Nitriding of Titanium and Its Alloys by N₂, NH₃, or Mixtures of N₂ + H₂ in a dc Arc Plasma at Low Pressures (≤10 torr)

Reuven Avni
Lewis Research Center
Cleveland, Ohio

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Reuven Avni*
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

SUMMARY

The dc glow discharges in different gas mixtures of Ar + N₂, Ar + NH₃ or Ar + N₂ + H₂ result in the surface nitriding of Ti metal and its alloy (Ti6Al4V). Various gas mixtures were used in order to establish the main active species governing the nitriding process, i.e., N, N₂, NH, or NH₂ as excited or ionized particles. The dc discharge was sampled and analyzed by quadruple mass spectrometry (QPMS) and optical emission spectroscopy (OES) and the nitrided samples were analyzed by scanning electron microscopy (SEM) with an EDAX attachment, microhardness, and Fourier transform infrared reflectance spectrometry (FTIR). It was found that the excited and ionized nitrogen and hydrogen atoms are the main species responsible for the nitriding process in a dc glow discharge.

INTRODUCTION

In a plasma nitriding process of steels, Hudis (ref. 1) was the first to isolate the active plasma ingredients. Sampling the plasma by mass spectrometry, the ionized atoms and molecules in the cathode region (in an inductive rf plasma of N₂ + H₂, Ar + N₂ + H₂ or Ar + N₂ at low pressures), Hudis (ref. 1) attributed to ionized species, bombarding the steel surface, the main role in the nitriding process of steels; specifically to the ΣNH positive ions (NH⁺, NH₃⁺, NH₄⁺, NH₅⁺, NH₆⁺ and N₂H₅⁺). Tibbetts (ref. 2) separated between the effects of ions and neutral species in the plasma (dc glow discharge of N₂ + H₂ mixtures) nitriding by introducing a grounded grid between the ±300 V anode and the ±300 V cathode. Tibbetts (ref. 2) concluded that neutral species of N atoms governs the nitriding process of steels rather than positive ions. Matsumoto et al. (refs. 3 to 5) investigating the plasma nitriding process (rf discharges in N₂ and N₂ + H₂ mixtures) of Ti, Zr and Si reached the conclusion that the absorption of nitrogen and NH⁺ in the surface is the rate determining step followed by the diffusion of nitrogen. Matsumoto et al. (refs. 4 to 5) reported the nitriding rates of Ti being larger in a N₂ + H₂ mixture than in a N₂ plasma.

From the above investigations (refs. 1 to 5) the species governing the surface nitriding of metals in a plasma process remains still an open question.

In the present investigation the plasma diagnostics was focused to answer the open questions of kinetics and mechanism of the plasma nitriding process of

*Ben Gurion University of the Negev, Beer Sheva, Israel and NRC-NASA Research Associate; presently at NRC-Negev, P.O. Box 9001, Beer Sheva, Israel.
titanium and its alloys. A dc glow discharge was sustained separately in gaseous mixtures of Ar + N₂; Ar + N₂ + H₂ and Ar + NH₃ between stainless steels (SS304) anode and cathode. The samples of Ti and Ti6Al4V were placed during the discharge on the cathode. Two general approaches were used in the investigation, namely:

(1) On-line approach in which the glow discharge plasma was sampled by: (a) QPMS for evaluating the kinetics of dissociation and formation of species in real time in the plasma and (b) optical emission spectroscopy (OES) in the near to cathode region for determining the excited species reaching the cathode and the Ti samples.

(2) Off-line approach in which the Ti nitride samples were analyzed for: (a) elemental distribution by SEM and EDAX; (b) by Fourier Transform IR (FTIR) in reflectance for the N-H stretch in the surface and (c) the microhardness of the Ti-N layer. It should be noted that no Auger Electron Spectrometry (AES) for surface and depth profiling, secondary ion mass spectrometry (SIMS) for hydrogen content and XPS for chemical bonding were used due to lack of time. The analysis will be performed later on in Israel on the nitrided samples, and reported in due time.

