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by

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Abstract

Many factors such as impurities in the oxide and metal, microstructure, gas impurities, and oxide thickness may influence the rate and location of the nucleation of hydride on uranium. This work has concentrated on isolating one of these variables, the oxide thickness, and measuring the effect of the oxide thickness on uranium hydride nucleation. Uranium samples, all from the same lot, were prepared with different oxide thicknesses. The oxide thickness was measured using Rutherford Backscattering Spectrosopy. Oxidized uranium samples were then exposed to ultra-high purity hydrogen gas under constant volume conditions. Decreases in pressure indicated hydrogen uptake by the sample. The time for hydride nucleation—as well as the maximum hydriding rate—was then calculated from the measured decreases in pressure. The time to nucleate a hydride was found to increase whereas the maximum hydriding rate was found to decrease with increasing oxide thickness. The density of hydride pits also decreased with increasing oxide thickness. The observed results support the argument that the nucleation of hydride is controlled somewhat by diffusion of hydrogen through the oxide layer. Vacuum outgassing of samples, thereby removing the oxide impurities and keeping the oxide thickness constant, dramatically decreased the nucleation time and increased the maximum hydriding rate. Again, this is consistent with hydrogen diffusion through the oxide controlling the nucleation of hydride. Impurities in the oxide layer can decrease the diffusivity of hydrogen and therefore delay the nucleation of uranium hydride.

Introduction and Background

The kinetics of uranium hydride formation have been extensively studied[1–8]. However, the nucleation kinetics on oxidized specimens has not been specifically measured as a function of oxide thickness. Since the first qualitative observations of the initiation of hydrides in uranium by Owen and Scudmore in 1966[8], steps are usually taken to minimize the oxide film thickness so that the reaction kinetics being measured is for the hydrogen gas/uranium metal system. Specimens are mechanically abraded or pre-hydrided[6] to remove most of the oxide before being exposed to hydrogen gas. Some previous studies activate the surface by exposing the uranium to temperatures ranging from 200°C to 630°C under vacuum before exposing it to hydrogen gas[3–5]. This method may affect the character of the oxide, for example, changing its stoichiometry or absorbed species content (such as hydroxyls). Other studies measure hydriding kinetics on uranium powder formed by hydriding/dehydriding reactions[2]. Typically the presence of an initiation time has been attributed to the presence of air impurities in the hydrogen gas stream[3,9], and precautions are taken to eliminate or reduce the incubation time. The present study was aimed at measuring the effect of different oxide thicknesses on the hydride nucleation kinetics. Our experimental conditions most closely parallel the experimental conditions used by Bloch et al.[6], except no prehydriding treatment was used in our work.

Experimental

Annealed high-purity uranium rods (3.18 mm in diameter and ~50 mm long) were used for this study. The samples contained < 300 ppm of impurities. The samples were prepared by an electropolish technique and subsequently baked at 100°C, then exposed to variations in cover gas purity or exposed to air, resulting in variations in apparent oxide thickness. This sample preparation resulted in samples within a batch having a relatively uniform oxide thickness. High-Energy Rutherford Backscattering (HERBS) at Los Alamos National Laboratory's Ion Beam Materials Laboratory[10] was used to characterize the amount of oxygen in the uranium. A 7.6-MeV alpha beam backscattered at 167° was used to measure the oxygen concentration. At this energy, the oxygen cross section is approximately 145 times (760 mb/sr) the Rutherford cross section, allowing for extreme sensitivity to the element. Data analysis was accomplished using the software RUMP[11,12]. For thin oxygen layers the surface peak was integrated, and for thicker layers the spectra were matched by simulations.

