Ion Nitriding Principles and Applications

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Ion nitriding is a case hardening process that has been in existence in Europe for many years. In the U.S., no attempt was made to use this process in production until after 1950. Furthermore, the promotion of production ion nitriding here was only accomplished within the past 10-15 years. Although there are many small to moderate quantity applications, the smaller user has considered the process more of a mystery than proven science and suspected everyday processing was only feasible in a university laboratory or a large corporation. This article attempts to make understandable the basics of ion nitriding including a brief discussion of the nitride forming elements and their respective layers. Applications and processing of parts such as gears, shafts, and dies of various alloys will also be discussed.

Basic Principles

To understand how ion nitriding can be made a relatively simple thermal process, one must first learn the basics. It is a case hardening treatment—the result of a reaction generated from a high voltage glow discharge between the workpiece (cathode) and the inside chamber wall of the vacuum furnace (anode). See Fig. 1. Various resultants of this glow discharge such as color of glow, glow intensity, glow seam width, as will be explained later, and rate of temperature rise are a function of operating parameters, i.e., applied voltage, vacuum level, and gas mixture.

Applied voltage from a controlled D.C. power supply energizes the workpiece and the hearth of the vacuum furnace (which are electrically insulated from earth ground). At the same time, a controlled flow of a hydrogen and/or nitrogen gas is bled into the vacuum chamber. The gas is ionized and the ions impinge upon the work to be processed raising its temperature to the 600°F to 1000°F range. This reaction causes a release of photons resulting in a blue-violet glow surrounding the work pieces. (A similar, more common reaction is that of an electric neon sign where neon gas is ionized releasing photons.)

The high velocity collision of the hydrogen ions on the work surface causes a reduction reaction and hence a cleaning or removing of oxides and small quantities of impurities from the surface. Nitrogen ions react with elements such as aluminum, chromium, molybdenum, and vanadium, forming hard nitrides and after time, resulting in a desired nitrided case depth. Process time can vary from as short as one hour up to 40 hours, depending on the type of alloy and case depth requirement. Fig. 2 shows a sample case depth curve[1] for 4140 steel.

Gases used in the ion nitriding process include hydrogen (H_2), nitrogen (N_2), and sometimes methane (CH_4). The standard nitriding mix is 75% H_2/25% N_2 and can be obtained premixed. It has been verified[2] that gas stratification problems do not exist with this type of mixture because of gas bottle filling techniques, very low freezing temperatures of each component of the mix, and the way in which it is introduced to the vacuum chamber—a highly turbulent flow. Typically, the H_2 gas is used for initial plasma generation and "heat up" of the work load. The switchover point to the gas mix is determined partly by the shape of the workpieces and the temperature at which the load is being nitrided. Where several holes exist, whether blind or through, care must be exercised to avoid locally overheating the surroundings of the hole because of the contained plasma energy within the hole. If the particular workpiece requires specific control of the compound zone, variations in the N_2 content can be made by individually controlling each gas. Increased amounts of N_2 will generate a thicker compound zone. Flow rates of less than 1 SCFH are normal and yield very good results.

Ion nitrided surfaces are made up of two types of layers: the outer compound zone, a thin and compact white layer (hard but brittle iron nitrides

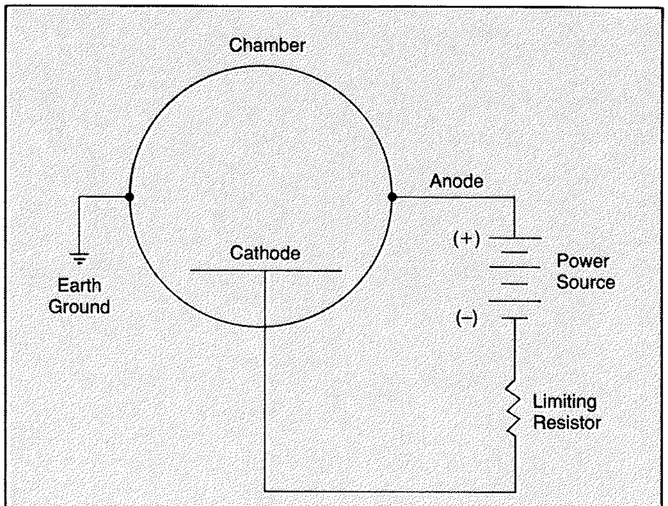


Fig. 1 Basic diagram of glow discharge.

