Advances in Plasma Ion Nitriding

Ralph Poor
Surface Combustion, Inc., Maumee, Ohio USA

Abstract

The ion or plasma nitriding process has been around for many decades. Developed in the late 1930s, the process was used extensively in Europe. During the 1980s, the process became more popular in the U.S., and many systems were purchased.

Early on, the process was not widely understood, and some applications were not a good fit. As plasma nitriding advantages and limitations became realized, the process found its niche in many different industries. Very demanding applications proved to be good applications for ion over gas nitriding.

In general, plasma nitriding uses high voltage power operating in the 500–1000 VDC range, often conducting hundreds of amps to power the process by activating the glow discharge.

The glow discharge is not only capable of heating the parts but also ionizes the atmosphere to allow the process to operate.

This paper provides insight into plasma nitriding and discusses new advances, widening the range of applications for the process. Many of the advances are in the form of advanced process control electronics, mass flow controllers for process gas flow, and, most importantly, newer high voltage power supply designs with high speed microprocessor arc detection technology.

Introduction

Ion nitriding is one branch of the three most common nitriding processes which are typically classified as atmosphere or gas nitriding, salt bath nitriding, and ion or plasma nitriding. Fig. 1 shows the characteristic purple glow around parts during ion nitriding.

Most nitriding processes are traditionally carried out between 800 to 1,150°F (426 to 621°C), however, some special materials may be processed at much higher or lower temperatures for unique properties. Processing at these lower than average heat-treating temperatures is generally preferred for reduced part distortion.

Plasma or ion nitriding can easily operate at even lower temperatures than other nitriding processes. Therefore, for applications wishing to minimize part distortion, ion or plasma nitriding may be preferred. Many stainless steels are even processed in the 400–500°F range.

Table 1: Chemistry of Nitralloy 135™ Modified, showing percentages of the individual alloying elements. [1]

<table>
<thead>
<tr>
<th>Nitralloy 135™ Modified - Typical Chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
</tr>
<tr>
<td>Manganese</td>
</tr>
<tr>
<td>Silicon</td>
</tr>
<tr>
<td>Chrome</td>
</tr>
<tr>
<td>Molybdenum</td>
</tr>
<tr>
<td>Aluminum</td>
</tr>
<tr>
<td>Iron</td>
</tr>
</tbody>
</table>

From an environmental standpoint, plasma or ion nitriding comes in ranking the greenest of the nitriding processes since no salts or salt disposal is required, and no ammonia gas, a necessity in all forms of the atmosphere gas nitriding process, is used.

Generally, these processes release a nitrogen atom to attach to the work piece’s alloying elements. In this atomic combination of a nitrogen atom in conjunction with the base iron and other alloy elements, a “nitride” is formed, which is an extremely hard ceramic that provides resistance to wear. Depending on the alloy, most individual elements of the base materials can also be nitried. This in turn allows many different nitrides to be formed.

These nitrides include, but are not limited to, iron nitride, chrome nitride, aluminum nitride, moly nitride, vanadium nitride, and titanium nitride. Some specialty alloys, such as...
Nitalloy 135™ (Table 1), have been specifically tailored for nitriding and have many of the “nitride formers” in the mix. These nitrides form in the white layer which is above the surface of the part, as well as in the diffusion zone below the white layer. See Fig. 2 for white layer example.

Typical nitriding applications include gears, crankshafts, camshafts, plastic mold extrusion dies, as well as enhancing a wide range of heat-treated tool steels.

**Direct Processing of Lower Grade Materials as Received from the Mill**

Ion nitriding can also be extremely beneficial for lower grade materials that are received directly from the mill. In this case, the nitriding temperature may lower the material’s core hardness but will add extreme hardness and subsequently wear resistance to the surface. In this instance, the material has usually high wear from a rubbing application and not subjected to high pressure or high impact loads. The material in these situations has a very high hardness on the surface, but directly below the high hardness layer, a relatively soft material exists.

In some cases, the very soft core may not be able to support the hard surface. In situations where the material is under high pressure loads, the base cannot support the high hardness surface and subsequent crushing of the hard surface takes place.

