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# Advances and Directions of Ion Nitriding/Carburizing

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# ADVANCES AND DIRECTIONS OF ION NITRIDING/CARBURIZING

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## ABSTRACT

Ion nitriding and carburizing are plasma activated thermodynamic processes for the production of case hardened surface layers not only for ferrous materials, but also for an increasing number of nonferrous metals. When the treatment variables are properly controlled, the use of nitrogenous or carbonaceous glow discharge medium offers great flexibility in tailoring surface/near-surface properties independently of the bulk properties. The ion nitriding process has reached a high level of maturity and has gained wide industrial acceptance, while the more recently introduced ion carburizing process is rapidly gaining industrial acceptance.

The current status of plasma mass transfer mechanisms into the surface regarding the formation of compound and diffusion layers in ion nitriding and carbon build-up ion carburizing will be reviewed. In addition, the recent developments in design and construction of advanced equipment for obtaining optimized and controlled case/core properties will be summarized. Also, new developments and trends such as duplex plasma treatments and alternatives to dc diode nitriding will be highlighted.

THE CASE HARDENING PROCESSES such as nitriding, carburizing and carbonitriding are well established thermochemical diffusion processes for surface/near-surface hardening of ferrous materials, mainly steel. These processes are widely used in the manufacturing and machining industries primarily to treat engine components, tools for hot/cold work, die castings, machine tools, and tribocomponents. These processes are based on diffusion of the nonmetallic interstitial elements, carbon, and/or nitrogen, into the surfaces. Hard surface compound nitride or carbide layers with an extended diffusion zone are formed. Nitrogen diffusion in steels is usually performed in the ferrite phase between 450 to 590 °C and is a ferritic treatment, whereas carbon diffusion is performed in the austenite phase between 925 to 1050 °C and is an austenitic treatment.

To obtain the best response to nitriding steels, they should contain nitride forming elements such as aluminum, chromium, titanium, molybdenum, vanadium, and tungsten. In carburizing the maximum amount of carbon that can be dissolved in the austenite phase can be determined from the $Fe\text{-}Fe_3C$ phase diagram. The nitriding and carburizing processes can be divided into two broad categories: conventional and ion assisted (plasma) processes. The conventional case hardening processes are performed in solid, liquid or gaseous mass transfer media. These processes have been extensively described in the literature and will not be discussed in this review.

The ion nitriding/carburizing processes are plasma activated thermodynamic processes for the production of case hardened surface layers not only for ferrous metals but also for an increasing number of nonferrous metals. The ion assisted diffusion processes are based on the energetic nature of the glow discharge. The high energy of the nitrogenous or carbonaceous plasma contains ions, electrons, radicals, and activated species. The interaction between the plasma and the solid surface is based on excitation, ionization, dissociation and acceleration. The use of the glow discharge offers great flexibility in tailoring surface/near-surface properties independent of the bulk properties when the treatment variables are properly controlled.

The ion nitriding process has reached a high level of maturity and perfection and has gained wide industrial acceptance primarily for increasing wear resistance and antigalling, and improving fatigue life and corrosion resistance. However, the more recently introduced ion carburizing process stands on the edge of industrial applications.

The objective of this introductory paper is to address the current status and understanding of plasma-mass transfer processes and plasma-surface interactions as to the formation of the compound layer and diffusion zone during case hardening. Further, the paper will highlight the recent accomplishments in equipment design/construction and the new trends in utilizing duplex plasma processes and the development of various improved/modified ion nitriding processes. Some general references (Refs. 1 to 5) on the subject described here are given in the references section.

## ION ASSISTED SURFACE TREATMENTS

The ion assisted surface modification/deposition treatments can be classified in three categories:

(1) **Ion assisted deposition** which covers physical vapor deposition (PVD) such as sputtering and ion plating, and chemical deposition (CVD) such as plasma enhanced deposition;
(2) **Ion beam techniques** which cover ion implantation, ion beam mixing, and ion beam enhanced deposition; and
(3) **Plasma thermochemical processes** such as ion nitriding, ion carburizing, ion carbonitriding, ion boriding, and ion oxidation.

Depending on deposition energies and surface interactions, the above processes can be classified as processes that produce distinct overlay coatings (ion assisted deposition) and processes forming no discrete coating but which modify the surface/near surface by diffusion, penetration and chemical reaction (plasma thermochemical processes, ion implantation). In this paper, the plasma thermochemical diffusion processes with regard to plasma-mass transfer/interactions will be described.

## GLOW DISCHARGE CONSIDERATIONS

The glow discharge used as a processing plasma for surface modification can be established and sustained in various ways: dc diode discharges, rf discharges, microwave discharges, electron emission configurations and magnetically enhanced discharges. In the plasma assisted diffusion treatment, processes such as ion nitriding/carburizing, the dc diode discharge is most widely used. In these nonequilibrium plasma only the temperature of the electrons is high and that of the reactive species is relatively low. Because the temperature of the electrons is high, excitation and ionization of neutral atoms/molecules increase, resulting in enhanced reactive chemical reactions and plasma heating. Since the interactions of the energetic ion species with the surface are localized, the results which are obtained are different from that of simple (conventional) thermal activation.