The following plasma's macrovariables were changed in this investigation: the gaseous mixtures, the gas pressure in the plasma reactor, the voltage and current of the discharge with and without Ti or Ti6Al4V samples on the SS304 cathode, in the order to find the influence of Ti samples on the dc glow discharge (ref. 6).

**EXPERIMENTAL**

The dc Glow Discharge Rig

The "rig" was planned and designed during the month of April 1983; in May the drawings (blueprints) were ready and went to the main machine shop for fabrication. In August 83 the fabrication was finished and the "rig" assembling started September 83 and ended in December 83. During January to February 84 the "rig" was tested. In March the experimental work on plasma nitriding began and continued until July 27, 1984.

Figure 1 shows the schematics of the "plasma rig". The gases used (Ar, N₂, H₂ and NH₃ UHP 99.999 percent, Matheson) were fed into the plasma reactor through flowmeters, mixed in a mixing chamber and a laminar flow was maintained. The dc power supply generates the discharge up to 1 kV and 200 mA through the SS304 anode with a surface of 5.0 cm²; the SS304 cathode with a surface of 11.4 cm² was grounded and mounted on a feedthrough which allows changes of the gap between the anode and the cathode. A rotary pump (two stages) and a valve maintained the pressure in the plasma reactor between 0.5 to 10.0 torr controlled by a thermocouple gauge. On the plasma reactor (in the line of sight) a differential pumping system (using a diffusion pump) was mounted between two nozzles; the first nearer to the plasma reactor with a diameter of 0.02 cm and the second has a diameter of 0.03 cm. On the second nozzle a quadruple mass spectrometer was mounted and its pressure controlled by an ionic pump. While the pressure in plasma reactor can be varied between 0.5 to 10.0 torr, the pressure in the differential pumping between the nozzles was of the order of 10⁻⁶ torr and the QPMS was maintained in the 10⁻⁷ torr pressure.
range. Due to this pressures regime the excited and ionized extracted particles, from the glow discharge reactor, passing through the two nozzles (in the line of sight) reach the ionization chamber of the QPMS. The extracted plasma particles will not interact between them after the first nozzle due to the mean free paths greater than $10^4$ cm in the differential pumping system and greater than $5 \times 10^4$ cm in the QPMS system. The particles reacting with the walls were lost and will not reach the QPMS.

The cathode region of the dc plasma system was focused through a quartz window and aligned on the entrance slit of a monochromator with an aperture, $f/4$, and spectral resolution of $10^{-4}$ nm. The photomultiplier (IP28) was operated at 900 V and the spectra recorded between 200 and 700 nm.

The Mass Spectra

The mass spectra output was recorded by an x-y scope equipped with a polaroid camera. Figure 2(a) shows the recorded mass spectra of an Ar + N$_2$ plasma. Starting from the left the following m/e were identified: 2, 14, 15, 16, 17, 18, 20, 27, 28, 29, 32, 37, 40, and 44. Because H$_2$ was not introduced to the plasma reactor the m/e 2, (H$^+$), 15 (NH$^+$), 16 (NH$^+$ or O$^+$), 17 (NH$^+$ or OH$^+$), 18 (H$_2$O$^+$) and 32 (O$_2^+$) were obtained from the dissociation of water vapor and oxygen from the reactor walls during the dc discharge. These mass peaks were present as well in the discharge of Ar + N$_2$ + H$_2$ and in the Ar + NH$_3$. To diminish the contamination from the reactor walls two mass spectra were recorded one without the discharge (ND) and the second with the discharge on (D). The results are always presented as the difference $I_D - I_{ND}$. In order to discern between NH$^+$ and H$_2$O$^+$ (m/e = 18) and N$_2$H$^+$ and O$_2^+$ (m/e = 32) discharges in Ar + N$_2$ + D$_2$ and Ar + NH$_3$ + D$_2$ were recorded. The presence of deuterium shifts the m/e for the formation of ND$_4$ to m/e = 22 and N$_2$D$_4$ to m/e = 36. Figure 2(b) shows the formation of those mass peaks as obtained on the polaroid camera while figure 3 shows the normalized concentration of the mass species obtained in Ar + N$_2$ + D$_2$ and Ar + NH$_3$ + D$_2$ discharges, at a pressure of 3.0 torr. The normalization was performed by measuring the intensity of each mass peak (I) and divided by the summation of all the mass peaks obtained ($\sum$ I) (Ar$^+$ peak excluded) in the same recorded mass spectra. The normalized concentrations ($I/\sum I$) is only relative, and represents in percent the mass species in the glow discharge, of a given gas mixture. To minimize the fragmentation of species in the quadruple's ionization chamber its electron energy was set at 50 eV for both ND (no discharge) and D (discharge) conditions. Figure 3 shows the formation and the isotopic shifts such as DH$^*$($^+$), NH$^*$($^+$), NH$_2$D$^*$($^+$), and N$_2$H$_2$D$^*$($^+$) excited radicals during the dc discharge. In the Ar + N$_2$ + D$_2$ discharge the dominant species formed are ND$_4^*$($^+$) and N$^*$($^+$) while in the Ar + NH$_3$ + D$_2$ mixture the N$_2$, NH$_2$D$_2$ and N have the highest concentration.

