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Surface & Coatings Technology 215 (2013) 431-439

Contents lists available at SciVerse ScienceDirect



Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

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ARTICLE INFO

Available online 6 November 2012

Keywords: Plasma Coatings Ionitriding Duplex Arc discharge

ABSTRACT

The gaseous plasma of low pressure arc discharges has been used extensively for various surface treatment applications including heat treatment, ion nitriding, ion implantation, PECVD and duplex processes. Highly ionized low pressure arc plasmas with electron density up to $\sim 10^{18}$ m⁻³ can be generated by a shielded vacuum arc cathode, a hollow cathode or by a thermionic cathode. In this paper, plasma properties are characterized by electrostatic probes and optical emission spectroscopy. A range of different species can be produced in low pressure arc plasma immersion processes via decomposition of precursor molecules by electron collisions. Surface treatment of different steels and metal alloys in such a dense plasma environment can substantially affect the surface profile. The ion nitriding of different types of steel in a low pressure arc plasma environment is investigated. The rate of ion nitriding as a function of plasma parameters, such as ion current density, pressure and gas composition is established for several types of steel and ranging from 0.1 to 1 µm/min. Ionitrided layers can be produced in arc plasma immersion processes at substrate biases as low as -30 V and substrate temperatures as low as 200 °C, depending on the type of steel. Alternatively, low energy ion implantation of nitrogen can be produced at bias voltages exceeding - 500 V and substrate temperatures less than 100 °C. The distribution of plasma density and the uniformity of ion nitriding layers in industrial scale vacuum processing chambers are investigated. Duplex coatings were also produced by ion nitriding in an arc plasma immersion environment followed by deposition of TiN coatings. The ion nitriding and duplex coating layers are characterized by structure, thickness, microhardness depth profile, surface roughness and coating adhesion. Surface treatment in conventional glow discharge compared to low pressure arc plasma immersion processes is presented. The results of processing complex shape components are discussed.

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1. Introduction

For the past 20 years, plasma immersion surface engineering technologies have been under increasing attention of the scientific and industrial communities. Following the pioneering work of Conrad [1] who introduced plasma immersion ion nitriding, it is now successfully applied to other processes, like ion implantation, ion cleaning, and coating deposition [2]. The basic approach of this technology is to split up two different tasks: creation of a plasma environment and providing ion bombardment of the substrates by the ions attracted from the surrounding plasma. In a traditional technology a high voltage bias is applied to the substrates, which creates anomalous glow discharge plasma surrounding the substrates. At the same time, the same bias voltage is used to attract the ions from the plasma. The characteristic pressure for glow discharge ion nitriding technology is 1-10 hPa, as determined by Paschen curve [2,3]. Plasma source ion nitriding and low energy ion implantation use an independent plasma source to ionize a nitrogen containing reactive gas atmosphere and then deliver a high flux of highly chemically active

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0257-8972/\$ – see front matter @ 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.surfcoat.2012.10.069 nitrogen-bearing atomic particles to the substrate surface [2]. The flux of nitrogen ions can be formed by ion beams as in the case of ion beam nitriding of titanium alloys in [4]. Alternatively a set of active nitrogen-bearing species can be generated by different plasma discharges such as glow discharge, MW (microwave), RF or DC arc discharge [2,5-7]. Low temperature ion nitriding and ion implantation processes can be performed in highly ionized dense plasma environments [2,5,8-10]. In the case of plasma immersed ion nitriding processes, the operating pressure is determined by an independent plasma source, while the bias potential applied to the substrate can be varied over a wide range, independently from the plasma generator. In most cases, RF or thermionic DC plasma sources were used to generate the plasma environment for plasma immersed processes. At the same time it was found that using a cold vacuum arc cathode to generate a plasma environment yields significant advantages over other electron emitters such as hollow cathodes or thermionic cathodes for plasma immersed processes [11-18]. The first experiments using vacuum cathodic arc sources integrated in conventional cathodic arc coaters were conducted in the 1980's-1990's to generate a remote arc discharge (RAD) plasma also known as arc enhanced glow discharge (AEGD) for ion nitriding, ion cleaning, ion implantation and coating deposition processes [19-24]. In this approach the dense and highly ionized plasma of the positive column of the remote low pressure arc or glow discharge is generated between the cathode of the primary vacuum arc discharge and the remote anode. It was found that vacuum arc generators are capable of providing a uniform distribution of dense and strongly ionized gaseous plasma over large industrial coating chambers. In addition, the cathodic arc source can operate in any reactive gaseous environment which makes this type of plasma generator more widely useful than hot filament or hollow cathode thermionic cathodes.

