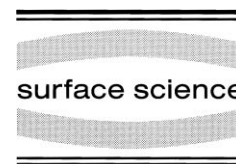




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The effect of a nitrogen-rich surface layer on the sub-surface deuterium (hydrogen) concentration distribution in titanium

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Abstract

Deuterium and nitrogen depth profiles in Ti with modified surfaces have been measured with Auger electron spectroscopy, secondary ion mass spectroscopy, and $D(^3\text{He},p)^4\text{He}$ nuclear reaction analysis. Nitrogen-rich surface layers of varying thicknesses were created on Ti by exposure to N_2 gas at 650°C . Deuterium loading was performed by exposure to 1 Torr of D_2 gas at 500°C . The deuterium distribution was influenced by nitrogen in the near-surface regions of all samples. Specifically, deuterium solubility was suppressed in surface regions of high (greater than 1%) nitrogen concentration. The deuterium solubility also remained low within the first few microns, well beyond the region of high nitrogen concentration. This effect is attributed to internal elastic stresses imposed by the non-deuterium absorbing nitrogen-rich layer on the Ti. These stresses prohibit the volume expansion associated with deuterium absorption. We estimate stresses on the order of 3–4 GPa are required to suppress the deuterium solubility to the values observed. The deuterium absorption kinetics were observed to depend systematically on the thickness of the nitrogen-rich layer. This is consistent with limited solubility near the surface or a surface poisoning effect influencing the overall deuterium diffusion from the gas phase into the Ti bulk. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Auger electron spectroscopy; Deuterium; Diffusion and migration; Hydrogen molecule; Nitrides; Nuclear reaction analysis; Secondary ion mass spectroscopy; Titanium

1. Introduction

The need for a quantitative study of the effect of nitride layers on the equilibrium hydrogen depth profile and absorption kinetics in Ti originates from both practical and fundamental concerns. Nitrogen, oxygen and carbon impurities are always present in the first few hundred angstroms of a Ti surface because of the extreme reactivity of tita-

nium to gases [1]. The existence of these impurities is important since hydrogen absorption kinetics in Ti, one of many possible hydrogen storage media [2], is strongly dependent on the surface [1,3]. In addition, bulk nitrogen impurities are known to modify hydrogen solubility in Ti [2–6].

The effect of pre-absorbed nitrogen and of a hydrogen–nitrogen gas mixture on the hydrogen absorption in a Ti particle bed has been studied by Fukada et al. [3]. The evaluation of nitrogen toxicity on the hydrogen absorption was made by chromatography analysis of the inlet and outlet gas from the sample column. Both the time dependency of the hydrogen absorption and total quan-

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tity of absorbed hydrogen were measured. The effect of flowing $H_2 + N_2 + Ar$ was found to depend on temperature and N_2 concentration in the gas. For example, the hydrogen absorption was reduced by a factor of 1.6 for 0.3 at.% N_2 at $600^\circ C$, while at $400^\circ C$ in the same flow mixture, hydrogen absorption was reduced to zero [3]. Pre-exposure to N_2 gas also decreased the absorbed hydrogen concentration by 20–30% [3]. The only explanation given by Fukada et al. is qualitative and based on the formation of a nitride film on the surface. However, X-ray diffraction did not indicate the formation of nitrides below $800^\circ C$, perhaps because the layers were too thin. No analysis of the surface and depth composition in the Ti material was performed.

In a separate study, measurements of the hydrogen and deuterium solubility in TiN_x samples, with 5–15 at.% nitrogen homogeneously distributed and exposed to H_2 or D_2 gas at pressures below 1 Torr over a temperature range of 600 – $850^\circ C$, are reported by Yamanka et al. [5]. The solubilities of hydrogen and deuterium were found to increase in the presence of nitrogen. A factor of two increase in solubility is reported for a $TiN_{0.176}$ alloy at $600^\circ C$. While the authors did not propose an explanation for this increase, it may be due to the formation of $N-H$ ($-D$) impurity couples in the Ti lattice.

