SANDIA REPORT

SAND2001-8361
Unlimited Release
Printed August 2001

Plasma Driven Permeation of Deuterium into Nitrided Ti-6Al-4V

D. F. Cowgill, R. A. Causey

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia is a multiprogram laboratory operated by Sandia Corporation,
a Lockheed Martin Company, for the United States Department of
Energy under Contract DE-AC04-94AL85000.

Sandia National Laboratories

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

Available to DOE and DOE contractors from
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Telephone: (865) 576-8401
Facsimile: (865) 576-5728
E-Mail: reports@adonis.osti.gov
Online ordering: http://www.doe.gov/bridge

Prices available from (703) 605-6000
Web site: http://www.ntis.gov/ordering.htm

Available to the public from
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Rd
Springfield, VA 22161

Telephone: (800) 553-6847
Facsimile: (703) 605-6900
E-Mail: orders@ntis.fedworld.gov
Online ordering: http;//www.ntis.gov/ordering.htm

SAND2001-8361
Unlimited Release
August 2001

Plasma Driven Permeation of Deuterium into Nitrided Ti-6Al-4V

D. F. Cowgill and R. A. Causey
Engineered Materials Department
Sandia National Laboratories
Livermore, CA 94551-0969

Abstract

Surface nitrided samples of Ti-6Al-4V alloy were exposed to deuterium plasmas simulating exposures for the TPX maintenance rails. Subsequent outgassing revealed all samples retained less than 1% of the incident ions and no observable uptake of the background deuterium gas. The thick nitride layers produced by Advanced Heat Treat Corporation's plasma process provided the most effective uptake barrier, limiting the total average hydrogen concentration to less than 2000 appm. This is significantly less than the levels required for embrittlement of the Ti-6Al-4V alloy. Though anticipated erosion of the nitride layers was not simulated by these tests, it is estimated that the 7-10 micron thick layer on this sample should withstand the normal sputtering and erosion by transient plasma events in TPX. Thinner nitride layers produced by laser and mechanical processes may not survive this erosion.

This work supported under United States Department of Energy, Contract No. DE-AC04-94AL85000.

CONTENTS

TABLES

FIGURES

Plasma Driven Permeation of Deuterium into Nitrided Ti-6Al-4V

Introduction

Ti-6Al-4V is the low activation material currently designated for structural uses inside the TPX fusion reactor. In most applications, it will be hidden behind carbon tiles and thus be protected from the deuterium plasma. The maintenance vehicle rail is an exception. It will be exposed to an energetic ion flux of approximately 1×10^{15} D/cm^2-s for 10^6 seconds during its lifetime in TPX. Titanium alloys are known to be subject to hydrogen-induced crack growth [1] if allowed to absorb substantial amounts of hydrogen. It is anticipated that the thin oxide layer normally present on titanium may be insufficient to prevent excessive uptake from the energetic hydrogen species. Thick protective layers of titanium nitride have been proposed to reduce this hydrogen uptake, while at the same time providing the abrasion resistance needed to support the vehicle wheels. This report describes experiments at Sandia National Laboratories in Livermore, California on the plasma driven permeation and retention of deuterium into surface nitrided samples of Ti-6Al-4V.

Procedures

The Ti-6Al-4V samples used in this experiment were fabricated from MIL-T-9047 material by Oak Ridge National Laboratory, and nitrided using three different processes: a plasma process (Advanced Heat Treat Corporation), a mechanical fluidized-vacuum process (Kemp Development Corporation), and a laser process (Iowa State University). They are denoted as AHT, KDC, and ISU, respectively. The samples were 0.64 cm thick x 2.54 cm diameter discs, nitrided on at least one face, with additional non-uniform layers on the back and edge surfaces. The AHT nitride was quoted to be composed roughly of a 1 micron surface layer of TiN over a 10 micron layer of Ti_2N, all over about a 100 micron N-diffusion layer. Nitride layers on the KDC and ISU samples were of unknown thickness and composition but had uniform gold TiN surfaces.