Low temperature and low pressure plasma immersion surface modification processes are also capable of supporting duplex surface treatment which consists of the combination of ion diffusion saturation of the surface layer followed by hard thin film coatings [2,14-17,20–27]. This approach is particularly effective in improving the load bearing capacity of surfaces. Thin film surface coatings deposited by PVD and CVD techniques are hard and can provide excellent tribological properties, but when they are deposited on a relatively soft metal substrate experiencing large plastic deformation at high loads, the egg-shell effect can reduce the load bearing capacity of the coated surface hence limiting its wear resistance [14,15,17,26-28]. Super hard DLC (diamond-like carbon) coatings have unique tribological properties with microhardness >50 GPa and coefficients of friction <0.1 at small loads P<P_c. However, when the DLC layer is deposited on relatively soft metal substrates it shows a rubber-like elastic behavior with negligible plastic deformation. When the substrate experiences large plastic deformation at increased loads P>Pc the DLC layer collapses. The value of the critical load, P_c, increases both with substrate hardness and with thickness of the coatings. For the loads larger than P_c, a macro failure of the coating over an area considerably larger than the indentation region is observed [14,15]. Duplex surface engineering is aimed at reducing the sharp gradient between the hard thin film coating and the soft metal substrate. The ratio of hard coating thickness to the thickness of the surface layer with improved hardness, such as an ion nitrided or a carburized layer may exceed 1:10 to achieve optimal results for load bearing capacity. This technique was applied to DLC coatings deposited on steel substrates in [14,15]. In these works, two coating layers, a 0.5 µm thick layer of DLC having hardness > 75 GPa, and a 0.5 μ m thick layer of TiN, having a hardness of 30 GPa were deposited on top of steel with a 30 µm ionitrided layer, having a hardness of 13 GPa, creating a nitrided steel-superhard coating system with improved load bearing capacity. It was shown in [26] that while untreated titanium and its alloys can hardly sustain 0.1 GPa at <5% sliding-rolling ratio, the novel titanium duplex system combining an oxygen diffusion treatment with a DLC coating can withstand 1.7 GPa under 100% sliding conditions. A similar approach was used in [27] where duplex surface engineered systems consisting of a nickel diffusion layer followed by TiN and DLC coatings were optimally designed and successfully tested.

Duplex coatings are found to improve wear resistance in large contact load applications when failure of the substrate system is by the egg-shell effect; effectively, a relatively soft metal substrate is unable to support a thin hard coating and under high loads the coating fails. In such cases the ion nitrided layer which has a hardness intermediate between a hard coating and a steel substrate can be adjusted to smooth the gradient in hardness distribution across the near-surface layer. Ion nitrided intermediate layers can also contribute to the improvement of corrosion resistance both in low temperature and in high temperature applications. Die casting dies have to survive a highly aggressive environment in an Al-Si foundry process. Duplex coatings on this tooling, deposited in the LAFAD system, were successfully utilized. In this application TiB₂containing multilayer coatings deposited by the filtered arc process on ion nitrided steel have demonstrated an order of magnitude improvement over samples which had only a coating or only an ion nitrided surface. This is due to the improvement in the strength and surface hardness of the substrate as well as diffusion barrier behavior provided by the combination of ceramic coatings and ion nitriding [21–24].

In the present work, ion treated surfaces of different steel produced in nitrogen and argon-nitrogen RAD plasma immersion processes are studied with emphasis on correlations between plasma characteristics and surface properties during initial stages of plasma-surface interaction. The modeling of nitrogen surface diffusion at the initial exposure of the steel substrate in a low pressure RAD plasma environment is discussed. This model is limited to the time until nitrogen concentration in a surface layer reaches its solubility limit. The modification of surface properties of different types of steel due to ion treatment in low pressure RAD plasma at later stages of the process is also discussed mostly for demonstration of the potential of this technology. Hardening of surface layer, formation of compound layer and examples of duplex coatings are also presented for illustration purposes, but detailed kinetics of RAD plasma ionitriding during later stages of the process (after surface reaches the nitrogen solubility limit) and functional properties of the RAD plasma treated surfaces are not discussed in this preliminary paper, which will be a subject for the further works.

2. Experimental details

A schematic illustration of the Large Area Filtered Arc Deposition (LAFAD) surface engineering system used in this study is shown in Fig. 1. It has a main chamber 600 mm dia \times 600 mm height with an attached Large Area Filtered Arc Source (LAFAS). This unidirectional dual filtered arc plasma source has a rectangular plasma guide chamber with two cathodic arc sources attached to the opposite walls of the plasma guide chamber. Each cathodic arc source utilizes a cylindrical "billet"-like target, 80 mm dia×50 mm long. The plasma guide has a deflecting, focusing, and scanning magnetic system which allows the plasma jet to be turned by 90° and focused toward the substrate to be coated. The positions of the cathode targets are displaced to each other by 50 mm in the vertical direction to compensate for the centrifugal drift of the vacuum arc plasma jets in a curvilinear magnetic field [14-17,20,22,29,30]. The remote anode is installed in the coating chamber opposite to the LAFAS opening. This allows operating in two modes: first, in a gaseous plasma processing mode and second, in filtered cathodic arc deposition mode. In gaseous plasma processing mode the deflecting magnetic field of the LAFAS is turned off which makes it a powerful source of electrons emitted by the cathodes of the primary arc sources. The influx of electron current propagating from the primary cathodic arc throughout the coating chamber creates highly ionized plasma on its way toward the remote arc anode. In the coating deposition mode, the magnetic deflecting field of the LAFAS is turned on bending the metal vapor plasma flow toward substrates to be coated in the coating chamber. The array of conventional tubular resistance heaters is set between the substrate holder platform and the auxiliary anode surrounding the substrate fixtures set. The coating deposition area of the system is 450 mm dia × 350 mm height. The substrate platform has 12 satellites, which can be provided with single or double rotation. The steel disks used as substrates for all trials were installed on a satellite position with single and double rotation [20,29,30].

