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Hydrogen Plasma Protection of Ti-3Al-2.5V Alloy by Ni Plating

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Hydrogen Plasma Protection of Ti-3Al-2.5V Alloy by Ni Plating

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Abstract

Nickel-plated samples of Ti-3Al-2.5V alloy tubing proposed for antenna structures in tokamaks were exposed to energetic deuterium plasmas simulating long term conditions. Subsequent high temperature outgassing revealed that no significant uptake of deuterium occurred for a thick-plated (50-75 μm) sample where the plating remained intact. Deuterium uptake observed for a thin-plated sample is believed to have occurred only after the plating layer was sputtered away. Uptake for an unplated sample was larger yet. None of the samples experienced uptake from exposure to the background gas.

It is argued that since hydrogen diffusion in Ni is large at typical exposure temperatures, the Ni plating does not reduce hydrogen uptake by providing a barrier to permeation. Rather, the observed large reduction is believed to result from enhanced H recombination at the surface. It is proposed that this approach to reducing plasma driven hydrogen permeation into materials could be made continuous in the presence of erosion by inclusion of Ni (or Fe) into the alloy. However, some of the beneficial enhanced-release effect of Ni may be countered by the buildup of over-layers produced by plasma redeposition.

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Introduction

Ti-Al-V alloys are low activation materials proposed for structural uses inside fusion reactors. In most applications they will be hidden behind plasma-facing tiles and thus protected from direct exposure to hydrogen plasmas. This is not the case for the rf antenna tubes, which will be exposed to energetic ion fluxes during both glow discharge conditioning processes and hydrogen plasma operation. 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. A thick Ni plating has been proposed to reduce this hydrogen uptake. This report describes experiments at Sandia National Laboratories in Livermore, California on the permeation and retention of deuterium into samples of Ni-plated Ti-3Al-2.5V alloy tubing planned for use in tokamak reactors.

Procedures

Samples of Ni-plated and bare Ti-3Al-2.5V tubing were provided by Oak Ridge National Laboratory. The tubing had been sawed lengthwise and flattened to provide a planar surface for plasma exposure. The samples were somewhat wavy, due to incomplete flattening. They were typically 2.5 gm and approximately 18x25 mm by 1mm thick. Two plating thicknesses were tested, specified at 25 and 50-75 microns, along with an unplated sample. The Ni plating appeared to cover all surfaces, including the sample edges.

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 held against a copper plate by a stainless steel mask and biased -185 volts to give the ions a net energy of 200 eV, or 100 eV D^+ ions. The three samples were exposed simultaneously for about

102 hours to an average flux of 5.0×10^{16} D/cm^2-s, giving a fluence of 1.8×10^{22} D/cm^2. They were heated by the plasma to a constant temperature of about 400 K after about 30 minutes of exposure. Sample temperatures were estimated to be 10-20 K higher than the measured copper plate due to the questionable thermal contact between the plate and "wavy" sample surfaces. In addition to the plasma, DPE has a background deuterium pressure of 0.5 Pa. Titanium is an exothermic hydride former with a hydride vapor pressure of about 10^{-4} Pa at 400 K. Thus, if the plating and native oxide layers are not effective, this background could produce a deuterium uptake even beyond the level of 100% plasma retention.

After plasma exposure, the samples were outgassed individually in a passivated, stainless steel tube furnace attached to Sandia's Armor Conditioning Experiment (ACX) apparatus. 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 the furnace background, 10^{-4} Pa. During the outgassing, hydrogen and deuterium species were monitored with a UTI mass spectrometer. The mass spectrometer was calibrated using standard hydrogen leaks and measured hydrogen flow rates from known volumes. Hydrogen and deuterium quantities were calculated from the amplitudes of mass peaks at 2, 3, 4 amu (P2, P3, P4) and corrected for molecular fractionation in the ionizer according to the expressions

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

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

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 2% of the outgassed amounts, were added to get total quantities for each species.

