Plasma-based nitrogen incorporation techniques for surface modification

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The article discusses various plasma-based nitrogen incorporation techniques for modification of solid surfaces, mostly applicable to iron and titanium-based alloys. While glow-discharge plasma nitriding (GDPN) is commercially successful and is widely investigated, other low-pressure plasma techniques are also gaining importance. A comparison of GDPN with shallow implantation and diffusion hardening is presented. The role of energetic neutrals in GDPN is also discussed. A brief description of mechanism of nitrogen incorporation in solid surfaces is also presented.

Introduction

Nitrogen has been widely used, along with carbon and boron, as elements introduced in iron and titanium-based alloys to increase the mechanical properties such as hardness, wear-resistance and corrosion resistance. These elements, having atomic dimensions much less than that of iron and titanium, can permeate the material as interstitial solid solution. These elements are added in bulk when the steel is in preparation or incorporated on the surface. Nitrogen incorporation on the surface of the finished alloy is called as nitriding. The conventionally used techniques are gas and liquid (salt-bath) nitriding.

Plasma made from nitrogen gas has an abundance of nitrogen ions and radicals and can also be used for nitrogen incorporation in iron and titanium alloys¹. This article discusses various plasma-assisted nitrogen incorporation techniques currently under investigation. The methods of incorporation of nitrogen in a plasma environment can be broadly classified into those based on diffusion^{1,2} or on implantation³. Hybrid processes based on implantation followed by diffusion inside the material have also been developed^{4,5}. The results from implantation at various energies⁶ and the role of energetic⁷ and excited neutrals are presented. A comparison between glowdischarge plasma nitriding (GDPN) and shallow implantation and diffusion hardening is presented⁸. A process of low-pressure nitrogen incorporation based on constricted anode plasma source is also described. A brief comparison between various nitrogen incorporation techniques is presented in Table 1. A brief review of nitrogen

incorporation mechanism in solid substrates is described. The problem of nitrogen incorporation in thin films during reactive physical and chemical vapour deposition is beyond the scope of this article.

Glow-discharge plasma nitriding

GDPN uses an abnormal glow discharge produced in a gas mixture of nitrogen and hydrogen (Figure 1). Abnormal glow discharges are discharges where the cathode of the discharge is fully covered by the glow. The substrate, which is also the cathode of the discharge, is typically biased negative between 400 and 800 V, and draws a current of 1–5 mA/cm². The operating pressure is typically between 1 and 10 mbar. The ratio of nitrogen in the nitrogen–hydrogen gas mixture varies from 5 to 95 volume% (ref. 1). The bias applied on the substrate may be dc or pulsed-dc. However, pulsed-dc is more favourable, as it gives rise to the formation of more radicals and prevents transition to an arc.

The cross-section of a GDPN-treated iron alloy has a compound layer of few microns thickness, which typically consists of Fe_3N followed by a diffusion layer of few tens

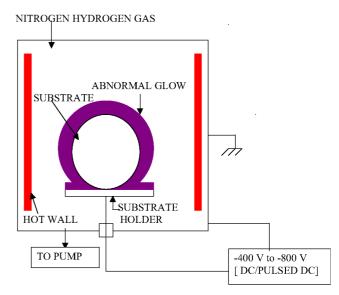


Figure 1. Schematic of a GDPN reactor. The abnormal glow surrounds the substrate uniformly. The hot walls are used usually in larger reactors where temperature uniformity across large substrates is difficult to maintain only by ion and neutral bombardment.

of microns consisting of mainly Fe₄N. The thickness of the compound layer and the diffusion layer together is usually referred to as the case depth. To get reasonable case depths, the substrate temperature is typically kept between 400 and 560°C for iron alloys and between 700 and 900°C for titanium alloys. The compound layer, also known as white layer, is responsible for wear-resistance improvement. The diffusion layer is mainly responsible for the improvement of the microhardness, fatigue life, etc. The compound layer thickness is usually controlled by the amount of hydrogen in the gas mixture; higher proportion of hydrogen gives a lower compound layer thickness.

