NASA-TM-83803 19850006859

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

November 1984

NASA

NITRIDING OF TITANIUM AND ITS ALLOYS BY N_2, NH_3, OR MIXTURES OF

N_2 + H_2 IN A dc ARC PLASMA AT LOW PRESSURES ($\leq$10 torr)

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

SUMMARY

The dc glow discharges in different gas mixtures of Ar + N_2, Ar + NH_3 or Ar + N_2 + H_2 result in the surface nitriding of Ti metal and its alloy (Ti6A14V). Various gas mixtures were used in order to establish the main active species governing the nitriding process, i.e., N, N_2, NH, or NH_2 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 N_2 + H_2, Ar + N_2 + H_2 or Ar + N_2 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 $\sum NH$ positive ions (NH^+, NH_2^+, NH_3^+, NH_4^+, NH_5^+ and $N_2H_2^+$). Tibbetts (ref. 2) separated between the effects of ions and neutral species in the plasma (dc glow discharge of N_2 + H_2 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 N_2 and N_2 + H_2 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 N_2 + H_2 mixture than in a N_2 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.

N85-15168#

titanium and its alloys. A dc glow discharge was sustained separately in gaseous mixtures of Ar + N_2; Ar + N_2 + H_2 and Ar + NH_3 between stainless steels (SS304) anode and cathode. The samples of Ti and Ti6A14V 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 than 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 Ti6A14V 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, N^2, H_2 and NH_3 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 cm^2; the SS304 cathode with a surface of 11.4 cm^2 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 excitated 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 5×10^4 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_2^+), 15 (NH^+), 16 (NH_2^+ or O^+), 17 (NH_3^+ or OH^+), 18 (H_2O^+) 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_4^+ and H_2O^+ (m/e = 18) and $N_2H_4^+$ 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 $N_2D_4^+$ 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 (ΣI) (Ar^+ peak excluded) in the same recorded mass spectra. The normalized concentrations ($I/\Sigma I$) 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 $DH^{*(+)}$, $NHD^{*(+)}$, $NHD_2^{*(+)}$, and $N_2H_2D_2^{*(+)}$ excited radicals during the dc discharge. In the Ar + N_2 + D_2 discharge the dominant species formed are $ND_3^{*(+)}$ and $N^{*(+)}$ while in the Ar + NH_3 + D_2 mixture the N_2, NH_2D_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

3

(3) 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/ΣI 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/ΣI 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-

4

sure. 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 $\sum I_{NH}$ 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_2^+, 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_2^+, 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_γ 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_2^+ and H while the $Ar + NH_3$ discharge supplies the highest relative concentration of excited and ionized $\sum NH$. Because both $Ar + N_2 + H_2$ and $Ar + NH_3$ plasmas nitrided the Ti and Ti6Al4V samples the uncertainity of which particle govern the nitriding process N, N_2^+ and H or $\sum NH$ 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 nitrided 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 reported earlier (refs. 1 to 5).

Edax – Elemental Analysis

Figures 10(a) to (d) shows an example of an EDAX spectrum taken on a nitrided Ti sample (R59); N, Si and Fe are shown besides the strong Ti lines

5

(fig. 10(d)). 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 + N_2 plasma. The presence of O in the Ti-N sample (R-63) is clearly shown in figure 10(a) and a segregation of Si 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 O_2 in the Ar + N_2 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 + N_2, Ar + N_2 + H_2 and Ar + NH_3, respectively. The same behavior of the IR reflectance spectra were obtained for the nitrided Ti6Al4V samples.

In the Ar + N_2 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 + NH_3 plasma (fig. 12) and in the Ar + N_2 + H_2 plasma (fig. 14). Moreover, the highest absorbance of the N-H stretch was obtained in the Ti samples nitrided in the Ar + N_2 + H_2 discharge (fig. 13) and not as expected in the Ar + NH_3 discharge (fig. 12). The amplification of the N-H bond in the Ar + N_2 + H_2 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 + NH_3 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 + N_2 + H_2 discharge, indicating that not the ΣNH excited or ionized particles dominate the nitriding process.

(2) The Ar + N_2 + H_2 discharge produces the highest relative concentration of excited and ionized N (tables I to III) and the highest relative concentration of $H\gamma$ (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

1. Hudis, Martin: Study of Ion-Nitriding. J. Appl. Phys., vol. 44, no. 4, Apr. 1973, pp. 1489-1496.

6

2. Tibbetts, Gary G.: Role of Nitrogen Atoms in "Ion-Nitriding." J. Appl. Phys., vol. 45, no. 11, Nov. 1974, pp. 5072-5073.

3. Konuma Mitsuhara, and Matsumoto Osamu: Nitriding of Titanium in a Radio Frequency Discharge. J. Less-Common Met., vol. 52, 1977, pp. 145-152.

