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OF URANIUM USING ION IMPLANTATION

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ABSTRACT

The hydriding of depleted uranium at 76 Torr hydrogen and 130°C has been significantly reduced by implantation of oxygen ions. The high-dose implanted specimens had incubation times for the initiation of the reaction after exposure to hydrogen that exceeded those of the non-implanted specimens by more than a factor of eight. Furthermore, the non-implanted specimens consumed enough hydrogen to cause macroscopic flaking of essentially the entire surface in times much less than the incubation time for the high-dose implanted specimens. In contrast, the ion-implanted specimens reacted only at isolated spots with the major fraction of the surface area unaffected by the hydrogen exposure.

DISCLAIMER

INTRODUCTION

The results presented here represent the first known use of ion implanta-
tion for the modification of the hydriding properties of a material. In
particular, oxygen ions were implanted in uranium up to concentrations
calculated to form surface oxides that should be stable under the hydriding
conditions (76 Torr hydrogen and 130°C). The inhibiting effect of surface
oxides on the hydrogenation of uranium has been recognized for many years
[1,2]. In addition, uranium hydride ignites in oxygen to form U_3O_8 or,
when insufficient oxygen is present, UO_2 and reacts at elevated temperature
with water to form UO_2 [1,2]. Since these oxides are thermodynamically more
stable than the hydride and inhibit the hydrogenation reaction, it is quite
logical to consider using oxide films for protection of uranium from hydrogen.
The oxide formed under ambient atmospheric conditions does not form a useful,
protective barrier, presumably because of its porosity, defects, impurities,
and tendency to spall off the surface. Oxidation at higher temperatures with
high-purity oxidizing gas would probably result in an improved barrier.
However, heating the uranium may be inconsistent with other constraints for
the bulk material (eg, grain size, precipitation of undesirable phases,
dimensional tolerances).

Implantation of oxygen into uranium surfaces under high energy, low
current conditions (ie, low power conditions) insures that the bulk properties
are retained while the oxygen concentration in the layer increases. Atomic
displacements and local thermal spikes caused by each oxygen ion should
provide a well-mixed layer approaching the thermodynamically favored oxide
normally formed at elevated temperatures. Furthermore, ion implantation
provides the highest lateral uniformity possible, because the ions are

electronically rastered over the area of interest. Finally, the purity of the
oxygen is unsurpassed because the oxygen ion beam is magnetically analyzed.

EXPERIMENTAL CONSIDERATIONS

The specimens used all came from one piece of high-purity depleted
uranium. Spectrochemical analysis revealed the following impurities or
detection limits (in ppm by weight): $Tm<60$; $Ba<40$; $Zr<10$; $Fe=7$; Zn, Al,
Si, Ca, Nb, $Sb\leq4$; $mg=2$; Cu, Mn, Ni, Bi, Co, Cr, Sn, $Sr\leq1$; B, Mo, Ti, Cd,
Tl, Pb, $V\leq0.4$; $Be<0.1$. Following EDM machining of the disk specimens from
the source piece, standard lapping procedures were used to achieve the nominal
dimensions of 27mm dia by 1.25mm thick. Inadvertent air exposure of the
lapped specimens necessitated a repolishing procedure that consisted of an
electropolish in perchloric acid to remove the gross oxide, a 600 grit polish
to remove pits, and a final mechanical polish with $1\mu m$ diamond paste. The
specimens were not annealed but were stored in kerosene and/or vacuum until
just prior to shipment (in all-metal UHV containers) to the implanters. The
last surface treatment immediately before shipment was an electropolishing
procedure in a solution of 450 ml ethanol (95%), 275 ml ethylene glycol, and
275 ml phosphoric acid (85%) at room temperature at 13V for 3 seconds.
Finally the specimens were rinsed in de-ionized water and dried in flowing
argon. These preparation procedures were applied to both the control and the
to-be-implanted specimens.