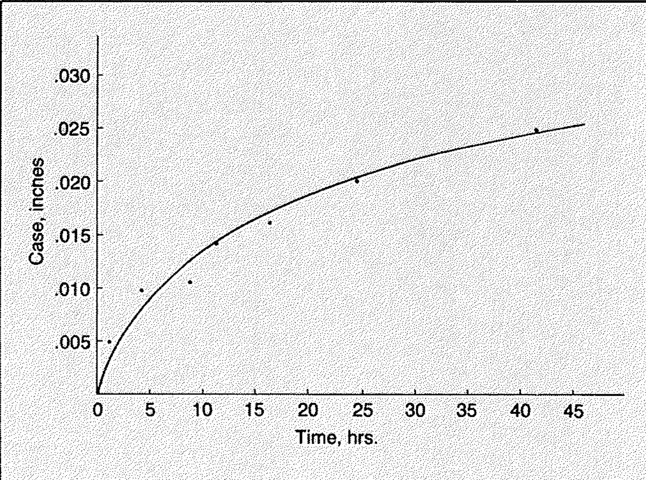


Fig. 2 Case depth vs. process time for 4140 alloy steel ion nitrided at 950°F.

and/or iron carbonitrides); and the inner diffusion zone of intermediate hardness between soft core and hard compound layer. The outer compound zone is extremely hard; if too thick, it is brittle and can crack and break away from the diffusion layer and parent material. This layer often is a desirable component of the nitrided surface because of its high hardness and may comprise one or two definitive phases, depending upon the material being processed and the processing conditions. When the plasma gas consists of a carbon-free mixture, a gamma-prime (γ') phase of iron nitride (Fe-N) develops. When the gas contains carbon, such as a methane (CH_4) mix, a multi-phase compound of gamma-prime (γ') and epsilon (ϵ) may be formed in the iron-carbonitride (Fe-C-N) layer. It also may be possible to suppress gamma-prime (γ') and form only epsilon (ϵ). To prevent too brittle and too thick a multiphase layer, the carbon content of the gas mix must be closely controlled, and is usually less than 1% of total.

The diffusion layer of hardness intermediate between core and compound layer, acts to increase overall material hardness while supporting the surface compound layer. It is comprised of alloy nitrides (Al, Cr, Mo, and V). Depending upon alloy composition, which influences hardenability of the metal, case depths attainable will vary from one material to another. However, the microstructure, thickness, and hardness of the compound and diffusion zones can be controlled, allowing optimum properties to be produced to suit service requirements of components in specific applications.

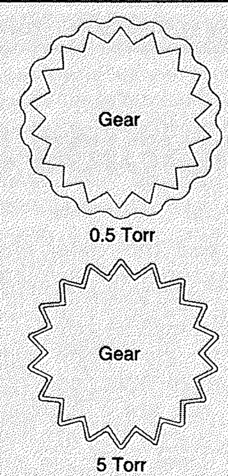


Fig. 3 Simulated plasma contours for gears under pressures shown.

Examples of Applications

Components applicable for ion nitriding range from gears and shafts to pump cylinders to punches and dies. The easiest work to process is exemplified by a 4140 Cr-Mo alloy steel gear with a broad tooth pattern or a 4140 Cr-Mo alloy steel shaft with gradual or no step changes. Case depths of .001″ to .030″ are easily attainable for this material and the rate of case development is faster than for most other materials. The narrower the tooth or the more abrupt the step changes, the higher the gas partial pressure must be to "drive" the glow seam (the thin intensely bright ribbon following the contour of the surface) tightly against the part surface. Fig. 3 shows simulated plasma contours around a gear at different gas pressures.

Cylinder surfaces for rotary type pumps involving bore wear or piston cylinders subjected to pressure and conditions for wear are candidates for ion nitriding to develop a harder and more wear resistant case. Punches and dies have benefitted from the ion nitriding process, too. Certain types of punches, primarily those without sharp edges but possibly subject to edge chipping, have better wear characteristics and also better release properties after ion nitriding. One case of ion nitriding an H-13 punch proved such a reduction in coefficient of friction that sticking of the punch to the part no longer occurred. Furthermore, ion nitriding of the die made for easier release of the part from the die while improving both punch and die life.