Plasma exposures were done in Sandia's Deuterium Plasma Experiment (DPE), a magnetically confined, rf heated plasma device capable of delivering a deuterium particle flux of about 10^{17} D/cm^2-s over 28 cm^2, for extended time periods. The DPE plasma is composed primarily of D_2^+ ions and has a positive potential of approximately 15 eV. During exposure, the samples were clamped to a copper plate by a stainless steel mask and biased -105 volts to give the ions a net energy of 120 eV, or 60 eV D^+ ions. TRIM calculations [2] show these ions have a penetration range of about 2 nm in TiN, TiO_2 or Ti. This range is less than normal oxide thickness, 5-10 nm. The samples were individually exposed to an average flux of 6.1×10^{16} D/cm^2-s for 16-18 hours giving fluences of $(3.6 \pm .4) \times 10^{21}$ D/cm^2. They were heated by the plasma to a constant temperature of 440 K, after about 30 minutes of exposure. In addition to the plasma, DPE has a background deuterium pressure of 0.5 Pa. Titanium reacts exothermically with hydrogen to form TiH_2 with a vapor pressure of about 10^{-4} Pa at 440 K. Thus, if the nitride and native oxide layers are not effective, this background could produce a deuterium uptake even beyond the level of 100% plasma retention.

After removal from DPE, the samples were individually outgassed in a passivated stainless steel tube furnace attached to Sandia's Armor Conditioning Experiment (ACX) apparatus. To provide material for additional analysis, the samples were cut in half along a diameter prior to outgassing. (It can be shown that rapid oxidation of the cut and slow H diffusion at room temperature prevent hydrogen isotope release resulting from this process.) During sample transfer, the furnace was kept warm and purged with dry nitrogen gas to minimize contamination by air exposure. After rapid evacuation, the furnace was heated to 1273 K at about 0.3 K/s, where it was held for several hours until the hydrogen partial pressures dropped to near zero. During outgassing, hydrogen, deuterium, and water vapor species were monitored with a UTI mass spectrometer. The mass spectrometer was calibrated using standard leaks and measured hydrogen flow rates from known volumes. Hydrogen and deuterium quantities were calculated from amplitudes of the mass peaks at 2, 3, 4 amu (P2, P3, P4) and corrected for molecular fractionation in the ionizer according to the expressions

$$\text{H atoms} = C\,[\,(P2 - B2) + 0.5(P3) - 0.05(P4)\,]$$

$$\text{D atoms} = C\,[\,0.5(P3) + (P4)\,].$$

Here B2 is the H_2 background of the furnace at temperature and C is a calibration constant. Residual H and D quantities within the samples were estimated by fitting exponentials to the decaying mass peaks. These residuals, which were less than 3% of the outgassed amounts, were added to get total quantities for each species. Water release was determined from the 18 amu peak using a slightly lower calibration constant.

Results

Microscopic examination of the surfaces revealed no effects of the plasma exposures, including gross erosion. After outgassing, the gold-colored TiN layers were no longer visible on the KDC and ISU samples and significantly reduced on the AHT sample. Integrated quantities of hydrogen, deuterium, and water found in each sample is summarized in Table 1. Average H/Ti and D/Ti atom fractions are calculated from sample masses after outgassing, using the Ti-6Al-4V composition. The deuterium fraction retained is given by the ratio of the observed D to the D ion fluence.

Table 1. Outgassing results for plasma-exposed, surface-nitrided Ti alloy samples. Plasma exposure: 440 K, 60 eV, 6.1×10^{16} D/cm^2-s, 4×10^{21} D/cm^2.

	AHT (plasma)	KDC (mechanical)	ISU (laser)
H ($\times 10^{20}$ atoms)	6.01	3.91	3.51
D ($\times 10^{20}$ atoms)	.83	1.58	3.07
H_2O ($\times 10^{18}$ molecules)	6.87	2.13	1.10
Fraction retained	.0024	.0052	.0090
Av. H/Ti (appm)	1590	1090	950
Av. D/Ti (appm)	220	440	830
"Peak" D/Ti (appm)	2260	4510	8470

Native hydrogen quantities varied from 1590 to 950 appm (34-20 wppm), consistent with H quantities normally found in Ti alloys. Deuterium quantities varied from 220 to 830 appm. The deuterium fraction retained is lower by a factor of two-to-four for the sample nitrided by the AHT plasma process. The AHT sample is also observed to outgas more water.