Results

Microscopic examination of the surfaces revealed no effects of the plasma exposures, other than slight discoloration. Integrated quantities of hydrogen and deuterium found in each of the samples are summarized in Table I. For comparison, two additional unexposed samples (plated and unplated) were also outgassed. Native H/Ti and total (H+D)/Ti atom fractions are calculated from the unplated sample mass after outgassing, using the Ti-3Al-2.5V composition. The deuterium fraction retained is defined as the ratio of the observed D to the D ion fluence.

Except for the exposed, bare sample, native hydrogen quantities were about 1100 appm (22 wppm H), consistent with the H quantities normally found in Ti alloys. After exposure, total H+D quantities varied from 1200 to 10,000 appm (24-200 wppm H). Comparison of native H for the unplated and plated samples shows that no additional hydrogen was introduced by the Ni plating process.

TABLE I. Outgassing results for plasma exposed Ti-3Al-2.5V tube samples. Exposure conditions: 400 K, 100 eV, 5.0×10^{16} D/cm^2-s, for 102 hrs. Fluence = 1.8×10^{22} D/cm^2.

Sample	Native H/Ti (appm)	Total H+D (appm)	Retained D (fraction)
Not plated Not flattened	996	------ No Exposure ------	
Not plated	457	9606	.0038
Thick Ni plating (50-75 μm)	1086	------ No Exposure ------	
Thin Ni plating (25 μm)	1257	7290	.0025
Thick Ni plating (50-75 μm)	1121	1153	.00001

Significant release of the implanted D occurred during the plasma exposure as evidenced by the small retained D fraction. The ratio of the integrated D fluence to number of Ti atoms in a sample is about 2.4 D/Ti, much greater than the outgassed amounts. Under the test fluence, the calculated retained D fraction is less than 1%, even for the unplated sample. For the exposed bare sample, addition of implanted D appears to have excluded some of the native H by dilution. Very little D was found in the thick-plated sample. After outgassing, the Ni plating appeared to be absent over a large fraction of the exposed surface for the thin-plated sample, but was intact for the thick-plated. This suggests the larger D retention for the thin-plated sample resulted from D uptake occuring after much of the coating was eroded away. Such erosion was not readily apparent during the microscopic inspection prior to the high temperature bake. Using a sputter coefficient of 0.007 Ni/ion [2] for normally incident 100 eV deuterons, produces an expected erosion of 14 microns. This is slight more than half the quoted plating thickness. The additional erosion may have resulted from plasma in homogeneity and by impurity sputtering.

Hydrogen and deuterium outgassing spectra for the samples are compared in Figures 1 and 2, respectively. For each sample, both isotopes begin releasing around the same temperature. The gas release often occurred in small transient bursts. For the unplated sample, the release began around 550°C; while it required nearly 800°C for the thick-plated sample. Gas release characteristics for the thin-plated sample support the hypothesis of a partial loss of the front surface plating. Here gas release began at a temperature only slightly higher than observed for unplated sample and the D release concluded before the H. At higher temperatures, H and D should rapidly mix by diffusion and should be released in proportion with the mixture. Using the H diffusivity [3] for α-Ti, gives a diffusion distance of about 0.5 mm, half the thickness of the sample, during a 102 hour exposure at 125°C. Thus, it appears gas was initially released through the front surface, where the D concentration was enhanced. This initial front surface release would also result in an earlier release for much of the D.

