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SUPPRESSION OF THE URANIUM-HYDROGEN REACTION
USING HIGH-DOSE CARBON IMPLANTATION

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This paper was prepared for submittal to
The MRS 1987 Spring Meeting
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ABSTRACT

We have previously reported the delay and reduction of the hydriding of uranium by implantation of oxygen. The reduced hydriding was attributed to the presence of the uranium oxide layer created near room temperature. In this paper we present results for the layers formed by implantation of 80 keV C^{+} to a dose of $8E17\ C/cm^2$. The carbide layers formed were characterized by Auger electron spectroscopy, Rutherford backscattering, and glancing angle x-ray diffraction. Hydriding properties of both non-implanted and implanted uranium were measured for 76 Torr hydrogen at 130°C. The implanted specimens had significantly longer incubation times for the start of the reaction after exposure to hydrogen and less area participating in the reaction.

INTRODUCTION

We have previously shown that ion implantation can markedly affect the hydrogenation of uranium [1]. In this earlier study we compared the hydriding characteristics of the implanted specimens with those of non-implanted specimens. In particular implantation of large doses (i.e. atoms/cm²) of O_2^{+} at 180 keV into uranium resulted in the creation of layers that were responsible for (a) increasing the incubation times for the initiation of the reaction after exposure to hydrogen and (b) reducing the area participating in the reaction. Probable explanations for the reduced hydriding included formation of a uniform, hydride-resistant oxide layer at the higher doses, reduction of the solubility of hydrogen in uranium at the lower doses, and ion-induced strain in the surface.

We have now implanted carbon ions in an attempt to create a uniform carbide layer inside the naturally occurring uranium oxide layer. The dose chosen was sufficient to synthesize a 244 nm thick layer of UC or a 154 nm layer of UC_2 . Both UC and UC_2 are thermodynamically stable with respect to UH_3 and should resist hydrogenation. In fact, one method of preparation of uranium carbides is to react fine UH_3 powder with fine graphite powder at elevated temperatures (e.g. > 900°C). Ion implantation offers the opportunity to form hydride-resistant uranium carbide layers near the surface of uranium at low temperatures while preserving the bulk properties.

In this paper we present results on the nature of the layers created by low-temperature (< 50°C) implantation of $8E17\ C/cm^2$ using 80 keV C^{+} and on the comparison of the hydriding characteristics for implanted and non-implanted uranium specimens. The layers have been characterized using Auger electron spectroscopy (AES), Rutherford backscattering (RBS), and glancing angle X-ray diffraction (GXR).

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EXPERIMENTAL CONSIDERATIONS

The specimens used all came from the same piece of high-purity, depleted uranium used in our previous study [1]. 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 < 4; Mg = 2; Cu, Mn, Ni, Bi, Co, Cr, Sn, Sr < 1; B, Mo, Ti, Cd, Tl, Pb, V < 0.4; Be < 0.1. After EDM cutting of the disk specimens from the bulk piece, standard lapping and mechanical polishing (final step with 1 μ m diamond paste) procedures were used to prepare surfaces for electropolishing. The polished specimens were stored in kerosene and/or vacuum until just prior to shipment in all-metal containers to the implanters. The final surface treatment immediately before shipment was an electropolish in a solution of 450 ml ethanol (95%), 275 ml ethylene glycol, and 275 phosphoric acid (85%) at room temperature at 13 V for about three seconds. Finally the specimens were rinsed in de-ionized water and dried in flowing argon gas. These preparation procedures were applied to both the control and the to-be-implanted specimens. The control specimens were shipped with the implanted specimens to insure they experienced the same environmental exposures.

Carbon ions (C^+) were implanted, using an electronically rastered beam, with energies of 80 keV to a dose of $8E17$ C/cm² over the central 25-mm-diameter area of each specimen. The range and standard deviation for 80 keV C^+ ions in pure uranium were calculated using the TRIM program [2] to be 88 and 45 nm, respectively. The maximum temperature during implantation was estimated to be 50°C. After implantation the implanted and control specimens were stored under vacuum except when (a) they were removed for mounting in the hydriding chamber or in an analysis chamber for AES or RBS and (b) GXR measurements were performed with the specimens at atmosphere for several hours.

Simultaneous RBS and particle induced X-ray emission (PIXE) measurements [3] using 2 MeV helium ions were combined to determine the depth distribution of the uranium and identify the elements causing the changes from the RBS spectrum for pure uranium. Depth profiles of carbon, oxygen, and uranium were obtained using argon ion sputtering and a 5 keV electrons for the AES analysis. GXR measurements were made using Cu(K) X-rays at angles of 5-10 degrees from the surface. Standard scanning electron microscopy (SEM) was used to determine the surface microtopography of polished only, implanted, and implanted and hydrided specimens.