4. Matsumoto Osamu, Konuma Mitsuhara, and Kanzaki, Yasushi: Nitriding of Titanium in an R.F. Discharge II. Effect of the Addition of Hydrogen to Nitrogen on Nitriding. J. Less-Common Met., vol. 84, no. 1, Mar. 1982, pp. 157-163.

5. Matsumoto, O.; Kanzaki, Y.: Plasma Nitriding Reaction of Metals. 6th International Symposium on Plasma Chemistry, vol. 2, M. I. Boulos and R. J. Munz, eds., McGill University (Montreal), 1983, pp. 340-345.

6. Veprek, S. and Venugopalan, M., eds.: Plasma Chemistry, Vol. IV. Topics in Current Chemistry, vol. 107, Springer Verlag, 1983.

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

[Cathode SS304; Φ_2 = 1.5 in; S_1 = 11.4 cm^2; titanium S_2 = 2(3.0 x 1.5 cm^2) = 9.0 cm^2; P_R = 4 to 4.5 torr; P_{QP} = 3·3.2x10^{-6} torr; eE = 50 eV; gap = 1.5 cm; t = 2 hr.]

m/e	Gas mixture					
	Ar + N$_2$ (4:1)		Ar + N$_2$ + H$_2$ (4.5/1; 2.5/1)		Ar + NH$_3$ (2:1)	
	I/$\sum$I, percent					
	SS304	+ Ti	SS304	+ Ti	SS304	+ Ti
H2$_2$	15.9	10.6	30.0	15.0	22.8	7.5
N	8.6	8.6	6.0	10.8	1.8	5.0
NH	----	----	----	1.6	1.8	3.0
NH$_2$	----	1.8	0.8	3.7	28.6	24.0
NH$_3$	----	4.6	3.3	5.6	34.9	27.0
NH$_4$	----	4.0	5.3	11.9	5.1	10.0
N$_2$	69.5	48.1	50.9	34.0	12.1	15.8
N$_2$H$_4$	----	2.2	1.0	2.8	1.0	2.5
N$_3$	1.0	----	0.8	1.2	----	----
dc	450 V; 130 to 150 mA		420 V; 100 to 120 mA		400 V; 100 to 120 mA	

m/e: 20 (Ar^{++}); 29; 31; 38; not in the $\sum$.

TABLE II. – NORMALIZED CONCENTRATIONS OF EXCITED PLUS IONIZED SPECIES IN THE dc DISCHARGES (ID – I_{ND})
TO THE PARTIAL PRESSURES IN THE GAS FEED

[Sample Ti6Al4V, 5.0 cm^2; Pr = 5 torr; electrodes gap, 1.5 cm; 400 V, 120 mA; P_{QP} = 2.4x10^{-6} torr; eE = 50 eV; t = 1 hr.]

Gas mixture feed	$\dfrac{\Sigma I_N}{aI}$ [a]	$\dfrac{\Sigma I_N}{I_{N_2} + I_{H_2}}$ [a]	$\dfrac{I_{H_2}}{I_{N_2} + I_{H_2}}$	$\dfrac{\Sigma I_{NH}}{I_{N_2} + I_{H_2}}$ [b]	$\dfrac{\Sigma I_N}{I_{NH_3} + I_{NH_2}}$ [a]	$\dfrac{I_{H_2}}{I_{NH_3} + I_{NH_2}}$	$\dfrac{\Sigma I_{NH}}{I_{NH_3} + I_{NH_2}}$ [b]
Ar + N_2 2:1 1.66 torr	66 percent 1.09 torr [c]67 percent	----------	----------	----------	----------	----------	----------
Ar + N_2 + H_2 2:1:1 2.50 torr	----------	88 percent 2.2 torr 2 percent(c)	30 percent 0.75 torr 46 percent(c)	40 percent 1.2 torr 18 percent(c)	----------	----------	----------
Ar + NH_3 1:1 2.50 torr	----------	----------	----------	----------	63 percent 1.56 torr	15 percent 0.38 torr	73 percent 1.82 torr

[a] $\Sigma I_N = I_{N^+} + I_{N_2^+} + I_{N_3^+}$

[b] $\Sigma I_{NH} = I_{NH^+} + I_{NH_2^+} + I_{NH_3^+} + I_{N_2H_4^+}$.

[c] Martin Hudis (ref. 1) – Positive Ions Ratio (Ar$^+$ = 33 percent): $\alpha = 10^{-4} - 10^{-5}\left(\dfrac{n_i}{\Sigma n}\right)$.

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.]

Excited species	nm	$I_{Ar+H_2+N_2}/I_{Ar+N_2}$	$I_{Ar+H_2+N_2}/I_{NH_3+Ar}$	Remarks
Ar_{ms} 14.53 to 11.55 eV	415.8	1.0	1.0	Ar^+ was not detected
N_2 2nd $C_3 - B_3$	380.5	1.0	3.0	
N_2^+ 1st $B^2\Sigma_u^+ - X^2\Sigma_g^+$	391.4	2.2	1.8	In each plasma $I_{N_2} > I_{N_2^+}$
N	411.0	2.5	1.4	
H_γ	434.1	> 10	5.5	
NH $A^3\Sigma - X^3\Sigma^{-1}$ (0 – 0)	336.0	> 10	0.6	Same ratios for the $0\nu = 0$ (1–1) at 337.0 nm

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.]

