

Title	Glow Plasma Behaviour in Nitriding Process(Physics, Process, Instruments & Measurements)
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Citation	Transactions of JWRI. 22(1) P.13-P.19
Issue Date	1993-08
Text Version	publisher
URL	http://hdl.handle.net/11094/4423
DOI	
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Glow Plasma Behaviour in Nitriding Process†

Yasuo TAKAHASHI*, Katsunori INOUE**, Yan LI*** and Isao KAWAGUCHI****

Abstract

Spectroscopic and some other diagnoses were carried out for investigation of DC glow plasma behaviour in ion nitriding process. A nitrogen-10% hydrogen mixture gas was used. The specimen was an austenitic stainless steel(SUS304), settled as the cathode. Current, voltage and gas pressure were mainly changed as plasma parameters. The spectral intensities are influenced by these parameters. N_2 and N_2^+ excited state were strongly detected. The intensity ratio N_2^+/N_2 depends on the gas pressure which was changed from 267 to 933 Pa. This dependence can be explained in terms of mean free path of particles. It was found that the ion nitriding process is largely controlled by ion density and cathode fall voltage. Also, the nitriding rate is the fastest at gas pressures from 533 Pa (4 torr) to 666 Pa (5 torr) which can be explained by taking into account the glow discharge behaviours.

KEY WORDS: (Glow Discharge) (Ion Nitriding) (Emission Spectroscopy) (Ion Density) (Cathode Fall) (Surface Hardening)

1. Introduction

DC glow plasma nitriding is a method for surface hardening ¹⁾. It offers several advantages over other conventional nitriding technologies. For example, it provides lower part distortion in comparison with gas and salt methods of nitriding.

The glow plasma introduces excited nitrogen to surfaces for subsequent diffusion into the material. The plasma and electric situation in the vicinity of metal surface (cathode) is, therefore, very important for ion nitriding process. We need investigate the plasma characteristics in the cathode region, so that the governing mechanisms of ion nitriding can be better understood and the nitriding process can be optimized.

A lot of emission spectroscopy investigation in cathode region have been performed ^{2, 3, 4)}, but these investigations were not related with the nitriding behaviour.

Titanium, the oxygen concentration limit of which is much greater than stainless steel can be surface-nitrided by radio frequency (RF) plasma alone ⁵⁾ or gas absorption at high temperatures ⁶⁾ (~1173 K). On the other hand, many stainless steels are hardly done by

either RF plasma ⁷⁾ or high temperature nitrogen gas ⁶⁾. We can, therefore, guess that the nitriding of stainless steels is governed by both ionization and potential gradient in cathode fall. In other words, ion nitriding mechanism of stainless steels cannot be explained only by ionization or nitrogen absorption. We need settle stainless steels as the cathode of DC glow discharge ^{6, 7)}, i.e. a certain cathode fall is necessary for nitriding stainless steels.

It is, therefore, necessary and important to investigate the situation around the cathode with respect to excited species and potential gradient. Then, in the present study, by using emission spectroscopy and other detective method, we investigate the plasma behaviour around the cathode. Further, we relate the discharge situation with the growth behaviours of nitride layer. In that stage, we change current density, cathode fall voltage and gas pressure to change the discharge situation around the cathode. The purpose of the present paper is to understand the governing mechanism in the plasma (ion) nitriding, based on the observation of discharge (plasma) situation during the ion nitriding process of an austenitic stainless steel.

† Received on July 30, 1993

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Transactions of JWRI is published by Welding Research Institute, Osaka University, Ibaraki, Osaka 567, Japan

2. Experimental

The experimental setup is schematically shown in Fig. 1. Upper half of the vacuum chamber (side wall) was made of fused silica and the lower side with electrodes for heating a specimen was made of an austenitic stainless steel ⁶⁾. The plasma is produced by a DC power source with a constant current characteristic. The length L between anode and cathode was 180 mm at first ⁶⁾ but was changed to 65 mm in order to increase emission intensity (ion density) even at the lower electric voltage. All nitriding processes mentioned below were performed at the length L of 65 mm. The material used was a SUS 304 stainless steel, the composition of which is shown in Table 1. The specimen (plate) was settled as the cathode. The width and thickness of the specimen were 10 mm and 1 mm, respectively. The both ends of the specimen were encased by a ceramic insulator so that the discharged surface area could be kept constant (660 mm²) for all nitriding tests. N₂ + 10% H₂ gas was used since the composition had been said to give the highest ion density under the constant current condition ⁸⁾. The gas pressure and discharge current ranges were, respectively, 267 to 933 Pa (2 to 7 torr) and 5 to 40 mA.

