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Title: A Model for the Initiation and Growth of Metal Hydride Corrosion

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23rd DOE Aging, Campatibility and Stockpile Stewardship Conference

23rd AGING, COMPATIBILITY AND STOCKPILE STEWARDSHIP CONFERENCE

CALL FOR PAPERS

MEETING LOCATION

The 23rd Aging, Compatibility and Stockpile Stewardship Conference will be held this year at the Livermore, CA site of Sandia National Laboratories on November 14-16, 2000 (Tuesday, Wednesday and Thursday). The host for the 23rd Conference will be Bob Bradshaw (925-294-3229, Fax 925-294-3410, Email rwbrads@sandia.gov).

PURPOSE OF CONFERENCE

This DOE-wide conference is held every 1-1/2 years to coordinate work on the reliability of the stockpile by bringing together experts from throughout the weapons complex. Assured reliability and safety of weapon systems imply that no important chemical reactions or physical changes occur in their materials or components that could compromise their performance or safety during stockpile life. Achieving this goal requires confident predictions of the effects of aging on the materials and assurances that important incompatibilities among the various materials do not exist. Because of the recent decisions to significantly extend the service lifetime of the enduring stockpile, further attention is being focused on these aging and reliability issues through the call for development of science-based, stockpile stewardship programs.

CONFERENCE TOPICS

Given the goals of the conference, there are many topics of potential interest and relevance to the weapons complex. Examples include, but are not limited to,

1. Studies to assure the safety and reliability of nuclear weapon designs and components throughout the lifetime of the weapon system in the enduring stockpile.
2. Aging studies of materials and environments of interest to weapon systems.
3. New or novel analytical techniques applicable to aging and reliability concerns.
4. Accelerated aging test design, and methodologies for lifetime prediction.
5. Modeling work being performed in support of stockpile stewardship.
6. Stockpile Laboratory Test (SLT) evaluations - test philosophy, results and use of information.
7. Studies on the importance of processing variables, such as cleaning, handling and packaging.
8. Impact on reliability and aging of new Environmental Safety and Health regulations.
9. Dismantlement issues such as reliability information available from dismantled components and the development of requisite handling and processing procedures.
10. Metals compatibility - oxidation, hydriding and other reactions with weapons environments and materials.
11. Studies on new materials/components that may be needed as replacement parts for upgrading the enduring stockpile.

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A Model for the Initiation and Growth Of Metal Hydride Corrosion

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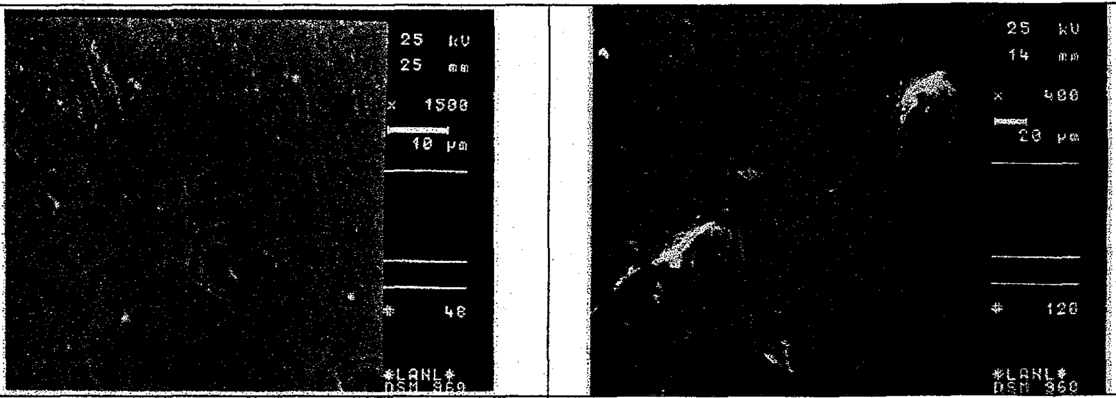
ABSTRACT

A mathematical model for the initiation and growth of metal hydride corrosion has been formulated that incorporates the processes of growth of subsurface hydride nuclei, their subsequent work-hardening of the local metal matrix, the onset of pit formation, pit growth and the shift to growth of the hydride film along the surface. The model has been applied in the investigation of uranium corrosion, wherein model parameters were experimentally obtained and then used in the prediction of corrosion.

