Chapter 2
Plasma Nitriding

Abstract Plasma nitriding technology, developed based on the glow discharge phenomenon, is reviewed in this chapter, ranging from its basic physical principle, main processing characteristics and technical advantages, as well as its industrial applications. Other nonmetal element plasma surface alloying technologies, such as plasma carburizing, plasma nitro-carburizing and plasma sulfurizing are briefly introduced. Further discussion is carried out on its limitation of the nonmetallic element for plasma nitriding technology and advanced technology development in China.

2.1 Glow Discharge and Its Characteristics

2.1.1 Characteristics of Glow Discharge

Plasma nitriding is a surface alloying technology which is developed based on the phenomenon and characteristics of the glow discharge plasma.

The phenomenon of glow discharge was first discovered and studied by applying a DC voltage across two electrodes in a vacuum diode. Characteristics of the Voltage–Current curve of the glow discharge were shown in Fig. 2.1 [1].

As seen in Fig. 2.1, the discharge can be separated in several regions along the current level. No visible light can be observed in the vacuum diode at the low voltage and current (the dotted line in the curve). As the voltage and current are changed, it goes through several discharge stages: Townsend discharge and normal glow discharge at low voltage and current, then jumping into abnormal glow discharge where any increase in the voltage gives an increase in the current density. The current density is uniform around the entire cathode surface, indicated by a uniform glow. The “abnormal glow discharge” region is used for plasma nitriding process. However, as the voltage is further raised, the glow discharge/arc discharge transition threshold point is approached, then the glow discharge collapses and high current density arc discharge forms.
The arc discharge is a severe discharge confined in a small area and would cause the working-piece ablation. It is critical to control cathode discharge to avoid arcing discharge and associated ablation-induced damage to the system.

### 2.1.2 Stratified Phenomenon

Figure 2.2 shows the typical visible glow distribution between the anode and the cathode. The stratified phenomenon can be observed. From the cathode to the anode, there exist several glow discharge spaces: Aston dark space, cathode glow, Crookes dark space, negative glow, Faraday dark, positive column, anode glow, and anode dark space. The total discharge width $D_k$ is a very important parameter, including Aston dark, cathode glow, Crookes dark, and negative glow. $D_k$ is also called as the width of cathode potential drop region. When the anode moves toward the cathode, only the width of the positive column reduced, but other parts remain unchanged. However, once the anode comes in the negative glow region, all of the glow discharge will be immediately extinguished. The higher the gas pressure is, the smaller the $D_k$ value would be. This is a very important feature for all applications of glow discharge process.
2.1.3 Interactions Between Ions and Material Surface

In plasma material surface process, the main process is the interaction between ions and the material surface. The basic physical and chemical interactions between ions and the substrate surface are schematically shown in Fig. 2.3.

Driven by the electric field, the positive ions from the glow discharge plasma, such as nonmetallic elements (argon and nitrogen) or metal elements, will bombard the cathode surface, resulting in some interaction effects as listed here [2]:

2.1 Glow Discharge and Its Characteristics
1. **Sputtering:** Any material with negative potential in the plasma equipment will be sputtered by positive incident ions and produce an atomic vapor of the cathode material. These sputtered-out atoms would deposit on the closed-by working-piece. We can use any negative electrode made of alloying element as a target for the alloying element supply.

2. **Heating:** From the discharge plasma, electrons and ions with high energy would bombard the surface of the substrate and releases energy for heating the substrate. The temperature of the working-piece can be higher than 1200 °C.

3. **Implantation:** When high energetic ions bombard the surface, they can jam (or implant) into the substrate surface to form an implantation layer. The depth of implantation layer is determined by the ion energy and the characteristics of the material to be implanted.

4. **Diffusion:** As is described above, the working-piece can be heated by electron-ion bombardments or other heating methods to enough high temperature. Under thermal driving, the incident ions and sputtered-deposited atoms can diffuse deeply into the surface of the working-piece to form a greater thickness alloying layer.

5. **Cleaning:** When the cathode surface is bombarded by ions, its light sputtering effect can be used to clean the oil stain and impurities at the surface, while thermal heating effect can induce oxides decomposition at the work object surface.

6. **Defects Creating:** Ion bombardment can make the atoms of cathode surface to be sputtered and creates a defect layer including a large number of vacancies and dislocations, which can be more active for dissolving and diffusion of alloying elements.