A Sievert's-type apparatus (constant volume and temperature, variable pressure) was used for the measurement of the initiation of hydriding in the uranium. The volumes were measured to within ±0.01 cc accuracy, and the temperature was maintained constant to within ±0.1 ^{o}C using a convection oven. Changes in pressure indicate an uptake of hydrogen by the sample. Ultra-high purity (UHP) hydrogen (99.9995% pure) was used for the reaction studies. Purified hydrogen from a palladium-alloy hydrogen purifier was also used for a few samples, but no appreciable difference was observed as compared to UHP H_2. Therefore, UHP H_2 was used for all of the results in this study. A uranium rod was removed from its inert gas vessel and immediately placed in the reaction vessel, which was purged three times with UHP Ar and evacuated to $< 10^{-4}$ Pa for 12 hours. The sample was then exposed to ~760torr H_2 at 70^{o}C, and the pressure was continuously measured with a computer-based data acquisition system to determine the initiation of hydriding. Each of the samples was reacted with the same amount of hydrogen so that ~10% of the sample would be converted to uranium hydride. After the sample was allowed to react with all of the hydrogen in the reaction vessel, it was removed and examined optically and by scanning electron microscopy.

Samples were then vacuum outgassed with a Thermal Desorption Mass Spectrometer (TDMS) to analyze the gases evolving from the uranium surface during heating. The samples were evacuated to ~$2x10^{-8}$ torr then heated to 600 °C at a rate of 5 °C/min.

Results and Discussion

A typical pressure vs. time plot is shown in Figure 1 and Figure 2. All samples show an initial drop in pressure of about 1 torr over a period of about 10 minutes. As seen in Table 1, both the pressure drop, Δp, and the time interval of the pressure drop, Δt, increase with increasing oxide thickness. An explanation for this is that the pressure drops as hydrogen dissolves in the oxide film and stabilizes when it reaches the solubility limit in the oxide. The solubility limit at 70^{o}C is constant; however, as the oxide thickness increases, the amount of hydrogen absorbed in the oxide (ΔP) will increase. Likewise, the time to reach the solubility limit will also increase with oxide thickness because of diffusion.

After this initial pressure drop, the pressure plateaus until the hydride pitting reaction begins. One sample was removed from the apparatus in the middle of the plateau region and examined optically and with a scanning electron microscope. No differences (i.e. blisters or hydride pits) between this H_2-exposed sample and an unexposed sample were observed. The pressure vs. time data was converted into hydriding rate vs. time to determine the hydride initiation parameters; an example is given in Figure 3. The hydride initiation time represents the time at which a hydride nucleus has grown to a size sufficient to break through the oxide layer and grow both laterally and into the sample. This time was measured as the intersection of the time axis with a line drawn through the linear portion of the curve. The actual initiation time is slightly less than the times quoted in Table 1; however, the applied method produced the best repeatability for comparison purposes. Figure 4 shows the effect of oxide thickness on the initiation time. The data appears to follow a $t^{1/2}$ dependence as would be expected if it were a result of diffusion. However, the data does not extrapolate to zero initiation time at zero oxide film thickness as might be expected. Another cause must be attributed to the finite initiation time at zero thickness. As will be shown later, vacuum outgassing will have a role in this result. The maximum hydriding rate is simply taken from the plot. As seen in Table 1, the hydride initiation time increases with increasing oxide thickness. Again, this result may be attributed to the effect of hydrogen diffusion through the oxide. A uranium rod with a thicker oxide will require a longer time for hydrogen to diffuse to the oxide/metal interface and establish a critical concentration for hydride nucleation and growth.

Figure 5 shows optical micrographs of two batches of hydride samples. A high density of small pits covers the surface of the sample with a thin oxide, whereas, the thicker oxide sample has fewer but larger hydride pits. Also, the pits on the thicker oxide sample are deeper than the pits on the thin oxide sample as seen along the edge of the specimens. This variation in hydride pit size and distribution is also evident in the maximum hydriding rate. The thin oxide sample, which has many small pits, has a higher maximum hydriding rate than the thicker oxide sample. Since more nucleation sites exist in the thin oxide sample and the hydriding kinetics is in the pitting regime, the hydriding rate will be higher.