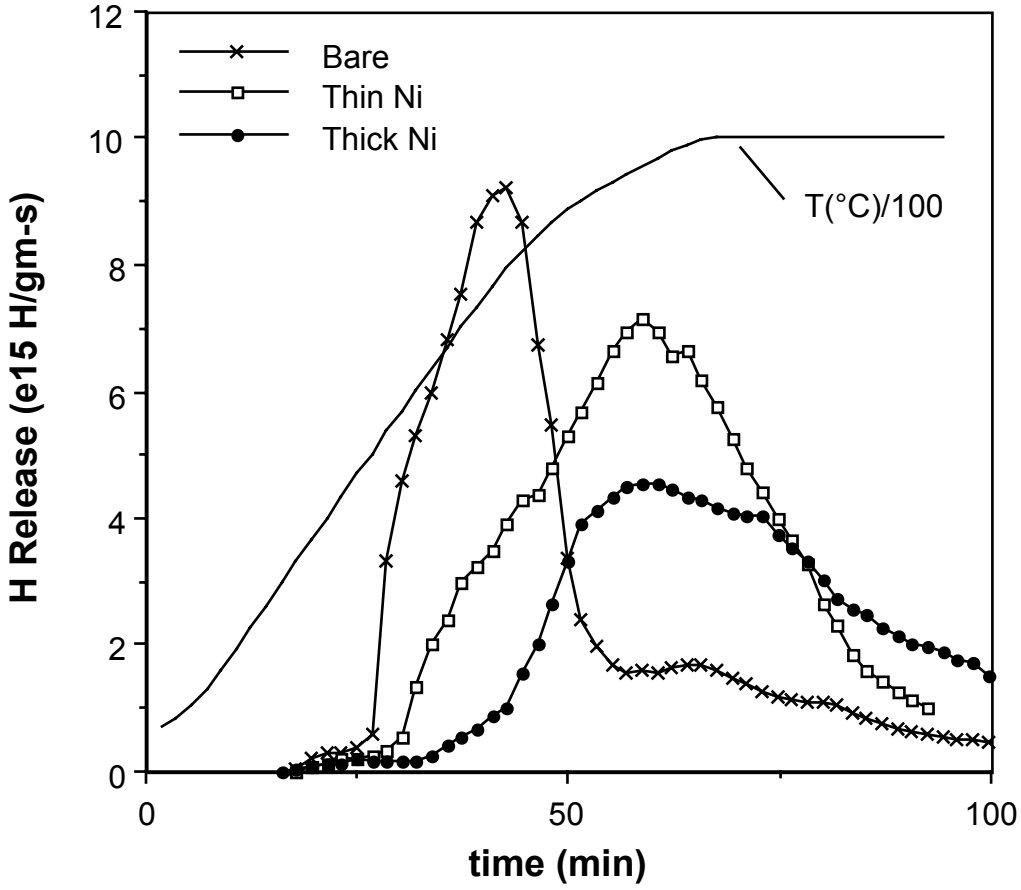

FIGURE 1. Thermodesorption of native hydrogen from the samples.