To increase the corrosion resistance of the nitrided surface, a small amount of carbon is also introduced in the modified surface. The process is then referred to as plasma nitrocarburizing. A small amount of methane is used in the gas mixture in that case along with nitrogen and hydrogen. For austenitic stainless steels, precipitation of CrN takes place in the compound layer, which reduces the corrosion resistance. To avoid CrN precipitation, the treatment temperature is usually kept below 400°C.

GDPN derives its effectiveness by suitable manipulation of the glow discharge, working under conditions in which the glow covers the entire cathode surface. This is usually the condition of the abnormal glow discharge, in which case the discharge has positive dynamic impedance. The substrate behaves as the cathode and the chamber wall as the anode. Surrounding the substrate conformally is a non-glowing region called as the ion sheath, after which there is the negative glow. In the ion sheath region, strong electric fields accelerate ions from the negative glow to the substrate. In GDPN, the substrate bias, background pressure and the substrate current are interrelated.

In abnormal glow conditions, the substrate surface is bombarded with nitrogen ions, energetic nitrogen molecules and nitrogen—hydrogen radicals^{6,9}. Detailed calculation shows that the number of energetic nitrogen molecules bombarding the substrate is much more than the number of nitrogen ions. These energetic molecules also deposit more energy and momentum and thus contribute to net

nitrogen flux, as well as energy to heat the surface to facilitate diffusion of nitrogen. Additionally, hydrogen attaches itself with nitrogen forming NH* radicals, which liberate nitrogen in contact with the surface^{9,10}. All these findings indicate that while ions in an abnormal glow-discharge plasma play a major role in generating the energetic neutral molecules and radicals, their role in nitriding is minimal.

Plasma source ion implantation

Plasma source ion implantation (PSII) derives its effectiveness by imparting kinetic energy to ions of the plasma and making them impinge on the substrate surface, and is thus an ion-dominated process (Figure 2). In PSII, the substrate is immersed in a low-pressure plasma and biased pulsed-negative between – 20 and – 250 kV. The plasma is usually of nitrogen and produced by impact ionization of nitrogen molecules by thermoionically emitted electrons from thoriated tungsten filaments. The pressure is usually much lower than GDPN and so are the plasma densities. Some amount of density enhancement is achieved, by putting a magnetic cusp along the vacuum chamber, which prevents the loss of primary electrons.

According to the theory of PSII, with the application of a large negative bias on the substrate¹¹, in the initial phase (for times less than an ion plasma period), ions remain stationary and electrons are repelled by the bias to create an ion matrix sheath (Figure 3). The potential profile in the ion matrix sheath is parabolic in nature. On longer time scales (for times ~ ion plasma period), ions begin to move towards the substrate. This phase is described by a quasi-static expansion of Child's law. On the assumption that the sheath is collisionless, the time-dependent sheath motion is described by

$$s = s_0 \left(1 + 2 w_{\rm pi} \ t/3 \right)^{1/3}, \tag{1}$$

where s is the dynamic sheath thickness, s_0 is the ion

Table 1.	Comparison of various plasma-based nitrogen incorporation techniques used for iron and titanium alloys

Process	Pressure (mbar)	Gas	Plasma source	Substrate bias (kV)	Substrate temperature (°C); achieved by	Mechanism of nitrogen incorporation
GDPN	1-10	$N_2 + H_2$	Abnormal glow	-0.4 to -0.8	400-900; by ion and energetic neutral	Diffusion of ion, neutral and radical
PSII	$10^{-3} - 10^{-4}$	N_2	Filament-assisted arc	-20 to - 250	Room temperature	Implantation of ion
PIII	$10^{-3} - 10^{-4}$	N_2	Rf inductive	-20 to -40	350-500; by ion energy	Implantation of ion followed by diffusion
RFPN	$10^{-3} - 10^{-4}$	N_2	Rf inductive	– 1	350–500; by auxiliary heater	Implantation of ion followed by diffusion
SIDH	$10^{-3} - 10^{-4}$	$N_2 + H_2$	Filament-assisted arc	-0.5 to - 1	350–500; by ion energy	Implantation of ion followed by diffusion and diffusion of radical
CAPS-PN	10^{-2}	$N_2 + H_2$	Constricted anode, hollow cathode	At ground potential. Anode at + 800 V.	350–500; by auxiliary heater	Diffusion of ion and radical