The effect of nitrogen-rich subsurface layers, created by nitrogen ion implantation, on the hydrogen depth profile in Ti was studied by Farshi et al. using nuclear reaction analysis techniques [6]. These authors found that nitrogen ion bombardment redistributed hydrogen, an effect that may be the result of defect generation during implantation. Especially interesting was the apparent segregation of hydrogen in the subsurface region with the heaviest ion-induced damage [6].

The concurrent measurements of the nitrogen and deuterium depth profiles in Ti samples pre-exposed to N_2 gas are reported here. The purpose of this work was to conclusively establish the correlation between hydrogen (deuterium) and nitrogen in the near-surface region of Ti. In addition, the deuterium absorption kinetics were recorded and demonstrate the effect of a nitrogen-rich surface layer on deuterium transport into bulk Ti.

2. Experimental

Ti samples with a typical mass of 0.2 g were prepared from 0.025 cm thick foil, supplied by Johnson Matthey Aesar, in a multi-step process. First, the samples were cleaned in a solvent and loaded into quartz tube that was part of a stainless-steel gas manifold system. This system was evacuated at room temperature under a vacuum of 10^{-9} Torr for 12 h. The samples were then annealed at $800^\circ C$ for 12 h in a vacuum of 10^{-8} – 10^{-9} Torr. The purpose of this annealing step was to outgas the samples and induce recrystallization of the rolled foil. This procedure resulted in an average grain size of approximately $100\ \mu m$ and gave very reproducible deuterium absorption results. The temperature was next lowered to $650^\circ C$ under vacuum and samples exposed to 1 Torr of N_2 gas for a pre-determined amount of time with the system isolated (closed volume). This resulted in the creation of a nitrogen-rich surface layer with a Ti_2N composition (the measured N variation with depth will be presented in the next section). After N_2 gas exposure, the sample temperature was lowered to $500^\circ C$ under the N_2 gas. The system was then evacuated and purged under low D_2 gas pressure (approximately 0.02 Torr) for several minutes. The system was isolated and the samples exposed to 1 Torr of D_2 gas at $500^\circ C$. The samples were allowed to reach equilibrium with the D_2 gas. The deuterium concentration was determined from the total D_2 gas-pressure change in the closed volume of $2570\ cm^3$. Finally, the samples were cooled to room temperature under the equilibrium D_2 gas pressure. Deuterium did not outgas from the Ti samples after removal from the gas manifold. The samples prepared in this manner are identified by $Ti/N\text{-xxx}/D$, where xxx is the N_2 gas exposure time in minutes. A reference sample without N_2 gas exposure, $Ti/N\text{-000}/D$, was prepared and investigated as well. A second set of samples were prepared under identical conditions *without* exposure to D_2 gas and were identified by $Ti/N\text{-xxx}$. The purpose of this set of samples was to investigate the influence of D_2 gas exposure on the nitrogen profile. Sample characteristics, including

N_2 gas exposure time and total deuterium concentration, are given in Table 1.

Three techniques were used to determine nitrogen and deuterium depth profiles in the Ti samples, Auger electron spectroscopy (AES), secondary ion mass spectroscopy (SIMS), and $D(^3He, p)^4He$ nuclear reaction analysis. Accurate, absolute-concentration depth profiles for all elements, except deuterium, present in the Ti sample were measured using the PHI 660 AES instrument. Sputtering was performed at rates of 36 and 162 Å/min. The typical sputtered area was approximately $0.4 \times 0.4 \text{ mm}^2$, while the analysis spot size was approximately $0.1 \times 0.1 \text{ }\mu\text{m}^2$. The sputtering rate was calibrated using silicon; data provided by Commonwealth Scientific Corporation indicate that the Ar sputtering rate in Si is equal to that for Ti under the conditions used here [7]. The detection of nitrogen in Ti is complicated by the overlap of the nitrogen and Ti2 Auger electron signals. The nitrogen concentration profiles reported here were obtained from the difference in Ti concentration derived from the Ti1 and Ti2 signals [8].