The typical LAFAD plasma processing parameters used in most of the deposition trials reported in this work include the following steps: after pre-heating to 300–350 °C using a radiant heater array, the substrates were subjected to fifteen or twenty minutes of ion etching at ~0.1 Pa in an argon RAD plasma generated by the LAFAS with the deflecting magnetic field turned off. After the ion etching step, nitrogen was added to the gas atmosphere at pressures ranging from 0.02 to 1 Pa and to carry out the ion nitriding stage. For the duplex treatment, filtered arc coatings of different architectures were deposited after the ion nitriding stage. During deposition of ceramic or cermet coatings, an ultra-thin metallic bond layer is deposited first to improve the coating adhesion. The metal coatings were deposited in argon, while during deposition of carbides, nitrides or oxiceramic layers, a reactive gas (methane, nitrogen and/or oxygen)



Fig. 1. Schematic view of the LAFAD-600C large area surface engineering system.

is added to the processing chamber, forming a reactive gaseous plasma atmosphere. The gas pressure in LAFAD processes typically ranges from 0.02 to 0.1 Pa for deposition of ceramic coatings, while it can be reduced below 0.001 Pa for the deposition of carbon DLC and related coatings [14,15]. Note that during deposition of near dielectric oxiceramic and oxinitride coatings as well as ta-C coatings, a 13.56 MHz RF generator was used as a substrate bias power supply, while for deposition of conductive coatings, an MDX-II (Advanced Energy) power supply, coupled with their Sparcle-V accessory, was used as a DC bias power supply. The substrate bias during ion nitriding did not exceed -100 V, while during the coating deposition stage the bias potential ranged from -30 to -50 V [14-17,20,29,30]. The ta-C coatings were deposited by LAFAD coating deposition process using the primary cathodic arc sources with graphite targets at primary arc current of ~70 A without input of any residual gas during 1 h at deposition rate of 0.5 µm/h. During this coating deposition run the substrate bias was applied by RF 13.56 MHz generator with the matching network which kept the substrate autopolarization potential at ~100 V. The drill bits of 1 mm and 10 mm diameter made of HSS and cemented carbide (WC/6% Co) were used as substrates in this coating deposition process. Portion of the HSS drills were subjected to 10 min of RAD plasma ionitriding prior to carbon coating deposition process.

The angular distribution of the ion saturation current density around the chamber was measured by an array of ion collector probes. These were cylindrical in shape with dimensions 0.35 m tall × 0.05 m diameter and were distributed equidistantly along the circumference of the round table at a radius of 0.2 m as illustrated in Fig. 1. The probe located in front of the LAFAS opening along the line of symmetry was assigned to the two angular positions of 0° and 360°. The ion collector probes were biased -100 V vs. ground similar to arrangement used in [14,15,20,29]. The coupons, 0.025 m dia×0.003 m thick, were also positioned along the circumference of the round table at the half height of the ion probes. The coupons were made of different steel which allows demonstrating the differences in RAD plasma ionitriding depending on substrate composition. The chemical compositions of steel samples used in this study are shown in Table 1. After plasma treatment the coupons were cross-sectioned and polished and the hardness distribution was determined by measuring Knoop indentations as a function of the distance from the surface. This was followed by etching for 4 min in Nital (2% nitric acid in ethyl alcohol solution) which reveals information about the morphology of the nitrided layer. A white layer on etching indicates a compound layer of either $\epsilon\text{-Fe}_{2-3}N$ phase or a mixture of Fe₄N or Fe₃N nitrides depending on substrate temperature during ionitriding process. Layers with less nitrogen are etched by the Nital and appear dark under the optical microscope. Substrate temperature was measured using heat treated 1045 steel coupons. The curve presented in Fig. 2 shows the relationship between the hardness of 1045 steel coupons vs. temperature after 1 h exposure in a furnace at different temperatures. The assessment of the temperature distribution in the coating chamber has shown that the