Hydrogen and deuterium outgassing spectra for the three samples are compared in Figures 1 and 2, respectively. For each sample, both isotopes begin releasing around 650°C. Absence of D release below this temperature suggests little implanted D resides weakly bound within the surface nitride or oxide layers. Small, transient gas bursts were observed at 650-750°C, indicative of cracking or dissolution of the surface layers.

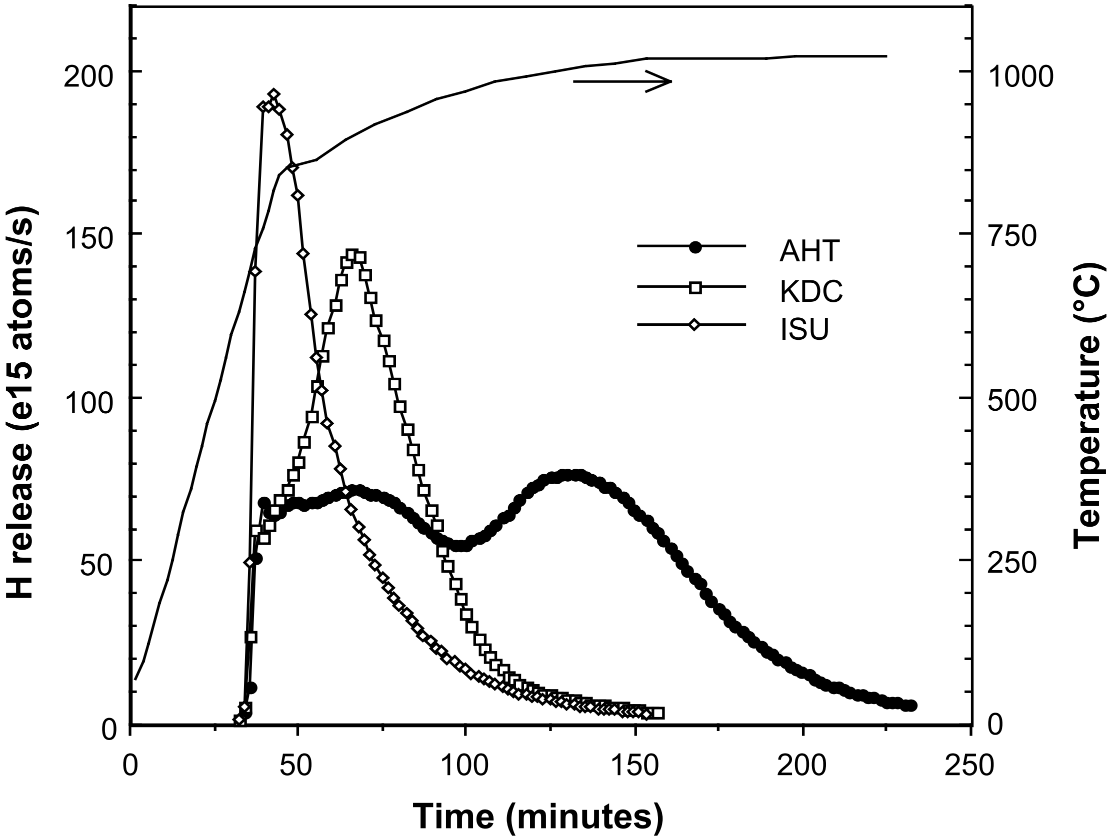

Figure 1. Thermodesorption of native hydrogen from the samples.

Both species are most rapidly emitted from the ISU sample, and somewhat slower from the KDC sample. For the AHT sample, release is delayed for approximately half of each species. The ratio of D/H release is plotted in Figure 3. At higher temperatures, H and D mix by diffusion within the sample and are released in proportion with the mixture. Near 650°C, before mixing, deuterium is preferentially released from the ISU sample. Only a small fraction of this D can come from traps within its nitride layer unless this layer is very thick. It is more likely that most of this D comes from the Ti alloy beneath the nitride layer.