matrix sheath thickness, w_{pi} is the ion plasma frequency and t is the time. The time-dependent ion current, j_c is

$$j_{\rm c} = (2/9) n_0 w_{\rm pi} s_0 (1 + 2 w_{\rm pi} t/3)^{-2/3},$$
 (2)

where n_0 is the background plasma density. Equations (1) and (2) are important in PSII, as they determine the spacing between substrates, the implanted ion dose, the power supply requirements and hence design parameters of the PSII reactor.

PSII, which was introduced as an alternate to beamline implantation, usually operates at room temperature. Thus the implanted ions have a Gaussian profile in the substrate with the mean at the range of the ion penetration. As the temperature is low, the diffusion of implanted ions is negligible. This renders the surface with a high hardness and also gives corrosion resistance and wear-resistance¹². PSII is also used as an intermediate step in diamond-like carbon deposition on aluminium, where methane is used as the plasma-forming gas. PSII finds it application in materials where there is a restriction on the maximum substrate temperature for surface modification.

Plasma immersion ion implantation

Plasma immersion ion implantation (PIII) is a high-temperature version of PSII with the plasma formed

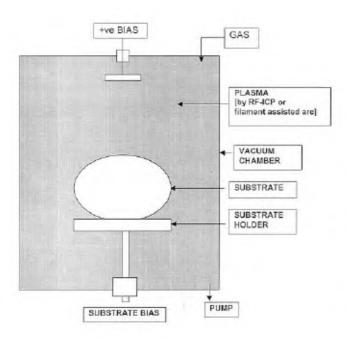


Figure 2. Schematic of a reactor typically used in PSII, PIII, RFPN and SIDH experiments. In RFPN an additional positive bias is applied to an electrode on the top (YAK) to make plasma potential more positive. As these experiments are carried out at a low-pressure, usually there is no additional ionization by the substrate bias around the substrate, unlike GDPN.

using a rf inductively coupled plasma source^{4,13,14}. The basic theory as described in the previous section on sheath dynamics holds good here also (Figure 3). In PIII, the substrate bias is usually varied between – 20 and – 40 kV. The ion bombardment to the substrate surface is applied at a much higher repetition rate, so as to increase the substrate temperature. This facilitates the diffusion of the implanted ions to depths significantly higher than their range of penetration. PIII has been successfully used to modify the surface properties of a wide variety of steels and titanium alloys.

The major contribution from the PIII technique is in understanding the formation and properties of the expanded austenite phase, formed typically at processing temperatures just below 400°C in austenitic stainless steels. Expanded austenite phase has nitrogen present in solid solution in the austenitic stainless steel, without precipitation as nitrides. This gives stainless steel a higher surface hardness without compromising the corrosion resistance¹⁵.

Radio frequency plasma nitriding

Radio frequency plasma nitriding (RFPN) is a recently developed technique for incorporation of nitrogen in steels in an inductively coupled nitrogen plasma at low-pressure (Figure 2). In RFPN, the plasma potential is controlled separately by drawing away electrons by a positive-biased yak¹⁶. The substrate is also biased negative (~1 kV) so as to accelerate ions. RFPN is not very popular as the nitrided layers are not very thick.

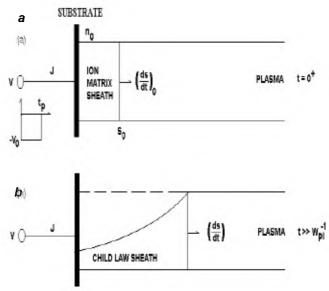


Figure 3. Schematic model of sheath expansion in PSII, PIII, RFPN and SIDH experiments; (a) at the time of application of pulse, and (b) at later times.