A Cameca IMS 5f SIMS instrument was used to track nitrogen (at lower concentration values) and deuterium. A Cs^+ ion beam at a current of 50 nA was used at two sputtering rates, 279 and 569 Å/min. The beam raster areas were 250 by 250 μm^2 and 175 by 175 μm^2 , respectively, and the analyzed area was 30 by 30 μm^2 . This instrument can, in principle, measure any element, including hydrogen and deuterium, at concentrations as low as a few ppm. However, SIMS provides only relative values for the concentration of each element. The deuterium concentration profiles were normalized to the known bulk value at a depth where the SIMS response reached a steady state. The nitro-

gen concentration measured with AES was used to normalize the SIMS nitrogen concentration for each sample. The total SIMS-sputtered depth, and hence average sputtering rate, for each sample was measured with a DEKTAK 3030 profilometry instrument.

Complex interactions of the incident ion beam and/or sample matrix ions at the surface occur in the SIMS analysis. As a result, the measured signals can depend on sample and measurement conditions. One possible artifact of SIMS analysis of our samples is the suppression of the deuterium signal in regions of low nitrogen concentration. The $D(^3He, p)^4He$ nuclear reaction analysis technique was used to confirm the deuterium profiles obtained from SIMS. A 1.7 MeV Tandatron accelerator provided the source of $^3He^{+1}$ ions with typical currents of 10–40 nA. Measurements were performed at four or five incident 3He energies; 0.6, 0.65 (for sample Ti/N-180/D only), 0.8, 1.2, and 2.2 MeV. The beam size at the sample was 1 mm^2 . The sampling depth was varied from the near-surface up to approximately 4 μm by changing the incident 3He energy.

3. Results

Preliminary AES measurements showed that samples annealed in vacuum, as described above, without subsequent N_2 or D_2 gas exposure, had C, N and O impurity concentrations falling to values below the sensitivity of the instrument (1%) within the first few hundred angstroms of the surface. Significant nitrogen levels, extending thousands of angstroms from the surface were observed in samples exposed to N_2 gas. The room-temperature AES measurements of the nitrogen depth

Table 1
Ti sample characteristics

| Sample | N_2 gas exposure time, T_N (min) | Deuterium absorption time constant, τ (1/s) | Deuterium concentration [D]/[Ti] |
|------------|--------------------------------------|--|----------------------------------|
| Ti/N-000/D | 0 | 204.0×10^{-5} | 0.048 |
| Ti/N-011/D | 11 | 24.0×10^{-5} | 0.048 |
| Ti/N-045/D | 45 | 5.9×10^{-5} | 0.046 |
| Ti/N-090/D | 90 | 2.4×10^{-5} | 0.046 |
| Ti/N-180/D | 180 | 0.6×10^{-5} | 0.037 |

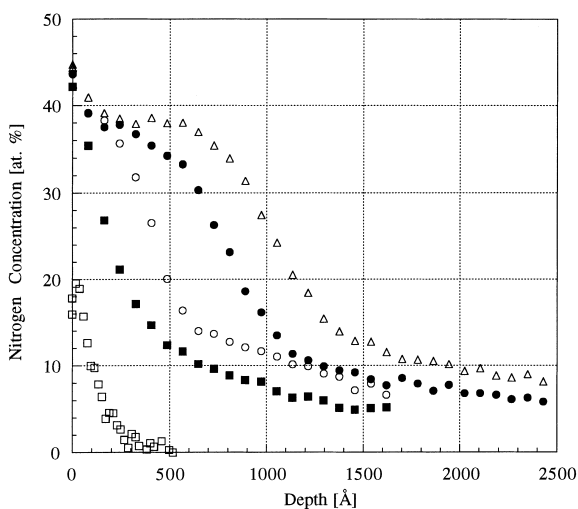


Fig. 1. Nitrogen depth profiles in Ti/N-000/D (open boxes), Ti/N-011/D (solid boxes), Ti/N-045/D (open circles), Ti/N-090/D (solid circles), and Ti/N-180/D (open triangles) measured with AES.