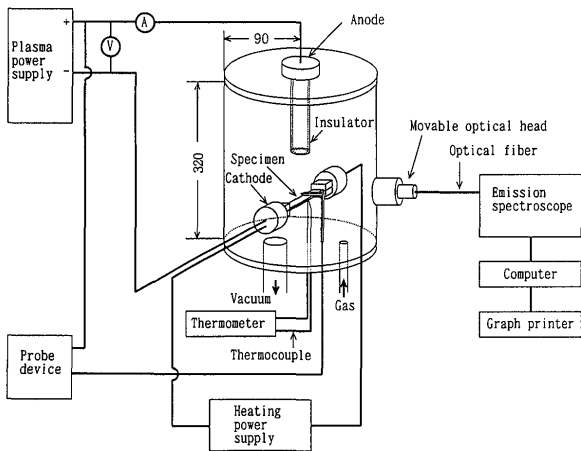


Fig. 1 Experimental setup for observation of an ion nitriding process.

Table 1 Chemical composition of the specimen (wt%).

C	Si	Mn	P	S	Ni	Cr	Fe
0.05	0.54	1.22	0.031	0.005	8.16	18.15	bal.

A Monochromator (CT-25C) made by JASCO was used for emission spectroscopic observation. The space on the specimen was focused by the optical head with a 1 mm aperture. The spectroscopic results were obtained through a rock-in-amplifier and sent to a computer for data processing. Langmuir probe method was used to measure the potential distribution along the center axis

of the vacuum chamber. The specimen temperature T_s have a great influence on the nitriding rate but the specimen was mainly kept at 873 K in an accuracy to within $\pm 2K$ in order to remove the temperature effect. The specimen temperature was measured by a thermocouple to control the specimen heating.

3. Experimental Results and Discussion

3. 1. Plasma Morphology in Ion Nitriding

We have reported about morphology of a process plasma in our previous papers ^{6, 9)}. According to them, the plasma morphology can be classified into four types (A, B, C, D). Type A is observed in the region of lower gas pressure and lower current density. Type A requires high voltage. Type B is a discharge in which negative glow extends all over the vacuum chamber but the negative glow area decreases to become that of Type C as the gas pressure increases. When the gas pressure is higher, the negative glow area further decreases, and positive column expands near by the cathode. This is type D. Type C is considered to be a transition region from type B to D. After we refer to in literature ^{1, 7, 10)}, the ion nitriding of stainless steels is generally conducted in the region from type C to D and mainly done under the situation of type D.

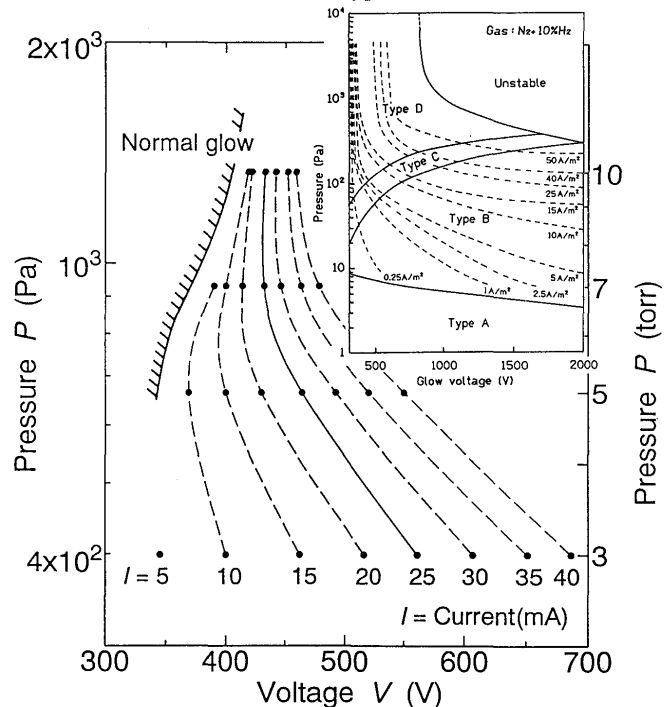


Fig. 2 A diagram of gas pressure P vs. voltage V for $L = 65$ mm The insertion is for $L = 180$ mm.