INTRODUCTION

The hydride corrosion of uranium and plutonium may have significant implications for the lifetime of uranium in nuclear weapons. The kinetics of the uranium-hydrogen reaction have been the subject of many studies and have been well characterized. In the reaction between hydrogen and bulk uranium metal at constant temperature and pressure, para-linear kinetics are observed. The initiation of the reaction has been the subject of some controversy. While early studies identified an "induction period" [1] prior to the reaction initiating, most later studies maintain that this is a product of low gas purity, that in high purity hydrogen the reaction begins immediately.[2] In order for the induction period to be eliminated at temperatures below 100° C it has been shown necessary to sensitize the surface with an anneal at 200-600° C.[3] Most studies have reported that the reaction initiates at discrete sites on the surface of the metal, the number and distribution of which have been observed to vary with surface preparation, grain size, purity, and inclusion size and distribution, among other variables.[4,5,6] The kinetics do vary considerably with the metallurgical condition of the specimen, which effect has been attributed to variations in the nucleation kinetics.[7] Currently there is a strong focus on uranium corrosion from the DOE in both the enhanced and core surveillance programs.

The mechanism of uranium hydride corrosion (pitting) starts with the presence of nuclei for the hydride to form. These nuclei may be reactive elemental impurities (e.g. S, Cl, F) or may themselves be composed of uranium hydride due to supersaturation of the as-cast metal. In either case the nuclei appear to be most concentrated near larger inclusions in a pattern that seems to be consistent with a solute rejection zone. This latter mechanism is demonstrated by the ring of pits observed in figure 1, and the scanning atomic force microscopy potentiostatic map shown in figure 2.

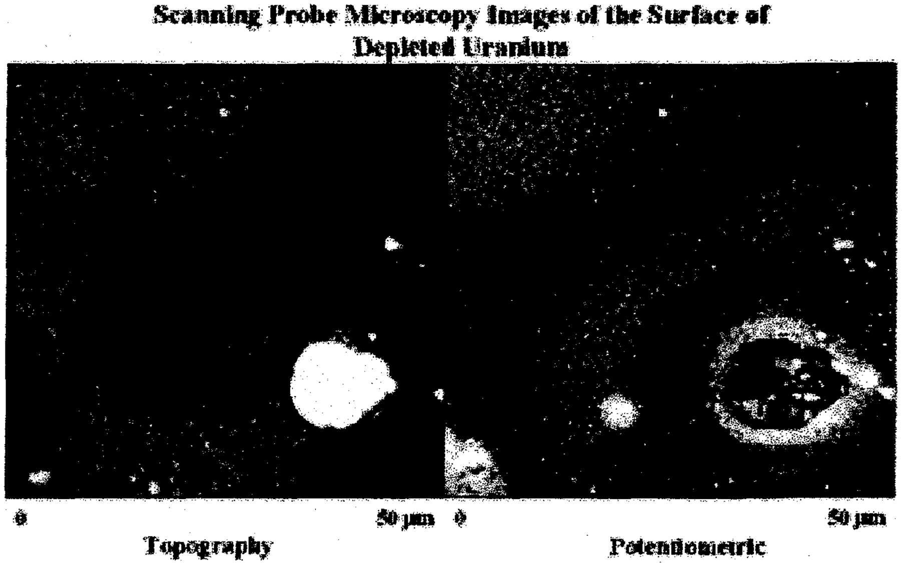


1a. A ring of hydride blisters formed around a pair of "carbide" inclusions after approximately 5 minutes exposure at 70° C in as-cast uranium.

1b. Larger blisters which have fractured the surface of the uranium, after approximately 10 minutes exposure at 70° C, as –cast uranium.

Figure 1. Early stages of hydride corrosion.

As the hydride grows, the local metal matrix is deformed due to volumetric change of metal to hydride. This deformation eventually results in the local failure of the metal matrix and work hardening of the matrix surrounding the failed metal matrix and hydride. The process of growth, matrix failure and work hardening continues and propagates in the presence of a varying hydrogen species field until the hydride ruptures the surface of the metal, as seen in Figure 1b. At this point the mechanism of "feeding" the hydride changes from diffusion of hydrogen through metal and oxide to direct contact with the gas.