Ti/Ar plasma	260 to 300
Ti6Al4V/Ar plasma	350 to 400
Ti/Ar + N_2	1200 + 150 ⎫ Y. Gold
Ti6Al4V/Ar + N_2	1400 + 100 ⎭ ~18K
Ti/Ar + NH_3	1500 + 50 ⎫ Y. Gold
Ti6Al4V/Ar + NH_3	1600 + 100 ⎭ ~14k
Ti/Ar + N_2 + H_2	1700 + 100 ⎫ Y. Gold
Ti6Al4V/Ar + N_2 + H_2	1800 + 50 ⎭ ~14k

Ar N₂ H₂ NH₃

Flow
meters

Gas diffuser

dc
Power
supply

Diffusion
pump

Rotary
pump

Scope

Mixer

Reactor

$+$ ≤ 10

$\leq 10^{-6}$

$\leq 10^{-7}$

Q. P.
mass filter

Electronics
for
Q. P.

Ionic
pump

0.2 mm

0.3 mm

Rotary
pump

Monochromator
OES

☐ Ionization gauge

⌂ Manometer

✕ Valves

✕ Needle valves
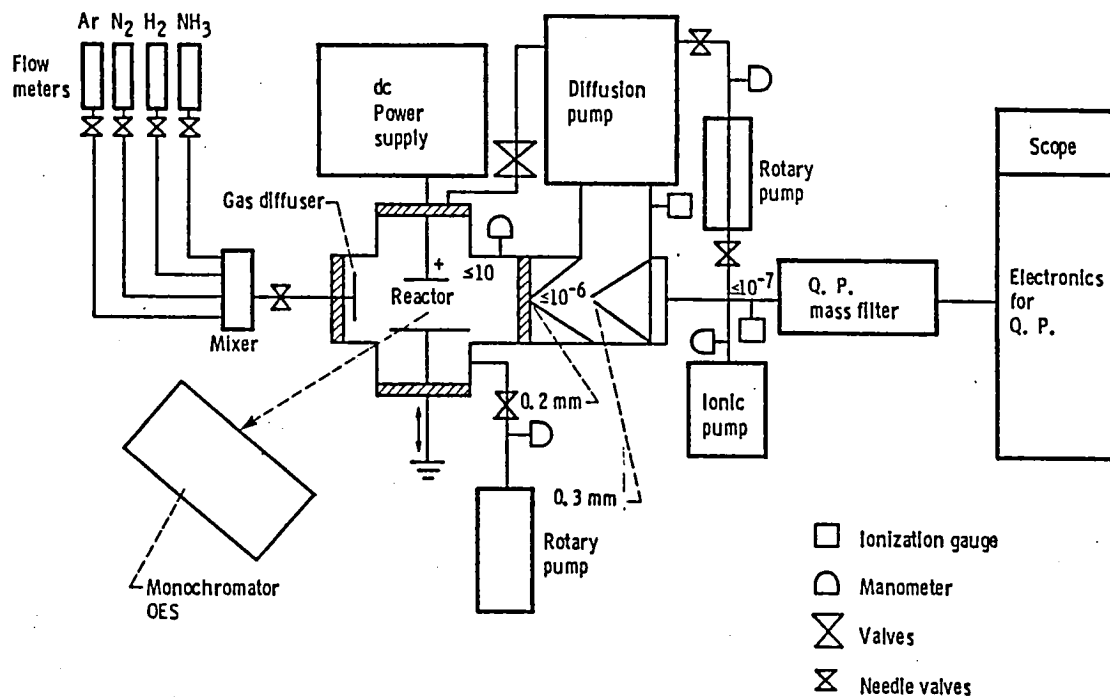
Figure 1. – d.c. Plasma rig – schematic.
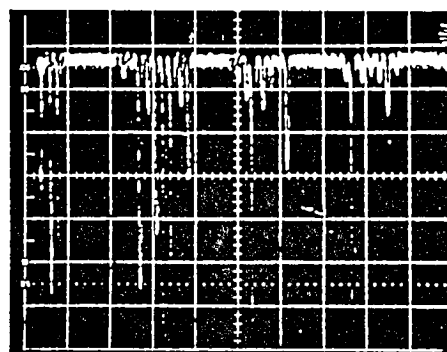
(a) Ar + N₂.
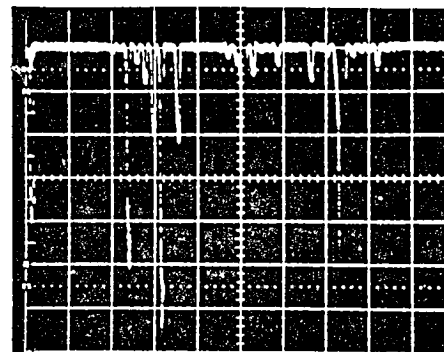
(b) Ar + N₂ + D₂.