Figure 2 is a diagram of gas pressure P versus discharge voltage V between anode and cathode. Another morphology map is together shown in Fig. 2. This has been drawn by Tanaka et. al ⁶⁾ who carried out ion

nitriding under a condition different from the present study with respect to length L between electric poles and surface area of cathode. The present condition of $L = 65$ mm somewhat changes the position of domain D from that of Tanaka ($L = 65$ mm). But, all experimental points in Fig. 2 belong to type D.

It is suggested from the results of Tanaka et al. 6, 11) that the ion nitriding is not able to be performed in the gas pressures greater than 933 Pa. In other words, a specimen surface is not ion-bombarded enough to sputter the oxide film, since the voltage V becomes low and the mean free path is small at $P > 933$ Pa. On the other hand, as V increases greater than 600 V, the sputtering phenomenon becomes very striking.⁶⁾ Besides, as indicated in Fig. 2, the normal glow is observed at lower currents. In the present study, we carried out experimental tests in the region of abnormal discharge. The current I was mainly kept at 25 mA denoted by a solid line in Fig. 2 (current density $i_d = 37.87 \text{ Am}^{-2}$).

Figure 3 shows discharge morphologies around the specimen (cathode) when the specimen is not heated. As P increases from (a) to (d), the negative glow area gradually shrinks. These belong to type D morphologies although photo. (a) is close to type C. As can be seen in Fig. 3, the space near the cathode only emitted light and other space was dark.

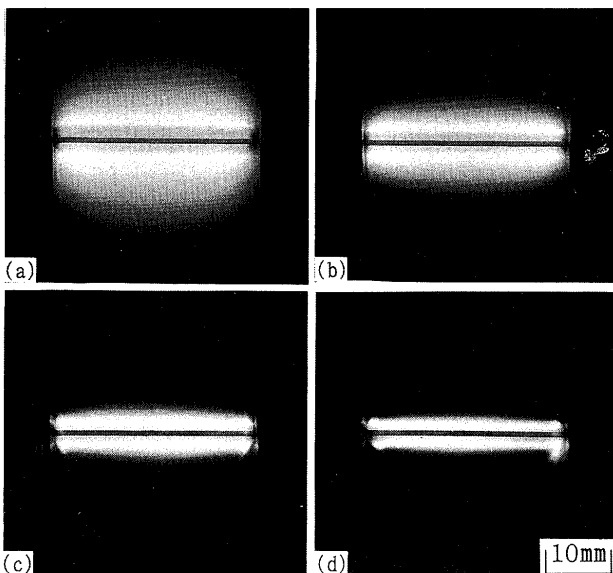


Fig. 3 Plasma morphologies during ion nitriding at $I = 25$ mA ($i_d = 37.87 \text{ Am}^{-2}$).
 (a) $P = 267$ Pa (2 torr), (b) $P = 400$ Pa (3 torr),
 (c) $P = 667$ Pa (5 torr), (d) $P = 933$ Pa (7 torr).

Figure 4 shows distributions of floating potential obtained by Langmuir's probe method. The anode drop is just about 50 ~ 70 V. Because the floating potential is considered to be roughly equal to the plasma potential,

it appears that the plasma potential changes gradually to the position of $d = 5$ mm, where d is the distance from the cathode surface. However, the potential sharply changes at $d < 5$ mm. Also, as the gas pressure increases, the anode drop increases while the cathode fall decreases. Besides, it was found that the cathode fall increases with increase in the current density, while the potential in plasma column changes only slightly.