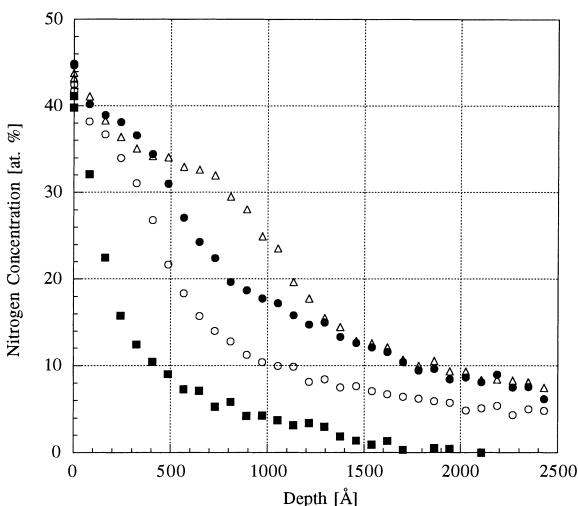


Fig. 2. Nitrogen depth profiles in Ti/N-011 (solid boxes), Ti/N-045 (open circles), Ti/N-090 (solid circles), and Ti/N-180 (open triangles) measured with AES. The profile for Ti/N-000 was not measured.

profile for the samples exposed and not exposed to D_2 gas are shown in Figs. 1 and 2, respectively. In general, D_2 gas exposure does not significantly alter the nitrogen depth profile. The variation of the nitrogen depth profile at different locations on the Ti/N-180/D surface is shown in Fig. 3. This

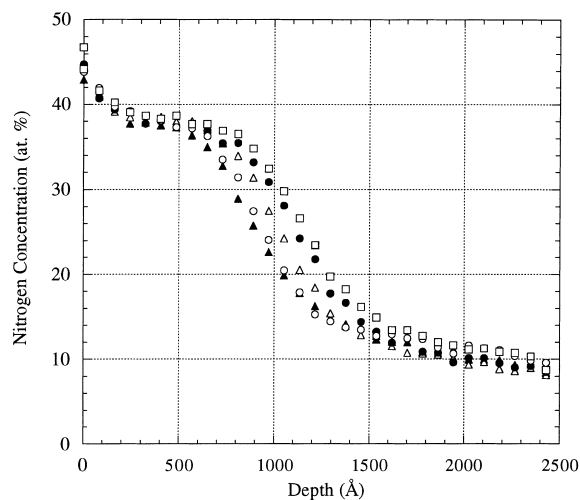


Fig. 3. Variation in nitrogen depth profile for Ti/N-180/D observed with AES at different locations on the sample surface.

spread in the near-surface profile was typical of the samples investigated here and is thought to be due to variations in the orientation of individual Ti grains affecting either the sputtering rate or the progression of nitrogen into the sample. The formation and progression of a plateau, corresponding to a Ti_2N composition, can be observed in Figs. 1 and 2. The evolution of this plateau with time is characterized by an effective diffusion constant, $D_N \cong L^2/4T_N$, where L is the characteristic thickness of the layer (arbitrarily defined here as the thickness corresponding to 20% nitrogen concentration), and T_N is the N_2 gas exposure time. The data from all four samples are well represented by $D_N \cong 3 \times 10^{-15} \text{ cm}^2/\text{s}$. This is approximately a factor of three smaller than the diffusion coefficient for nitrogen in TiN quoted by McQuillan and McQuillan [9], consistent with nitrogen diffusion through the Ti_2N surface layer dominating the kinetics.

The combined nitrogen and deuterium depth profiles measured simultaneously with SIMS at room temperature are shown in Figs. 4–8 for Ti/N-000/D, Ti/N-011/D, Ti/N-045/D, Ti/N-090/D, and Ti/N-180/D, respectively. As mentioned previously, the nitrogen concentration has been placed on an absolute scale by normalization with respect to the AES measurements, while the deuterium concentrations have been normalized to

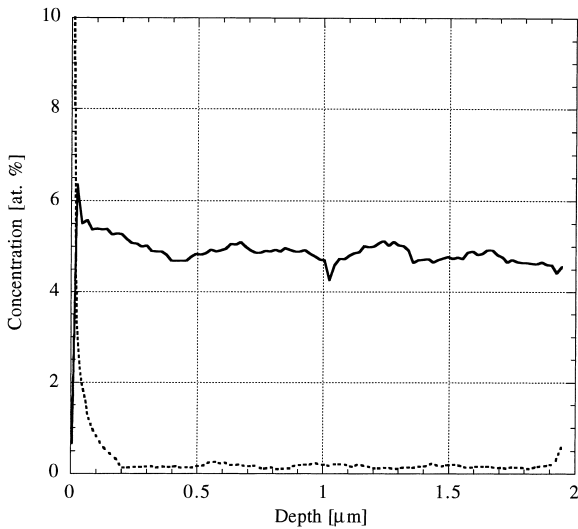


Fig. 4. Nitrogen (dotted line) and deuterium (solid line) depth profiles in Ti/N-000/D measured with SIMS.