Shallow implantation and diffusion hardening

Shallow implantation and diffusion hardening (SIDH) is a process which incorporates implantation and diffusion of nitrogen in a low-pressure nitrogen plasma formed by filament-assisted arc as in PSII (Figure 2). However, in SIDH the substrate bias is pulsed negative and has a magnitude $\sim 1~\rm kV$, and the repetition rate and pulse duration chosen to be high enough that the substrate temperature rises and there is diffusion of implanted ions 6,17,18 . A cross-sectional hardness profile for SIDH-treated AISI52100 steel is presented in Figure 4. It can be seen that in the same treatment duration, nitrogen diffuses to larger depths when the temperature is increased. The results indicate that when the treatment is performed at high temperature, then diffusion is the dominant process.

A comparison of SIDH and PIII-treated SS304 is done by varying the substrate bias from -1 to -20 kV (ref. 19). It is seen that if the temperature is maintained constant by ion bombardment only, then under similar plasma conditions for the same duration, the hardness values are similar at all substrate biases. This suggests that SIDH is probably as competitive as PIII in surface modification of materials at a much lower voltage and hence at a lower hardware cost.

Low-pressure plasma nitriding

Low-pressure plasma nitriding is another technique for introducing nitrogen inside materials. We have developed a variant of this technique using a constricted anode plasma source (CAPS) (Figure 5). Nitrogen ions can be accelerated to a substrate if a suitable potential difference exists between the plasma and the substrate. In most cases, the plasma potential is close to ground potential and the substrate is biased negative. In CAPS, the plasma

1200 1000 800 microhardness (HV) 600 400 received 200 20 40 6.0 8.0 100 120 depth from surface (μm)

Figure 4. Variation of hardness with depth from the surface after SIDH at 500°C for 3, 4 and 5 h for AISI52100 steel. The depth of hardened layer increases with time. The diffusion coefficient of nitrogen is 3.3×10^{-13} m²/s, which is higher than that typically obtained in plasma nitriding.

potential is positive and the substrate is at ground potential. The plasma is produced between a constricted anode and the vacuum chamber is the cathode. The samples are heated using an auxiliary heater to facilitate diffusion of nitrogen. On comparing the diffusion coefficients of nitrogen in stainless steel SS304, it is clear that CAPS plasma nitriding has the highest value, which may be explained because of the high availability of nitrogen from the high plasma density and the presence of nitrogen radicals in a nitrogen—hydrogen gas mixture²⁰.

Comparison between SIDH and GDPN

SIDH and GDPN use similar substrate bias, gas composition and temperature. However, the operating pressure and hence plasma-production mechanism are different.

A thorough comparison between these techniques is reported by Guenzel et al.⁸. The experimental parameters are reported in Table 2. The issue was to evaluate the relative efficiency of GDPN or SIDH for nitrogen incorporation in SS304 under similar substrate bias conditions, temperature, gas composition and treatment duration. The nitrogen concentration profile (Figure 6), shows that for identical gas mixtures, SIDH can deliver a larger amount

Table 2. Parameters for comparison between GDPN and SIDH

	GDPN	SIDH
Substrate	SS304	SS304
Pressure	4 mbar	$5 \times 10^{-4} \mathrm{mbar}$
Plasma production	Abnormal glow discharge	Hot filament arc
Treatment voltage	$-700\ ilde{ ext{V}}$	-700 V
Treatment temperature and time	380°C/2 h	380°C/2 h
Pulse duration and rep. rate	50 μs/10 kHz	50 μs/10 kHz
Gas	N2 and 20%	N2 and 20%
	$N_2 + 80\% H_2$	$N_2 + 80\% H_2$

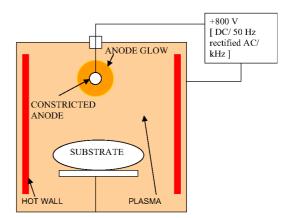


Figure 5. Schematic of a constricted anode plasma source for plasma nitriding applications. On the application of the positive bias on the constricted anode, an anode glow is observed first and then a plasma fills the entire chamber. The hot walls control the substrate temperature.

of nitrogen inside the sample. With pure nitrogen, GDPN is unsuccessful. With the gas mixture, the amount of nitrogen increases, because of the formation of excited neutrals. Glancing-angle X-ray diffraction reveals the formation of expanded austenite phase, indicating that nitrogen is present inside the sample in solid solution (Figure 7). Wear-testing is carried out with sliding tungsten carbide ball at a load of 3 N, with 60% humidity at room temperature on the treated substrates. This also indicates that SIDH with nitrogen as well as the gas mixture, has better wear properties than GDPN (Figure 8).