As shown in Fig. 2, the ion nitriding process yields a very tight and uniform white layer and is seen as the vertical white region on the right side of the image below. Since this material is designed for low temperature tempering, the core of the material is significantly reduced in hardness and therefore cannot hold up to heavy mechanical loading, however, the surface is extremely resistant to sliding wear.

**Nitriding and Ferritic Nitrocarburizing in conjunction with other heat treatments**

For applications requiring only high resistance to sliding wear, the example of the AR-500 material demonstrates that high hardness is accomplished on material received directly from the mill.

Therefore, the nitriding process can be performed as a standalone heat treatment where no other in-house hardening operations are done prior to the nitriding process.

For applications requiring high wear resistance on the surface in conjunction with resistance to high mechanical loading, a material such as 4140 is often used (Fig. 3).

The 4140 would be first austenitized, oil quenched, and tempered at 1,000°F (538°C) prior to the ion nitriding process.

This procedure allows the nitriding process to take place below the tempering temperature and therefore eliminates further reduction of part hardness through additional tempering.

**Ion Plasma Processing**

The ion plasma nitriding process operates in a special type of vacuum furnace often called the vacuum vessel (Fig. 4). After a load is charged into the vessel, a vacuum pump is activated to remove all air and water vapor from the parts and vessel. When most of the air has been removed, the workload is heated either by the plasma glow discharge directly or by auxiliary resistance heating elements. By heating the load first with resistance heating elements, the load can be heated rapidly without the worry of arc damage. Arc damage typically occurs when the high voltage supply is first applied to parts which may be still dirty from machining processes or castings which typically are more difficult to preclean.
Fig. 4: Industrial “pit style” ion nitriding installation. The major portion of the ion nitriding vessel and vacuum pumping system is located below the floor line. The control cabinet and power supply are shown on the far left.

Heating under resistance heat in conjunction with a high vacuum and sometimes in the presence of hydrogen, allows the vacuum to clean the parts. Once parts are heated, the contaminants are vaporized away and sputter cleaning under glow discharge can take place.

The ion or plasma nitriding process uses a high voltage power supply operating in the 500–1000V direct current (DC) range, often conducting hundreds of amps for larger loads to power the process and activate the glow discharge. This glow discharge is capable of both heating the workload parts and ionizing the atmosphere to allow the process to operate.

When using resistance heating, the glow discharge is typically turned on at approximately 650–750°F. However, many units are manufactured without resistance heating, and glow discharge is used to heat parts from room temperature.

There are many process variables to be monitored and controlled in the process. Typical process variables are given in Table 2. The hard-vacuum levels initially obtained for cleaning are later reduced by raising the partial pressure of the vessel. Partial pressure is accomplished by flowing in the process gas mix.

Gas mixes are typically controlled by mass flow controllers that meter the individual process gases. Typical gases used in plasma/ion nitriding are hydrogen and nitrogen. Nitrogen later becomes the nascent nitrogen for the process to work. Hydrogen is used for part cleaning and also diluting the nitrogen. Too high a nitrogen gas level can generate a porous white layer. For applications wishing to add carbon to the work piece or for ductile, gray, or cast iron, methane is added to the mix. Argon is also often added for glow seam control. Precision mass flow controllers meter individual gas flows to yield an endless array of nitriding atmospheres, providing significantly different properties for different materials.

<table>
<thead>
<tr>
<th>Typical Plasma Nitriding Process Variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistance Heating Temperature</td>
</tr>
<tr>
<td>Part Temperature</td>
</tr>
<tr>
<td>Vacuum Level</td>
</tr>
<tr>
<td>Total Gas Flow Rate</td>
</tr>
<tr>
<td>Gas Mix</td>
</tr>
<tr>
<td>DC Voltage</td>
</tr>
<tr>
<td>DC Amps</td>
</tr>
<tr>
<td>Power Frequency</td>
</tr>
<tr>
<td>Duty Cycle</td>
</tr>
<tr>
<td>Arc Rate</td>
</tr>
<tr>
<td>Incoming Water Temperature</td>
</tr>
</tbody>
</table>

Table 2: Typical process variables to be monitored as the cycle progresses. Many additional load thermocouples are often used to assure part temperature is correct.