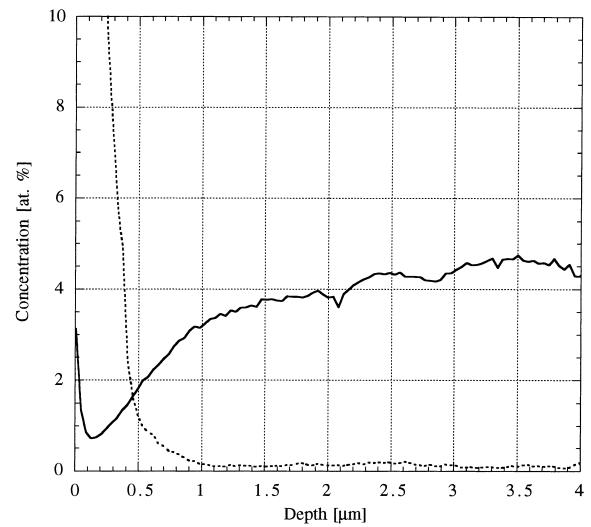


Fig. 6. Nitrogen (dotted line) and deuterium (solid line) depth profiles in Ti/N-045/D measured with SIMS.

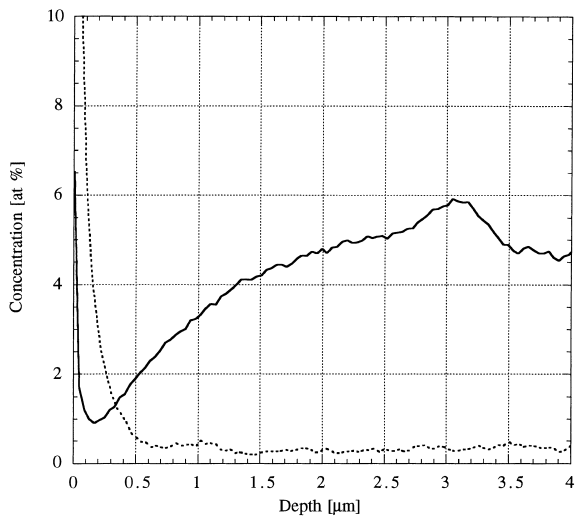


Fig. 5. Nitrogen (dotted line) and deuterium (solid line) depth profiles in Ti/N-011/D measured with SIMS.

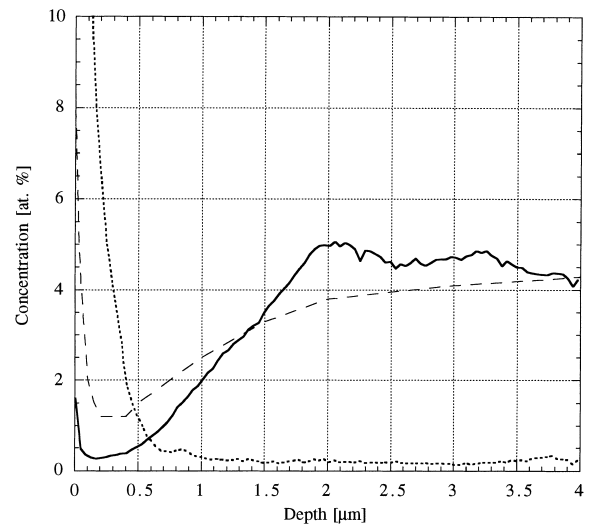


Fig. 7. Nitrogen (dotted line) and deuterium (solid line) depth profiles in Ti/N-090/D measured with SIMS. The deuterium profile obtained from deconvolution of $D(^3\text{He}, p)^4\text{He}$ nuclear reaction analysis data (dashed line) is also shown.