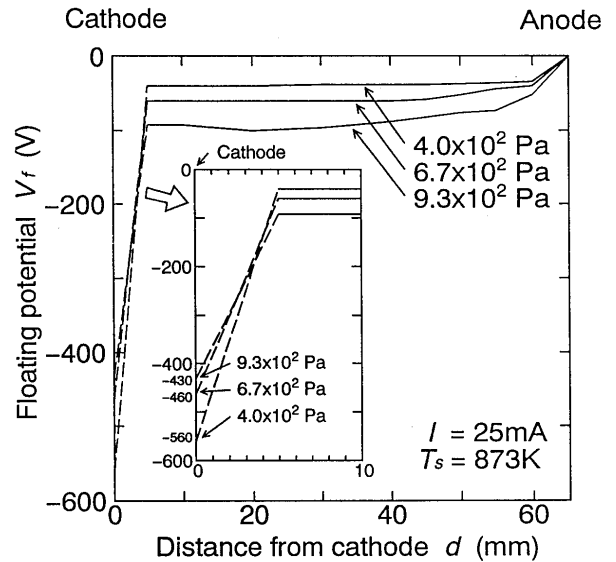


Fig. 4 Floating potential distribution along the center axis of the vacuum chamber. The insertion exactly shows the cathode potentials.

Because of the probe size, we could not measure the potential distribution near the cathode ($d = 0 \sim 5$ mm). Also, because plasma state is not established owing to expand ion sheath in the vicinity of the cathode, we might not be able to measure it by the probe method. The real cathode fall area is narrower than 5 mm but we define the voltage drop from $d = 5$ to 0 mm as the cathode fall voltage. We should not estimate the gradient (electric field) from these data but we can say that this voltage drop roughly equal to the true cathode fall voltage. The authors consider that the voltage gradient near the cathode is very important for comprehending ion nitriding behaviour, and intend to measure the floating potential close to the cathode surface by using a smaller probe.

Figure 5 shows both of total and cathode fall voltage as a function of the gas pressure P . Although the total voltage does not largely change at $P > 800$ Pa, the cathode fall voltage decreases as P increases. On the other hand, in the region of $P < 800$ Pa, both of them rapidly increase as P decreases. This rise of the cathode fall voltage increases the ion energy for bombarding (sputtering) specimen surface. In other words, the lowering of the cathode fall voltage causes the original

surface oxide film to remain long on the stainless steel, i.e. it takes longer to remove the oxide film.

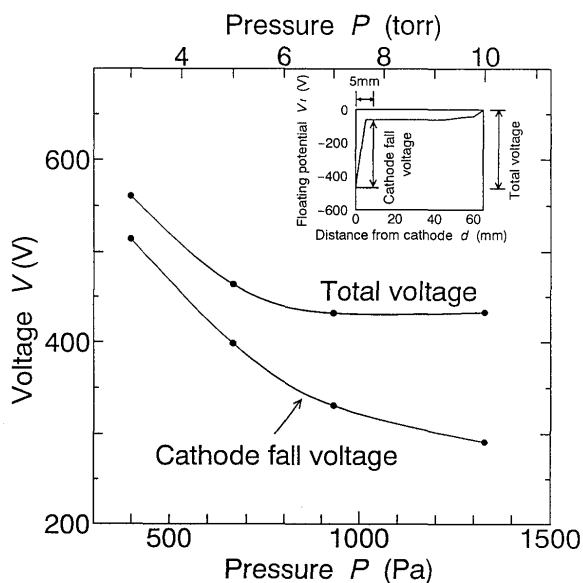


Fig. 5 Voltage depending on gas pressure. The insertion shows a definition of the cathode fall voltage.

3. 2. Emission Spectroscopic Diagnosis

The first observation was carried out from 0 to 1000 nm in wavelength λ . It was found from this diagnosis that all spectra are observed in $\lambda = 290$ nm to 870 nm. In particular, spectra in the range of $\lambda = 300 \sim 500$ nm were changed largely with change in the gas pressure.

Figure 6 shows the emission spectra obtained during nitriding. (a) is for full range of $\lambda = 290 \sim 1000$ nm and (b) is for $\lambda = 300 \sim 500$ nm. The intensity of all spectra gradually decreases as the ion nitriding progresses in order of hours. The results obtained at about 1200 s after starting ion nitriding are reported in the present paper. Because it took 400 ~ 600 s to measure emission spectra, Fig. 6 shows the results obtained from $t = 1200 \sim 1800$ s, where t is the nitriding time. However, the measuring period of 400 ~ 600 s does not largely change the intensities.