Parts subjected to corrosive atmospheres are frequently made of a 300 series stainless steel. Hydrogen cleaning of the surface tends to remove the protective chromium oxide layer. The case depth imparted by ion nitriding improves part life by reducing wear. As an added benefit, the corrosive resistant epsilon case formed makes up for some of the corrosion resistance lost upon removal of chromium oxide layer.

Changing the processing gas to a 25% N_2 - 1/4% CH_4 - balance H_2 and raising process temperature allows for carbonitriding to be performed. This treatment applies to those materials that do not contain the elements required to develop diffusion case nitrides but do need a very hard surface combined with required strength. Carbonitriding of 45P anchor steel (99.54 Fe, 0.45 P) powder metallurgy parts and subjecting them to a high humidity atmosphere for one year showed extended corrosion

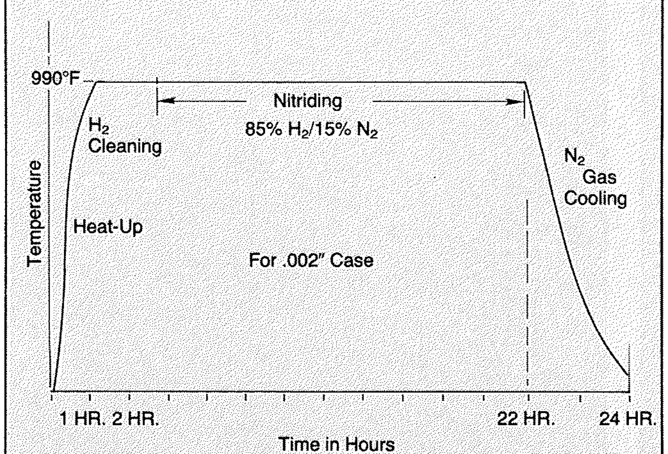


Fig. 4 Ion-nitriding cycle for stainless steel grade 17-4PH.

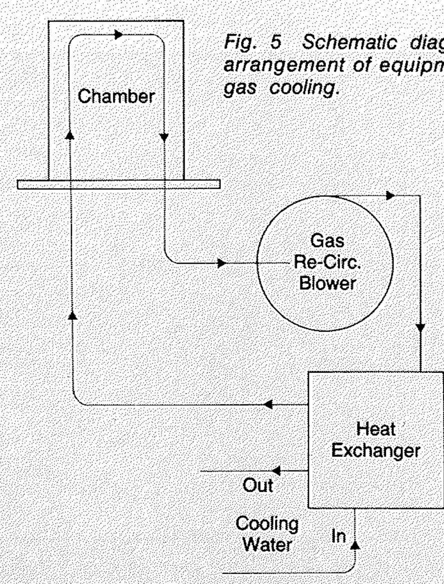


Fig. 5 Schematic diagram of arrangement of equipment for gas cooling.

prevention capabilities by more than ten times over that provided by the previous standard steam treating operation.

Typical Process Cycle

The first step of processing work is inspection. Parts should always be checked for damage such as cracks, chips, or nicks and for suitability to the process. Some parts contain caution spots, as will be explained later.

Although not as stringent as for a thin film coating or ion plating operations, cleaning of the parts is imperative. Heavy greases should be avoided. Removal with several "wipe downs" with clean rags is advisable before proceeding. Parts that can fit into a vapor degreaser are best handled that way. Those that are too big or awkward can be wiped down using a lint-free cloth with alcohol or mineral spirits first, then with acetone. This leaves a clean, acceptable surface. Blind holes, through holes, tapped or smooth holes must be cleaned of any chips and oils.

Proper fixturing, which can be made of mild carbon steel, may be attached at this time. Fasteners can be plain carbon (unplated), or stainless steel and should have their threads coated with moly-disulfide or equivalent. This coating prevents high temperature sticking of the threads to the tapped hole in the part. Any holes not used for fixturing should be blanked off if they are not the subject of the nitride requirement. If they are left open to the processing gas, and parameters are not carefully monitored and adjusted, localized overheating may occur due to trapped plasma (glow) energy within the hole.