The intrinsic sites for hydride nucleation in the uranium rods should be identical because they have virtually identical metallurgical histories. Therefore, microstructural variations such as grain size, texture and/or inclusion types, and distribution should not exist and hence cannot explain the differences observed in the hydride initiation kinetics or the hydride initiation sites. The variation in the number of observed hydride pits is directly correlated to the oxide thickness. Fewer hydride pits exist in the sample with a thicker oxide as compared with the thin oxide sample. This variation may again be attributed to hydrogen diffusion through the oxide layer. The thicker oxide will require a longer time to achieve steady state than the thinner oxide. Perturbations in a perfectly planar oxide film may exist, e.g. because of spallation, chemical variations in the oxide film from absorbed species, or chemical variations from inhomogeneities in the sample. These perturbations will affect the hydrogen diffusion through the oxide, either increasing or decreasing hydrogen diffusion. Therefore, any perturbations in the hydrogen diffusion through the oxide will be magnified in the thicker oxide case and result in fewer hydride initiation sites. The thin oxide sample may still have perturbations in the hydrogen diffusion; however as a result of the shorter times required to achieve steady state, the magnitude of the perturbations will remain small, and more hydride nucleation sites will initiate and grow. This suggests that a sample with no oxide film should nucleate a very large number of hydride sites and have an even faster hydriding rate. However, Balooch and Hamza[13] note that the low sticking probability of H_2 on clean uranium would make hydride initiation on wide areas of uranium surfaces unlikely. Therefore, the density of hydride initiation sites may approach a constant maximum value with decreasing oxide thickness because of the low H_2 sticking probabilities.

A uranium sample with an air-grown oxide (~250nm) was vacuum outgassed in the TDMS to analyze the gases evolving from the sample. During the heating of this sample, large amounts of various gases (H_2, CO_2, H_2O, CO/N_2) evolve from the surface with CO_2 and H_2 being the predominant desorbed gases. The TDMS spectra in Figure 7 show that the gases begin to desorb at about 100–150°C and peak at about 275°C. In comparison, the TDMS spectra for a different batch of “clean” uranium are shown in Figure 6. Hydrogen is the predominant desorbed gas with CO_2, H_2O, and CO/N_2 present at lower quantities. The appearance of the outgassed sample changed from a dark gray color before outgassing to a shiny silver color after outgassing. RBS measurements showed that oxide thickness on the outgassed sample remained the same at 250 nm; however, the carbon concentration in the oxide layer decreased to below the limit of detection following vacuum outgassing. An outgassed sample was subsequently reacted with hydrogen in a manner similar to the previous initiation experiments. The initial pressure drop was immeasurable because of the time resolution of the experiment, and the sample began hydriding within 20 seconds. The maximum hydriding rate, 7.5 mmol H/m^2sec, was also much higher than previously measured. Figure 8 shows the surface of the uranium sample after the reaction consumed all of the hydrogen. Almost the entire surface has hydrided with only a few unreacted areas visible. As in the previous experiments, the volume and initial pressure of hydrogen in the system are the same as those used earlier, and the mass is the same within 5%. Therefore, the volume of uranium converted to hydride is the same. The large increase in the maximum hydriding rate is again explained by the increase in the number of nucleation sites. Vacuum outgassing has a much larger effect on hydride nucleation than does the oxide thickness. Outgassing causes the initiation time to decrease from about 12,000 sec to 20 sec; however, the oxide thickness remains constant. Clearly, the impurity content of the oxide film has a strong effect on hydride nucleation. Impurities may limit the sites in which hydrogen can reside, thereby decreasing the hydrogen diffusion rate through the oxide. The oxide thickness will still play a role because it determines the length scale of the hydrogen diffusion.

Conclusions

The hydriding kinetics of oxidized uranium rods was studied to investigate the effects of oxide film thickness and vacuum outgassing on the nucleation of hydride pits. Four main conclusions can be drawn from this work:

- The initiation time for nucleating hydride pits increases with increasing oxide film thickness;
- The maximum hydriding rate increases as the oxide film thickness decreases;
- As the oxide film thickness increases, the density of pits decreases and the average pit size increases; and
- The nucleation kinetics of uranium hydride is strongly increased by vacuum outgassing and is believed to be a result of removing impurities from the oxide film, namely CO_2.

These conclusions can be explained by considering the diffusion of hydrogen through the oxide layer, giving rise to longer initiation times in samples with thicker oxide films. Also, oxide films with impurities can have slower hydrogen diffusion rates so that when the impurities are removed, the reaction will initiate almost immediately. Hydrogen diffusion through the oxide layer also explains the initial 1-torr drop in pressure as well as the hydride pit morphology.