the known bulk values. Notice that the deuterium concentration is very low in the near-surface regions of all samples where high levels of nitrogen are present. This is consistent with low deuterium solubility in TiN_x ($0.1 \leq x \leq 1$) alloys. However, the deuterium concentration does not reach the bulk level until a depth of at least a few microns, well beyond the region of significant nitrogen

concentration. This unexpected suppression of deuterium solubility, especially evident in Ti/N-090/D and Ti/N-180/D, was our motivation to perform an independent measurement of the deuterium depth profile. Figs. 7 and 8 include the deconvoluted $D(^3\text{He}, p)^4\text{He}$ nuclear reaction

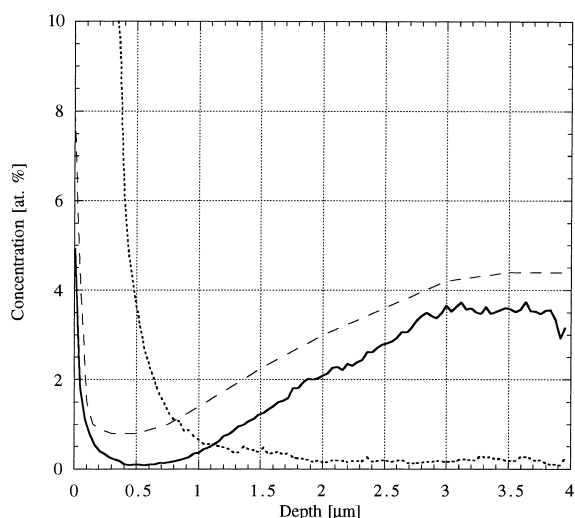


Fig. 8. Nitrogen (dotted line) and deuterium (solid line) depth profiles in Ti/N-180/D measured with SIMS. The deuterium profile obtained from deconvolution of $D(^3\text{He,p})^4\text{He}$ nuclear reaction analysis data (dashed line) is also shown.

analysis data, confirming, albeit with a poorer depth resolution, the suppression of the deuterium concentration observed with SIMS.

A similar trend in the deuterium depth profile was observed in a sample with an approximately 2 μm thick TiN layer fabricated by chemical vapor deposition (CVD) and supplied by the Goodfellow Corporation of Cambridge, UK. Deuterium loading of this material, facilitated by removal of the TiN layer from one side of the sample by mechanical grinding, was carried out under the conditions described above (except without N_2 gas exposure). The nitrogen and deuterium depth profiles measured in this sample with SIMS are shown in Fig. 9. The peak in the deuterium depth profile at the TiN–Ti interface is attributed to interfacial trapping of the interstitial solute. As with the samples fabricated by N_2 gas exposure, the deuterium solubility in the CVD sample is reduced well beyond the depth at which the nitrogen concentration goes to zero. We therefore consider the deuterium solubility behavior observed in the vicinity of nitrogen-rich surface layers to be generic, independent of the procedure used to create the nitrogen-rich surface layer.

4. Analysis and discussion

The suppression of the deuterium solubility in regions of very low nitrogen concentration contradicts the results discussed in Section 1, namely an increase in hydrogen solubility in the presence of low concentrations of uniformly distributed nitrogen [5]. However, the nitrogen in our samples is not uniformly distributed. The observed deuterium solubility behavior is thought to be due to the non-absorbing, nitrogen-rich surface layer; the volume expansion associated with deuterium absorption in the Ti matrix is inhibited in the regions adjacent to this surface layer. The non-absorbing surface layer elastically constrains the adjoining matrix, preventing the volume expansion required for deuterium incorporation into the Ti lattice. This elastic constraint would, in principle, propagate indefinitely and must be terminated by arrays of dislocations with predominately edge character.