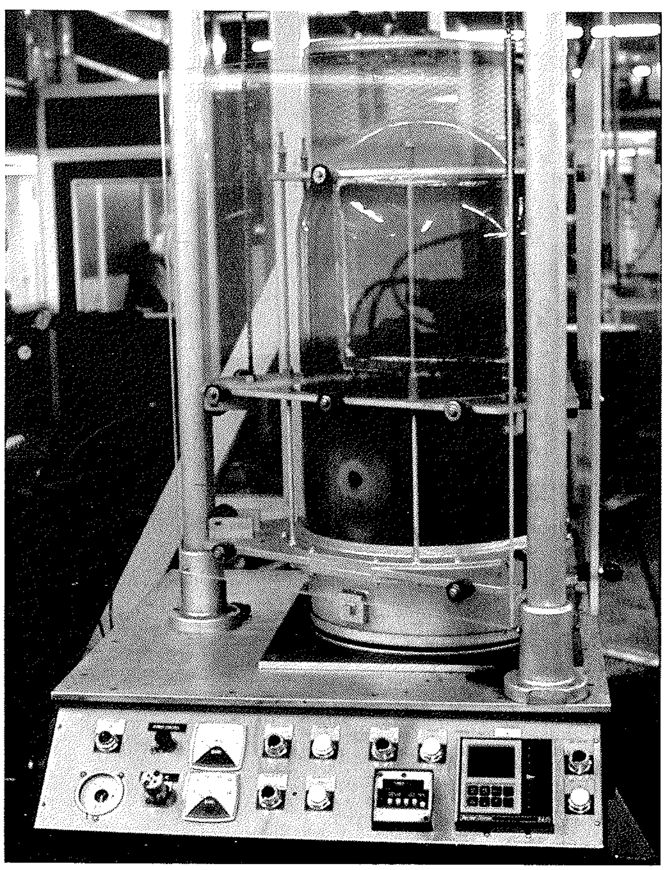
Once parts are cleaned and fixtured, the vacuum pumping system is started and the chamber is evacuated to at least 100 microns (0.1 Torr). The preprogrammed cycle, a simplified example of which is shown in Fig. 4, is initiated by bleeding in a controlled flow of hydrogen for the initial sputtering and heat up. The work load is heated to temperature and the chamber is switched over to the nitriding mix (H_2/N_2 blend) for the predetermined time at temperature to achieve the desired case depth. Cooling is automatic with nitrogen gas at near atmospheric pressure and circulated with a recirculating blower and heat exchanger to speed cooling. Fig. 5 shows the layout of the gas recirculating system. Once below 200°F (95°C) the chamber is opened and the parts are removed. If desired, the parts can be protected with a light oil such as Rust-pel.[3]

Cautions and Operating Tips

There are many aspects of the ion nitriding process that simply require experience to learn. First, small diameter bores in long thin-walled tubes pose overheating problems because of the small mass to absorb the contained heat energy. A ratio of length to diameter (L/D) of a through hole on the order of ten is comfortable. Ratios larger than this can be accommodated; however, process parameters must be modified, and some knowledge of the process is advisable to avoid overheating and, in turn, tempering (softening) the workpiece. For example, if D2 tool steel is nitrided above 975°F (525°C), which is above the secondary hardening temperature[4], the core hardness will be tempered.

Blind holes require twice the attention because the energy is contained in the hole with no way to get out. When the energy reaches a certain level, a "fireball" occurs, which is the "explosion" of energy from the inside of the hole out. The best prevention is to block off this hole. This can be a simple matter if it is tapped. By threading a stainless or carbon steel machine screw or hex head bolt into the hole, the plasma (glow-discharge) will wrap around the screw instead of penetrating inside the hole. Again, coating the threads with a moly-disulfide compound will prevent sticking of the screw to the part. If the hole is not tapped, fitting a segment of smooth round bar or the closest size bolt into the hole will usually prevent problems.