Figure 7 details the spectra between 330 and 340 nm. The spectrum of NH at 336 nm cannot be seen in Fig. 6. This spectrum could not be observed unless the slit width of the monochromator was set very narrow.

From the spectral graph of Figs. 6 and 7, it can be seen that ; firstly, the excited ion mainly observed in the present study is N_2^+ . Secondly, the excited neutral particles are a molecular and the very most dominant is N_2 although NH particles are slightly excited. Besides, with respect to the excited species N_2^+ and N_2 , the spectral intensities change with discharge current, I , gas pressure, P and specimen (cathode) temperature, T_s , although T_s has not so large effect as shown in Fig. 8, where the intensity of N_2^+ ($\lambda = 391.4$ nm) increasing

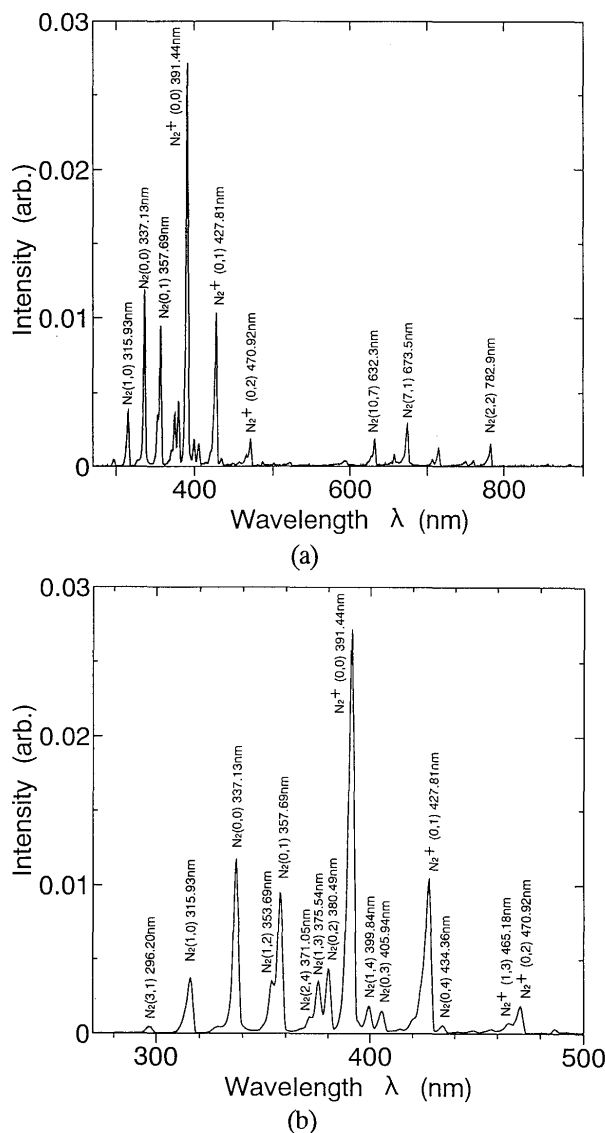


Fig. 6 Emission spectra during ion nitriding. (a) For $\lambda = 0 \sim 1000$ nm, (b) For $\lambda = 290 \sim 500$ nm

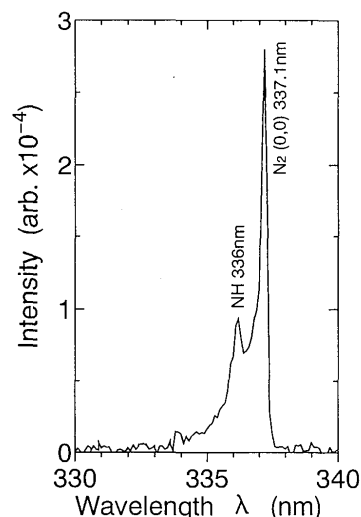


Fig. 7 Detail emission spectra in the 330 to 340 nm.

somewhat with T_s . Of course, the gas temperature has a large influence on the spectral intensity. Fig. 8 suggests that the temperature of the plasma close to the specimen is increased by heating the specimen.