Scanning Probe Microscopy Images of the Surface of Depleted Uranium

DU surfaces from the same batch of material used for the hydriding experiments were imaged within the same region using potentiometric AFM.. Note that there is a bright ring (indicating low conductivity) around the inclusion at a distance of approximately 10 μm. This region corresponds to the areas that are also observed to nucleate hydride.

The mathematical model consists of a reaction diffusion equation with a boundary mass transfer-like condition at the surface and a no flux condition is applied to the remaining domain boundaries. The reaction kinetics are those found in Condon [8]. This is expressed as:

$$\frac{\partial C}{\partial \tau} = \nabla \bullet (D \nabla C) - \lambda\, C_{UH}\left(C - \frac{1}{K_e}\right); D = \begin{cases} D_{UH}\ ; C_{UH} \le C_{UH}^{M}(C_{UH}) \\ D_{H}^{U}\ ; C_{UH} > C_{UH}^{M}(C_{UH}) \end{cases}$$

$$C(t = 0, x_i) = C^0$$

$$-D_H^U \frac{\partial C}{\partial x_i}\bigg|_{i = surface} = \frac{D_H^O}{L_O}\left(C\big|_{i = surface} - C^B\right); C_{UM} \le C_{UH}^{M}\left(C_{UH}\right)\Big|_{i = surface}$$

$$C\big|_{i = surface} = C^B\ ; C_{UM} > C_{UH}^{M}\left(C_{UH}\right)\Big|_{i = surface}$$

$$\frac{\partial C}{\partial x_i}\bigg|_{S \notin surface} = 0$$

where;

C	is the concentration of hydrogen in the uranium matrix
C^B	is the concentration of hydrogen in the gas phase
C^0	is the initial concentration of hydrogen in the uranium metal
C_U	is the concentration of uranium metal
C_U^0	is the initial concentration of uranium metal
C_{UH}	is the concentration of uranium hydride
C_{UH}^0	is the initial mean concentration of uranium hydride
C_{UH}^M	is the concentration of uranium hydride require to rupture the metal matrix (CHRM)
D	is the hydrogen diffusivity in either uranium metal or uranium hydride
D_H^U	is the diffusivity of hydrogen in uranium metal
D_{UH}	is the diffusivity of hydrogen in uranium hydride

D_H^0	is the diffusivity of hydrogen in the oxide layer
L_O	is the dimensionless thickness of the oxide layer
K_e	is the equilibrium constant for the hydride reaction
N	is a normal deviate function with mean C_{UH}^0
x_I	is a dimensionless coordinate for the computational domain
α	is a stoichiometric coefficient for the hydride reaction
γ_1	is the molar density ratio of uranium hydride and hydrogen in uranium
γ_2	is the molar density ratio of uranium and hydrogen in uranium
λ	is the ratio of hydride reaction rate to hydrogen diffusivity in uranium metal
τ	is dimensionless time.

Note that to account for the autocatalytic nature of the hydride reaction, the reaction term is a function of the local concentration of uranium hydride. This is probably related to the area of the hydride entity, the increase in area allows for increasing reaction. Once the local hydride concentration in the metal is above the value required to "crack" the matrix and allow the hydride to grow, the diffusivity becomes that for hydrogen in uranium hydride.

Two additional equations are required, that for the hydride growth and depletion of uranium metal, and are:

$$\frac{\partial C_{UH}}{\partial \tau} = \lambda \gamma_1 C_{UH}\left(C - \frac{1}{K_e}\right)$$