Figure 2. – Examples of QPMS spectra of dc glow discharge.
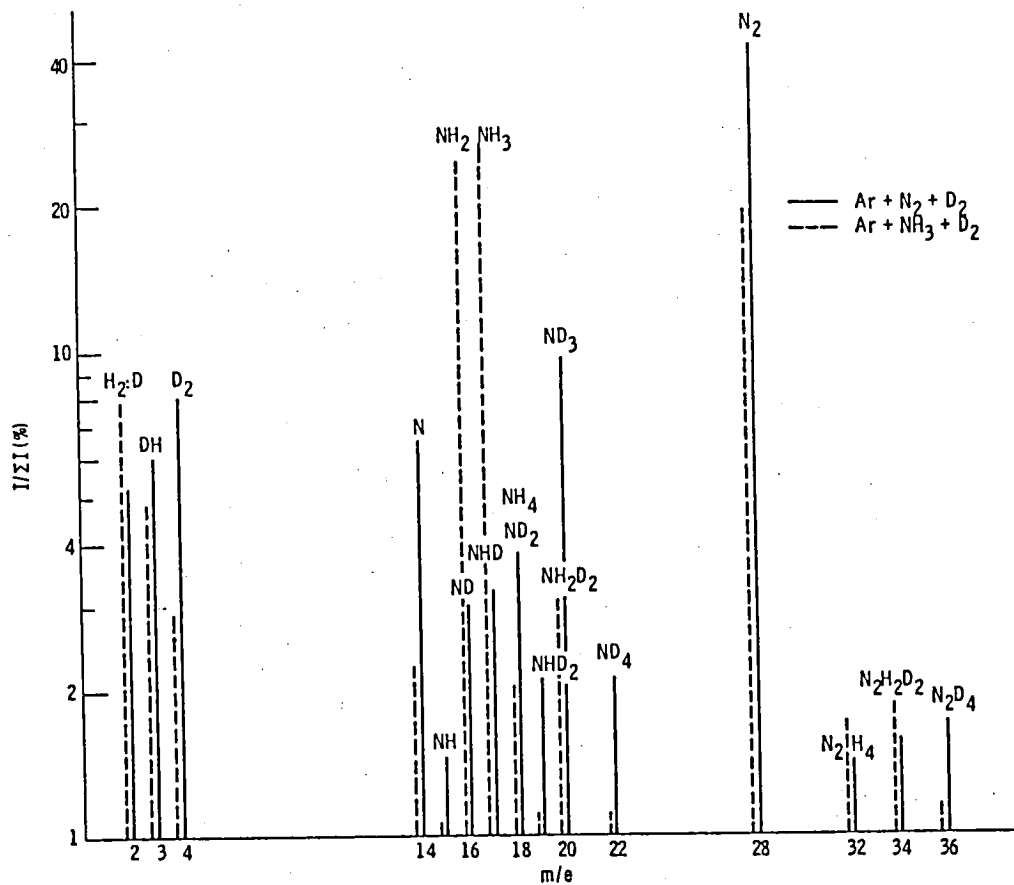
Figure 3. - Normalized concentrations ($I/\Sigma I$) OF m/e's in dc glow discharges. Ar/N$_2$ = 4/1; D$_2$/N$_2$ = 3/1; Ar/NH$_3$ = 2/1; D$_2$/NH$_3$ = 1/1; P$_R$ = 3.0 torr; P$_{QP}$ = 9.0 10^{-7} torr; eE = 70 ev.
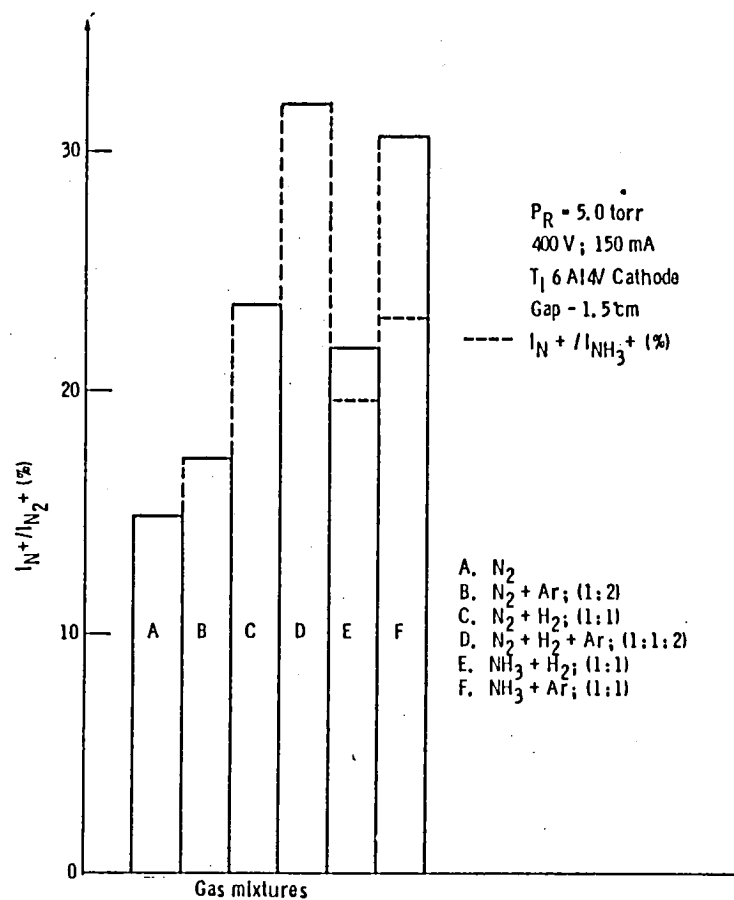