Table 1

| Typical elemental composition | on of steels used in this | work, at.% (balance iron). |
|-------------------------------|---------------------------|----------------------------|
|-------------------------------|---------------------------|----------------------------|

| Steel | С | Cr | Мо | W | V | Ta | Со | Ni | Mn | Cu | Si |
|---|--|--|------------------------------|-------------|-----------------------|-----------|----|----------------------|---------------------------------------|-----------|--|
| HSS (T1) M2 H13 SS17-4 AISI 4340 AISI 1045 | 0.75 0.95 0.37-0.42 0.07 0.36-0.44 0.43 | 4.2 5.0–5.5 15.00–17.50 1–1.4 | 5.0 1.2–1.75 0.25–0.35 | 18.0 6.0 | 1.1 2.0 0.8–1.2 | 0.15-0.45 | | 3.00–5.00 1.3–1.7 | 0.2–0.5 1.0 0.45–0.7 0.6–0.9 | 3.00-5.00 | 0.8–1.2 1.0 0.1–0.35 0.15–0.3 |



Rockwell C 45 40 Hardne ss, 35 30 -0.0612x 69.112 25 20 750 150 250 350 450 550 650 Temperature, Deg. C

Fig. 2. Tempering curve for 1045 Steel for 1 h tempering.

maximum temperature difference due to radiation heating for different locations within the processing chamber does not exceed 30 °C. The elemental distribution within the near-surface layer was determined by Auger electron spectroscopy, as described previously [21,29]. This analysis was done using a Varian model 981-2707 Auger electron spectrometer. Electron beam energy of 5 keV was used. The modulation voltage on the lock-in amplifier was 10 V peak-to-peak. The data was digitized and processed using custom software. A Varian model 981-2043 ion gun was used to obtain the depth profiles. The ion beam energy was 2 keV. A sputter rate of 8 nm/min was measured on a CVD silicon nitride thin film.

3. Results and discussion

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3.1. Characterization of RAD plasma processing

The density of the ion saturation current impinging upon the substrates immersed in the RAD plasma is shown in Fig. 3. The density of the nitrogen atoms in the RAD argon-nitrogen plasma is also shown in Fig. 3. The concentration of the atomic nitrogen in the RAD plasma was measured by an optical emission actinometry technique using radiation of atomic nitrogen and argon at spectral lines NI(410.0 nm) and ArI(415.9 nm) [15,17,31]. An unexpected feature of the RAD plasma is that the ion flux and its resultant current density increase when gas pressure decreases. The concentration of atomic nitrogen increases with an increase of gas pressure, as a result of decomposition of nitrogen molecules, excited nitrogen molecules, and molecular ions by electron impacts [5,8,15,17,31-33].



Fig. 3. Ion flux and concentration of nitrogen atoms vs. nitrogen pressure.

The relationship between ion saturation current and RAD current is shown in Fig. 4. The ion flux current increases with an increase of the RAD current and decreases with an increase of the gas pressure. It can be seen that the magnitude of the ion saturation current is approximately in direct proportion to the RAD current. Under conditions typical for RAD plasma immersion processes the pressure p<1 Pa, the plasma sheath is collisionless, and the ion flux of ionized particles of k-sort follows Bohm's relationship [3]:

$$J_{ik} = cez_{ki}n_{ik}v_{kBohm}, v_{kBohm} = \sqrt{\left(\frac{k_B T_e}{M_k}\right)}, \tag{1}$$

where e is electron charge, z_k, M_k and n_{ki} are charge number, atomic mass and density of ionized atomic particles of k-sort, Te is electron temperature, k_B is the Boltzmann constant, and c is a coefficient on the order of unity. The total ion flux of all ionized atomic particles reaching the substrate is:

$$j_i = S_k(j_{ik}) \tag{2}$$

In a RAD plasma the electron temperature ranges from 1 to 3 eV over a wide range of pressure and remote arc current making Bohm's velocity nearly independent from discharge parameters [3,15,31]. In the case of argon RAD plasma, as follows from the results shown in Fig. 4 and from Eq. (1), the density of argon ions, n_{iAr}, is proportional to the RAD current. Direct proportionality between discharge current and plasma density in the RAD plasma was also proved by optical emission spectroscopy measurements. The main channel of excitation of argon atoms in a low pressure (p<1 Pa) RAD plasma is single electron impact followed by radiative decay, which is governed by the following reactions:

$$e + Ar \Longrightarrow e + Ar \Longrightarrow Ar \Longrightarrow Ar + h\nu.$$
(3)