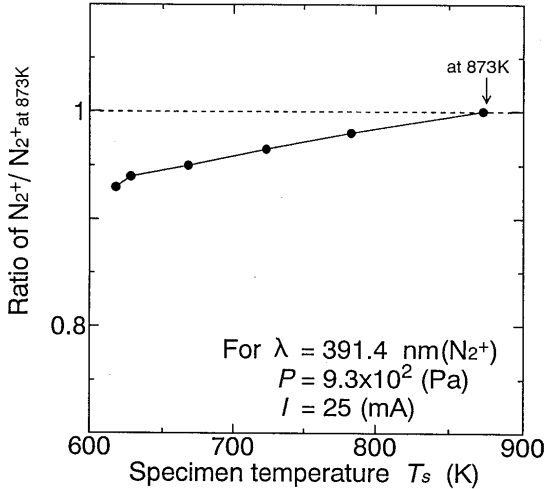


Fig. 8 Effect of specimen temperature on the intensity ratio (N_2^+ at T_s / N_2^+ at 873 K for $\lambda = 391.4$ nm).

Figure 9 shows the influence of gas pressure P on the spectral intensities of $N_2^+(0,0)$ ($\lambda = 391.44$ and 427.81 nm) and $N_2(0,0)$ ($\lambda = 337.13$ nm) under the test condition of $I = 25$ mA ($i_d = 37.87$ Am⁻²) and $T_s = 873$ K. The intensity of N_2 neutral species somewhat decreases at $P < 400$ Pa, but is roughly constant. On the other hand, the intensities of N_2^+ give a maximum value at $P = 400$ Pa and decrease as P increases from 400 Pa.

Figure 10 shows the intensity ratios of N_2^+ to N_2 of $\lambda = 337.13$ nm. The rise of the gas pressure reduces ionic species even if the current density is constant. The intensities of neutral $N_2(0,0)$ and $N_2(0,1)$ both increase in comparison with ionic species as P increases.

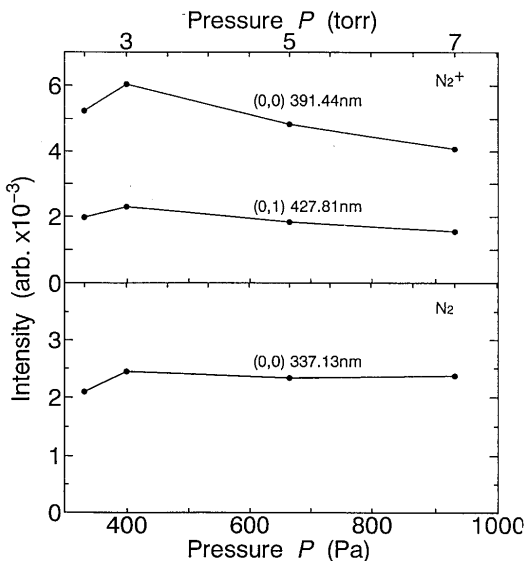


Fig. 9 Spectral intensities of N_2^+ and N_2 depending on the gas pressure.

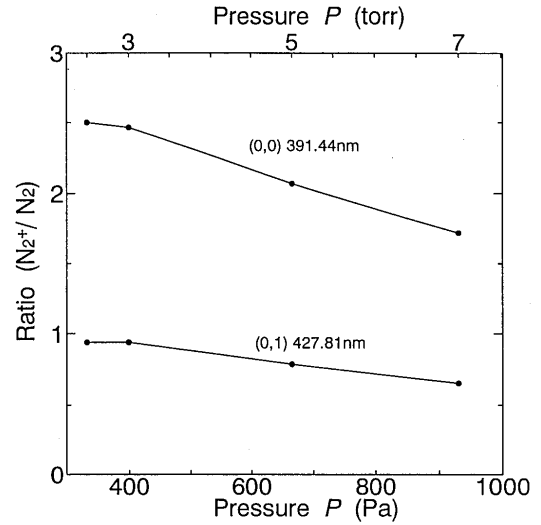


Fig. 10 Intensity ratio of N_2^+ / N_2 . The N_2 of 337.13 nm is adopted as an intensity of neutral particles

It was also observed that the relative intensity N_2^+ / N_2 decreases and the intensities of neutral $N_2(0,0)$ and $N_2(0,1)$ increases, as i_d and T_s decreases, which means worse from the view of the ion nitriding process.