Figure 4. — Normalized concentration of N (atom + ions) in the different gas mixtures.
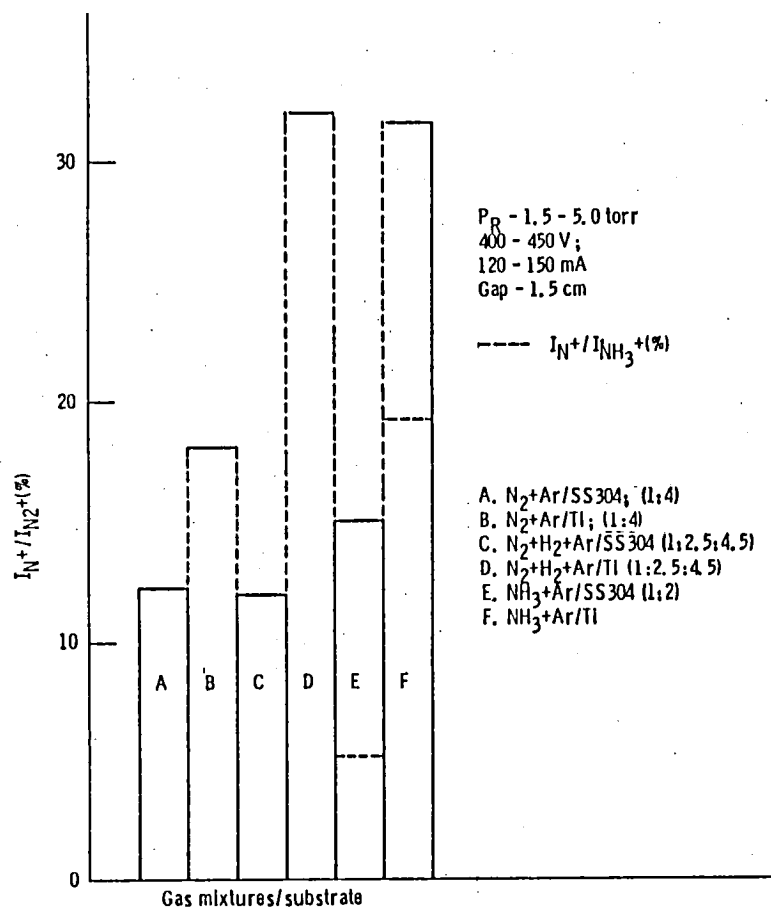
Figure 5. – The influence of titatium samples on the normalized concentrations of N (atoms + ions) in the different gas mixtures.
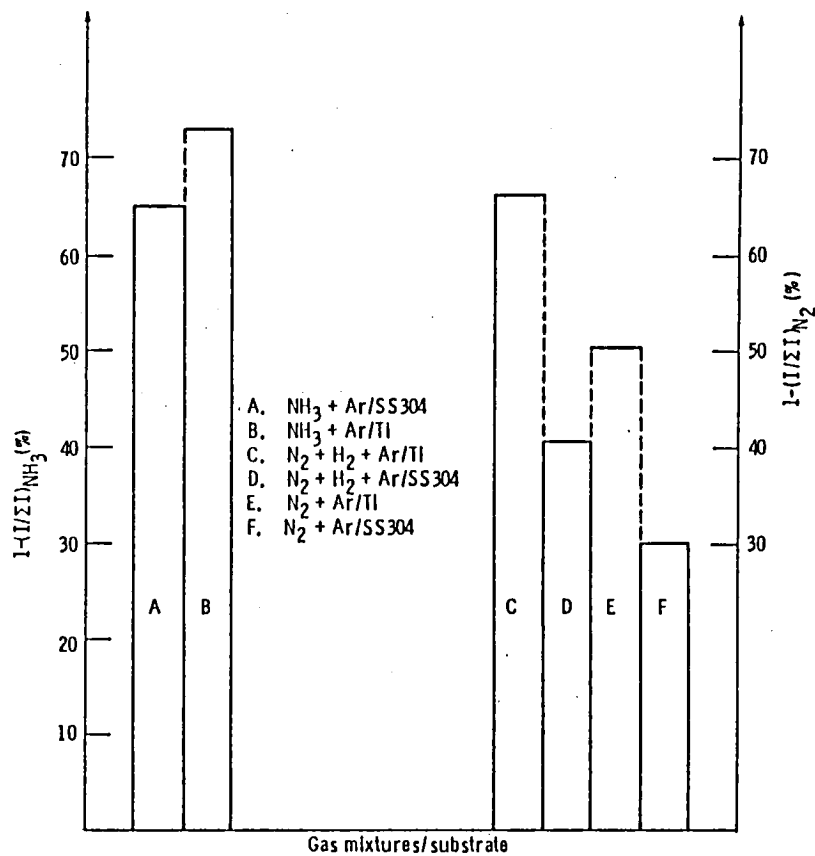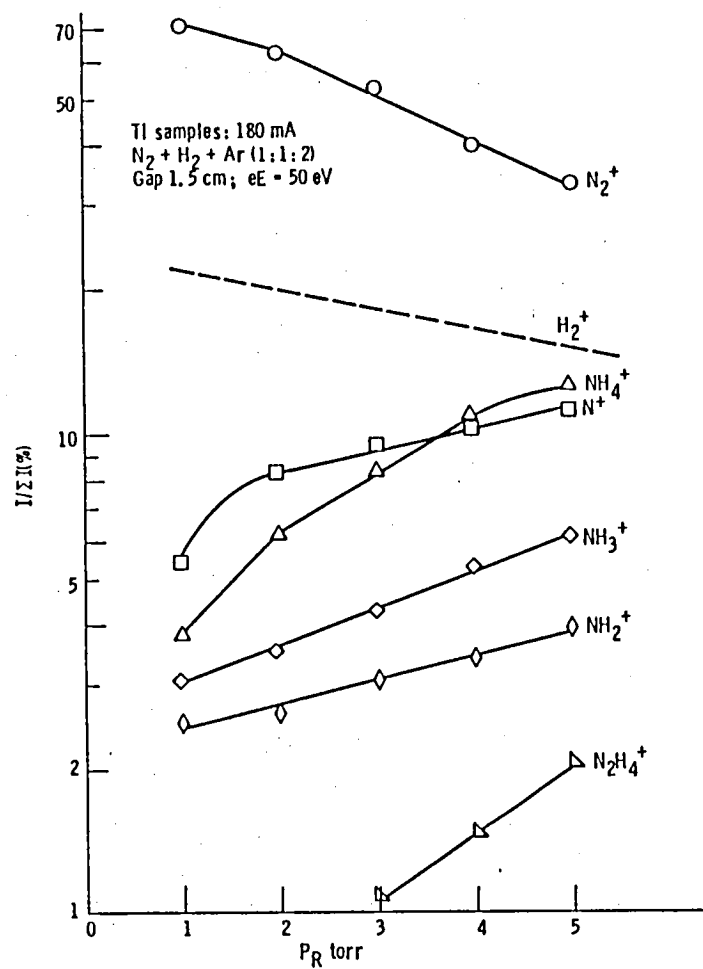
Figure 6. - The normalized dissociation rate of N_2 and NH_3 on titanium samples.