7. **Surface Etching:** Similar to the surface cleaning, ion bombardment can erode and strip off the surface layer of the cathode material through ion sputtering process. This effect has been used as an important method for the glow discharge analyzer of surface composition distribution.

8. **Chemical Reaction Accelerating:** Glow discharge plasma contains high energy in ions and electrons, which would stimulate the activation of chemical species and acceleration of many chemical reactions that cannot be achieved under the routine condition. Experiments on the chemical reaction with gas discharge have been carried on for a hundred years. In 1967, F.K. McTaggart first used the concept of “plasma chemistry” [3] to stimulate the chemical reactions occurring in the discharge.
2.2 Plasma Nitriding Process

Plasma nitriding was invented by Berghaus [4]. It is considered as “the Foundation Stone of Modern Plasma Surface Engineering” and one of “the most important achievements of surface engineering” in the development of material surface technology [5, 6].

Nitriding or carburizing is used as an effective method to improve the surface hardness, wear resistance fatigue strength and corrosion resistance of metal materials. Plasma nitriding has been used in the fields of mechanical manufacturing, chemical engineering, aviation, and national defense and so on.

2.2.1 Basic Principle

The schematic diagram of the plasma nitriding process experimental setup is shown in Fig. 2.4, where the working-piece, anode, and cathode are arranged as shown.

Under the condition of glow discharge, the refilled gases (nitrogen + hydrogen, or ammonia NH₃ gas) are ionized into N⁺ and H⁺. Driven by a high voltage electric field, H⁺ and N⁺ ions move to bombard the surface of the working-piece. The kinetic energy of ions will be converted into heat energy so that the surface of the working-piece is heated to a required temperature. At the same time, the nitrogen atom is adsorbed and diffused into the surface of the working-piece to form a nitriding layer.

![Schematic diagram of plasma nitriding experimental setup](image)

Fig. 2.4 Schematic diagram of plasma nitriding experimental setup [1]
Commonly used plasma nitriding process parameter range:

- nitriding temperature, 450–650 °C;
- gas pressure, $1.33 \times 10^2$–$1.33 \times 10^3$ Pa;
- discharge voltage, 400–800 V;
- current density, 0.5–5 mA/cm$^2$;

Nitriding processing time can range from a few minutes to more than 10 h, according to the process condition such as the working-piece material and nitriding temperature, as well as the required nitriding layer depth.

### 2.2.2 Advantages

Compared with thermal gas nitriding, plasma nitriding has the following advantages:

1. **High diffusion speed**: Driving under plasma energy and high temperature, nitrogen ions can diffuse into the material subsurface faster and deeper. To obtain the same thickness of a nitriding layer, the plasma nitriding time is only about $1/3$–$1/5$ of the time by gas nitriding.

2. **Energy saving**: Ion bombardment on the surface generates the local heating on the working-piece surface without heating the whole furnace body, thus the process can greatly minimize energy consumption.

3. **Controllable microstructure of the nitride layer**: In contrast to gas nitriding process, the composition and microstructure of the nitride layer are controllable during plasma nitriding process. It can be controlled by adjusting the ratio of nitrogen and hydrogen contents in the feed gas during the plasma nitriding process.

4. **No requirement for any treatment for the passive film of stainless steel**: During plasma nitriding, ion bombardment can destroy the passive film on the surface, both to simplify the process and save the labor cost.

5. **No chemical pollution**: plasma nitriding only use a small amount of ammonia or nitrogen, hydrogen, the environment pollution is negligible.

6. **Used as the final step**: After plasma nitriding, the part surface is silver gray and good smoothness. Structure deformation is also very small. They do not need regrinding, annealing, or another retreatment in the post process.

### 2.2.3 Industrial Applications

Plasma nitriding has been used for a long time to improve wear resistance and fatigue strength, with a minimum distortion. It has been widely applied in
machinery, petroleum, chemical industry, metallurgy, automobile, aviation and national defense and other industrial fields. The application of plasma nitriding for surface modification is still expanding, such as for various engine crankshaft, cylinder liner, plastic extrusion screw, aluminum profile extrusion die, gear, etc., leading to remarkable economic and social benefits.

Plasma nitriding on nonferrous metals, especially on the titanium alloy, has also made good applications in significant improvement effect in the wear resistance and corrosion resistance of the titanium alloy [6].

2.3 Other Plasma Surface Alloying Technology

2.3.1 Plasma Carburizing

Carburizing is the first surface alloying method for improving the surface hardness and wears resistance of steels. In the late 1970s, the plasma carburizing had been applied to replace the traditional carburizing process.