References

1. W.M. Albrecht and M.W. Mallett: *J. Electrochemical Society*, 1956, **103**, 404-409.

2. J.B. Condon and E.A. Larson: *J. Chem. Phys.*, 1973, **59**, 855-865.

3. R.M. Alire, B.A. Mueller, C.L. Peterson, and J.R. Mosley: *J. Chem. Phys.*, 1970, **52**, 37-46.

4. G.L. Powell, W.L. Harper, and J.R. Kirkpatrick: *Journal of the Less-Common Metals*, 1991, **172**, 116-123.

5. G.L. Powell, R.N. Ceo, W.L. Harper, and J.R. Kirkpatrick: *Zeitschrift Für Physikalische Chemie-International Journal of Research in Physical Chemistry & Chemical Physics*, 1993, **181**, 275-282.

6. J. Bloch and M.H. Mintz: *J. Less Common Metals*, 1981, **81**, 301-320.

7. J. Bloch and M.H. Mintz: *Journal of Alloys and Compounds*, 1997, **253**, 529-541.

8. L.W. Owen and R.A. Scudmore: *Corr. Sci.*, 1966, **6**, 461-468.

9. J.E. Burke and C.S. Smith: *J. Amer. Chem. Soc.*, 1947, **69**, 2500-2502.

10. J.R. Tesmer, D.M. Parkin, and C.J. Maggiore: *Nuclear Instruments & Methods in Physics Research, Section B*, 1989, **40**, 718-721.

11. L.R. Doolittle: *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions With Materials and Atoms*, 1986, **15**, 227-231.

12. L.R. Doolittle: *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions With Materials and Atom* , 1985, **9**, 344-351.

13. M. Balooch and A.V. Hamza: *Journal of Nuclear Materials*, 1996, **230**, 259-270.

Table 1: Measured hydride initiation parameters.

Sample	Oxide thickness (nm)	ΔP (torr)	Δt (sec)	Initiation Time (sec)	Max. Pitting Rate (mmol H/m^{2}sec)
Outgassed	**250**			**20**	**7.5**
C_1		0.8	810	11005	2.80
C_2		0.8	865	12362	2.65
average	**250**	**0.8**	**838**	**11684**	**2.73**
std. dev.	**50**	**0.0**	**39**	**960**	**0.11**
B_1		0.6	523	6231	3.49
B_2		0.5	581	6191	3.52
B_3		0.7	669	5789	3.47
B_4		0.5	654	5628	3.44
average	**102**	**0.6**	**607**	**5960**	**3.48**
std. dev.	**30**	**0.1**	**68**	**298**	**0.03**
A_1		0.4	360	3940	4.63
A_2		0.3	400	4146	4
A_3		0.2	250	2613	4.3
A_4		0.3	350	4422	3.4
average	**20**	**0.3**	**340**	**3780**	**4.08**
std. dev.	**3**	**0.1**	**64**	**803**	**0.52**