The superior performance of SIDH in comparison to GDPN has been attributed to decoupling the method of plasma production from the substrate bias in SIDH. In

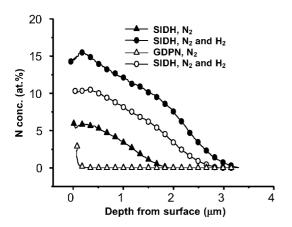


Figure 6. Nitrogen concentration profiles in SS316Ti, measured with glow-discharge optical emission spectroscopy, after 2 h of SIDH and GDPN treatment with nitrogen and a mixture containing 20% nitrogen and 80% hydrogen as working gas.

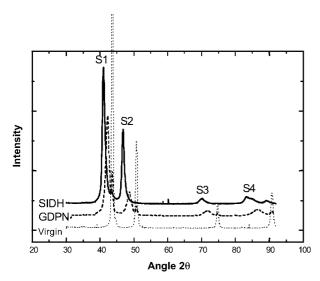


Figure 7. Glancing-angle XRD-spectra showing the austenite peaks (virgin) and peaks of the S-phase (expanded austenite) with the characteristic shift due to lattice expansion.

GDPN, the substrate bias, gas pressure and plasma properties are all coupled with each other, and hence the amount of ions supplied is fixed. Specially, for nitrogen incorporation in austenitic stainless steels, SIDH is suitable as the much-desired hard, expanded austenite phase is formed, which retains the corrosion resistance of steel.

Role of neutrals in nitrogen incorporation

A large number of experiments have been performed to understand the role nitrogen radicals and nitrogen atoms produced in a nitrogen abnormal glow-discharge plasma. The ion sheath, which is collisional with charge exchange as the dominant collision mechanism, provides a rich source of energetic neutrals bombarding the substrate surface. A detailed theoretical analysis has been carried out recently⁷.

The ion distribution function at the cathode of an abnormal glow discharge, which is typically used in GDPN can be expressed in one dimension as

$$f_{i}(u, z) = (6/5) \left[(u s^{5/3}) / \left\{ (u_{m}^{2} z^{2/3} (1 - u^{2} s^{5/3} / u_{m}^{2} z^{5/3})^{2/5} \right\} \right]$$

$$\exp\left[-(z/\lambda) \left\{ 1 - (1 - u^{2} s^{5/3} / u_{m}^{2} z^{5/3})^{3/5} \right\} \right],$$
 (3)

where s is the collisional ion sheath thickness, λ is the collisional mean free path, u is the velocity ranging between 0 and maximum velocity ($u_{\rm m}$) corresponding to the full potential difference, z is the distance from the plasma–sheath interface and has values between 0 and s.

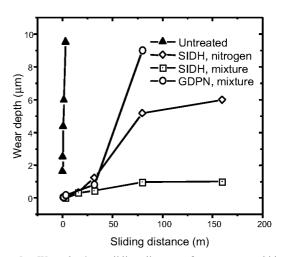


Figure 8. Wear depth vs sliding distance of a tungsten carbide ball (load 3 N) after 2 h of GDPN and SIDH treatment with different gas mixtures compared to the wear of an untreated substrate. The wear obtained after GDPN treatment with nitrogen as a working gas is similar to that of the untreated sample and not shown in the figure. SIDH with the mixture has the highest wear resistance.