Molecular oxygen ions (O_2^+) were implanted, using an electronically
rastered beam, with energies of 180 keV to various doses up to 8×10^{17} O_2^+/cm^2
over the central 25 mm-diameter area of each specimen. The range and standard
deviation for 90 keV O^+ ions in pure uranium were calculated using the TRIM

program [3] to be 830 Å and 440 Å, respectively. The ion flux during implantation was approximately 1μA/cm^2 (ie, 0.18 W/cm^2). Since the uranium specimens were mounted on a copper plate that was attached to a water cooled platen and the input power was low, the maximum temperature reached during implantation was estimated to be 50^{0}C. Electropolished control specimens accompanied the specimens for implantation in each UHV shipping container; thus, the control and implanted specimens experienced the same atmospheric exposures. After return from the implanters, all specimens were held under vacuum until they were mounted in the hydriding chamber.

The hydriding studies were performed using a vacuum chamber for edgeless studies of gas-metal reactions which has been detailed previously [4]. In essence, the chamber consisted of two separate vacuum regions with most of the front (ie, implanted) surface of the specimen exposed to the hydrogen while the other surfaces remained under vacuum ($<10^{-5}$ Torr). The extent of the reaction was determined, quantitatively, by measuring the quantity of hydrogen taken up by the exposed area (3.0 cm^2) under isobaric (76 Torr) and isothermal (130°C) conditions. To insure uniform temperature across the specimen, the entire chamber was heated to the desired temperature as measured by a sheathed thermocouple in contact with the back of the specimen. Visual observation of the front surface was made through a sapphire window. Hydrogen gas was used directly from tanks of 99.999 percent pure hydrogen. The gas was expanded several times into evacuated, baked volumes of the gas-handling system before each hydriding experiment. The relatively short induction times for the non-implanted specimens that were given a 600-grit polish immediately prior to mounting in the hydriding chamber attest to the cleanliness of the

hydrogen over the reacting surface. The reaction was stopped by simply evacuating the hydrogen and removing the heating power.

The reaction conditions were chosen to fulfill several criteria. A relatively slow reaction rate was desired to permit observation of unambiguous distinctions for the various implantation conditions; however, the rate needed to be sufficient to insure fairly prompt reaction with the 600-grit polished specimens. The temperature of 130°C meets the above conditions and, in addition, provides a reaction that follows a linear law [1] and a hydride attact typical of lower temperatures (ie, formation of funnel-like hydride pits which penetrate into the reacting sample) [5]. The gas handling system for hydriding was limited by the available pressure transducers to 1000 Torr in the supply reservoir and 100 Torr in the reaction chamber. We chose to use 800 and 76 Torr, respectively. For our reaction conditions the linear reaction rate was estimated from published data [6] to be approximately 0.8 μm of pure uranium per minute. The reaction was considered initiated when the amount of hydrogen consumed clearly exceeded the drift in the barometric sensors (ie, after consumption of 0.025 Torr-liters). For uniform hydrogen up-take and reaction 0.025 Torr-liters of gas would consume about 0.04 μm of pure uranium (ie, 1.6μm/Torr-liter).

RESULTS AND DISCUSSION

The hydrogen consumption results are displayed in Fig. 1. Reactions of the two 600-grit polished specimens and one electropolished specimen were terminated after consumption of about 7 Torr-liters of hydrogen because macroscopic flaking of essentially the entire surface was observed. The reactions with the other specimens were terminated before 4 Torr-liters had

been consumed to minimize the surface damage and, hopefully, permit reuse after repolishing. The reaction rates at the end of the exposures were 0.7 and 0.9 μm/min for the two 600-grit polished specimens. These rates are consistent with the anticipated result of 0.8 μm/min for the linear reaction rate [6]. In contrast, the final rates for the two electropolished specimens were 1.3 and 1.5 μm/min. Presumably, the different rates observed for 600-grit polished and electropolished specimens is a consequence of differences in the surface conditions (eg, surface strain). The open circles on the abscissa of Fig. 1 represent the induction times (ie, the times for initiation of the reaction after exposure to hydrogen). Clearly, oxygen-ion implantation can increase the induction time by a considerable amount. In fact, for the oxygen-ion doses employed the induction time increased monotonically with implanted dose. Comparison of the induction times t_i for the two electro-polished specimens (t_i = 4 and 8 mins) with the high-dose implanted specimens (t_i = 69 and 163 mins) shows that the induction time can be increased by factors of 8 to 40. The small induction time difference between the electropolished specimens was most probably due to slight differences in the hydrogen gas purity or to differences in the surface films present (these two measurements were made approximately three months apart). For the high dose implanted pair the large discrepancy is presumably a consequence of the nature of the hydriding process for implanted specimens.