Several types of glow discharges depending on the relationship between voltage and current exist as shown in Fig. 1. All plasma thermochemical processes are performed in the abnormal glow

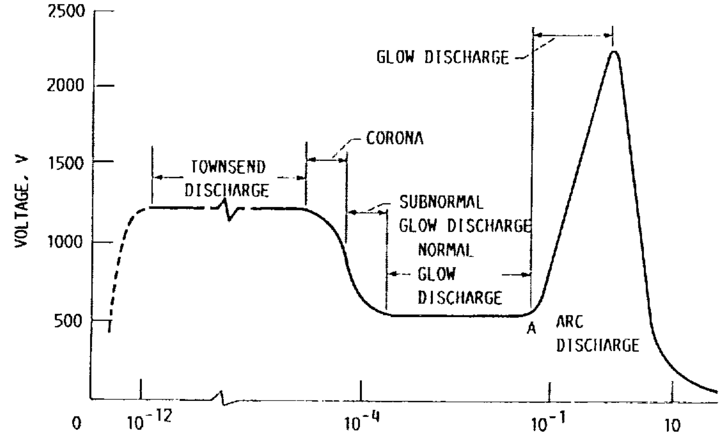


FIGURE 1. - VOLTAGE - CURRENT CHARACTERISTICS OF DIFFERENT TYPES OF DISCHARGE IN ARGON. (EDENHOFER) (REF. 6.)

in which the current increases with the voltage. In the abnormal region, the glow covers the specimen uniformly and therefore, uniform treatment can be expected. Further, the control of this unstable abnormal glow discharge is the critical feature in the production of uniform reproducible layers. With the advancement of technology, new plasma power generators have been introduced to prevent the formation of arcs, so that the glow discharge can be safely maintained at high current densities in the abnormal region.

The thermochemical processes such as ion nitriding are performed over a fairly well defined range of pressure and voltage (typically 1 to 10 torr and 0.3 to 0.8 kV) under dc diode plasma conditions. A typical ion nitriding system is schematically shown in Fig. 2.

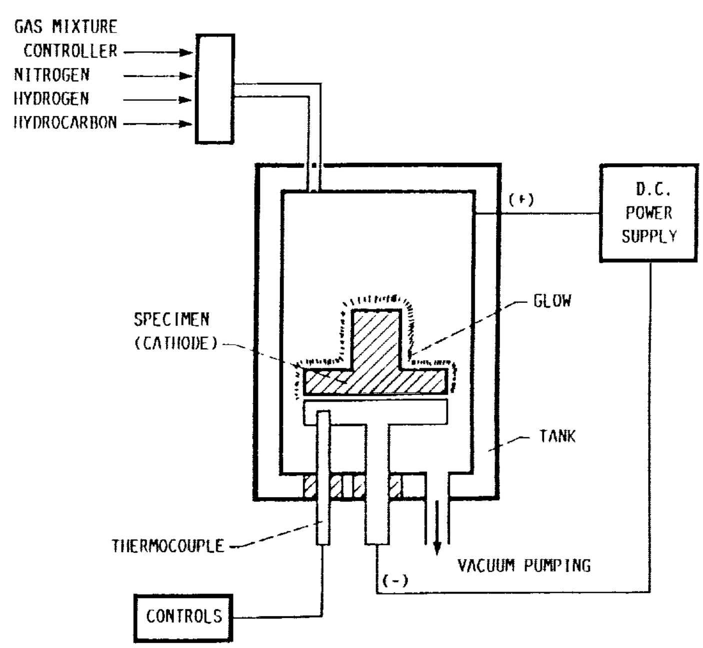


FIGURE 2. - ION NITRIDING SYSTEM.

## ION NITRIDING/CARBURIZING MECHANISMS

Presently there is no universal model which explains the ion nitriding process. However, numerous mechanisms have been proposed to explain this concept. The fact remains that the exact reactant species in the glow discharge during ion nitriding are not well identified. As to ion carburizing, which is a more recent process, the basic explanations are derived from the more widely proposed ion nitriding concepts.

Basically, the ion nitriding/carburizing processes are controlled by plasma mass transfer (nitrogenous/carbonaceous species) and plasma-surface interactions. All the proposed mechanisms are essentially derived from these basic contributing factors:

(1) Sputtering,
(2) Ion excited atom implantation,
(3) Adsorption, and
(4) Condensation/deposition.

The numerous proposed mechanisms can be categorized and summarized as follows:

(1) Adsorption of atomic N;
(2) Sputtering: sputtered Fe and subsequent FeN condensation on surface (Kölbel's model) (Ref. 6), and sputter cleaned and activated surface; and
(3) Impact of molecular ions ($NH^+$, $NH_2^+$) and subsequent penetration.

