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URANIUM HYDRIDE INITATION KINETICS: EFFECT OF OXIDE THICKNESS

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Introduction and Background

The kinetics of hydride formation in uranium have been extensively studied. (1-8) ~~in the literature[1-8]~~. However, the initiation or nucleation kinetics on oxidized specimens have 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 are for the hydrogen gas/uranium metal system. Specimens are mechanically abraded or pre-hydrided[6] to remove most of the oxide before exposing to hydrogen gas. Some previous studies vacuum outgas the uranium at temperatures ranging from 200 °C to 630 °C before exposing to hydrogen gas[3-5]. This 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, 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. The oxide thickness of each batch was measured using Rutherford Backscattering Spectroscopy (RBS).

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 °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, purged three times with UHP Ar and evacuated to < 10^{-4} Pa for 12 hours. The sample was then exposed to ~ 760 torr H_2 at 70°C; and the pressure was continuously measured with a computer-based data acquisition system to determine the initiation of hydriding. 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.

Results and Discussion

A typical pressure vs. time plot is shown in Figure 1. 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°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 due to 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 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 2. 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. The maximum hydriding rate is simply taken from the plot. As seen in Table 1, the hydride initiation time increases with increasing oxide thickness. This 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 3 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 are 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 initiation sites appear to exist in the sample with a thicker oxide as compared to the thin oxide sample. This 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. due to spallation, chemical variations in the oxide film due to absorbed species, or chemical variations due to 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 due to 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[10] 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 due to the low H_2 sticking probabilities.

Conclusions

The hydriding kinetics of oxidized uranium rods was studied to investigate the effects of oxide film thickness on the nucleation of hydride pits. Three 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 increases, the density of pits increases but the average pit size decreases.

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. Hydrogen diffusion through the oxide layer also explains the initial 1 torr drop in pressure as well as the hydride pit morphology.

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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)
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**

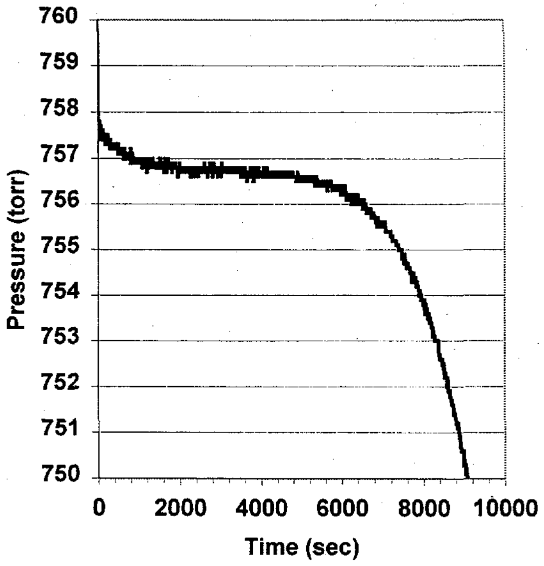


Figure 1: Hydrogen pressure versus time over sample A_1 showing the initiation of hydriding.

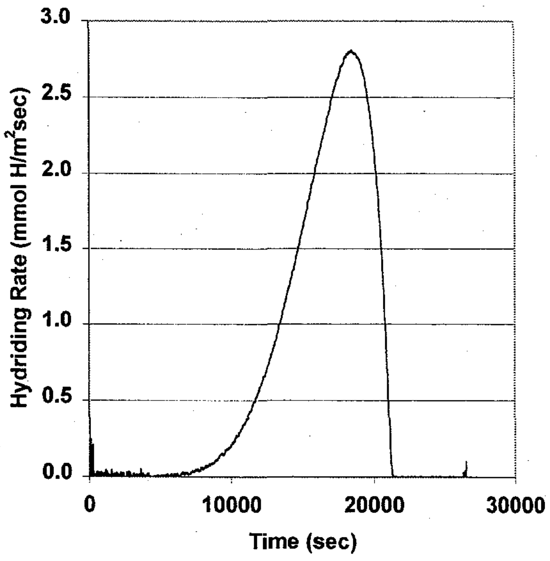
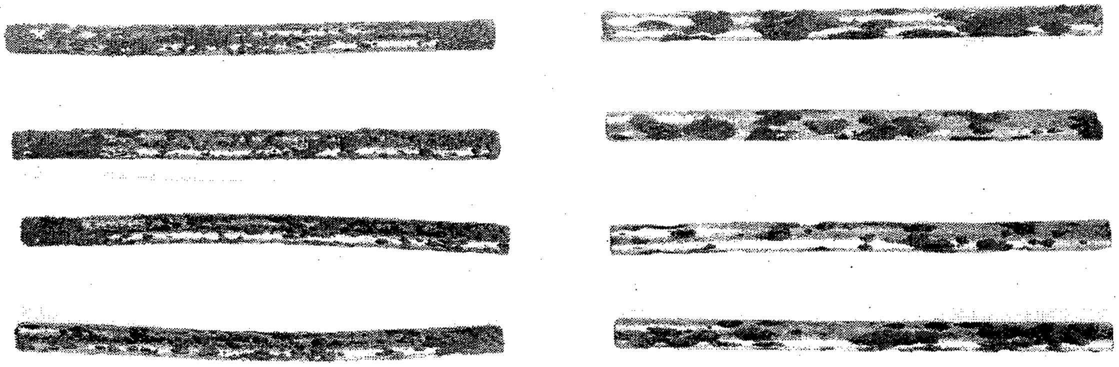


Figure 2: Hydriding Rate data for sample A_1. The sample was exposed to 760 torr H_2 at 70 °C



thin oxide batch (A)

thick oxide batch (C)

Figure 3: Optical micrographs of two batches of hydrided specimens. The set on the left, A, have a thin oxide; whereas the set on the right have a thick oxide.