The mean free path, s , of particles is given by

$$s = \frac{kT}{\sigma P} \quad (1)$$

where σ is the cross section of collision, P the gas pressure; T the gas temperature in Kelvin, and k is Boltzmann's constant. The mean free path becomes smaller with the gas pressure increasing or gas temperature decreasing, which means the reduction of kinetic energy of charged particles just before collision. It becomes difficult for ionic particles and electrons to excite other neutral particles to be charged as the mean free path decreases. Decrease in the mean free path also implies relative increase in the density of neutral particle since current keeps constant. This can be a reason of the variation in the relative intensities of N_2^+ / N_2 . It can be easy to explain the change in the intensities if we take into account the mean free path s .

As seen in the region of $P < 400$ Pa of Fig. 9, all spectral intensity decreases as P decreases from 400 Pa. This is due to the expanded plasma as can be seen in photo. (a) in Fig. 3. The ion density can be increased by increasing the current density, but the discharge voltage is simultaneously increased and finally becomes higher than 600 V as indicated in Fig. 2.

As pointed out elsewhere,^{6, 12)} the sputtering phenomenon becomes striking at pressures less than 400 Pa and total voltage higher than 600 V. It is also expected that the specimen surface is sputtered in some degree even under the present conditions of $P = 266 \sim 933$ Pa, V

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= 400 ~ 600 V. ¹⁾ The sputtering rate may increase as P decreases, because the current density in the vicinity of the cathode, i_d , does not change.

Marchand et al.⁴⁾ and Petitjean et al.⁸⁾ observed excited species such as NH ($\lambda = 336 \text{ nm}$) and Fe ($\lambda = 558.7$ and 561.6 nm) other than N_2^+ and N_2 by using an emission spectroscopy, but the intensities of NH and Fe were very poor. In the present study, a poor NH peak could be observed at 336 nm as shown in Fig. 7, if we precisely measured but Fe was not detected. Because the sputtering occurs somewhat during nitriding, metallic atoms such as Fe and Cr naturally exist in the plasma close to the cathode. But, it is suggested from the spectroscopic results that they are not strongly excited.

The grating used by Marchand et al. had $1200 \text{ grooves mm}^{-1}$ but ours has only 600 grooves , which might not be enough to detect a Fe spectrum. The resolution limit $\delta\lambda$ was 0.1 nm for Fig. 7. The value was less than that of Marchand et al. (0.3 nm),⁴⁾ but it may be necessary to measure the spectral line emission with $\delta\lambda$ less than 0.1 nm .

Hudis⁷⁾ observed the active ingredients (ions) such as NH^+ , NH_3^+ , N^+ , and H^+ by using a mass and energy analyzer. In particular, the mass analyzer seems to make it possible to observe many H^+ ions, but the mass analyzer hardly measured N_2^+ particles. As indicated in Fig. 6, many N_2^+ ions obviously exist around the cathodes. Marchand et al. and Petitjean et al. did not observe any NH^+ , NH_3^+ , N^+ , and H^+ . These ionic species seem not to be observed at all by the emission spectroscopy. In Hudis's experiments, there remains a question that while the excited species in plasma go through his mass and energy analyzer they may change to another ionic state, because many N_2^+ ions were not detected. The answer of this question is, however, not known.

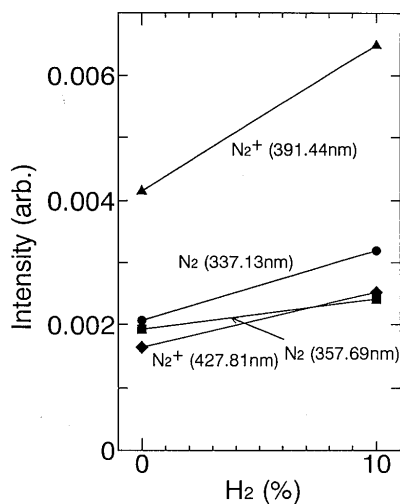


Fig. 11 Effect of gas mixture ($\text{N}_2 + 10\% \text{H}_2$) on the spectral intensities.

The ionic hydro-particles may play an important role as suggested by Hudis. But, in the present paper, we have examined ion nitriding behaviour, by taking into account the peaks emitted strongly. Even if ionic species other than N_2^+ exist in plasma, we consider that they increase and decrease proportionally to N_2^+ ions. In other words, we can regard the N_2^+ intensity as a representative parameter for the ion nitriding. If we take into consideration the results obtained in the present study, we can say that the ion density increases when N_2^+ peak becomes larger.