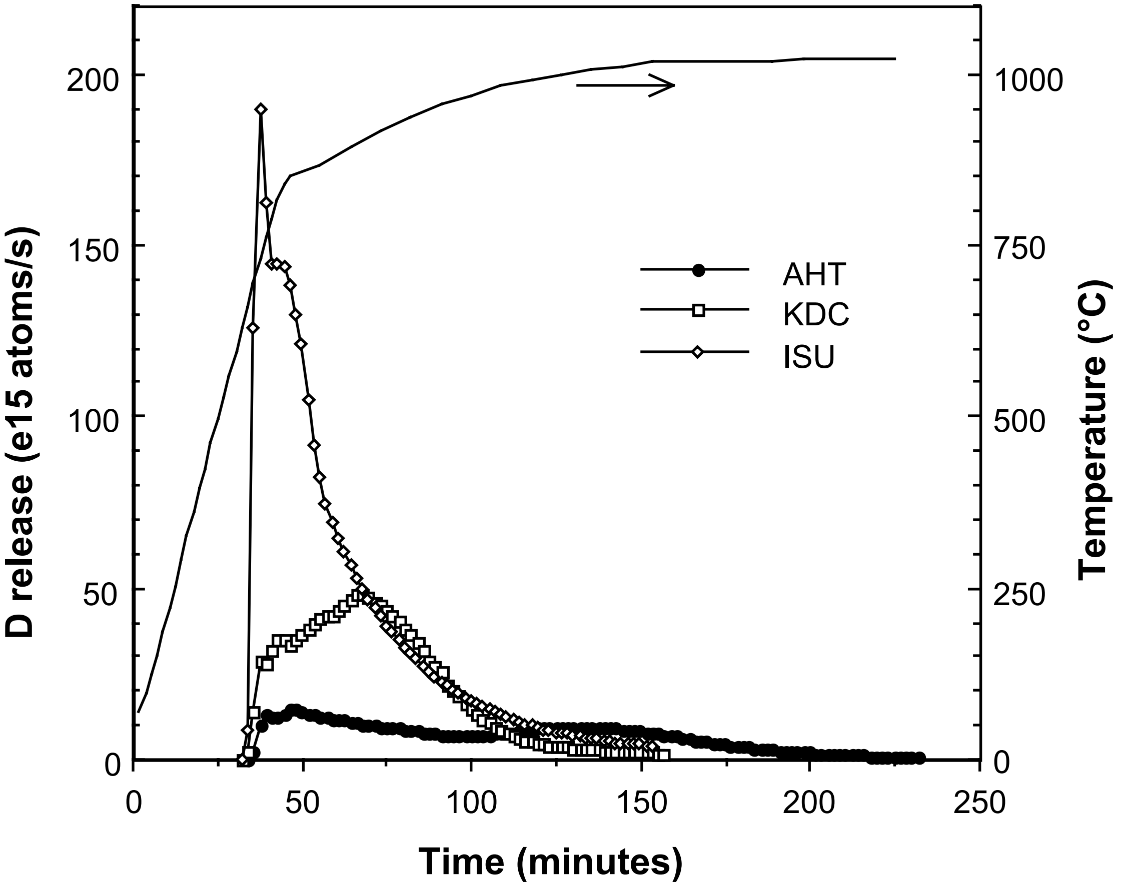

Figure 2. Thermodesorption of retained deuterium from the samples.