In this case, the concentration of the excited argon atoms in the RAD plasma is proportional to electron density: $n_{Ar^*} \propto n_e$. It can be seen from Fig. 4 that the intensity of the radiation at wavelength 763.79 nm (ArI) from the radiative decay of the excited argon atoms is proportional to the RAD current hence the electron density is also proportional to the RAD current. Direct proportionality of electron density to discharge current is a common feature in positive column plasmas such as low pressure arcs and glow discharges [3]. Using expression (1) and assuming an electron temperature, T_e , of 1–3 eV one can estimate the RAD plasma density to be in the range of 10^{16} – 10^{18} m⁻³. In low pressure discharge plasmas (p<1 Pa), the electron-heavy particle collisions are the dominant reactions generating both excited neutral and ionized species. In pure nitrogen or N₂-Ar plasmas the following nitrogen-bearing species can contribute to the ion nitriding process: atomic nitrogen N, N⁺ ions, vibrationally excited nitrogen molecules N₂ and molecular ions N₂⁺. The concentrations of these particles in the positive column of low pressure arc discharges are proportional to the electron concentration n_e and, consequently, to the discharge current [3,6,7,31-33]. In the ion nitriding process the nitrogen-bearing atomic particles conveyed from the plasma environment stick to the surface. The neutral particles, N and N₂, as well as N_2^+ molecular ions, can stick to the substrate surface by physical and chemical absorption, while atomic nitrogen ions N⁺ can be implanted into the surface even at low substrate bias [3,5–7,31–35]. The vibrationally excited nitrogen molecules and molecular ions can produce atomic nitrogen via heterogeneous decomposition at the substrate surface. The flux of neutral atoms and molecules conveyed from the nitrogen plasma to the substrate surface can be defined as follows

$$g_n = \Sigma_k g_{nk} = 1/4\Sigma_k n_{nk} v_{kT}, v_{kT=} \sqrt{\left(\frac{2k_B T_g}{M_k}\right)}$$
(4)

where g_{nk} and n_{nk} , are the flux and density of the neutral atomic particles of k-sort respectfully and v_{kT} is their thermal velocity, T_g is gas

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Fig. 4. Ion flux radiation intensity emitted by excited Ar atoms and depth of the nitriding layer as a function of RAD current.

temperature [3]. The mass flux of the ionized atomic particles toward the substrate surface can be calculated on the basis of Eqs. (1) and (2):

$$g_i = \Sigma_k(n_{ik} v_{kBohm}). \tag{5}$$

Therefore the total mass flux of nitrogen-bearing atomic particles which can contribute to the ion nitriding process can be expressed as follows:

$$\mathbf{q} = \Sigma_k (\mathbf{n}_{nk} \mathbf{v}_{kT} + \mathbf{n}_{ik} \mathbf{v}_{kBohm}). \tag{6}$$

In the low pressure RAD plasma the concentration of these particles is proportional to the RAD current, and, at the same time, it is a function of the nitrogen pressure. Therefore the flux of nitrogen-bearing species which can contribute to the low pressure RAD plasma immersion ion nitriding process can be expressed as the following:

$$q_{N} = q(P_{N})j_{RAD},\tag{7}$$

where j_{RAD} is the RAD current density and $q(P_N)$ is a function of nitrogen pressure. The portion of the total flux of the nitrogen-bearing species delivered to the substrate surface from the surrounding plasma environment which is trapped at the substrate surface and contributing to the solid-state nitrogen diffusion into the substrate is defined by the substrate temperature. Taking into account Eq. (7), this flux can be expressed as the following:

$$\mathbf{q}_{s} = \mathbf{q}'(\mathbf{P}_{N}, \mathbf{T}_{s})\mathbf{j}_{\text{RAD}},\tag{8}$$

where q_s is a flux of plasma-born nitrogen atoms trapped by the surface of the substrate, P_N is nitrogen pressure, T_s is substrate temperature and q'(P_N ,T s) is a function of nitrogen pressure and substrate temperature [4–6,34–36].

3.2. Modeling of the initial stage of RAD plasma ionitriding

The following model can be used to estimate relationships between the main parameters of the RAD plasma ion nitriding process. This model is similar to the integral heat-balance model developed in [37–39]. The Fick's equation which governs the diffusion transport of nitrogen in a substrate is given as follows [37,38,40]:

$$\partial C_{\rm N} / \partial t = D_{\rm N} \left(\partial^2 C_{\rm N} / \partial x^2 \right) \tag{9}$$

where D_N is the diffusivity of nitrogen in steel, C_N is the nitrogen concentration in the substrate. Taking into account Eq. (8), the boundary condition to Eq. (9) at the substrate surface can be expressed as follows:

$$D_{N}(\partial C_{N}/\partial x)_{s} = -q_{s} = -q'(P_{N}, T_{s})j_{RAD}, \qquad (10)$$

where $(\partial C_N/\partial x)_s$ is a gradient of the nitrogen concentration at the substrate surface. In the case of metals which do not initially have dissolved nitrogen, both the nitrogen concentration and nitrogen flux at the end of the diffusion layer within the substrate are near zero:

$$C_N(d_N) = 0, (\partial C_N / \partial x)_{dN} = 0 \tag{11}$$

where $d_{N}(t)$ is the depth of the nitrogen diffusion layer.