Of course, it is important for N_2 gas to contain $10\% \text{H}_2$ gas. As indicated by Marchand et al.⁴⁾, N_2 gas with $10\% \text{H}_2$ gives the highest ion density. **Figure 11** also indicates that N_2 gas with $10\% \text{H}_2$ increases ion particles, in comparison with neutral particles.

3. 3. Ion nitriding process controlled by plasma behaviour

Figure 12 shows the nitriding layer thickness δ formed for $t = 4 \text{ hr}$ and the current density of 37.87 Am^{-2} depending on gas pressure P . As seen in Fig. 12, the nitriding layer reaches $70 \mu\text{m}$ at $P = 667 \text{ Pa}$ (5 torr). It is suggested that the nitriding rate reaches the maximum at $P = 533 \sim 667 \text{ Pa}$ (4 to 5 torr).

According to Tanaka et al.¹¹⁾, the lowering in the cathode fall voltage makes oxide film remaining on the specimen surface. This means the lowering in the nitriding rate. This is a reason why the nitriding rate has a maximum value around $P = 667 \text{ Pa}$, even if the specimen temperature is kept constant.

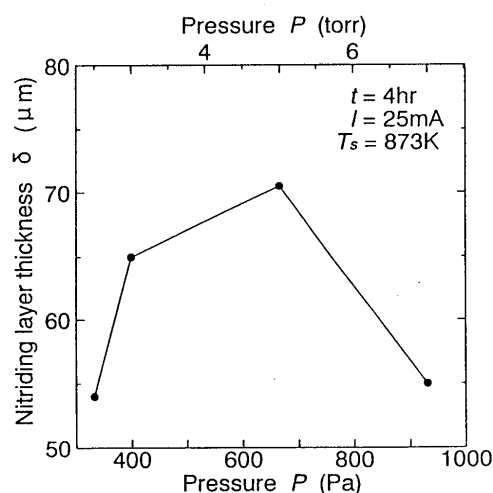


Fig. 12 Nitriding layer thickness produced for 4 hr, depending on the gas pressure.

As mentioned above, the ion density increases as P decreases, and also the discharge voltage simultaneously becomes higher with decreasing P . This means that the sputtering rate increases with decreasing P .

The exited nitrogen concentration increases on the specimen surface with the ion density of N_2^+ and naturally becomes higher as P decreases. The oxide film disappears from the specimen surface by sputtering. The sputtering phenomenon also becomes strong as P decreases. Active metallic atoms or active specimen surface can be exposed to the cathode fall region (or plasma) by this sputtering. It is easy to produce the nitriding reaction, because the free energy change for production of nitride must be negative at $T_s = 873$ K. The nitrogen atoms is supersaturated at the specimen surface, and raises the concentration gradient of nitrogen from the surface to the matrix, resulting in the diffusing process facilitated. But, if the sputtering occurs too much then the nitride layer is simultaneously removed too much. The maximum point of nitride layer thickness, therefore, exists at $P \approx 667$ Pa.

4. Conclusions

We have discussed DC glow discharge for ion nitriding process. We have found that the glow discharge behaviour has an important influence on the ion nitriding. The main results obtained in the present study are as follows,

- (1) The ion nitriding of a SUS 304 stainless steel should be conducted under the conditions of $P = 533$ to 666 Pa ($4 \sim 5$ torr), using the mixture gas $N_2 + 10\%H_2$. Under these conditions, the negative glow area expands only around the cathode. The plasma morphology of type D is suitable for the ion nitriding.
- (2) The exited spectra N_2^+ is strongly observed but other ionic spectra such as H^+ NH^+ are hardly measured, if we use the emission spectrometer.
- (3) The intensities (N_2 and N_2^+) are influenced by the current density, specimen temperature and gas pressure. As the current density decreases and the specimen temperature becomes low, or as the gas pressure increases, the intensity of N_2^+ becomes weaker. This can be explained in terms of the mean free path of particles in plasma.

- (4) The ion nitriding is very influenced by the cathode fall voltage and the ion density around the cathode. With respect to the cathode fall voltage, there is an optimal value for the ion nitriding.

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