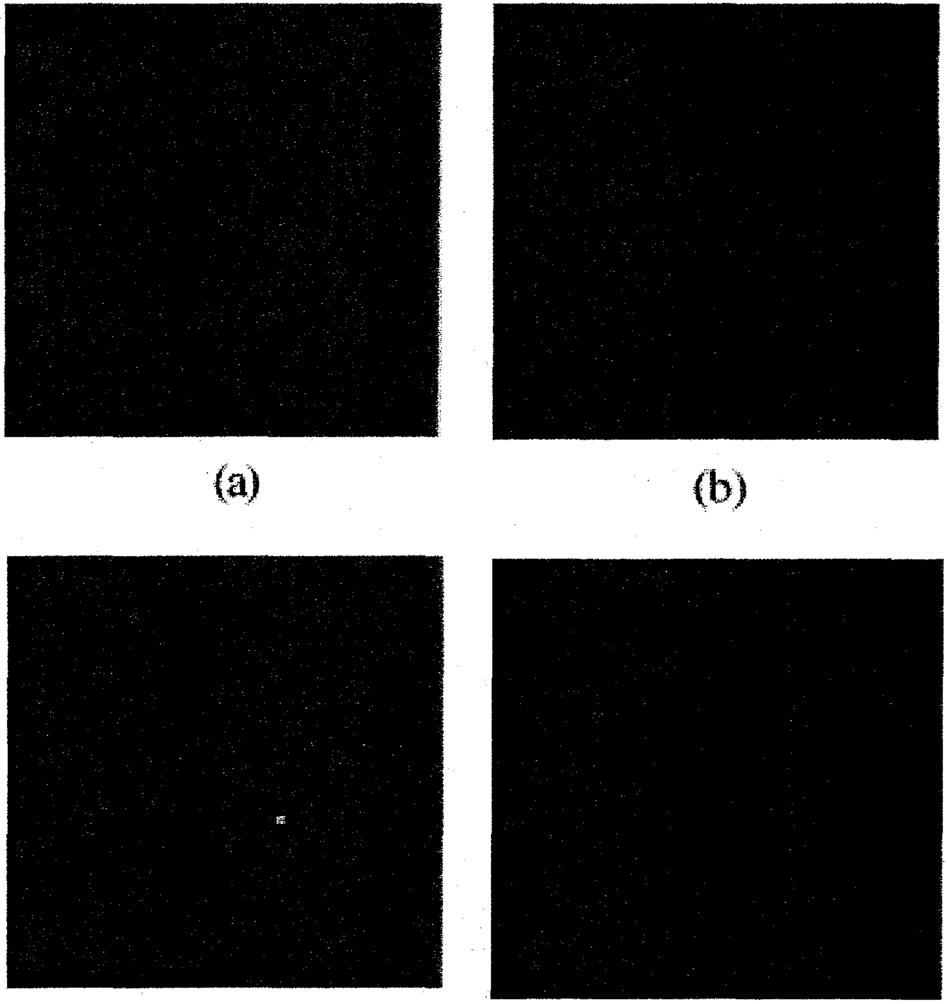
$$C_{UH}(\tau = 0) = N\left(\overline{x} = C_{UH}^0, 0\right)$$

$$\frac{\partial C_U}{\partial \tau} = -\alpha \lambda \gamma_2 C_{UH}\left(C - \frac{1}{K_e}\right)$$

$$C_U = C_U^0$$

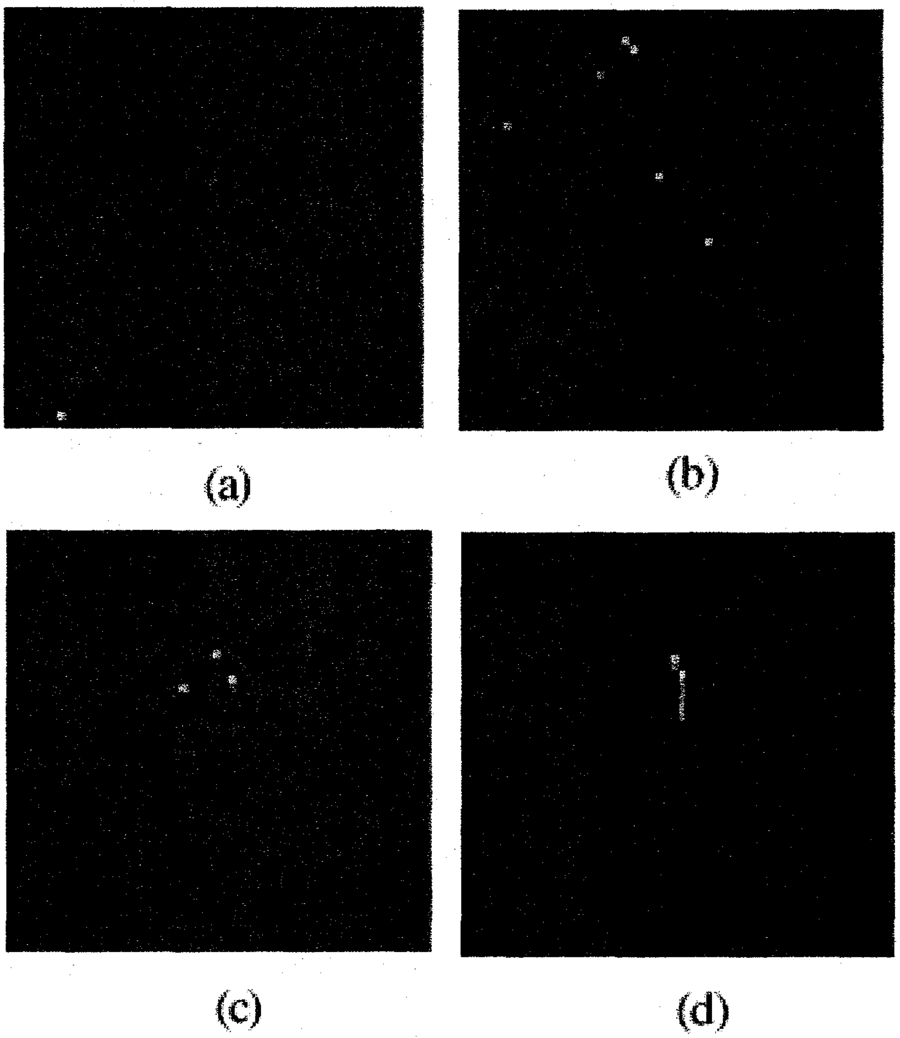
where the initial concentration of hydride is a random distribution in both position within the computational domain and in local concentration whose mean is that for the nominal concentration for hydride in the metal. Numerically, this is accomplished by seeding the entire domain with random deviates and then for each element, adding the values of all neighboring elements. This addition is done for a predetermined number of iterates and results in filtering the domain with only a few locations (nominally 2 to 10 in a 50x50 matrix) with peak values that have a local gaussian distribution (Calef [9]).