The Analysis of Ti-N Layer

The nitrided Ti and Ti6Al4V samples were analyzed by:

1. SEM + EDAX
2. FTIR Reflectance by Nicolet 7000 on a KSR-5 crystal, and
Microhardness VHN under a load of 25 g and expressed in kgf mm$^{-2}$.  

RESULTS AND DISCUSSION

The dc glow discharges of Ar $+$ N$_2$, Ar $+$ N$_2$ + H$_2$ and Ar $+$ NH$_3$ mixtures result in the nitriding of Ti and Ti6Al4V samples. The difference being the color and the microhardness (VHN$_{25}$) of the Ti-N layer. A deep yellow gold color was obtained in the Ar $+$ N$_2$ discharge and a lighter yellow gold color was obtained in both Ar $+$ N$_2$ + H$_2$ and Ar $+$ NH$_3$ discharges. The highest VHN$_{25}$ was obtained in the Ar $+$ N$_2$ + H$_2$ discharge for both Ti and Ti6Al4V samples.

On-Line Measurements

Formation of N atoms and positive ions ($N^{*+}$) in the glow discharge of the various gas mixtures are shown in figures 4 to 6 and table I. The normalized concentration (relative) of $N^{*+}$ in percent is expressed as the peak intensity ratio $I_{N}/I_{N_{2}}$ and $I_{N}/I_{NH_{3}}$. Figure 4 shows the highest value of $I_{N}/I_{N_{2}}$ in the Ar $+$ N$_2$ + H$_2$ (Ar/N$_2$ = 2/1 and H$_2$/N$_2$ = 1/1) mixture compared to the discharge in other gas mixtures such as: N$_2$ alone; N$_2$ + Ar; N$_2$ + H$_2$; NH$_3$ + H$_2$ and NH$_3$ + Ar. The discharge conditions, electrodes gap and gas pressure were kept constant for the different gas mixtures. The Ti6Al4V samples used were fresh and identical in size in each gas mixture.

Figure 5 shows the formation of $N^{*+}$ as influenced by the Ti samples in the glow discharge. The ratio of Ti samples surfaces to the SS304 cathode was kept constant at 0.8. The $I_{N}/I_{N_{2}}$ values are higher in the presence of Ti samples than on the SS304 cathode without Ti for all the gas mixtures, and reaches its maximum value in the Ar $+$ N$_2$ + H$_2$ mixture. In figure 6 the normalized dissociation rate of N$_2$ and NH$_3$ expressed as $1 - I/ZI$ is shown for the different gas mixtures with and without Ti samples on the cathode. The dissociation rate is enhanced by the Ti samples compared to the SS304 cathode without Ti in any gas mixture glow discharge. Both figures 5 and 6 indicate a higher Ti catalytic effect (ref. 6) in the glow discharge for the dissociation of N$_2$ and NH$_3$ and $N^{*+}$ formation, when compared to SS304 (ref. 6). The titanium's catalytic effect in the dissociation of N$_2$ and NH$_3$ and the formation of new excited and ionized species is directly shown in percent normalized concentrations in table I for Ar $+$ N$_2$, Ar $+$ N$_2$ + H$_2$ and Ar $+$ NH$_3$ gas mixtures.