Eq. (9) can be also given in integral form as follows:

$$\frac{d}{dt}\int_{0}^{d_{N}}C_{N}dx = -D_{N}(\frac{\partial C_{N}}{\partial x})S.$$
(12)

A simple approximation to the solution of Eq. (12) with boundary conditions (10) and (11) can be found by using a polynomial profile:

$$C_{N} = (q_{s}/2d_{N}D_{N})(d_{N}-x)^{2}. \tag{13}$$

Solution of Eq. (12) gives the following expression for the depth of the nitriding layer:

$$d_N = \sqrt{6D_N t}.$$
 (14)

The surface concentration of the nitrogen determined by Eq. (13) is

$$C_N = q_s d_N / 2D_N. \tag{15}$$

Therefore, the time needed to reach the maximum nitrogen concentration C_{Nmax} determined by the solubility limit of nitrogen in steel at the substrate surface is given as follows:

$$t_{max} = 2/3 \left(D_N C_{Nmax}^2 / q_s^2 \right), \tag{16}$$

or, taking into account Eq. (8):

$$t_{max} = 2/3 \left({D_N {C_{Nmax}}^2 / \left({q^2 (P_N , T_s)j_{RAD}}^2 \right)}, \tag{17} \right)$$

where C_{Nmax} is the maximum solubility level of nitrogen in the substrate determined by steel composition and substrate temperature; t_{max} represents so-named incubation time which starts from the beginning of the ionitriding process until the nitrogen concentration at the substrate surface reaches the solubility limits of the bulk [26,36–38,40,41]. Eq. (17) shows the inversely proportional relationship between incubation time and the square of the RAD current density. Substituting Eq. (17) into Eq. (14) yields the maximum depth the ion nitriding layer reaches when nitrogen is reaching its maximum solubility level:

$$d_{N} = 2D_{N}C_{Nmax}/(q(P_{N},T_{s})j_{RAD}), \qquad (18)$$

which shows that the thickness of the nitrided surface layer produced during the incubation period of time is inversely proportional to the RAD current density.

3.3. Characterization of RAD plasma ionitriding of the different type of steel

The direct measurement of the rate of ion nitriding of HSS coupons subjected to the RAD plasma at the same substrate temperature and nitrogen pressure has demonstrated an almost directly proportional relationship between RAD current density and depth of ionitrided layer as illustrated in Fig. 4. It was found that the most effective pressure range of the RAD plasma immersion process is from 5×10^{-3} to 1 Pa due to higher plasma density of the RAD plasma at lower pressures.

The uniformity of plasma distribution along with temperature and ion nitriding rate of coupons made of HSS positioned at different locations around the circumference of the coating area of the plasma processing chamber is presented in Fig. 5. The coupons made of HSS along with temperature sensitive coupons made of heat treated 1045 steel were also distributed equidistantly around the substrate table. The coupons were attached to the ion collectors in the middle of each cylinder-probe on its side facing the chamber walls. During the first 30 min of this process (process stabilizing/conditioning stage) the chamber was filled with argon at 0.04 Pa and radiation heaters were turned on to stabilize the thermal conditions in the chamber. After this stage the argon was replaced with nitrogen at the same pressure of 0.04 Pa. The RAD discharge was then established with a remote anode current of 60 A. The ion probes along with the steel coupons were biased at -100 V vs. ground. The process lasted 1 h in pure nitrogen at 0.03 Pa. The ion saturation current density distribution has two maximums: near 0/360° in front of the LAFAS and near 180° in the vicinity of the remote anode. A slight asymmetry in the plasma density distribution can be attributed to the vertical displacement of the primary arc cathode targets of the LAFAS. It can be seen from Fig. 5 that during this process the temperature of the coupons was distributed quite uniformly around the processing area of the chamber at $550 + (-50 \degree C)$. The ion nitriding layer is composed mostly of diffusion zone which after etching in Nital solution looks like a thick dark layer and sometimes a very thin, hard and brittle surface nitride-enriched layer which looks like a white layer after etching. The rate of ion nitriding of HSS reached approximately 0.5 µm/min. The ion nitriding rate increases in the area of the chamber where the plasma density is higher. Maximal coupon temperatures are located in the vicinity of the heaters and remote anode (180° position) where the rate of ion nitriding reaches its maximum as well. A thin nitride-enriched compound layer (a white layer) was detected only at the locations with highest temperature of the coupons. Preliminary XRD analysis of samples made of mild steel and HSS subjected to ionitriding in RAD plasma at 0.5 mtorr of nitrogen pressure and substrate temperatures below 500 °C has revealed the formation of ϵ -Fe₂₋₃N phase after the first 30 min of ionitriding process, when the formation of the white surface layer started, in agreement with iron-nitrogen equilibrium diagram [14,37]. However, the detailed analysis of phase composition and kinetic of formation of nitriding phases during later stages of RAD plasma ionitriding, after surface layer reaches the maximum solubility level of nitrogen in steel, is not included in a scope of this preliminary work. At the locations where ion current density and temperature are smaller the RAD



Fig. 5. Distribution of ion saturation current, temperature of 1045 Coupons and ionitriding rate of HSS steel vs. its position around the substrate platform of LAFAD-600C system. RAD current 60 A, nitrogen pressure 0.03 Pa, substrate bias - 100 V, process duration 1 h.

plasma ion nitriding process creates only diffusion layer without forming the hard and brittle nitride phases on the surface. Photographs of cross sections of M2 and H13 steel coupons subjected to RAD plasma immersion ion nitriding followed by 4 min etching in Nital solution are shown in Fig. 6. The dark layer with thickness of 30–100 µm represents a diffusion zone while a white surface layer 2–3 µm thick represents a nitride-enriched compound zone [25,42,43].