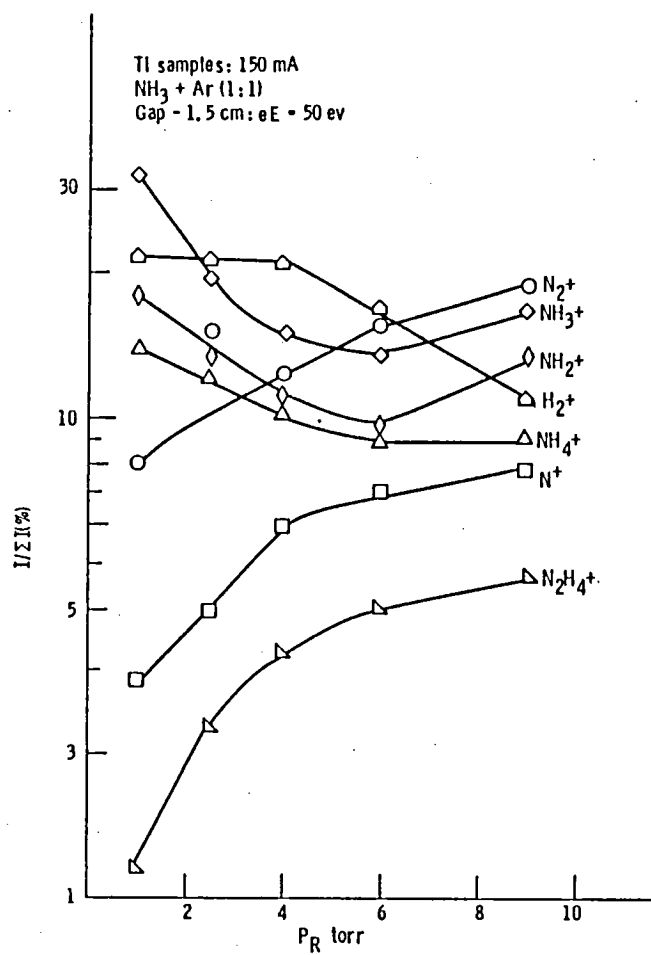Figure 7. - Normalized concentrations (I/ΣI) versus gas pressure.