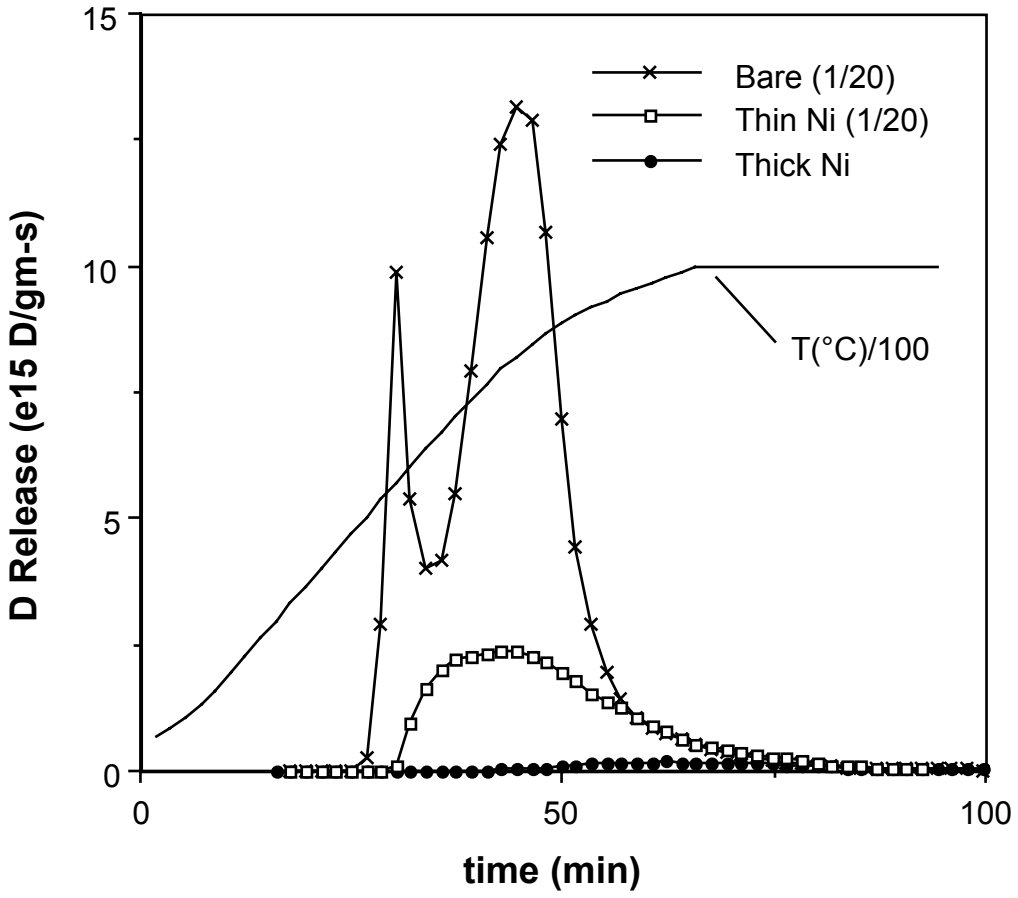

FIGURE 2. Thermodesorption of retained deuterium. Note that the spectra have been reduced by a factor of twenty for the bare and thin-plated samples.

Discussion

Although no sample retained more than a small fraction of the plasma exposure, nickel plating is found effective in further reducing the hydrogen uptake and retention. The low retention for all samples indicates surface recombination of the diffusing species is very rapid and eventually results in a hydrogen release approaching the implant rate. The addition of Ni further increases the release rate, probably by increasing density of recombination sites. Following recombination, D_2 (HD) gas molecules are released from these sites into the gas phase. Vacated sites are apparently refilled preferentially by diffusing species rather than from the overpressure gas. This is in agreement with the dynamics of the Baskes model [4].

Although gas analysis showed partial pressures of water vapor and other oxidizing species were of sufficient quantities to rapidly reoxidize exposed Ti atoms on the surface, the plasma appears effective in keeping these sites active. The net result is that implanted hydrogen is released and the overpressure hydrogen gas is not absorbed. This results in a low average hydrogen saturation level within the bulk. The surface concentration under the test conditions is greater than the average concentration since the D diffusion distance is only about half the sample thickness. This concentration is expected to be both flux and temperature dependent. Additional studies will be required to characterize these dependences.

Conclusions

From this study it is concluded that if they remain intact, Ni-plating layers on the Ti-3Al-2.5V alloy at 400K will enhance embrittlement protection from the normal hydrogen plasmas expected in tokamaks. No additional hydrogen appears introduced into the alloy by the Ni plating process and no significant uptake occurs from the background gas overpressure. A thick plating provides better plasma protection for high fluence, since thin platings may not withstand the normal plasma erosion. The estimated annual sputter erosion for $2x10^{22}$ D^+/cm^2 at 400 eV (sputter coefficient = .033 Ni/ion [2] at normal incidence) is about 70 microns. Additional erosion 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.

It should also be noted that if D retention is controlled by surface recombination, as suggested by these results, then the beneficial, enhanced-release effect of Ni may be negated by the addition of a low-Z plasma facing coating over the Ni-plating or by coatings of redeposited material. The effects of such additional coatings should be tested prior to use.

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. Roth, J. Nucl. Materials 176-7, 132 (1990).
3. R.J. Wasilewski and G.L. Kehl, Metallurgia 50, 225 (1954).
4. M.I. Baskes, J. Nucl. Mater. 92, 318 (1980).

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