The kinetics of dissociation ($k_d$) and formation ($k_f$) in the dc glow discharge is shown for Ar $+$ N$_2$ + H$_2$ in figure 7 and for Ar $+$ NH$_3$ in figure 8 as normalized concentration $I/ZI$ versus the gas pressure in the plasma reactor with Ti samples on the SS304 cathode (surface ratio 0.8). In figure 7 the dissociation of both N$_2$ and H$_2$ molecules increases with increasing gas pressure while the formation of N, NH$_2$, NH$_3$, NH$_4$ and N$_2$H$_4$ excited and ionized species increases with increasing pressure. The behavior of the dissociation and the formation follows a pseudo first order kinetics. (The rate constants $k_d$ and $k_f$ for each particle will be evaluated later on in Israel and will be reported. (as soon as possible). The same behavior is shown in figure 8 for the Ar $+$ NH$_3$ mixture; the dissociation of NH$_3$, NH$_2$ and NH$_4$ decreases with increasing gas pressure while the formation of N$_2$, N and N$_2$H$_4$ increases with increasing pres-
Both $k_d$ and $k_f$ for each particle shows a more complex behavior when compared to the glow discharges in Ar + $N_2 + H_2$ (fig. 7).

Excited and ionized particles reaching the sample surface are shown in table II (from QPMS measurements) and in table III (from OES measurements of spectral line and band intensities). The values in table II are expressed as normalized concentration of particles in percent and as partial pressure in the dc glow discharge. Following Hudis (ref. 1) the normalized concentrations are given as a summation of the excited and ionized particles as indicated in table II. The $\Sigma_{N_{NH}}$ values reaching the sample surface is higher in the Ar + $NH_3$ plasma as compared to the Ar + $N_2 + H_2$ plasma while the highest concentration of hydrogen particles $I_{H_2}$ was obtained in the Ar + $N_2 + H_2$ plasma.

The spectral lines and bands intensity of Ar, $N_2$, $N_3$, N, H and NH are shown in table III as a ratio for the same excited or ionized particle (at same wavelength) in the Ar + $N_2 + H_2$ plasma and Ar + $N_2$ or Ar + $NH_3$ plasmas. The spectral intensity ratio $I_1/I_2$ is shown in figure 9 as related to the ratio of (the same) particle concentration $n_1/n_2$. Accordingly the highest concentration of $N_3$, and N was obtained in the Ar + $N_2 + H_2$ discharge while the highest concentration of NH was obtained in the Ar + $NH_3$ plasma. The highest concentration of $H_2$ was obtained in the Ar + $N_2 + H_2$ plasma; compared to the other gas mixtures.

Summarizing the on-line measurements it was found that the Ar + $N_2 + H_2$ plasma supplies the highest relative concentration of excited and ionized N, $N_3$ and H while the Ar + $NH_3$ discharge supplies the highest relative concentration of excited and ionized $\Sigma_{NH}$. Because both Ar + $N_2 + H_2$ and Ar + $NH_3$ plasmas nitrided the Ti and Ti6Al4V samples the uncertainty of which particle govern the nitriding process N, $N_3$ and H or $\Sigma_{NH}$ remain unresolved? The off-line measurements will supply a partial answer.

**OFF-LINE MEASUREMENTS**

**Microhardness of Ti-N Layer**

Table IV shows the values of microhardness expressed as Vickers using a 25 g load in kgf mm$^{-2}$. Each sample was measured in five different locations on the surface taken at random. The highest VHN value for either Ti or Ti6Al4V nitried samples were obtained in the Ar + $N_2 + H_2$ plasma, about 6.5 times harder than Ti sample treated in Ar plasma and about five times harder than Ti6Al4V sample treated only in the Ar plasma. The Ar plasma was applied for a 1.0 hr period. This treatment of only Ar plasma was used as standard procedure for cleaning the surface of the Ti and Ti6Al4V samples prior to nitriding in the Ar + $N_2$, Ar + $N_2 + H_2$ or Ar + $NH_3$ discharges. The harder nitride layer obtained in the Ar + $N_2 + H_2$ plasma compared to Ar + $N_2$ gas mixtures was re-reported earlier (refs. 1 to 5).