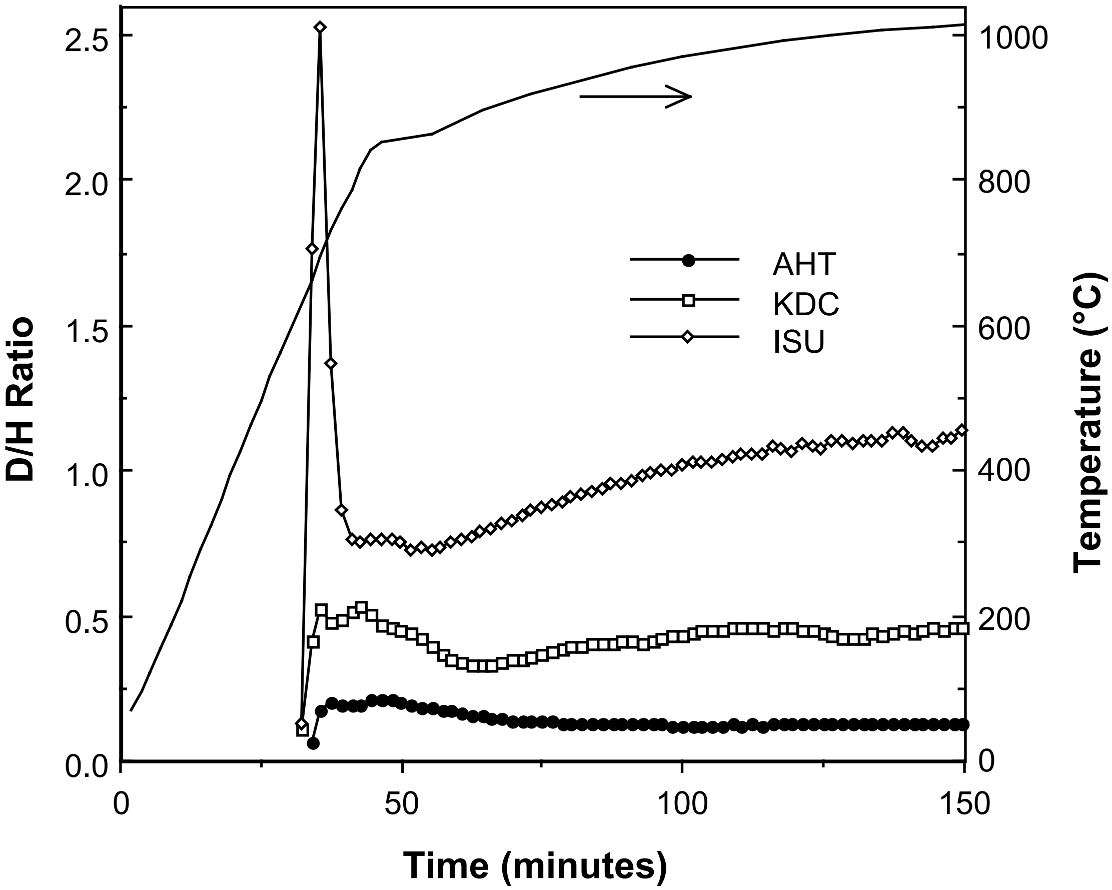

Figure 3. Ratio of D/H desorbed from the samples.

Water outgassing spectra are compared in Figure 4. This water was probably desorbed from the hygroscopic surface layers. Water release begins around 300°C and is completed by 650°C, where the hydrogen release begins. At this point the water signal drops significantly. This abrupt decrease may result in part from residual water reacting with freshly exposed Ti, as the surface layers crack or dissolve into the bulk. From the magnitude of the ordinate in Figure 4 and from the water listed Table 1, it is concluded that the hydrogen contributed by water dissociation is negligible. The HDO and D_2O were observed to be much smaller yet, indicating very little deuterium was excluded by the analysis.