A Quick Review of a Lab Ion Nitriding System

The metallic parts to be processed are placed inside the vessel on an electrically isolated hearth or work support. Here the parts themselves will be connected to the negative side of the high voltage power supply. Once placed inside the vessel, the door is closed, and the vacuum pumping system removes all ambient air. This portion of the process takes roughly 15 minutes.

After pump down is complete, the electrical high voltage supply is activated, and the glow discharge begins. A work thermocouple measures the increasing temperature of one or more parts and the parts are ramped to nitriding temperature.

During this portion of the process, the gas partial pressure setpoint is automatically changed as parts rise in temperature. This change in pressure is necessary since cold parts need a higher vacuum or excess arcing can take place. As the parts heat, the pressure is increased, the glow seam becomes closer to the parts, and more current will flow. This increase in current is necessary to increase the part temperature. The control system automatically adjusts pressure by changing the gas flow of the epsilon, gamma prime, or other process gas. Increasing the gas flow increases or raises the partial pressure.

The graphs shown in Fig. 5 and 6 shows the effect on gas flow to pressure, and likewise the effect of pressure on system amperage draw. An increase in pressure causes the glow seam to tighten, and the tightening of the seam has several immediate effects. The current flow increases, and a corresponding drop in voltage occurs. As noted on the graph, the relative kW input to the load remains relatively constant at approximately 4kW.

Looking closer at the graph of Fig. 6 shows the amperage increasing from 4 amps to approximately 7.5, and likewise the system voltage drops from approximately 1000VDC to just over 500VDC.
Power and Process Variables for Larger Systems

As we move from small laboratory systems to very large industrial processing centers, most components simply scale up. Hearth load capacities increase from a few hundred pounds to tens of thousands of pounds. Resistance heating systems scale up in kilowatts but typically continue to use graphite heating elements if the elements are exposed to the vacuum.

Computer and PLC process control panels usually remain the same, however, ranges on mass flow controllers increase as well as pipe sizes and vacuum pumps.

Figures 7 and 8 show higher current flow for maintaining glow for loads in excess of 10,000 lb. Voltage behavior remains very much like that of smaller units, and the control of frequency and duty cycle is also quite similar between small and large units.

Pulse Power Supply Discussion

The older technology power supplies typically would take 480 VAC 3 phase power and step this voltage upwards to 1000VAC. From this high voltage AC power, silicon-controlled rectifiers (SCR) were used to rectify the alternating current to direct current (DC). The SCR’s were also used to regulate the voltage and/or current flow during the process. By delaying when the SCR’s are fired in the 60 Hertz line frequency, the power could be reduced and controlled. Two SCR’s were used per phase or

six in total. The system was similar in concept to a conventional lamp dimmer one might find in a home.

These systems were rugged and designed to handle hundreds of amps at 1000VDC. Arc detect circuitry would monitor voltage and current levels. If a sudden drop in voltage occurred or a sudden rise in current, the system assumed an arc was occurring, and the SCR’s were gated completely off. Once sufficient time in milliseconds elapsed, the SCR’s would turn back on. Adjustments to the circuits were done by adjusting small ten turn potentiometers. When an “arc-detect” circuit card
needed to be initially installed and set up or replaced, numerous adjustments were required to set up new components.

Modern power supplies operate internally at very high frequencies and use high speed microprocessors to manage the supply, detect arcs, and digitally communicate with companion control systems. The days of potentiometer adjustments have been eliminated.

Arc detect settings are now set through menu screens (Fig. 9) or can be set up by external process controllers on a recipe basis through digital communication. Therefore, settings can be dialed in for different applications, part types, geometries, and load configurations.

The arc detect settings are automatically changed from cycle to cycle as process requirements change. Many applications with large loads will require more power than a standard power supply can deliver. In this situation, multiple power supplies can be ganged together to support the high-power demands of large vessels processing large loads.

