotopic SIMS profiles show these product profiles clearly between isotopic layers and therefore, when Δx (the distance for the product concentration to drop by a factor of 10) is measured as a function of temperature, a second test of the model can be made. The outcome of this test is illustrated in Figure 4.
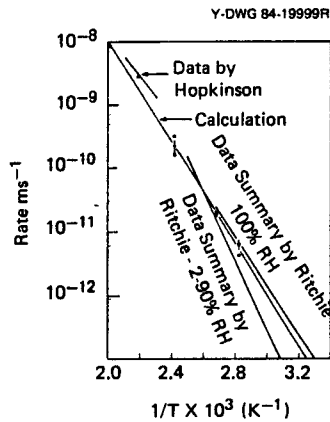
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Figure 3. Calculated vs. experimental rates of oxidation of uranium by water
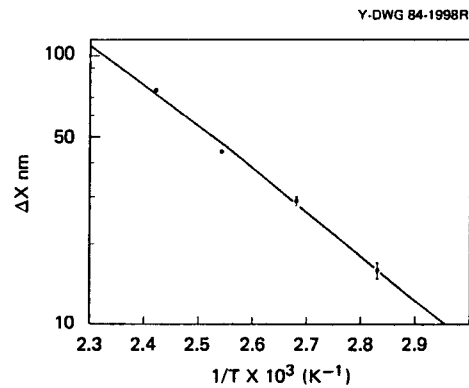


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Figure 4. Calculated vs. experimental $\Delta x$ (Points experimental)

It has long been known that the oxidation of uranium by water is retarded by the presence of oxygen gas and the retardation has been assumed to occur by site blocking at the surface[1],[2]. However, when alternate isotopic exposures were made, followed by exposure to a mixture of $^{16}O_2$ and $^{18}OH_2$, the rapid exchange of $^{16}O$ and $^{18}O$ occurred in the oxide layer, but the further oxidation by water in this and subsequent exposures was retarded for up to 21 hours (Figure 5). This shows graphically that $OH_2$ is not held up at the surface and that the retarding mechanism is effective at the oxide/metal interface rather than at the surface. The effectiveness of the $O_2$ to retard the further water oxidation was much reduced if no water-formed oxide layer were present. The effectiveness was also crystallite related.
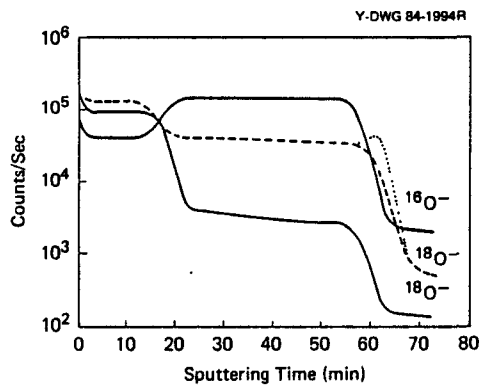


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Figure 5. Profiles showing inhibition of water oxidation by oxygen at oxide/metal interface. Exposures are 0.6kPa (4.6 torr) $^{18}OH_2$ for 6.5h, 0.6kPa $^{16}OD_2$ for 18h at 80°C (solid lines). After exposure to 1.3kPa $^{16}O_2$ and 0.6kPa $^{18}OH_2$ for 6h, the $^{18}O$ profile shifted to the dashed line. Additional exposures to pure $^{18}OH_2$ for 12 hours result in the $^{18}O$ final profile (dotted line).

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