**Edax - Elemental Analysis**

Figures 10(a) to (d) shows an example of an EDAX spectrum taken on a nitried Ti sample (R59); N, Si and Fe are shown besides the strong Ti lines.
EDAX spectra taken for the nitrided Ti or Ti6Al4V samples in the different gas mixtures discharges show no significant differences. The reason for the almost identical spectra stems from the EDAX techniques in which the X-rays penetrates about 3 μm below the nitrided surfaces. The SEM + EDAX analysis made on Ti-N crosssections show a layer thickness ranging between 2 to 3 μm after a maximum nitriding period of 6 hr. The only difference in the EDAX spectrum was obtained when an air leak was introduced in the Ar + N₂ plasma. The presence of O in the Ti-N sample (R-63) is clearly shown in figure 10(a) and a segregation of S and Fe from the Ti bulk towards the Ti-N surface was measured in figures 10(b) and (c), respectively. It may be concluded that for a 6 hr nitriding period the presence of O₂ in the Ar + N₂ plasma enhances the elemental segregation toward the surface.

Fourier Transform IR Reflectance

The IR reflectance spectra are shown in figures 11 to 13 for Ti samples nitrided in Ar + N₂, Ar + N₂ + H₂ and Ar + NH₃, respectively. The same behavior of the IR reflectance spectra were obtained for the nitrided Ti6Al4V samples.

In the Ar + N₂ plasma no N-H bonds were detected in the IR reflectance spectra of the Ti-N surface (fig. 11). The IR reflectance spectra show the N-H stretch only on the Ti samples nitrided in Ar + NH₃ plasma (fig. 12) and in the Ar + N₂ + H₂ plasma (fig. 14). Moreover, the highest absorbance of the N-H stretch was obtained in the Ti samples nitrided in the Ar + N₂ + H₂ discharge (fig. 13) and not as expected in the Ar + NH₃ discharge (fig. 12). The amplification of the N-H bond in the Ar + N₂ + H₂ mixtures is the most important result of the FTIR technique for the nitrided Ti or Ti6Al4V samples for the following reasons:

1. If the NH excited or ionized particles would be responsible for the nitriding process of titanium it would be expected to have the highest IR absorbance of the N-H bond. The Ar + NH₃ plasma which produces the highest relative concentrations of ΣNH particles (tables I to III) shows a smaller N-H bond (fig. 12) than the one measured in the Ar + N₂ + H₂ discharge, indicating that not the ΣNH excited or ionized particles dominate the nitriding process.

2. The Ar + N₂ + H₂ discharge produces the highest relative concentration of excited and ionized N (tables I to III) and the highest relative concentration of H atoms (atoms) as shown in table III. Both N and H particles are responsible for the highest IR-absorbance of N-H bonds shown in figure 13.

The results shown in figure 13 for the N-H bonding in the Ti-N layer should be crosschecked by other surface techniques besides the FTIR, namely by SIMS in which the hydrogen content in the Ti-N layer can be analyzed both on the surface and depth profiling. The SIMS technique was not available.

REFERENCES


TABLE I. - MASS SPECTRA IN THE GLOW DISCHARGE WITH AND WITHOUT TITANIUM SAMPLES (AT THE CATHODE)

[Cathode SS304; \( \phi = 1.5 \) in; \( S_1 = 11.4 \) cm\(^2\); titanium \( S_2 = 2(3.0 \times 1.5 \) cm\(^2\) = 9.0 cm\(^2\); \( P_R = 4 \) to 4.5 torr; \( P_{QP} = 3 \times 3.2 \times 10^{-6} \) torr; \( eE = 50 \) eV; gap = 1.5 cm; \( t = 2 \) hr.]