Fig. 2a is an optical micrograph of electropolished uranium (U4) after 40 minutes of exposure to hydrogen and removal of most of the loose hydride powder. The high density of pits that are remanents of the macroscopic flaking process covers essentially the entire surface. Figs. 2b-d are scanning electron micrographs of a spot where the density of pits was lower

than typical. The field of view in Fig. 2b includes all three of the major features of the surface: (1) irregularly shaped pits, (2) pre-flaking hydride mounds, and (3) apparently virgin uranium. Fig. 2c provides a magnified view of the center of Fig. 2b and shows hydride mounds in various stages of development. The small bright spots are residual hydride powder particles. A highly magnified view of the center of Fig. 2c is given in Fig. 2d, which has in its lower right hand corner the edge of a mound. The upper left region of Fig. 2d is typical of the virgin uranium.

Fig. 3 is a display of the surface morphology typical of the implanted specimens after exposure to hydrogen. The optical micrograph of Fig. 3a shows that, even after 87 minutes exposure, a surface implanted with 10^{17} $0_2^+/cm^2$ was attacked only in a few clearly distinguishable spots. Since the attack occurred only over a small fraction of the total surface, the apparent rate of hydrogen consumption (Torr-liters/min) should be less than that for the 600-grit polished and electropolished specimens, which were attacked more uniformly. Thus, for a given amount of hydrogen consumption, the lower rates observed for the implanted specimens (Fig. 1) is a direct measure of the fraction of the surface participating in the reaction. The reaction area decreased with increasing implanted dose. Figs. 3b-d are scanning electron micrographs with magnifications directly comparable to those of Figs. 2b-d. The center of Figs. 3b-d is an apparently undisturbed or virgin uranium area near one of the pits. Removal of the hydride powder debris was more difficult for this specimen as evidenced by the higher density of bright spots in Figs. 3b-d relative to that in Figs. 2b-d. In contrast to the electropolished specimens, there was no evidence of hydride mounds on the implanted samples, except for the lowest dose ($4x10^{16}$ $0_2^+/cm^2$) specimen. This result was

consistent with the visual observations made during the hydriding reactions. The electropolished samples reacted by a combination of (a) creation of small black spots (ie, pits) over the entire surface and (b) growth of the previously created pits by repeated ejection of hydride particles and reaction with the freshly exposed metallic uranium until essentially the entire surface was covered by pits. For doses greater than 4×10^{16} O_2^+/cm^2, the implanted specimens reacted by creation of a few small, isolated pits and growth of these pits. The relative rate of creation of new pits was very low for these higher dose specimens.

The reasons for the hydriding being restricted to a few isolated spots on the implanted specimens are not known at present. However, assuming that all high-dose implanted uranium surface areas were protected, the hydriding sites must correspond to small areas that were not modified the same as the vast majority of the surface. This could result from implantation into impurity inclusions and from the absence of implantation in surface areas inaccessible to the ions (eg, sides of some defects or areas masked by dust particles). The virgin uranium areas displayed in Figs. 2d and 3d are typical of these areas for exposed specimens and of all non-exposed surfaces. The dark spots shown at this magnification are presumed to be defects in the surface resulting from the preparation procedures and/or voids in the bulk material. Some of these defects may have had nearly vertical or undercut sides, and consequently, the ion implantation process, which is inherently a line-of-sight process, would have been ineffective on such surfaces. Of course, defects with exposed sides would have been implanted.

Combined Rutherford backscattering and ion-induced x-ray analysis [7] using 2 MeV helium ions of the as-implanted specimens showed that only the specimens that received 4×10^{17} O_2^+/cm^2 had a thick, uniform surface compound (ie, oxide). However, this was inconsistent with the highest does (8×10^{17} O_2^+/cm^2) specimens, which had a high concentration of oxygen only at a depth approximately equal to the projected range R_p for 90 keV O^+ ions by the TRIM program [3]. The specimens that received 4×10^{17} O_2^+/cm^2 had a blue color in the implanted region, which would be consistent with the formation of a uniform oxide layer by either implantation or by excessive air-exposure of the implanted sample. Scanning electron micrographs of the specimens implanted with the highest dose showed evidence of blister formation, which would be consistent with a implantation flux that greatly exceeded the flux of oxygen diffusing away from the implanted depth. The specimens implanted with the lower doses had oxygen concentrations near the expected R_p that were considerably below that necessary for uniform oxide formation.