Pieces of angle-iron (carbon or stainless steel), channel, flat bar, and pipe



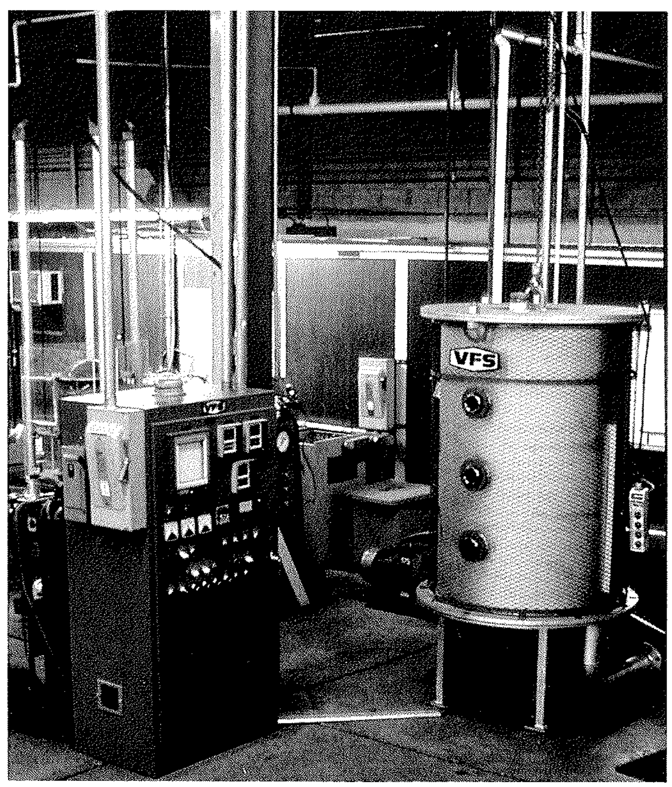


Fig. 6 Two ion-nitriding furnaces and their instrumentation at commercial heat treating shop.

are all good shapes from which fixtures can be fabricated. They can be used for work supports, hanging fixtures, masks, etc. Hex-head bolts of carbon steel or stainless steel can be used as pedestals to support work or lift certain areas off of the hearth plate.

Stop-off materials, to prevent selected surfaces from nitriding, are available for ion nitriding. It is suggested that tests be carried out to determine the best stop-off materials before applying them to actual work. Removal of all paint-on stop-off materials requires mechanical means such as by wire brush, coarse cloth or other semi-abrasive material. This eliminates the use of stop-offs in small, hard-to-reach locations because of the difficulty in their removal after ion nitriding. Copper plating is probably the oldest and most effective means of masking. This procedure requires a plating operation, with subsequent removal of plating at areas where a nitrided case is desired and then ion nitriding. Following nitriding, a stripping operation removes the balance of the plating. Use of flat, annealed copper sheet stop-off can be an aid in flat or gradual bend applications. On flat surfaces carbon steel sheets often are used to mask and prevent nitriding.

A problem encountered on occasion is attributed to decarburized parts prior to ion nitriding. Tell-tale signs of this decarburized state often are not found until after nitriding is complete. These post-nitriding signs are most obvious, however, and consist of the following: inconsistent scaley-like surfaces, flaking of the nitrided surface, and blotchy, inconsistent layer development as seen by the typical hazy, matte gray color.

Initial heating occurs due to the collisions of the hydrogen ions with the workpiece. The rate of temperature rise is greater with H_2 than with the H_2/N_2 nitriding mix. If for some reason a small area of a part begins showing signs of color (red radiation—as evidenced upon momentarily turning the ion power off and viewing the part) when using H_2, switching to the nitriding mix will cool that portion; this allows a more uniform part temperature while still raising the temperature to the set point. This is one good reason to have large and numerous sightports for operator observation.

Fig. 6 shows two typical ion nitriding units in operation at a sister company—Solar Atmospheres, Inc., a commercial heat treating shop.

Conclusions

Even when the number of parts is small and the repetition of a given job is unknown, ion nitriding is a viable case hardening process. Various materials will develop case depths by ion nitriding, as other literature will support.[1,5] Gears, shafts, punches and dies are the most common candidates, but new applications are discovered every week. Processing costs are competitive, conditions are clean and environmentally safe and repeatability is achievable. Ion nitriding is certainly worth considering when a harder, more wear resistant and quality surface is required for part in service.

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