<table>
<thead>
<tr>
<th>m/e</th>
<th>Gas mixture</th>
<th>SS304 + Ti</th>
<th>SS304 + Ti</th>
<th>SS304 + Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ar + N(_2) (4:1)</td>
<td>15.9</td>
<td>10.6</td>
<td>30.0</td>
</tr>
<tr>
<td></td>
<td>Ar + N(_2) + H(_2) (4.5/1; 2.5/1)</td>
<td>6.0</td>
<td>10.8</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>Ar + NH(_3) (2:1)</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>I/(\Sigma), percent</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(_2)</td>
<td></td>
<td>30.0</td>
<td>30.0</td>
<td>22.8</td>
</tr>
<tr>
<td>N</td>
<td></td>
<td>6.0</td>
<td>10.8</td>
<td>1.8</td>
</tr>
<tr>
<td>NH</td>
<td></td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>NH(_2)</td>
<td></td>
<td>1.8</td>
<td>3.7</td>
<td>28.6</td>
</tr>
<tr>
<td>NH(_3)</td>
<td></td>
<td>4.6</td>
<td>5.6</td>
<td>34.9</td>
</tr>
<tr>
<td>NH(_4)</td>
<td></td>
<td>4.0</td>
<td>5.3</td>
<td>5.1</td>
</tr>
<tr>
<td>N(_2)</td>
<td></td>
<td>69.5</td>
<td>50.9</td>
<td>12.1</td>
</tr>
<tr>
<td>N(_2)H(_4)</td>
<td></td>
<td>2.2</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>N(_3)</td>
<td></td>
<td>1.0</td>
<td>0.8</td>
<td>1.2</td>
</tr>
<tr>
<td>dc</td>
<td>450 V; 130 to 150 mA</td>
<td>420 V; 100 to 120 mA</td>
<td>400 V; 100 to 120 mA</td>
<td></td>
</tr>
</tbody>
</table>

m/e: 20 (Ar\(^{++}\)); 29; 31; 38; not in the \( \Sigma \).
TABLE II. - NORMALIZED CONCENTRATIONS OF EXCITED PLUS IONIZED SPECIES IN THE dc DISCHARGES (ID - IN0) TO THE PARTIAL PRESSURES IN THE GAS FEED

[Sample Ti6Al4V, 5.0 cm²; Pr = 5 torr; electrodes gap, 1.5 cm; 400 V, 120 mA; Pgp = 2.4 x 10⁻⁶ torr; eE = 50 eV; t = 1 hr.]

<table>
<thead>
<tr>
<th>Gas mixture feed</th>
<th>$\frac{I_{IN}}{I_1}$</th>
<th>$\frac{I_{IN}^a}{I_{N_2}^a + I_{H_2}^a}$</th>
<th>$\frac{I_{H_2}}{I_{N_2}^a + I_{H_2}^a}$</th>
<th>$\frac{I_{NH}}{I_{NH_2}^a + I_{NH_2}^b}$</th>
<th>$\frac{I_{NH}}{I_{NH_2}^b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar + N₂ 2:1</td>
<td>66 percent</td>
<td>88 percent</td>
<td>40 percent</td>
<td>63 percent</td>
<td></td>
</tr>
<tr>
<td>Ar + H₂</td>
<td>2.10 torr</td>
<td>2.2 torr</td>
<td>1.2 torr</td>
<td>1.56 torr</td>
<td>15 percent</td>
</tr>
<tr>
<td>Ar + NH₃ 1:1</td>
<td>67 percent</td>
<td>2 percent(c)</td>
<td>18 percent(c)</td>
<td>0.38 torr</td>
<td>73 percent</td>
</tr>
<tr>
<td>Ar + N₂ + H₂</td>
<td>2.50 torr</td>
<td>2 percent(c)</td>
<td>18 percent(c)</td>
<td>1.82 torr</td>
<td></td>
</tr>
</tbody>
</table>

\[ a \frac{I_{IN}}{I_1} = \frac{I_{N}^+ + I_{N_2}^+ + I_{N_3}^+}{I_1} \]

\[ b \frac{I_{NH}}{I_{NH_2}} = \frac{I_{NH}^+ + I_{NH_2}^+ + I_{NH_3}^+ + I_{NH_4}^+}{I_{NH_2}^b} \]

\[ ^c \text{Martin Hudis (ref. 1) - Positive Ions Ratio (Ar^+ = 33 percent): } a = 10^{-4} - 10^{-5} \left( \frac{I_1}{I_1^0} \right) \]
TABLE III. - SPECTRAL INTENSITY RATIOS FOR THE SAME EXCITED SPECIES IN THE VARIOUS dc DISCHARGES IN THE CATHODE REGION

[No Ti samples; 400 V; 150 mA; Pr = 5 torr; gap 1.0 cm.]