Even with the microscopic differences revealed by RBS and SEM, all the implanted specimens produced similar optical micrographs (eg, Fig. 3a) after consumption of the same amount of hydrogen. In general, the specimens implanted with higher doses had fewer hydride pits. This suggests that reduction of the hydrogenation of uranium may be achieved without formation of a uniform oxide layer. Two other possibilities may be responsible for the observations: (1) ion-induced stress in the surface and (2) reduction of the solubility of hydrogen in uranium by implanted oxygen. Ion implantation generally induces stress in surfaces. The ion-induced stress may retard the formation of the hydride mounds and, hence, quench the growth of any hydride nuclei that may have formed. Bloch and Mintz [5] noted that strain effects

can prevent the development of bulk precipitation even when the concentration of the dissolved hydrogen inside the specimen reaches saturation, which is approximately 2 ppm for α-uranium at temperatures below 668°C [1]. The importance of oxygen inside the uranium during hydrogenation has been discussed by Condon [8, 9]. Hydrogen, occupying interstitial positions, diffuses rapidly in the metal before nucleation and growth of the β-phase UH_3. Oxygen (or other anions) compete for these interstitial sites and considerably modify the kinetics. Thus, the oxygen can limit the hydrogen solubility and reduce the probability of hydride formation.

Although the reason for the reduced hydriding is not clear at this time, the data show conclusively that ion implantation can have a marked influence on the reaction of hydrogen with uranium. Our work is continuing in an effort to understand and refine the processes involved.

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Figure Captions

Figure 1: Reaction of hydrogen with uranium.

Figure 2: Micrographs of electropolished uranium (U4) after exposure to 76 Torr H_2 at 130°C for 40 minutes: (a) optical micrograph and (b-c) scanning electron micrographs.