In ion carburizing, the presently proposed mechanism is by C transfer from the $CH_4/H_2$ plasma to the specimen through the dissociation of $CH_4$ within the glow and forced attraction of the carbon species to the specimen (cathode) and finally reaction at the surface. All the above contributing factors are responsible for the enhanced plasma carburizing kinetics.

## OPTIMIZATION OF PLASMA PROCESS VARIABLES

Up to now, only four process variables (temperature, composition of gas, pressure of gas and treatment time) have been controlled to optimize the microstructure, thickness, microhardness of the compound layer and diffusion zone. By varying the process variables such as composition of the gas mixture (nitrogen, hydrogen or hydrocarbon gases) one can custom tailor the metallurgical structures as shown in Fig. 3 to meet any specified requirements. The various nitride compound layers can be produced on the surface with a diffusion zone which may be 100 times thicker than the compound layer.

Recently, a fifth control variable, namely current density or power density can be regulated independently from the work-load temperature with the development of a plasma current density (pcd) sensor. In ion nitriding by controlling the power density/current density the compound layer thickness and composition can be accurately controlled, whereas during ion carburizing, the rate of carbon build-up on the surface can be monitored as shown in Fig. 4. Higher current densities increase the carbon build-up on the surface.

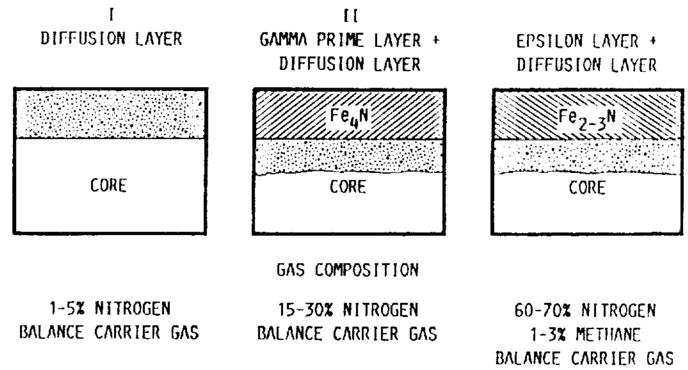


FIGURE 3. - METALLURGICAL CONFIGURATIONS DURING PLASMA NITRIDING.

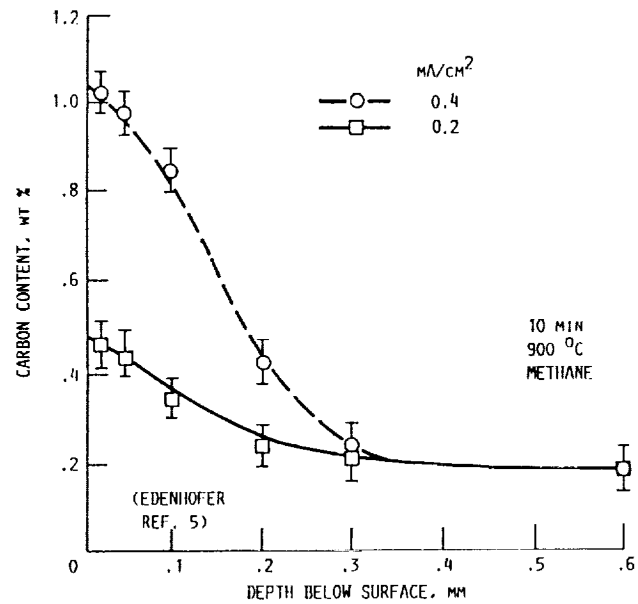


FIGURE 4. - EFFECT OF CURRENT DENSITY ON CARBON BUILD-UP DURING PLASMA CARBURIZING IN METHANE AT 900 °C.

## RECENT DEVELOPMENTS AND FUTURE TRENDS

The current developments and improvements in the thermochemical diffusion treatment technology have been primarily in design/construction of more advanced equipment such as plasma power generators, and microprocessor controllers with computerization and programming. The objective is to optimize plasma and surface sensoring and to monitor/control all the process variables.

The future trends in the surfacing/modification technology are twofold: the development of duplex plasma treatments and alternatives to dc diode nitriding. The duplex plasma treatments are combined treatments where ion nitrided surface is subsequently coated by PVD (ion plating or sputtering) or by CVD coating techniques. Significant improvements have been achieved in the cutting tool industry where pre-nitrided drill bits are ion plated with TiN (Ref. 7). The numerous alternatives to dc diode nitriding which are presently investigated may be categorized as follows:

(1) Enhanced low pressure plasma nitriding which utilizes a dc triode configuration (Refs. 5 and 8),
(2) rf-nitriding which produces an enhanced discharge (Ref. 5),
(3) Pulsed-plasma nitriding at microsecond intervals for blind hole penetration (Ref. 5),
(4) Magnetically enhanced ion-nitriding for achieving deeper penetration (Ref. 5), and
(5) Plasma nitriding with air where gas mixture of air (nitrogen as donor) and $H_2$ (conc. critical) is used (Ref. 5).

Finally, the above techniques are extended to new materials such as powder metallurgy (P/M) products, powders and complex geometrical surfaces.

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16. Abstract

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