The hydriding studies were performed using a vacuum chamber for edgeless studies of gas-metal reactions [4]. In essence, the chamber consisted of two separate vacuum regions with most of the front (i.e. implanted) surface of the specimen exposed to the hydrogen while the other surfaces remained under vacuum (< $1E-5$ Torr). For the present experiments two significant improvements were made to the original chamber design [4]: (a) the specimen was mounted in a vertical plane to ensure the release of loose reaction products and unimpeded access of the gas to the exposed surface and (b) a low-power (~60X) optical microscope on a XYZ stage was combined with a light source to permit improved observations of the exposed surface through the sapphire window.

The extent of the reaction was determined by measuring the quantity of hydrogen taken up by the exposed area (3.0 cm²) under isobaric (76 Torr) and isothermal (130°C) conditions. 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, which were the same as previously used [1,4], 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 ensure 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 [5] and a hydride attack of non-implanted uranium that was typical of lower temperatures (i.e. formation of funnel-like hydride pits which penetrate into the reacting sample) [6].

For our reaction conditions, the linear reaction rate was estimated from published data [7] to be approximately $0.8 \mu\text{m}$ of pure uranium per minute. The reaction was considered initiated when the amount of hydrogen consumed clearly exceeded 0.017 Torr-liters. For uniform uptake and reaction, 0.017 Torr-liters of hydrogen would consume about $0.03 \mu\text{m}$ of pure uranium (i.e. $1.6 \mu\text{m/Torr-liter}$).

RESULTS AND DISCUSSION

Characterization of Implanted Layers:

GXRD measurements indicated that alpha-uranium and UC_2 were the major phases present in the non-pitted region of an implanted specimen after the hydrogen exposure. UO_2 was detected as a trace phase.

AES sputter profiles were measured to determine the depth distributions of carbon, oxygen, and uranium. Figure 1 shows the profile of an implanted specimen after exposure to hydrogen. Within the high-carbon region, the carbon Auger peak had the sharp and symmetrical shape typical of carbon in carbides. From the similarity of this carbon peak structure to that measured for a known UC crystal and that given for UC by Dilliard et al. [8], we concluded that a uranium carbide layer had been formed. The composition of the uniform region of the implanted layer below the surface oxide was taken to be UC_2 because that was the only carbide phase found by GXRD. Since the sensitivity factor for the uranium OVV peak near 72 eV was taken to be that measured as 0.86 while sputtering the UC crystal, the sensitivity factor for the carbon KLL peak near 270 eV was set at 0.18 for all times after the first six minutes. The dashed lines are indicative of

Fig. 1: Auger sputter profile of carbon-implanted uranium after exposure to hydrogen at 76 Torr and 130°C . Data taken from a non-pitted region (i.e. center of light spot of Figure 3).

the uncertainties with the measurement of the carbon peak heights due to interference near 270 eV with part of the uranium NVV signal. For the first six minutes of the profile, the carbon peak was clearly that of graphitic carbon, and we used the sensitivity factor measured using a polished graphite standard. The sensitivity factor for oxygen was measured to be 0.36 using an Al_2O_3 layer on aluminum.

For an as-implanted specimen, the average C/U ratio in the implanted layer was in very good agreement (within two percent) with that for the hydrogen-exposed specimen, but the time to sputter through the layer (i.e. the full width at half maximum or FWHM) was about 30 minutes less than the 128 minutes shown in Figure 1. This apparent discrepancy may have resulted from slightly different sputtering conditions or real differences in the nature of the carbide layer caused by heating to 130°C for two days and/or exposure to hydrogen. For both specimens, the oxygen content in the implanted layer was below the detection limit of about one atomic percent.

Simultaneous RBS and PIXE measurements showed that carbon, oxygen, and uranium were the only $Z > 5$ elements present in the as-implanted specimens. The RBS spectra was dominated by the scattering events from uranium and the distribution of the other elements was inferred from the PIXE, AES, and GXRd results and the change in the uranium scattering height from pure uranium to that in the implanted condition. There was evidence for a surface layer (i.e. oxide) and an interior layer (i.e. implanted layer). Since essentially the same RBS spectrum was found for both the as-implanted and the implanted and hydrogen-exposed specimens, the 23% difference in the FWHM of the implanted layers by AES sputter profiling was apparently due to variations of the profiling conditions; however the possibility of different layer densities cannot be excluded.

Assuming only carbon and uranium were present in the interior layer, the ratio of the shallow minimum in the back-scattering amplitude from uranium in the implanted layer relative to that in pure uranium at the same detected energy was used to calculate the maximum C/U ratio following standard RBS calculational procedures [9] coupled with Bragg's rule of linear additivity of atomic stopping cross sections. The pure elemental stopping cross sections were obtained from the program of Zeigler et al. [10]. Since deviations from Bragg's rule are known to occur for compounds, particularly those containing low-Z elements [11], we used the UC crystal to determine a correction factor (.62) to the stopping cross section for carbon that produced a C/U ratio of 1.00. Although this correction factor may not strictly apply for all C/U ratios, we expect that it is better than no correction factor. With this limitation, the peak C/U ratio was found to be 2.57 for two different specimens. The corresponding atomic percents would be 72 for C and 28 for U. Since this result applies to the minimum in the uranium scattering signal, it corresponds to the maximum in the C/U ratio. Consequently, the average layer composition would be in reasonable agreement with the atomic percents for UC_2 : 67 for C and 33 for U. However, the apparent carbon richness may be explained by a region of the layer containing some implanted carbon in excess of that required to form UC_2 .