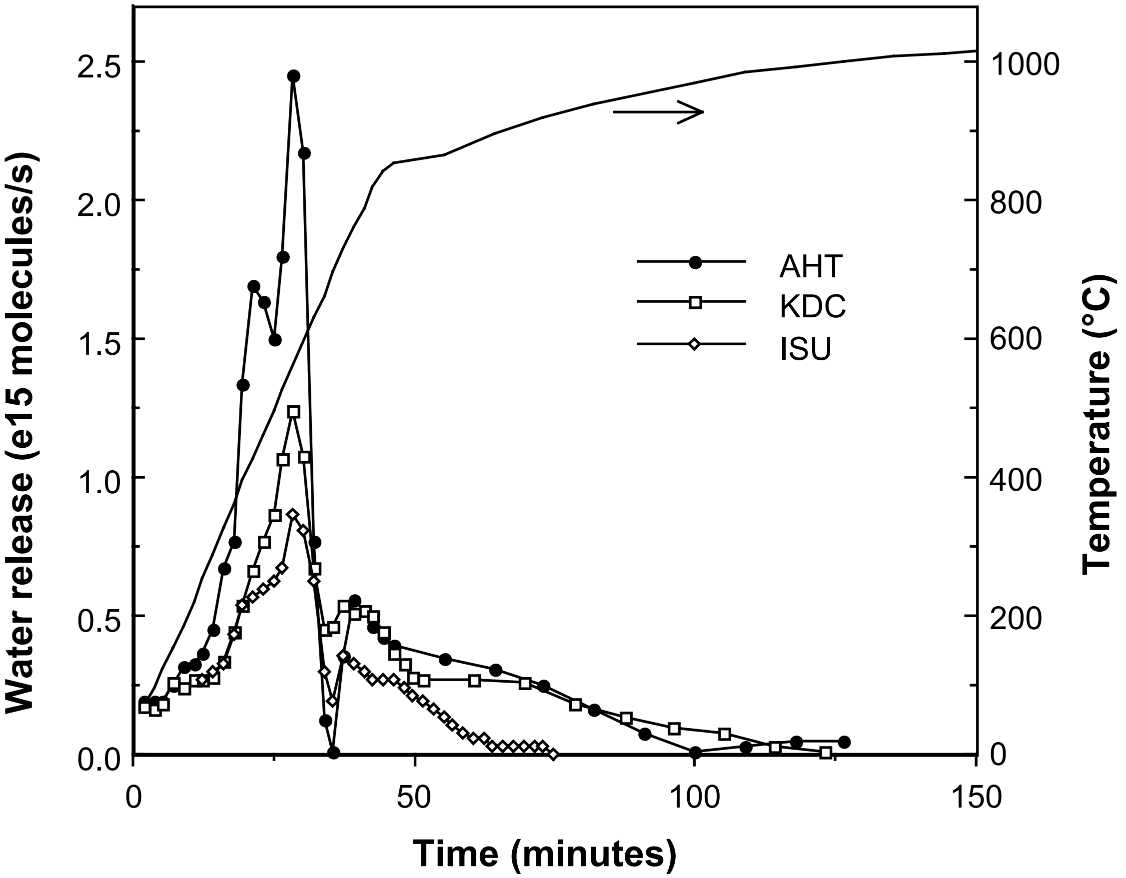

Figure 4. Thermodesorption of water from the samples.

Discussion

The absence of observable erosion is not surprising since the ion energy was too low to produce significant sputtering. The sputtering coefficient [3] for 100eV d^+ on Ti is 0.002 Ti/ion (normal incidence), and drops to about 10^{-4} at 60eV. For the test fluence, this gives an erosion of $4x10^{17}$ Ti/cm^2 or about 70nm. This is much less than the typical sample roughness, making the surface recession unobservable.

Native hydrogen found in the three samples differs by a factor of two. It is speculated that the additional hydrogen in the AHT sample was introduced by the plasma nitriding process. This sample was nitrided in equipment previously used for nitriding steels, where a mixture of hydrogen and nitrogen is employed. It is likely that outgassing from this system's walls produced a significant partial pressure of hydrogen during the nitriding process. The thick nitride layers on the AHT sample delayed desorption of half the H and D species. The similar delay for both species indicates it results from a more tenatious permeation barrier, rather than from traps within the surface layers. These layers also appeared more resistant to removal by the high temperature bake, than nitrides on the other samples. After outgassing, the gold TiN color was still partially visible on the AHT sample. Apparently, longer time is needed at high temperature for dissolution of these thick layers into the bulk. By contrast, surface layers on the laser nitrided ISU sample produced little resistance to the H desorption.

Deuterium desorption from the samples has similar characteristics. It is rapidly released with little resistance from ISU sample, but with more significant bursts than found for H isotope. Deuterium diffusion at 440 K is not sufficient to achieve uniform loading during the 16-18 hour exposures. Using the diffusivity for a-Ti [4], indicates that most of the deuterium should be located within 0.4-0.6 micron of the surface (ignoring the coating). The D concentrations in the near-surface regions are estimated to be approximately 10 times the average D for the samples. These "peak" values are also listed in Table 1. A near-surface deuterium enhancement is clearly visible in Figure 3 for each sample, as a large initial value for the D/H release ratio. The peak H+D concentration is lowest, 0.4 at%, in the AHT sample and reaches about 1 at% in the ISU sample. In terms of simulation of the TPX exposures, this concentration peaking is an artifact of the current test conditions. It is a result of compression of the plasma exposures into a time frame too short for deuterium to diffuse out of the near-surface region. Such peaking is expected to be much lower in TPX, where the plasma exposures are spread out over a much longer time frame.