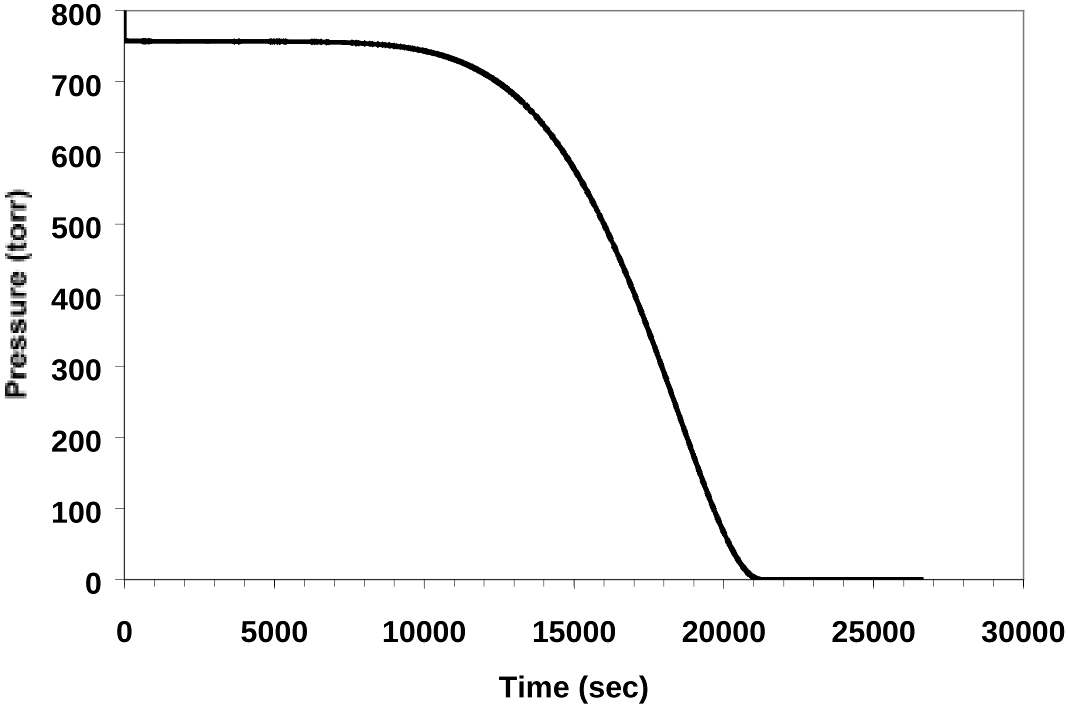

Figure 1: Hydrogen pressure versus time over sample C_1 showing the entire reaction.

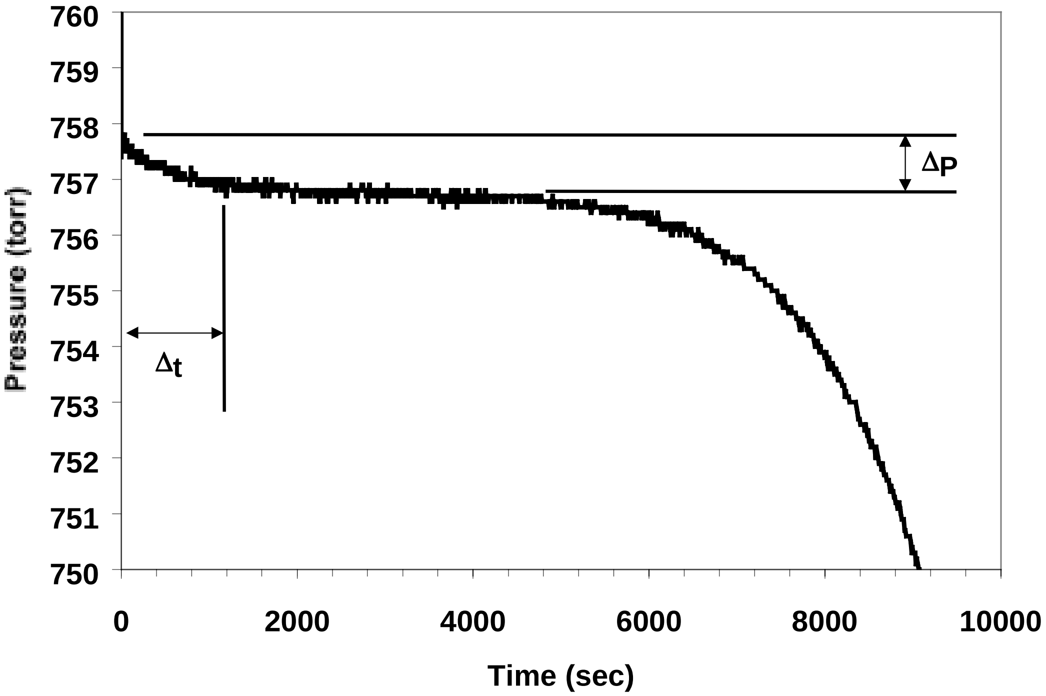

Figure 2: Hydrogen pressure versus time over sample C_1 showing the initiation of hydriding.