The neutral velocity distribution at the cathode is

$$f_{\rm n}(u, z=s) = \int_0^s f_{\rm i}(u, z) \, \mathrm{d}z/\lambda, \tag{4}$$

where (dz/λ) is the probability of occurrence of a charge exchange collision in the element dz and f_i is given by eq. (3). The results are computed by assuming that the plasma comprises only of N_2^+ ions. These ions undergo

charge exchange collision with N_2 molecules only in the ion sheath. The charge exchange cross-section is assumed to be 4×10^{-19} m². In Figure 9, the ion and the neutral distributions are plotted. The neutral distribution peaks at a lower velocity than the ions, however the neutral density is much higher than those of the ions. The peak values of the distribution and other parameters are tabulated in Table 3. The ratio of total momentum and kinetic

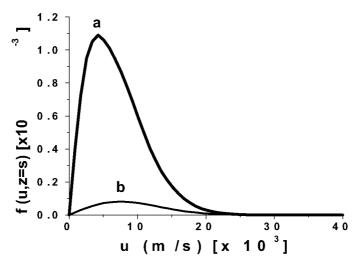


Figure 9. The normalized (a) neutral and (b) ion velocity distributions are plotted for $V_0 = -1000 \text{ V}$, p = 10 Torr and $j = 10 \text{ mA/cm}^2$ at the substrate. The area under the ion curve is unity. For actual values, it has to be multiplied by the ion flux coming from the plasma.

 Table 3.
 Various features of ion and neutral distribution functions

(-)ve Substrate bias [V]	500	500	500	500	1000	1000	1000	1000
Ion current density [mA/cm ²] Pressure [Torr] s [mm] Peak position of f_n ($u, z = s$) [m/s] Width of f_n ($u, z = s$) [m/s]	1 1 2.23 6567 11343	1 10 1.4 2388 4776	10 1 0.88 9850 17910	10 10 0.56 3582 8358	1 1 3.38 6752 13504	1 10 2.13 2532 5908	10 1 1.35 10218 20256	10 10 0.85 4220 9284
$\int_{0}^{u_{\text{max}}} f_{\mathbf{n}}(u, z = s) du$ $\int_{0}^{u_{\text{max}}} f_{\mathbf{i}}(u, z = s) du$	28	174	11	70	42	266	17	106
$\int_{0}^{u_{\text{max}}} u f_{\text{n}}(u, z = s) du$ $\int_{0}^{u_{\text{max}}} u f_{\text{i}}(u, z = s) du$	20.4	13.1	7.5	5.2	31.2	19.9	12.1	7.9
$\frac{\int_{0}^{u_{\text{max}}} u^{2} f_{\mathbf{n}}(u, z = s) du}{\int_{0}^{u_{\text{max}}} u^{2} f_{\mathbf{i}}(u, z = s) du}$	16.1	10.4	6.1	4.1	24.7	15.9	9.3	6.3

energy dumped by the neutrals and by the ions is estimated. In all the cases, the neutrals carry more momentum and kinetic energy to the electrode than the ions.

The results can be used to understand the role these energetic neutrals play in GDPN. In GDPN, the nitrogen ions strike the substrate surface, which is also the cathode, and raise the temperature. These ions and excited nitrogen atoms from the plasma diffuse inside the cathode and cause the necessary sub-surface modification. The role of energetic neutrals, created by charge exchange reaction inside the ion sheath, was not taken into consideration. However, the above analysis indicates that a large number of energetic neutrals can be generated by charge exchange reaction. These energetic neutrals also raise the sample temperature as they carry substantial amount of momentum and energy with them and also diffuse inside the cathode.

Nitrogen incorporation mechanism in solid substrates

The previous sections describe various techniques for nitrogen incorporation in the substrate. The various mechanisms that are prescribed for nitrogen incorporation are described in this section. The possible mechanisms described are mostly theoretical and have a large number of experiments, which either prove or disprove the theory.

One of the models for nitrogen incorporation²¹ in GDPN or iron alloys is based on sputtering of iron from the substrate. On the bombarding of the substrate surface by nitrogen ions, iron gets sputtered as Fe and enters the plasma. These iron atoms react with the nitrogen to form FeN. This FeN gets redeposited on the substrate surface and releases N. This goes on till Fe₄N is formed. The released nitrogen diffuses inside the surface because of high temperature. A large number of experiments²² support the sputtering theory, as iron deposits are seen everywhere in the GDPN reactor. There are, however, experiments²³, which demonstrate nitriding even when the substrate is biased positive, indicating that sputtering alone is not responsible for nitriding. The sputtering model cannot also explain the role played by hydrogen in nitriding.