The deuterium solubility behavior in the presence of an applied or internal stress, n_s , is given by

$$n_s = n \exp\left(\frac{-\sigma V_D}{RT}\right), \quad (1)$$

where n is the concentration in the absence of stress (given by Sievert's law for solid solutions), σ is the stress, V_D is the molar volume of deuterium in Ti (1.6 cm^3/mol [10]), T is the temperature, and R is the gas constant. The internal stress therefore varies logarithmically with the n_s/n ratio. At $n_s/n=0.1$, a typical value in the vicinity of the nitrogen-rich layer, the internal stress calculated using Eq. (1) is approximately 3.5 GPa. This stress is to be compared with the yield stress and shear modulus of pure Ti, 0.3 and 45 GPa, respectively. Significant internal stresses — well beyond the yield limit, but not exceeding the theoretical shear strength — are therefore required to suppress the deuterium solubility to the values observed here.

Deuterium absorption kinetics were found to vary systematically with N_2 gas exposure time. The D_2 gas pressure fell exponentially with time for all samples during deuterium loading. The

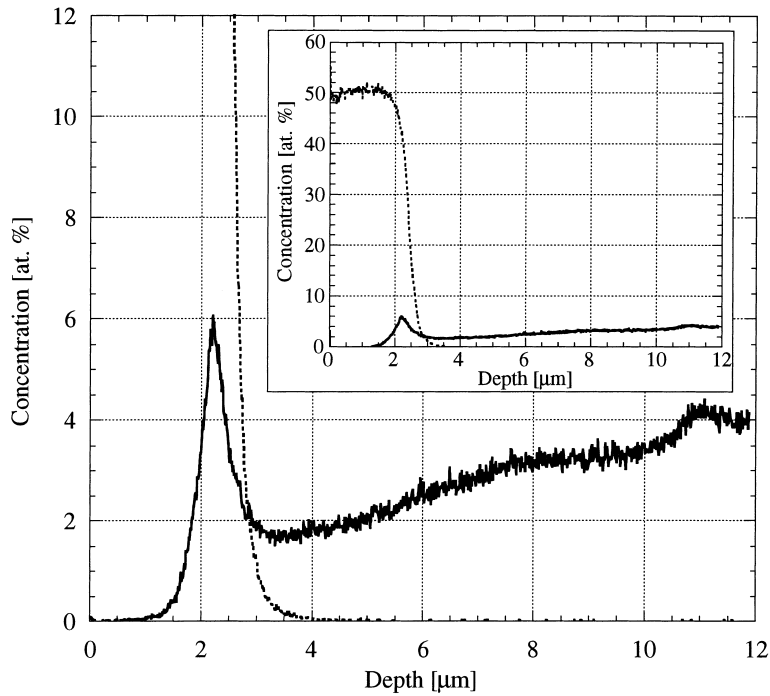


Fig. 9. Nitrogen (dotted line) and deuterium (solid line) depth profiles in the Ti/N-surface sample prepared using CVD measured with SIMS. The inset shows the profiles over a larger concentration range.

exponential rate constant, τ , is given by

$$\tau \cong \frac{\pi^2 D_D}{L^2} \cong \frac{\pi^2 D_D}{4D_N T_N} \quad (2)$$

where D_D is the effective deuterium diffusion coefficient. The right-hand side of Eq. (2) makes use of the correlation between the nitrogen-rich surface layer thickness (L), N_2 gas exposure time (T_N) and nitrogen diffusion coefficient (D_N) discussed previously. A plot of the exponential time constant observed during deuterium loading versus T_N^{-1} is shown in Fig. 10. The linear relationship for the three samples with the longest N_2 gas exposure times demonstrates that deuterium transport into the sample scales with the inverse of the N_2 gas exposure time. The downward deviation of Ti/N-011/D in Fig. 10 from the linear extrapolation of Eq. (2) to shorter exposure times indicates that deuterium mobility in this sample is not completely controlled by the nitrogen-rich surface layer.