<table>
<thead>
<tr>
<th>Excited species</th>
<th>nm</th>
<th>$I_{\text{Ar}+\text{H}_2+\text{N}<em>2}/I</em>{\text{Ar}+\text{N}_2}$</th>
<th>$I_{\text{Ar}+\text{H}_2+\text{N}<em>2}/I</em>{\text{NH}_3+\text{Ar}}$</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar$_{\text{ms}}$</td>
<td>415.8</td>
<td>1.0</td>
<td>1.0</td>
<td>Ar$^+$ was not detected</td>
</tr>
<tr>
<td>N$_2$</td>
<td>380.5</td>
<td>1.0</td>
<td>3.0</td>
<td>In each plasma $I_{N_2} &gt; I_{N_2}^+$</td>
</tr>
<tr>
<td>C$_3$ - B$_3$</td>
<td>391.4</td>
<td>2.2</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>N$_2^+$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B$_2^+$ - X$_2^+$</td>
<td>411.0</td>
<td>2.5</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>434.1</td>
<td>&gt; 10</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>NH</td>
<td>336.0</td>
<td>&gt; 10</td>
<td>0.6</td>
<td>Same ratios for the 0$_v$ = 0 (1-1) at 337.0 nm</td>
</tr>
</tbody>
</table>

Ar + N$_2$ + H$_2$ (Ar/N$_2$ = 2 : H$_2$/N$_2$ = 1).
Ar + NH$_3$ (Ar/NH$_3$ = 1).
Ar + N$_2$ (Ar/N$_2$ = 2).
TABLE IV. - MICROHARDNESS OF THE Ti-N SURFACE

[VHN 25 g load (kgf mm⁻²); 5/sample.]

<table>
<thead>
<tr>
<th>Process</th>
<th>VHN (kgf mm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti/Ar plasma</td>
<td>260 to 300</td>
</tr>
<tr>
<td>Ti₆A₁₄V/Ar plasma</td>
<td>350 to 400</td>
</tr>
<tr>
<td>Ti/Ar + N₂</td>
<td>1200 + 150</td>
</tr>
<tr>
<td>Ti₆A₁₄V/Ar + N₂</td>
<td>1400 + 100</td>
</tr>
<tr>
<td>Ti/Ar + NH₃</td>
<td>1500 + 50</td>
</tr>
<tr>
<td>Ti₆A₁₄V/Ar + NH₃</td>
<td>1600 + 100</td>
</tr>
<tr>
<td>Ti/Ar + N₂ + H₂</td>
<td>1700 + 100</td>
</tr>
<tr>
<td>Ti₆A₁₄V/Ar + N₂ + H₂</td>
<td>1800 + 50</td>
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Figure 1. - d.c. Plasma rig - schematic.

Figure 2. - Examples of QPMS spectra of d.c. glow discharge.
Figure 3. - Normalized concentrations (I/I\textsubscript{0}) of m/e's in dc glow discharges. Ar/N\textsubscript{2} = 4/1; D\textsubscript{2}/N\textsubscript{2} = 3/1; Ar/NH\textsubscript{3} = 2/1; D\textsubscript{2}/NH\textsubscript{3} = 1/1; P\textsubscript{R} = 3.0 torr; P\textsubscript{QP} = 9 \times 10^{-7} torr; eE = 70 ev.
Figure 4. - Normalized concentration of N (atom + ions) in the different gas mixtures.