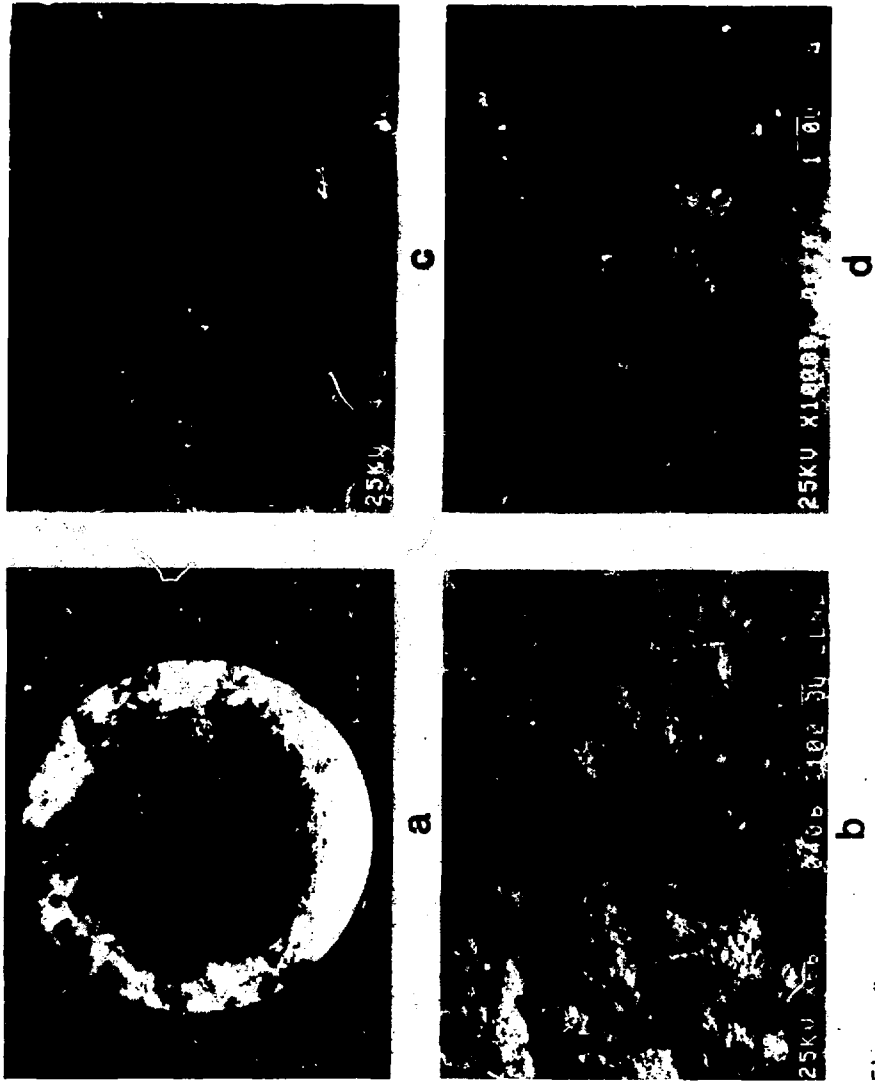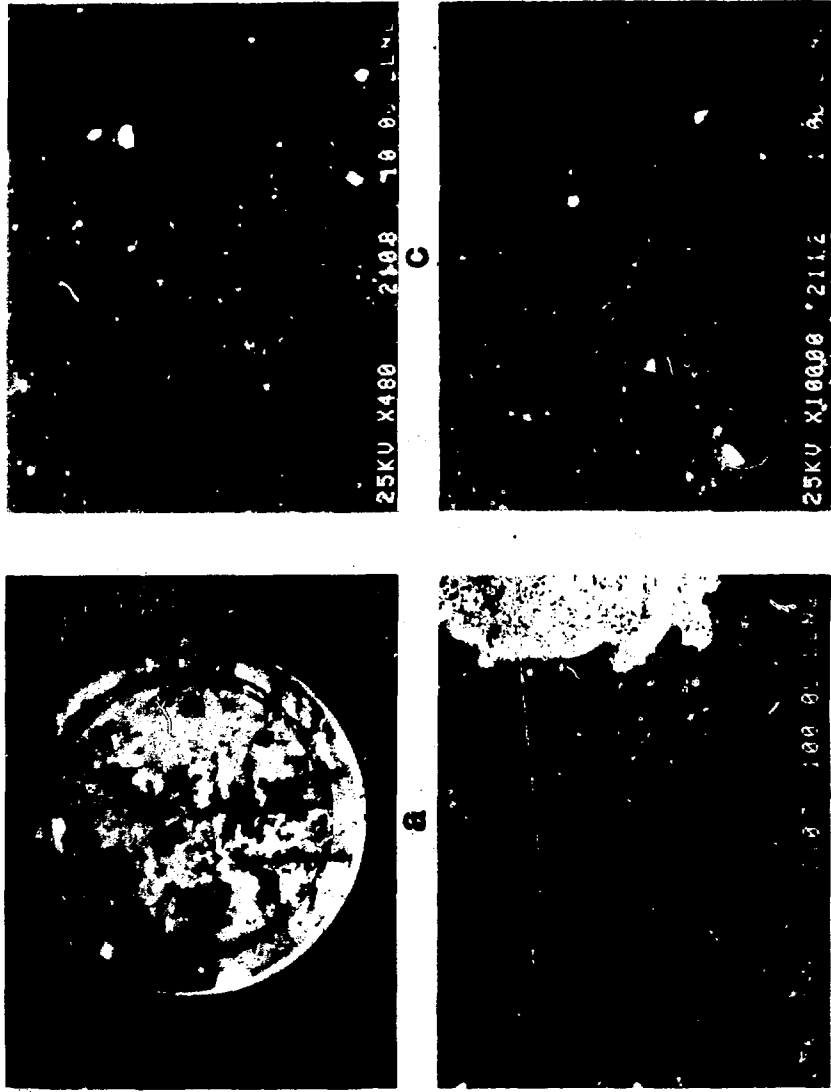Figure 3: Micrographs of uranium (U21) implanted with $10^{17}O_2^{\frac{1}{2}}/cm^2$ at 180 keV after exposure to 76 Torr H_2 at 130°C for 87 minutes: (a) optical micrograph and (b-c) scanning electron micrographs.