The nitrogen distribution measured by AES analysis in a nearsurface layer of H13 steel after 0.5 h nitriding in the RAD plasma at low substrate temperature, less than 300 °C, and at a relatively low substrate bias ~ -200 V is shown in Fig. 7. In this process, which is a borderline between low temperature ionitriding and low energy ion implantation, the characteristic concentration of nitrogen at the substrate surface is saturated at the level of about 1 atom % which corresponds to the nitrogen solubility level in H13 steel. This analysis only indicates that the saturation level of the nitrogen concentration at the surface of the substrate and is not intended to describe the depth profile of the nitrogen within the surface layer, which is not expected to form at such a low substrate temperature during initial stage of the ionitriding process. The same level of nitrogen concentration at the substrate surface can be reached in RAD plasma low energy ion implantation process at substrate temperature less than 100 °C and substrate bias ~ -500 V during the processing time not exceeding 2– 3 min. This time is in good agreement with characteristic incubation time estimated from the Eq. (17). The typical rate of remote arc plasma immersion nitriding of high-alloy steels ranges from 0.1 $\mu\text{m}/\text{min}$ to 1 µm/min depending on type of steel and plasma processing parameters, including substrate temperature, ion flux density and substrate bias. Structure and morphology of the surface layer can be



Fig. 6. Photographs, in cross-section: (a) H13 steel (a) and (b) M2 steel, after 1 h of ionitriding at substrate temperature ~500 °C in pure nitrogen RAD plasma at p = 0.04 Pa, ion current density 5 mA/cm², ×400 magnification (after 4 min etching in Nital solution).



Fig. 7. AES analysis of elemental distribution across the surface layer of M2 steel after 30 min ionitriding at substrate temperature $T_s \le 300$ °C in pure nitrogen RAD plasma at p = 0.04 Pa, ion current density 5 mA/cm².

controlled by adjusting the plasma processing parameters. The RAD current magnitude can be adjusted to influence the overall thickness of the nitride layer. Thickness control is achieved by the control of the ion density and therefore the ion impingement rate during RAD plasma processing because of a strong dependence of ion density on RAD current. A high RAD plasma density allows a high flux of ions to impinge upon the plasma immersed substrate surface. In this case, the high rate of ion nitriding can be achieved without a need of high bias voltage which can damage the surface and increase surface roughness. The rate of ion nitriding vs. substrate temperature in the RAD plasma immersion process at a nitrogen pressure of 0.05 Pa and a RAD current of 60A is shown in Fig. 8. It can be seen that the ion nitriding rate increases with an increase of the substrate temperature. An increase of substrate temperature can also result in an increase of the hardness of the steel surface. The hardness profiles of different steels which were subjected to RAD plasma immersion ion nitriding when discharge current and pressure were kept unchanged have demonstrated an increase of the hardness and thickness of the ion nitriding layer when temperature increases as illustrated in Fig. 9. Further increase of the substrate temperature can result in softening of the ionitrided layer as a result of substrate annealing. The ion nitriding rate strongly correlates with type of steel as shown in Fig. 10. It can also be seen that a compound (white) layer, composed of a nitride enriched phase also forms on selected types of steels



Fig. 8. Nitriding rate vs. substrate temperature for different types of steel ionitrided 1 h in pure nitrogen RAD plasma at p = 0.04 Pa, ion current density 5 mA/cm².

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while other steels, which were subjected to the same conditions of RAD plasma ion nitriding process do not develop such a layer.

3.4. RAD plasma immersion duplex treatment

It is also noted that a combination of ion nitriding and hard coating (Duplex approach) provides a much greater improvement of performance than a simple hard coating. The smoothness and low density of surface defects which is typical in ion nitrided surfaces prepared by RAD plasma immersion processes are suitable for the further deposition of hard ceramic coatings in a duplex process. Duplex treatment is found to be especially useful in case of DLC or ta-C superhard carbon coatings which are very brittle and usually develop catastrophic failure at small substrate deformation. Typical distribution of hardness vs. indentation depth of ta-C coating deposited on SS304 steel with CrN interlayer is shown in Fig. 11. In this case the ratio of the superhard ta-C layer to CrN bondcoat interlayer is 1:10, which allows improving the adhesion of the ta-C coating by accommodating surface deformation. Further improvement of the loadbearing capacity of ta-C coating can be achieved by ionitriding the substrate prior to deposition of CrN bondcoat. The hardness of ionitrided layer is ~13 GPa vs. 4 GPa hardness of untreated SS406. The effect of substrate hardness on wear resistance of ta-C coatings in interrupted cutting application was demonstrated during the



Fig. 9. Microhardness depth profile for different types of steel ionitrided during 1 h in pure nitrogen RAD plasma at p = 0.04 Pa, ion current density 5 mA/cm²: H13; b-M2 and HSS.