It was earlier demonstrated that hydrogen plays a crucial role in GDPN. Without addition of hydrogen it is difficult to have significant amount of nitrogen diffuse inside the substrate in a GDPN environment. It is also observed that hydrogen content in the nitrogen—hydrogen gas mixture controls the properties of the nitrided layer. Earlier experiments^{24,25} demonstrated that along with atomic nitrogen ions, molecular nitrogen and hydrogen ions, NH_x^+ (x = 1 to 3) are also produced. NH_x^+ on interaction with the surface forms $FeNH_{2-3}$ phase at the surface which dissociates and liberates nitrogen that diffuses inside. There are various other models based on the

presence of the NH⁺ radicals in the plasma and their role in nitriding. It was also demonstrated that there is a critical amount of nitrogen that has to be accelerated to the surface for any effective nitriding to take place^{26,27}. Hydrogen also reacts chemically with the oxygen present on the surface (as oxides) and activates the surface for nitrogen incorporation.

To facilitate the diffusion of nitrogen, high substrate temperature is needed. Using Fick's law and based on diffusion equations and boundary conditions, the observed diffusion profile can be explained to some extent. The depth of the diffusion zone is observed to depend on the available amount of nitrogen, the concentration gradient, temperature, time, material composition and composition of phases formed dynamically. The diffusion zone consists of nitrogen in solid solution as long as the temperature-dependent solubility limit is not exceeded. If the solubility limit is exceeded, nitride formation occurs and precipitation takes place. The precipitation usually starts at the grain boundaries and spreads in the bulk with increase in temperature or nitrogen concentration 2,28,29.

When the impinging ions have some kinetic energy, which is the case with PSII, PIII, RFPN and SIDH, then the surface also gets modified. The role of hydrogen gets minimal with increase in ion energy²⁸. Simultaneously, sputtering from the surface becomes dominant and so is the secondary electron yield. The surface undergoes radiation damage, generation of defects, amorphization, all of which help in enhancement of diffusion. Additionally, the top surface where most of the ions kinetic energy is dissipated, has a higher temperature and causes phases to form which are different from those formed at low energy. The kinetic energy of the ion aids in the penetration through the oxide layer on the surface and thus reduces the necessity of hydrogen²⁸.

There are many models explaining the mechanism of nitrogen incorporation. Experimental variables include ion energy, dose, angle of incidence, surface roughness, surface microstructure, substrate temperature, thickness of natural oxide layer, presence of hydrogen ions and excited and energetic nitrogen neutrals, presence of molecular and atomic nitrogen ions, etc. A review of the mechanisms of nitrogen incorporation is given by Michel *et al.*³⁰.

Conclusions

In this article a comparison of various plasma-based nitrogen incorporation techniques is described. Though GDPN is the most popular, commercially successful and simpler in operation than other techniques, there are certain other aspects in which other processes are better. For alloys, where the substrate cannot be heated to temperatures higher than 200°C due to metallurgical constraints, PSII is the alternative. In cases where better process control is desired, which can be done by

decoupling the plasma production from the substrate bias, SIDH is a better alternative than GDPN. The commercial acceptability of low-pressure nitriding techniques is yet to be demonstrated for a wide variety of steels. The role of energetic neutrals is presented which indicates that they contribute significantly to GDPN. Various mechanisms responsible for nitrogen incorporation are described.