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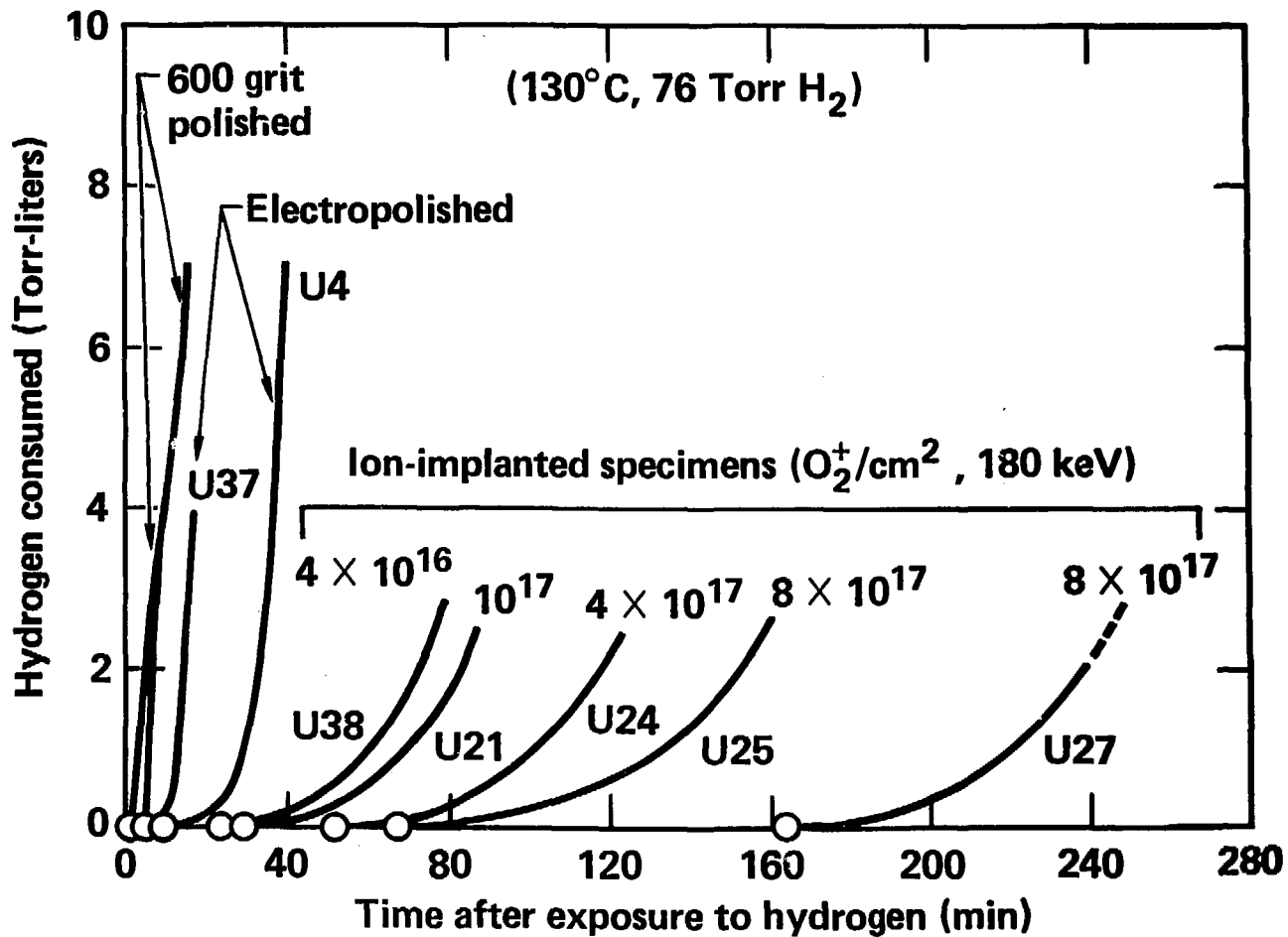
Figure 1.

Figure 2.

Figure 3.

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