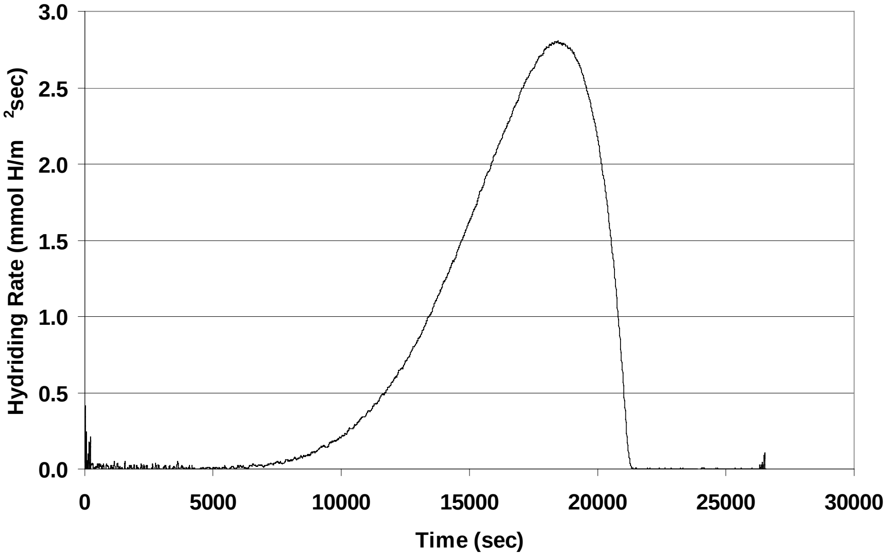

Figure 3: Hydriding Rate data for sample A_1. The sample was exposed to 760-torr H_2 at 70°C.

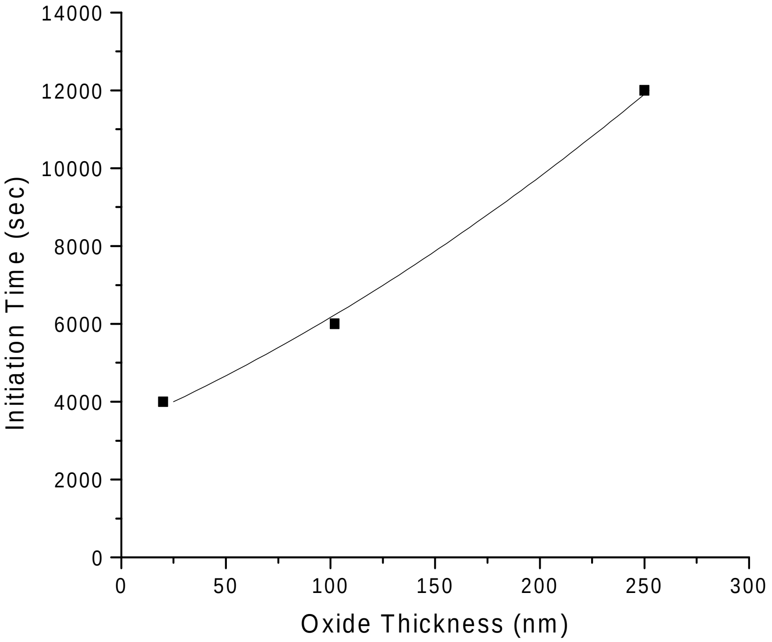

Figure 4: Effect of oxide thickness on the hydride initiation time. The data is fit to a square-root time dependence.