On the other hand, the enhanced near-surface concentration can lead to an increase in the D release fraction. Significant release of implanted D occurred during the plasma exposures as evident from the low retained D fraction. The release rate probably depends on the near surface D concentration. Thus the test-dependent concentration peaking may lead to an artificially-reduced retention fraction. The tabulated retained D fraction provides a quantitative comparison of the samples only under the specific test conditions. The ratio of the integrated D fluence to the number of Ti atoms in each sample is about 0.1 D/Ti. This is much greater than the outgassed D quantities and results in a retained D fraction which decreases with increasing fluence. Thus under these specific exposure conditions the AHT plasma treatment produces the most protective nitride layer, with a retained fraction of 0.0024. The KDC surface layer is about half as effective, at 0.0052, and the ISU is about one-fourth as good at 0.0090. This difference is evident in Figure 3 as a lower value for retained D/H. It is also evident from a comparison of the average D/Ti found in the samples.

Conclusions

These TPX simulation exposures produce no visual damage to surface nitride layers on Ti-6Al-4V. Under the test conditions, samples retain only a small fraction of the deuterium that impinges on the surface. Less than 1% of the incident D ions were found during subsequent sample outgassing. Also, there is no observable uptake of the background deuterium gas.

In terms of plasma protection, this test indicates the nitride layer produced by Advanced Heat Treat Corporation's plasma process is the most effective. It is about twice as good as the Kemp Development Corporation's mechanical process and four times as effective as Iowa State University's laser process. However, it appears that currently the AHT process introduces measurable quantities of hydrogen. It is likely that this additional H could be reduced by appropriate cleanup of the plasma nitriding system prior to processing. Even with this additional H, the total average H+D concentration following plasma exposure was only 1800 appm. This is still significantly less than the bulk hydrogen level required for embrittlement of the Ti-6Al-4V alloy, observed to be greater than 50,000 appm [4]. However, these test conditions produce concentrations which may differ from the longer term TPX exposures.

Anticipated erosion of the nitride layers on Ti-6Al-4V was not simulated by these tests. Thick layers will be needed to survive sputtering by higher energy ions and erosion by transient plasma events. At 400 eV normal incidence, sputtering increases to .01 Ti/ion [3], which produces an estimated erosion of 1.8 microns for 10^{21} D^+/cm^2. Additional sputtering may be produced by impurities within the plasma. Alternatively, some of the eroded material (and carbon from graphite tiles) may be redeposited during the sputtering process, reducing the net erosion rate.

References

1. N.R. Moody and J.E. Costa, "A Review of Microstructural Effects on Hydrogen-Induced Sustained Load Cracking in Structural Titanium Alloys," in Microstructure/Property Relationships in Titanium Aluminides and Alloys, Y. Kim and R. Boyer eds., (Minerals, Metals and Materials Society, 1991), 587-603.
2. J.P. Biersack and L.G. Haggmark, Nucl. Instr. and Meth. 174, 257 (1980).
3. J. Roth, J. Nucl. Materials 176-7, 132 (1990).
4. R.J. Wasilewski and G.L. Kehl, Metallurgia 50, 225 (1954).
5. J.W. Davis, McDonnell Douglas Aerospace, St. Louis, MO, private communication.

Distribution

1	MS 9001	M. E. John, 8000
		Attn: R. C. Wayne, 2200, MS 9005
		J. Vitko, 8100, MS 9004
		W. J. McLean, 8300, MS 9054
		D. R. Henson, 8400, MS 9007
		P. N. Smith, 8500, MS 9002
		K. E. Washington, 8900, MS 9003
		D. L. Crawford, 9900, MS 9003
1	MS 9405	R. H. Stulen, 8700
		Attn: R. Q. Hwang, 8721, MS 9161
		W. R. Even, 8722, MS 9403
		J. Wang, 8723, MS 9403
		J. Garcia, 8725, MS 9401
		E-P Chen, 8726, MS 9161
		J. Handrock, 8727, MS 9043
		M. Horstemeyer, 8728, MS 9042
		C. Henderson, 8729, MS 9401
		J. Goldsmith, 8730, MS 9409
		B. Replogle, 8731, MS 9409
		G. Kubiak, 8732, MS 9409
1	MS 9402	K. L. Wilson, 8724
5	MS 9402	R. A. Causey, 8724
5	MS 9402	D. F. Cowgill, 8724
3	MS 9018	Central Technical Files, 8945-1
1	MS 0899	Technical Library, 9616
1	MS 9021	Classification Office, 8511/Technical Library, MS 0899, 9616
1	MS 9021	Classification Office, 8511 For DOE/OSTI