The thickness of the implanted layers was determined from the RBS spectra by considering the energy difference between helium scattered from uranium near the oxide/carbide and the carbide/uranium interfaces. Essentially the same thickness was found for the as-implanted and the implanted and hydrogen-exposed specimens. The calculation was performed assuming two different C/U ratios: 2.00 and 2.57. For C/U = 2.00 the layer thickness was about $4.2\text{E}17 \text{ UC}_2/\text{cm}^2$; for C/U = 2.57 the thickness corresponded to about $4.0\text{E}17 \text{ UC}_2/\text{cm}^2$. In both cases the calculated quantity of carbon/ cm^2 (i.e. $8.5\text{E}17$ and $10.3\text{E}17$, respectively) was in reasonable agreement with the implanted dose of $8\text{E}17 \text{ C/cm}^2$.

Hydriding Experiments:

The hydrogen consumption results are displayed in Figure 2. Times for the initiation of the reaction were < 1 and 23 minutes for the 600-grit polished and electropolished control specimens, respectively. These times

Fig.2: Comparison of the reaction of 76 Torr of hydrogen at 130°C with two implanted and two non-implanted uranium specimens.

are consistent with those measured at other times for similar specimens. Induction times for the specimens implanted with carbon were both about 45 min. This increase in the induction time is significant and clearly shows the effect of the implanted layer. The reaction rates at the end of the exposures for the 600-grit polished and electropolished uranium specimens both corresponded to consumption of about $0.86 \mu\text{m}$ of uranium per minute, which agrees with that expected from the literature [7]. In contrast, the final rates for the two implanted specimens were both approximately $0.23 \mu\text{m}$ U/min. The apparently lower reaction rate of the implanted specimens is a consequence of the smaller fraction of the surface participating in the reaction allowing for the internal surface areas of the pits (Figure 3). The AES profile data of Figure 1 was obtained from the center of the bright, sputtered spot of Figure 3.

In agreement with the morphology attendant with the oxygen-implanted and hydrogen-exposed surfaces [1], the surfaces of the carbon-implanted, hydrogen-exposed specimens, as revealed by SEM at 10KX, had large, non-pitted areas very similar to the smooth, pre-exposed surface. Thus, the implanted layer greatly suppressed the uranium-hydrogen reaction over most of the exposed surface area. Identification of the mechanisms responsible for this suppression has not been unambiguously made, but the potential candidates are similar to those proposed for the oxygen implantations [1]: (a) a uniform, hydride-resistant carbide layer, (b) reduction of the solubility of hydrogen in uranium below the carbide layer where the carbon

Fig.3: Optical micrograph of carbon-implanted uranium after exposure to hydrogen at 76 Torr and 130°C for 95 minutes.

concentration is lower, and (c) ion-induced strain in the surface. Experiments are in progress to evaluate the importance of ion-induced strain on the hydrogenation of uranium.

The occurrence of hydriding at isolated spots is also similar to that previously observed for the oxygen-implanted specimens [1]. Presumably the hydriding sites correspond to small areas that were not modified the same as the vast majority of the surface. Such small areas could have resulted from (a) implantation into impurity inclusions and/or (b) lack of implantation in surfaces inaccessible to the ions (e.g. sides of some defects, or areas masked by dust particles). Some effects of the presence of dust particles are presently being evaluated.

CONCLUDING REMARKS

Implantation of 80 keV C^+ into uranium to a fluence of $8E17 \text{ C/cm}^2$ near room temperature results in the formation of a uranium carbide layer with a composition near that of UC_2 . The presence of this layer modifies the reaction of hydrogen at 76 Torr and 130°C with the uranium. Implanted specimens exhibited significantly longer incubation times for the start of the reaction after exposure to hydrogen and considerably smaller areas participating in the reaction. Combining this result with our previous results for oxide layers formed by implantation of oxygen [1], we can conclude, in general, that formation by ion implantation of compound layers that are thermodynamically stable with respect to hydrogen should suppress the uranium-hydrogen reaction. Future studies should address the detailed phenomena responsible for the reduced reaction.

This work and our previous study with oxygen-implanted uranium [1] demonstrated reduced hydriding for ion implanted uranium specimens. Hoffmann et al. [12] have shown that implantation of palladium enhances the uptake of hydrogen by titanium. Although these effects of ion implantation have only been reported for uranium and titanium, there are most certainly other materials whose hydriding properties could be markedly modified by ion implantation.

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