- **A.** $N_2$
- **B.** $N_2 + Ar$ (1:2)
- **C.** $N_2 + H_2$ (1:1)
- **D.** $N_2 + H_2 + Ar$ (1:1:2)
- **E.** $NH_3 + H_2$ (1:1)
- **F.** $NH_3 + Ar$ (1:1)

**Parameters:**
- $P_R = 5.0$ torr
- $V = 400$ V; $I = 150$ mA
- $T_{16} A 16$ cathode
- Gap = 1.5 cm

$I_N + I_{NH_3}^+$ (%)

![Graph showing normalized concentration of N (atom + ions) in different gas mixtures.](image-url)
Figure 5. - The influence of titanium samples on the normalized concentrations of N atoms (as + ions) in the different gas mixtures.
Figure 6. - The normalized dissociation rate of N₂ and NH₃ on titanium samples.
Figure 7. Normalized concentrations (I/I₀) versus gas pressure.
Figure 8. Normalized concentrations $I/I_{II}$ versus gas pressure.
\[ I_1 = \frac{h \nu}{4\pi} g A n_1 (\alpha_1) \frac{1}{\Sigma g_1} \exp \left( -\frac{\Delta E}{k T_1} \right) \]

1 = Ar + N_2 + H_2 mixture

\[ I_2 = \frac{h \nu}{4\pi} g A n_2 (\alpha_2) \frac{1}{\Sigma g_2} \exp \left( -\frac{\Delta E}{k T_2} \right) \]

2 = Ar + N_2 mixture

For an ionic spectral line, for example:

\[ \frac{I_1}{I_2} = \frac{n_1}{n_2} \frac{\alpha_1}{\alpha_2} \frac{\Sigma g_2}{\Sigma g_1} \exp \left( \frac{\Delta E}{k \left( \frac{1}{T_2} - \frac{1}{T_1} \right)} \right) \]

In which:

- \( I \) spectral line or band intensity
- \( \nu \) spectral frequency
- \( h \) Planck's constant
- g statistical weight of the spectral transition
- A transition probability (Einstein's coeff, spontaneous emission
- n total particle concentration of a given atom or molecule
  (i.e., \( n_{\text{atoms}} \) + \( n_{\text{molecules}} \) + \( n_{\text{ions}} \))
- \( \alpha \) degree of ionization
- 1-\( \alpha \) degree of neutrality (atoms or molecules)
- \( \Sigma g \) partition function
- \( \Delta E \) energy of the upper state (excited)
- \( k \) Boltzmann's constant
- \( T \) excitation temperature of the particle

Figure 9. - Correlations between spectral intensity and particle concentrations in the plasma-near-to-surface region.
Figure 10. - EDAX spectrum of the Ti-N sample (R59) and Ti-N-O sample (R63).
Figure 11. - FTIR reflectance spectrum of Ti-N sample in Ar + N₂ dc glow discharge.

Figure 12. - FTIR reflectance spectrum of Ti-N sample in Ar + NH₃ dc glow discharge.

Figure 13. - FTIR reflectance spectrum of Ti-N sample in Ar + N₂ + H₂ dc glow discharge.
**Title and Subtitle**

Nitriding of Titanium and Its Alloys by N₂, NH₃, or Mixtures of N₂ + H₂ in a dc Arc Plasma at Low Pressures (≤10 torr)

**Abstract**

The dc glow discharges in different gas mixtures of Ar + N₂, Ar + NH₃ or Ar + N₂ + H₂ result in the surface nitriding of Ti metal and its alloy (Ti6Al4V). Various gas mixtures were used in order to establish the main active species governing the nitriding process, i.e., N, N₂, NH₂, or NH₂ as excited or ionized particles. The dc discharge was sampled and analyzed by quadruple mass spectrometry (QPMS) and optical emission spectroscopy (OES), and the nitrided samples were analyzed by scanning electron microscopy (SEM) with an EDAX attachment, microhardness, and Fourier transform infrared reflectance spectrometry (FTIR). It was found that the excited and ionized nitrogen and hydrogen atoms are the main species responsible for the nitriding process in a dc glow discharge.

**Key Words (Suggested by Author(s))**

Nitriding
Titanium
Friction
Wear

**Distribution Statement**

Unclassified - unlimited
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