Figure 8. - Normalized concentrations (I/ΣI) versus gas pressure.

$$I_1 = \frac{h\nu}{4\pi} \, g\,A\,n_1 \frac{(\alpha)_1}{(1-\alpha)_1} \frac{1}{\Sigma g_1} \exp\left(-\frac{\Delta E}{kT_1}\right)$$

1 - Ar + N_2 + H_2 mixture

$$I_2 = \frac{h\nu}{4\pi} \, g\,A\,n_2 \frac{(\alpha)_2}{(1-\alpha)_2} \frac{1}{\Sigma g_2} \exp\left(-\frac{\Delta E}{kT_2}\right)$$

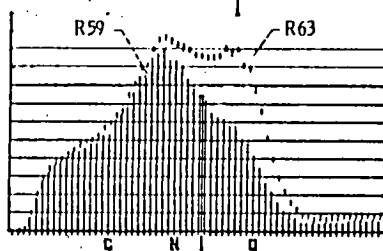2 - Ar + N_2 mixture

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
    ν spectral frequency
    h   planck's constant
    g   statistical weight of the spectral transition
    A   transition probability (Einstein's coeff. spontaneous emisson
    n   total particle concentration of a given atom or molecule
          (i.e. $n_{atoms} + n_{molecules} + n_{ions}$)
    α degree of ionization
  $1-\alpha$ degree of neutrality (atoms or molecules)
   Σg partition function
  ΔE energy of the upper state (excited)
    k   Boltzman's constant
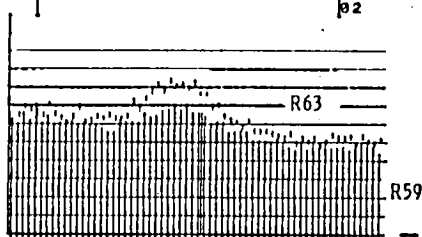   T   excitation temperature of the particle

Figure 9. - Correlations between spectral intensity and particle con-
centrations in the plasma-near-to-surface region.

38-MAY-84 14:33:25 EDAX READY
RATE: 472CPS TIME   575LSEC
00-20KEV:10EV/CH PRST: OFF
A:AVNI-45YEL   B:AVNI-45 DEG
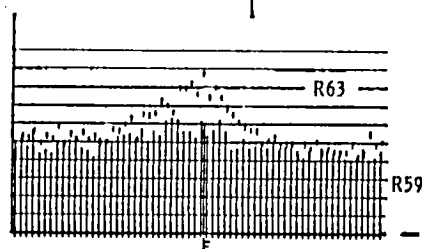FS=   6282   MEM:A/B FS=   9329

R59   R63

C   N   O

CURSOR (KEV)=00.440   EDAX
(a)

38-MAY-84 14:34:35 EDAX READY
RATE: 534CPS TIME   575LSEC
00-20KEV:10EV/CH PRST: OFF
A:AVNI-45YEL   B:AVNI-45 DEG
FS=   392   MEM:A/B FS=   503

R63

R59

CURSOR (KEV)=05.420 ·   EDAX
(c)

38-MAY-84 14:34:05 EDAX READY
RATE: 523CPS TIME   575LSEC
00-20KEV:10EV/CH PRST: OFF
A:AVNI-45YEL   B:AVNI-45 DEG
FS=   1570   MEM:A/B FS=   2332
                          02

R63

R59

5

CURSOR (KEV)=01.770   EDAX
(b)

38-MAY-84 14:35:27 EDAX READY
RATE: 790CPS TIME   575LSEC
00-20KEV:10EV/CH PRST: OFF
A:AVNI-45YEL   B:AVNI-45 DEG
FS= 25130   MEM: A   FS=   37318
                      02   04

C O   5   t
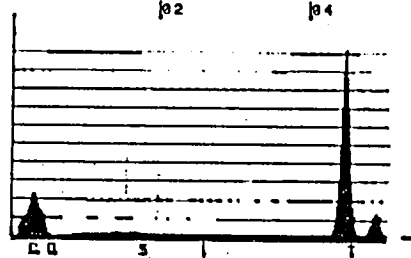
CURSOR (KEV)=02.540   EDAX
(d)

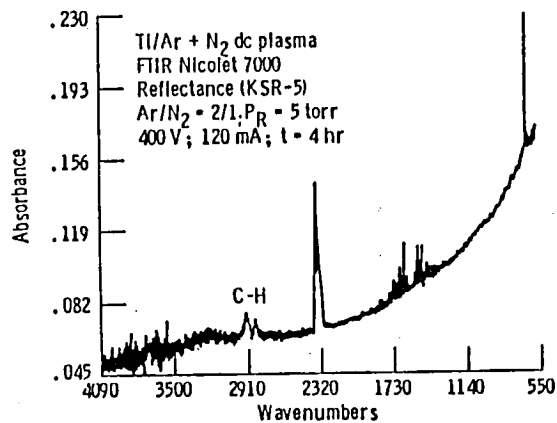Figure 10. - EDAX spectrum of the Tl-N sample (R59) and Tl-N-O sample (R63).