The model accounts for strength by altering the local value of the CHRM of the elements surrounding the element that has exceeded its CHRM. The form of alteration is simply the multiplication of the elements CHRM by a fixed value of one or greater. This is done at every solution iteration until the CHRM reaches a preset maximum value. For a multiplication factor of one, the material does not have any work hardening, and for values greater than one, work hardening occurs. This effect can be seen in following sets of figures. The first set in Figure 3 has a multiplier of one. The second set in Figure 4 has a multiplier of two.



(a) (b) (c) (d)

Figure 3. Progression of hydride growth with a work-hardening factor of 1.0. Gas is at top of box. Dimensionless time (a) is 0.02, (b) is 0.25, (c) is 0.40, and (d) is 0.60.



(a) (b)

(c) (d)

Figure 4. Progression of hydride growth with a work-hardening factor of 2.0. Gas is at top of box. Dimensionless time (a) is 0.02, (b) is 0.25, (c) is 0.40, and (d) is 0.60.

In Figure 3, all the entities grow without preferenceto direction until they coalesce into a single large pit. Whereas, in Figure 4, which is a simulation with work-hardening, the entities grow in the direction of highest local hydrogen gradient until one entity ruptures the surface. Then the growth is preferential along the surface, which is the region with least work-hardening. In the simulation, pit coalescence occurs with the surviving entity. In both cases, the entity that “wins” the race to the surface consumes hydrogen in the metal and from the gas phase. The reduction of hydrogen in the matrix results in some entities decomposing, as is seen experimentally.

CONCLUSIONS AND RECOMMENDATIONS

Experimental work has demonstrated that the formation of uranium hydride pits starts as a sub-surface nucleation and growth process. This explains the dependence of the kinetics on the flow stress of the material (which was introduced by Condon without an explicit explanation of mechanism). The nucleation occurs on inhomogeneous sites in the metal matrix, which appear most consistent with the segregation of impurities, particularly reactive non metals and/ or excess hydrogen picked up in casting. In any case the early stages of hydride nucleation, which controls the sites at which visible corrosion develops, is controlled by diffusion of hydrogen through both the metal and oxide, nucleation and growth within the near surface metal. We have developed a numerical model which incorporates all of these features and predicts nucleation and growth kinetics qualitatively very similar to those observed experimentally. Further work on the distribution and effects of specific impurities, variation of metallurgical history (and consequent strength) of the material and improved ambient temperature diffusion measurements will be incorporated into the model as the data is obtained. The ultimate objective of this work is a fully detailed quantitative predictive model for the location and growth rate of hydride on uranium of known composition and history.

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