- Rie, K. T., Menthe, E., Matthews, A., Legg, K. and Chin, J., MRS Bull., August, 1996, p. 46.
- 2. Jindal, P. C., J. Vac. Sci. Technol., 1978, 15, 313.
- Rej, D. J., in Handbook of Thin Film Process Technology, IOP Publishing, 1996.
- Collins, G. A. and Tendys, J., J. Vac. Sci. Technol., 1994, B14, 875.
- Baldwin, M. J., Fewell, M. P., Haydon, S. C., Kumar, S., Collins, G. A., Short, K. T. and Tendys, J., Surf. Coat. Technol., 1998, 98, 1187.
- 6. Mukherjee, S. and John, P. I., ibid, 1997, 93, 188.
- 7. Mukherjee, S., Phy. Plasmas, 2001, 8, 364.
- 8. Guenzel, R., Betzl, M., Alphonsa, I., Ganguly, B., John, P. I. and Mukherjee, S., Surf. Coat. Technol., 1998, 112, 307.
- 9. Petitjean, L. and Ricard, A., J. Phys. D. Appl. Phys., 1984, 17, 919.
- Ricard, A., Henrion, G., Michel, M. and Gantois, M., Pure Appl. Chem., 1988, 60, 747.
- 11. Lieberman, M. A., J. Appl. Phys., 1989, 66, 2926.

- Malik, S. M., Sridharan, K., Fetherson, R. P., Chen, A. and Conrad, J. R., J. Vac. Sci. Technol., 1994, B12, 843.
- Guenzel, R., Brutscher, J., Maendl, S. and Moeller, W., Surf. Coat. Technol., 1997, 96, 16.
- Blawert, C., Knoop, F. M., Weisheit, A. and Mordike, B. L., *ibid*, 1996, 85, 15.
- 15. Blawert, C., Surf. Eng., 1999, 15, 1.
- Baldwin, M. J., Collins, G. A., Fewell, M. P., Haydon, S. C., Kumar, S., Short, K. T. and Tendys, J., *Jpn. J. Appl. Phys.*, 1997, 36, 4941.
- 17. Mukherjee, S. and John, P. I., Surf. Coat. Technol., 1998, 98, 1437.
- 18. Rao, K. R. M., Mukherjee, S., Raole, P. M. and Manna, I., *Surf. Coat. Technol.*, (submitted).
- 19. Mukherjee, S., Raole, P. M. and John, P. I., submitted to *Surf. Coat. Technol.*, (submitted).
- 20. Kumar, R., M Phil thesis, Devi Ahilya University, 1999.
- O'Brien, J. M. and Goodman, D., in ASM Handbook, ASM International, USA, 1992, vol. 4, p. 420.
- 22. Keller, K., HTM, 26, 120, 1971.
- 23. Tibbetts, G. G., J. Appl. Phys., 1974, 45, 5072.
- 24. Hudis, M., ibid, 44, 1489, 1973.
- 25. Szabo, A. and Wilhelmi, H., HTM, 1984, 39, 148.
- Bell, T., Staines, A. M. and Loh, N. L., Neue Hüette, 1983, 28, 373
- 27. Hombeck, F. and Bell, T., Surf. Eng., 1991, 7, 45.
- 28. Blawert, C., Ph D thesis, TU Clausthal, 2000.
- Chakraborty, J., Alphonsa, I., Mukherjee, S. and John, P. I., submitted to J. Mater. Res.
- 30. Michel, H., Czerwiec, T., Gantois, M., Ablitzer, D. and Ricard, A., Surf. Coat. Technol., 1995, 72, 103.

MEETINGS/SYMPOSIA/SEMINARS

National Workshop on Geo-Technical Investigations and Highway Material Testing (GIHMT-02)

Date: 24 August 2002

Place: Indore

Topics include: Geo-technical Investigations: Field and laboratory tests including Lab Session; Highway Material Testing: Field and laboratory tests including Lab Session.

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Date: 27–28 September 2002

Place: Coimbatore

Topics include: 1. Plant genetic engineering methods; 2. Development of transgenics for improvement of agricultural and horticultural crops through (i) Resistance to pest and diseases, (ii) Tolerance to herbicides, (iii) Tolerance to abiotic stresses, (iv) Improvement of horticultural crops; 3. Role of GM crops in human health: (a) Nutritional improvement of agricultural and horticultural crops by genetic engineering, (b) Pharmaceutical improvement of medicinal plants by genetic engineering, (c) Edible vaccines, (d) Plant-based antibodies.

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