Fig. 10. Comparison of the nitriding rate of different types of steel ionitrided during 1 h at substrate temperature ~500 °C in pure nitrogen RAD plasma at p = 0.04 Pa, ion current density 5 mA/cm².

testing of the drills made of HSS and cemented carbide (WC/6% Co) in drilling the resin board with protective lacquer coating and graphite substrates. The testing results of these drills are shown in Table 2. During this comparative testing the drilling conditions were identical for the drills of the same diameter drilling the same counterpart material. Each drilling test ended when the quality of the holes started declining. It can be seen that the number of holes which can be produced by the drills with ta-C coating increases dramatically when the substrate hardness increases either because of the initial material hardness as in case of the carbide drills or because of ionitriding of the HSS drills [14,15]. These results are preliminary and more future works are necessary to fully investigate the influence of substrate hardening on wear resistance of complex multi-stage plasma treated surfaces combining ion diffusion saturation with different coatings in specific applications.

4. Conclusions

In the present study, ion nitriding and duplex coatings were prepared, using the LAFAD technique. The dual rectangular filter operates both in filtered arc coating mode and in gaseous plasma immersion mode, created by auxiliary arc discharge between cathodes of primary cathodic arc sources of filtered arc source and auxiliary anodes positioned in the coating chamber. RAD plasma is characterized as a dense and highly ionized environment. It is found that ion current density in RAD plasma increases when gas pressure decreases with the optimal pressure range from 0.01 to 1 Pa. The RAD positive column low pressure arc plasma is characterized by high electron density which is directly proportional to the RAD current. The incubation time when the surface concentration of nitrogen reaches its solubility limit in steel is inversely proportional to the square of the RAD current density. At the same time, the thickness of the nitride layer increases with an increase of the RAD ion current density. The ionitriding rate of different types of steel ranges from 0.1 to 1 µm/min. At the low pressure end of the RAD plasma



Fig. 11. Hardness vs. indentation depth in ta-C film, thickness ~300 nm deposited on CrN bond-coating interlayer, thickness ~3000 nm, substrate SST-304. (Courtesy of K. Brondum).

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| Table 2 | |
|---|-------------|
| Comparative testing of drills with ta-C coating and with duplex coating | <u>۲</u> .* |

| Item # | Drill material/diameter, mm | ta-C coating thickness, μm | Ionitrided layer thickness, µm | Material treated | Number of holes | Strengthening factor |
|--------|-----------------------------|----------------------------|--------------------------------|----------------------------------|-----------------|----------------------|
| 1 | HSS/1 | 0 | 0 | Resin board with lacquer coating | 10 | 1 |
| 2 | HSS/1 | 0.5 | 0 | Resin board with lacquer coating | 120 | 12 |
| 3 | HSS/1 | 0.5 | 5 | Resin board with lacquer coating | 190 | 19 |
| 4 | HSS/10 | 0 | 0 | Graphite | 100 | 1 |
| 5 | HSS/10 | 0.5 | 0 | Graphite | 430 | 4.3 |
| 6 | HSS/10 | 0.5 | 5 | Graphite | 770 | 7.7 |
| 7 | WC-6% Co/1 | 0.5 | 0 | Resin board with lacquer coating | | |
| 8 | WC-6% Co/1 | 0 | 0 | Resin board with lacquer coating | 3730 | 1 |
| 9 | WC-6% Co/1 | 0.5 | 0 | Resin board with lacquer coating | 5900 | 1.6 |

* Testing in drilling of resin boards was performed at microelectronics "Kyivprylad" plant in Kiev, Ukraine.

processing range, the ionization rate in auxiliary arc discharge and rate of nitriding increase when the pressure decreases, indicating a direct influence of ions on the nitriding rate. Both thickness and hardness of the ionitrided layer increase with an increase of the substrate temperature during RAD plasma ionitriding treatment. The white layer appears when ion flux and bias voltage are high, which can be attributed to increase of substrate temperature under intense ion bombardment conditions. It is found that both ionized nitrogen-bearing species and excited neutral nitrogen atoms and molecules are contributing to the ionitriding rate in RAD plasma immersion process. Thanks to high ion flux density, the RAD plasma ionitriding can be prepared at low substrate bias, which does not affect the initial substrate roughness making this treatment compatible with the following filtered arc coating deposition process. The temperature and pressure range of RAD plasma ionitriding overlap with plasma assisted PVD coating processes, which allows one to design duplex surface engineering processes combining ionitriding and hard ceramic coating deposition in one uninterrupted vacuum plasma processing cycle.

Acknowledgments

We acknowledge the technical assistance of T. Wittberg for AES analysis.

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