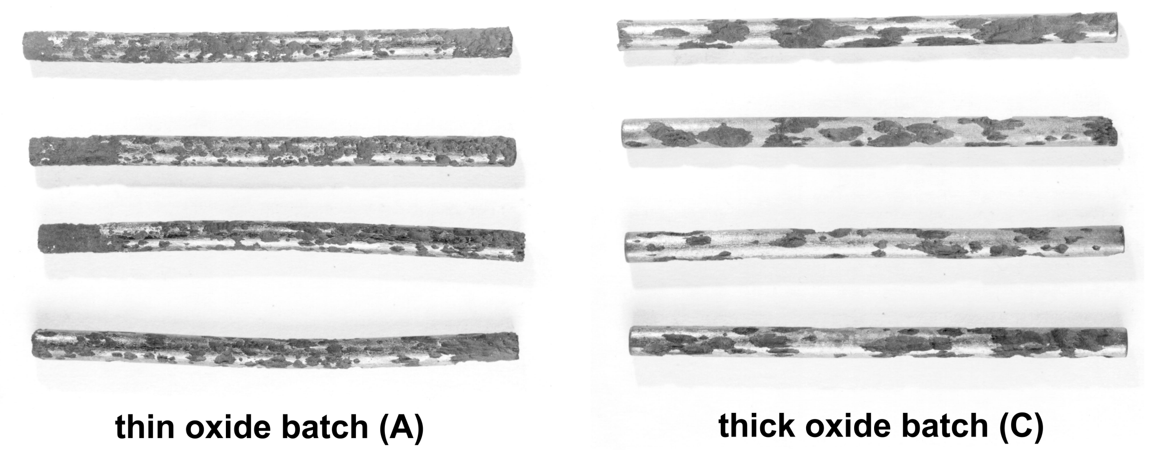

Figure 5: Optical micrographs of two batches of hydrided specimens. The set on the left, A, has a thin oxide, whereas the set on the right has a thick oxide.

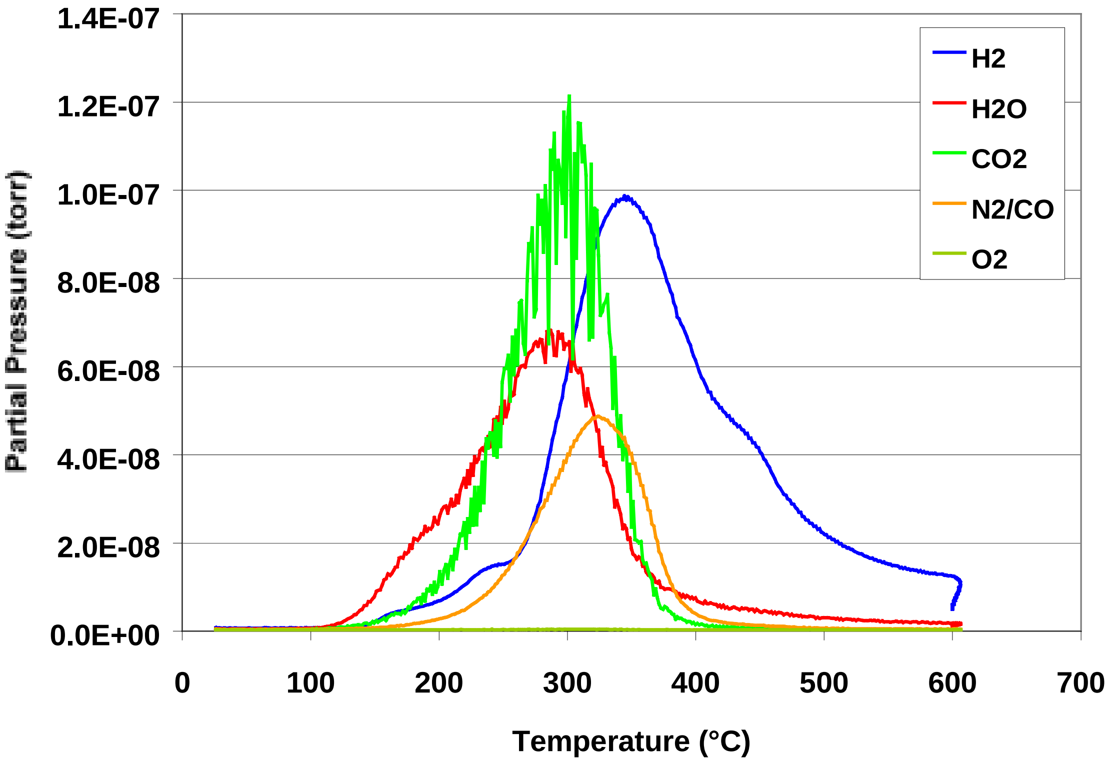

Figure 6: Thermal desorption spectra from "clean" uranium, heating rate 5°C/min.