Figure 11. – FTIR reflectance spectrum of Ti-n
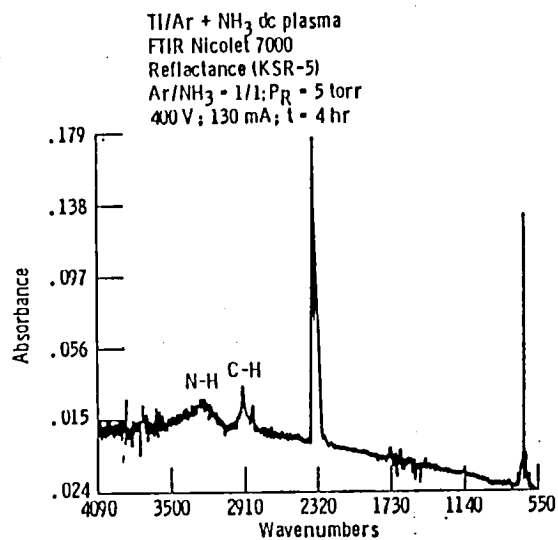sample in Ar + N_2 dc glow discharge.

Ti/Ar + N_2 dc plasma
FTIR Nicolet 7000
Reflectance (KSR-5)
Ar/N_2 = 2/1; P_R = 5 torr
400 V; 120 mA; t = 4 hr

Figure 12. – FTIR reflectance spectrum of Ti-N
sample in Ar + NH_3 dc glow discharge.

Ti/Ar + NH_3 dc plasma
FTIR Nicolet 7000
Reflactance (KSR-5)
Ar/NH_3 = 1/1; P_R = 5 torr
400 V; 130 mA; t = 4 hr
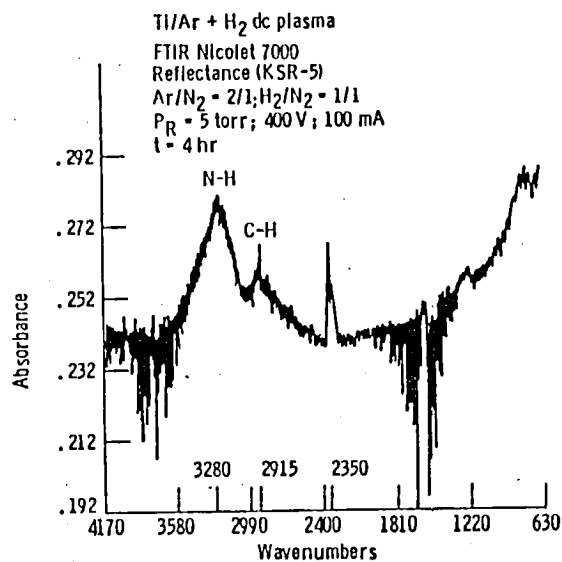
Figure 13. – FTIR reflectance spectrum of Ti-N sample
in Ar + N_2 + H_2 dc glow discharge.

Ti/Ar + H_2 dc plasma
FTIR Nicolet 7000
Reflectance (KSR-5)
Ar/N_2 = 2/1; H_2/N_2 = 1/1
P_R = 5 torr; 400 V; 100 mA
t = 4 hr

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TM-83803		

4. Title and Subtitle	5. Report Date
Nitriding of Titanium and Its Alloys by N_2, NH_3, or Mixtures of $N_2 + H_2$ in a dc Arc Plasma at Low Pressures (≤10 torr)	November 1984
	6. Performing Organization Code
	506-53-1B

7. Author(s)	8. Performing Organization Report No.
Reuven Avni	E-2254
	10. Work Unit No.

9. Performing Organization Name and Address	11. Contract or Grant No.
National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135	
	13. Type of Report and Period Covered

12. Sponsoring Agency Name and Address	Technical Memorandum
National Aeronautics and Space Administration Washington, D.C. 20546	14. Sponsoring Agency Code

16. Abstract

The dc glow discharges in different gas mixtures of $Ar + N_2$, $Ar + NH_3$ or $Ar + N_2 + H_2$ 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, N_2, NH, or NH_2 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.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Nitriding Titanium Friction Wear	Unclassified - unlimited STAR Category 37

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of pages	22. Price*
Unclassified	Unclassified		

National Aeronautics and
Space Administration

Washington, D.C.
20546

U.S.MAIL

NASA

POSTMASTER: If Undeliverable (Section 158
              Postal Manual) Do Not Return