One possible explanation for the observed

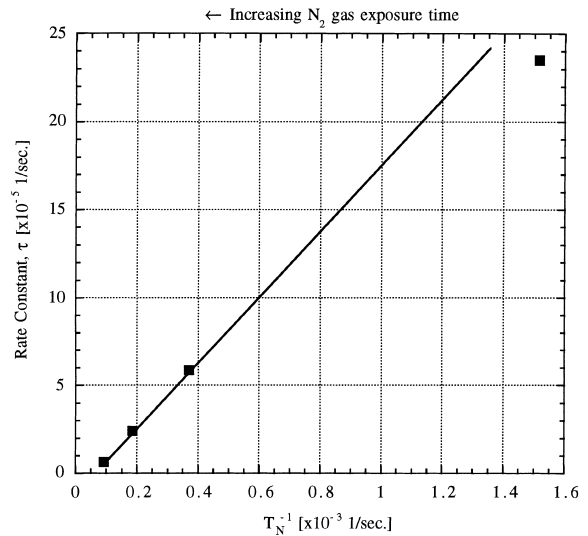


Fig. 10. Deuterium absorption exponential time constant, τ , versus T_N^{-1} the inverse of the N_2 gas exposure time. The linear behavior observed for the samples with the longest exposure is consistent with deuterium transport scaling with the nitrogen-rich surface layer thickness.

kinetic behavior is the suppression of deuterium solubility in the nitrogen-rich surface layer and extending region of elastic stress. Recall that the driving force for diffusion is the chemical potential gradient. Equilibrium during D_2 gas exposure implies equal deuterium chemical potential in all regions of the sample with respect to the D_2 gas. The approach to equilibrium (in other words, the absorption kinetics) will be influenced by suppressed deuterium solubility. The lower solubility limit in the nitrogen-rich surface layer and vicinity will be reached faster, thereby reducing the local chemical potential gradient. At the same time, the difference between the deuterium chemical potential in the gas phase and in the bulk Ti can remain high, still providing a driving force for deuterium diffusion. The stress-induced reduction in deuterium solubility that extends beyond the nitrogen-rich surface layer represents an additional permeation barrier on the overall mass transport of deuterium into the Ti bulk. This effect will exist in all metal–hydrogen systems with modified, non-hydrogen absorbing surfaces. A second effect that may influence the deuterium absorption kinetics is poisoning of the surface. The consistence of the absorption kinetic data with Eq. (2) indicates that such an effect must scale with the square of thickness of the nitrogen-rich surface layer. The presence of N_2 gas molecules, the logical source of surface poisoning, in the D_2 gas could very well depend on the nitrogen inventory in the near-surface regions of the sample. Such an effect would also be consistent with the work of Fukada et al. [3].

5. Conclusions

SIMS and AES measurements of the deuterium and nitrogen depth profiles in Ti with nitrogen-rich surfaces layers have been performed. Five samples were investigated in which the thickness of the modified surface layer was systematically increased by exposure to N_2 gas. Deuterium loading of the modified Ti samples was performed by exposure to 1 Torr of D_2 gas. The following conclusions are drawn from these measurements:

1. The nitrogen depth profiles measured with AES

are consistent with the progression of a Ti–N solid solution \rightarrow Ti_2N reaction from the surface inward as the N_2 gas exposure time is increased. The AES measurements also demonstrate that the nitrogen profile extends well into the sample at a relatively low concentration. Subsequent deuterium absorption does not alter the nitrogen depth profile.

2. The combined deuterium and nitrogen depth profiles measured with SIMS demonstrate that the deuterium solubility is suppressed in regions of high (greater than a few per cent) nitrogen concentration. Further, the deuterium concentration is reduced well beyond the measurable nitrogen concentration, especially for the two samples with the longest N_2 gas exposure time. This observation is attributed to a stress-induced suppression of the deuterium solubility caused by the non-deuterium absorbing nitrogen-rich surface layer. $D(^3He,p)^4He$ nuclear reaction analysis measurements confirm the deuterium depth profile and rule out the possibility that the SIMS profiles are an experimental artifact. A simple expression for this effect indicates that large internal stresses, of the order of 3–4 GPa, are required to suppress the deuterium solubility to the observed values.
3. The deuterium absorption kinetics were found to vary systematically with the thickness of the nitrogen-rich surface layer. The application of a one-dimensional diffusion model demonstrates that deuterium diffusion is influenced by the nitrogen-rich surface layer. The correlation between the deuterium absorption kinetics and N_2 gas exposure time is consistent with an effect that scales with the square of the thickness of the modified surface layer. We suspect that either (i) the limited deuterium solubility in the near surface region or (ii) a surface poisoning effect reduces the overall deuterium transport from the gas phase to the Ti bulk.

Acknowledgements

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