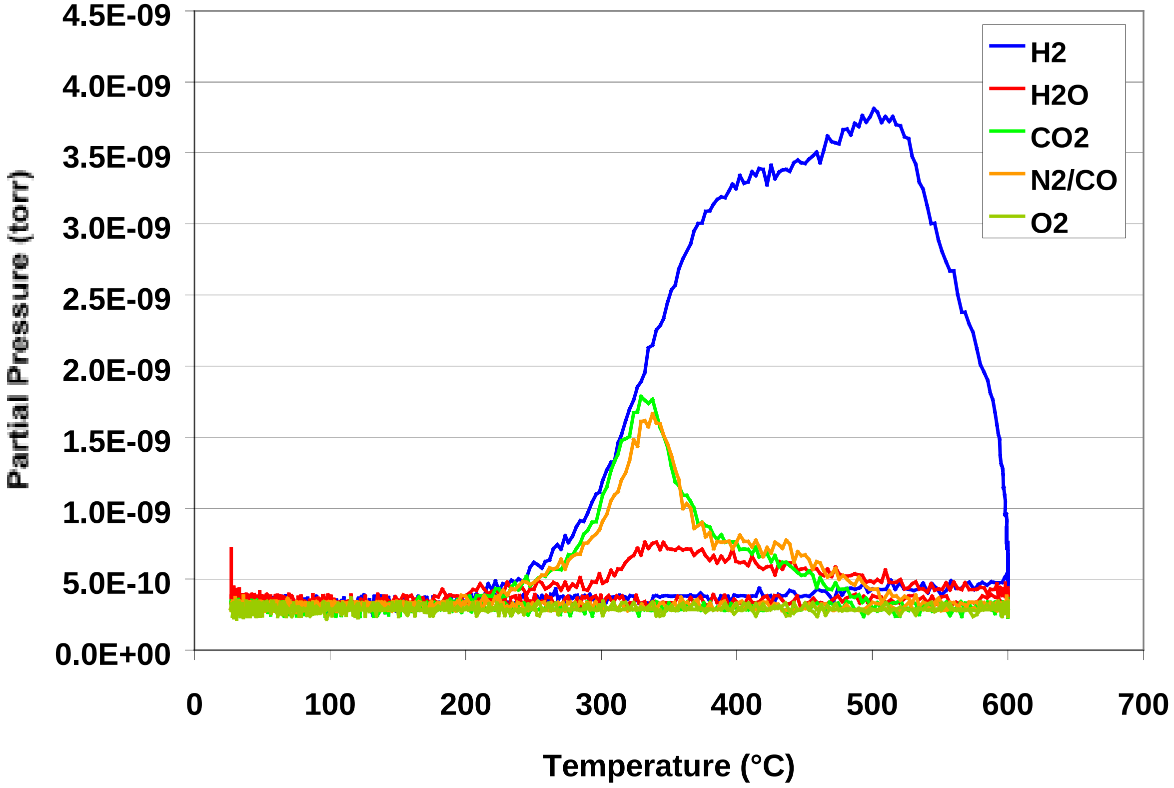

Figure 7: Thermal desorption spectra from batch C, heated at 5°C/min.

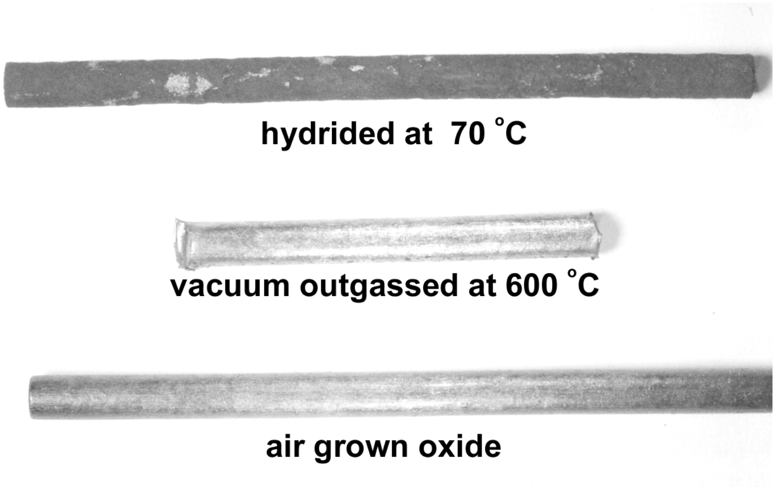

Figure 8: Micrographs of the surface of the uranium rod before outgassing, after outgassing, and after hydriding.

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