Carburizing gaseous medium for the use of the plasma carburizing is methane CH₄ or propane C₃H₈, with hydrogen or argon as the carrier gas. The volume ratio of 1:10 is used for propane dilution.

The alloy material treated with the method of plasma carburizing has higher wear resistance and fatigue strength than that by the conventional carburizing method. It is commonly used for the carburizing cycle with energy saving and no pollution.

2.3.2 Plasma Nitro-Carburizing

Plasma nitro-carburizing is processed in the condition of plasma nitriding with adding a small amount of carbon [3], commonly known as plasma soft nitriding. This treatment process is usually carried out with the medium of nitrogen or nitrogen–hydrogen mixture with Ethanol (C₂H₅OH) or Methane CH₄. Plasma nitro-carburizing is commonly used to improve the gear, shaft, piston rings, valve plate, mold, tool and so on for surface wear-resisting improvement.

2.3.3 Plasma Sulphurizing

Plasma sulfurizing is processed with H₂S or CS₂ gas at a temperature of 150–300 °C. Because of the low solubility of sulfur in the a-Fe (only 0.02%), no diffusion layer is formed after ion sulfurizing process. The resulting ferrous sulfide
compound surface layer is soft with low shear resistance and easy to slip, good for friction reducing and anti-bite application [7].

2.4 Restriction of Plasma Nitriding

The invention of plasma nitriding technology has opened up a new direction for the traditional surface nitriding process and adopted as a major development in the field of surface alloying. However, in the 86 years since its advent, the plasma nitriding technology can only be applied to nonmetallic elements. In order to break the limit of the plasma nitriding technology, people have been trying to apply the glow discharge phenomenon to the metal elements.

Liquid metal halide was once used as a source of supply material for metal elements after its gasification. As an example, the mixed gas of TiCl₄ with hydrogen gas as a carrier had been used for plasma surface titanium-alloying. Another example is surface silicon alloying, the source of silicon is SiCl₄ and hydrogen gas mixture, and the silicon alloying layer on the surface of the steel is Fe₃Si.

The main problem in these above processes is serious corrosion to the process equipment due to the toxic chlorine produced by the ionization from the metal halide. Therefore, this method has no practical significance, and it has not been further developed.

2.5 Development of Plasma Nitriding in China

To its technical advantages and the glow of the beautiful color appearance, plasma nitriding technology has attracted the great attention and development interest globally. Scientists and engineers in many countries have devoted their effort to the research and promotion of this technology. Taking China as an example, since 1972 there are more than 20 universities and research institutions and a few hundreds of scientific and technological workers have devoted their effort to this technology research and development. “Academic Committee for Chemical Heat Treatment of Plasma Bombardment” was once set up, responsible for the promotion of plasma nitriding technology development, the annual technical meeting, and academic information exchange. So far, nearly 3000 units of plasma nitriding furnaces and processing systems have been established in China. However, due to a poor quality of the early equipment design and fabrication, as well as a lack of good understanding of the plasma nitriding process, only about 30% of the equipments can be used in the application practice.

Starting in 1972, Author’s research group in China had got engaged in the study of plasma nitriding technology, following the initiative in Germany. A coating machine in the laboratory was modified as our first small plasma nitriding process
system. In 1975, a 30 kW large plasma nitriding furnace was built. Inspired by the
titanium-plating gas nitriding, the titanium gas nitriding was developed successfully
by placing sponge titanium in the gas nitriding furnace. On the basis of titanium gas
nitriding, we have further developed the titanium plasma nitriding process by
placing a titanium sponge on the anode and the cathode during plasma nitriding
processing. The nitriding layer formation speed of the titanium plasma nitriding is
double of the ordinary plasma nitriding process.

Furthermore, based on the titanium plasma nitriding, we developed a new
technology of “Titanium-carbon plasma nitriding” in 1976. The micro hardness of
carbon alloyed steel resulted from this process has reached up to 1000 HV_{0.1}.
Titanium-carbon plasma nitriding technology has won an award in the Chinese
National Science Conference in 1978 and won the third-grade award of Chinese

In the 1990s, with the development of the pulsed power supply and the appli-
cation of computer technology, the stability and reliability of the plasma nitriding
system equipment are greatly improved.

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Plasma Surface Metallurgy
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Xu, Z.; Xiong, F.F.
2017, XX, 269 p. 226 illus., 94 illus. in color., Hardcover
ISBN: 978-981-10-5722-9