For a large system, load weight can easily exceed 10,000 lb. and vessel size could be 9 feet in height and 5 feet in diameter. In Fig. 10, three 60kW units are ganged together and can deliver up 360 amps of current for glow discharge.

The power supply located in the upper slot is the main unit which communicates to the control equipment. This supply also sends signals to the lower supplies instructing them to operate at the same frequency and duty cycle. All three supplies are synced together.

Figures 11 and 12 show examples of different duty cycles from the pulse power supply. The power supply sets the on-time of the voltage based on the recipe setting. These settings change as the cycle progresses and can be tailored to individual part type and load conditions. Fig. 11 shows an 85% duty cycle while Fig. 12 shows a 30% duty cycle. The applied DC voltage is a negative voltage.

Since the supply voltage is negative, and the positive lead of the power supply is grounded to the furnace casing, then that means the parts are at a negative voltage potential in respect to ground.

**Other Major Equipment Components Required to Support the Process**

The equipment requires a vacuum tight vessel. Most units are built vertically. However, horizontal units are also manufactured and have some advantages such as easier loading, no required pits, and no required high bays for cranes.

Pumping systems can be either dry pumps or liquid ring piston style. Diffusion pumps are generally never installed, and since the process runs at higher partial pressures, oversized vacuum pumps are usually not required.

Fig. 9: Modern microprocessor controlled digital pulse power supply. Courtesy Trumpf Group, Hüttiger Elektronik

Fig. 10: Modern “ganged” pulse power supplies in industrial mounting enclosure. Three individual power supplies with one “master” and two “slave” units. All three supplies operate in unison and deliver three times the power as one unit would deliver.

Both cold wall designs and hot wall units with internal retorts are popular. Water cooled cold wall designs have several radiation shields separating the work zone from the casing. Hot wall designs are refractory lined and often have centrifugal
blowers attached to the wall to regulate the temperature outside the retort.

Process gases for smaller units may be provided by premixed gas cylinders. Larger units generally use mass flow controllers to create tailored gas mixes from separate tanks of nitrogen, hydrogen, etc. The mass flow controllers are vacuum tight, accurate, and provide the correct flow rate regardless of supply conditions. The gas mix can also be changed, if desired, while the process is under way. Both gamma prime gas, which is typically 75% hydrogen and 25% nitrogen, as well as epsilon gas, with 2–5% methane added, are quite common. Gas mixtures high in hydrogen can be used to reduce white layer, if desired. As mentioned earlier, argon is often added. Hydrogen can be used to preclean workloads, removing surface impurities.

After nitriding, load cooling is accomplished by raising system pressure with nitrogen to atmospheric pressure. Internal fans cool the workload to a safe handling temperature. This also reduces the load temperature to a range where air will not discolor the parts.

A control system is used for interlocks, alarms, valve control, resistance heat control, partial pressure control, DC power supply control, cooling, and data recording.

Data recording can be through analog communication or, preferably, direct digital communication between the recording device and the process control system. With direct digital communication, the exact digital values are recorded either via computer, or electronic strip chart recorder. Digital communication also allows a wide range of power supply values to be recorded. These include pulse rate or frequency, system voltage, system amperage, system kilowatts, duty cycle, on/off times, and arc counts. Other recorded process variables are process gas flowrates, cooling water temperatures, system partial pressure, work thermocouples, wall temperature, setpoints, and percent outputs of the heating systems.

**Conclusions**

In the Surface Combustion lab and also in large production units, the solid-state pulse power supplies have proven to be flexible, repeatable, and reliable. The most noticeable improvement has been the microprocessor-based arc detect circuitry which provides high resolution numerical adjustments in conjunction with extremely high-speed detection and suppression of arcs. This capability allows the glow discharge to be turned on earlier in the cycle reducing cycle time by 20%.

**Acknowledgments**

Jerry Wright and Cameron Aldrich of Ariel Corporation for their help in providing data and commentary on the equipment and its performance as well as metallurgical and production insight.

**References**

[1] Latrobe Specialty Steel Company, Nitralloy 135™ Modified Data Sheet