

# DEEP DIVE ON GAS NITRIDING

## Summary

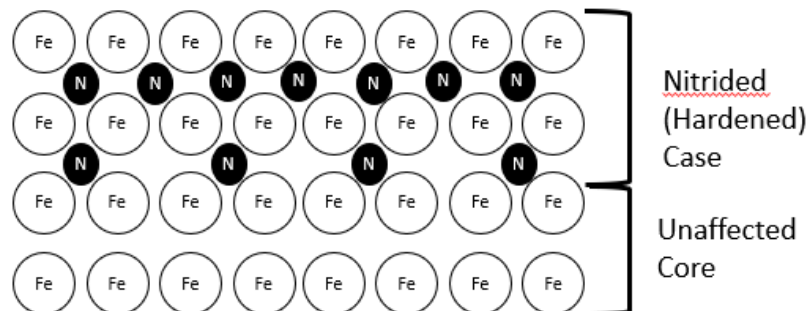
Gas Nitriding is a low temperature diffusion hardening process known for fatigue-resistance, corrosion-resistance, anti-galling, and lowered coefficient of friction. The process is suitable for mild steels, alloy steels, tool steels, cast irons, stainless steels, and more. Because of the low temperatures used, quenching is not required, which makes warpage unlikely and maintains the mechanical properties of the core. Nitriding is ideal for:

- Finished Components
- Complex geometries
- Maintaining dimensional tolerances
- Hardening large areas simultaneously

The nitriding process is a complex metallurgical process, and procedures are not one-size-fits-all for every alloy. Our team of Ph.D. Engineers develop individualized treatments for each material and application. Contact us to find out which treatment is right for your material and application.

## Nitriding Overview

Nitriding hardens steel by fitting Nitrogen atoms in the gaps between Iron (Fe) atoms known as interstitial sites. Picture a bucket of basketballs and trying to fit golf balls into the air pockets between balls. The nitrogen atoms can then contribute to hardening either by occupying interstitial sites, or by interacting with Fe and other alloying elements (Ti, V, Al, Cr, etc.) to form precipitates.



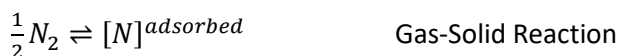
All nitriding, whether Gas, Liquid or Plasma are fundamentally the same in that they impart nitrogen atoms into the near surface of a material to harden through a combination of precipitation hardening and solid solution strengthening. There are two steps for any nitriding process:

1. Adsorption (Delivery) of atoms to the surface
2. Diffusion of atoms into the surface to a prescribed Depth

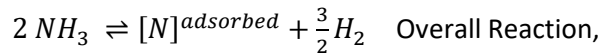
Gas, Liquid, and Plasma nitriding differ in the way that they deliver nitrogen to the surface, but the diffusion step is identical in all methods. The diffusion step accounts for the majority of the processing time, taking hours (up to tens of hours) compared to minutes for adsorption step. The adsorption step can be important in white layer growth kinetics, and in the activation stainless steels. Plasma nitriding requires line of sight to deliver nitrogen atoms, but since nitrogen ions are accelerated to strike the surface, nitriding can be done at lower temperatures. Salt-bath (liquid) nitriding is less capable of controlling the amount of nitrogen delivered to the surface, but the aggressive salts make activation of stainless steels relatively easy. Gas nitriding uses ammonia gas to deliver nitrogen to the surface, and combines the best of both worlds with activation of stainless steels being possible with proper surface preparation. Ammonia gases are easier to control than the molten salts used in liquid nitriding, and offers several benefits:

1. Better control over the process and product consistency.
2. Process can be monitored and automated using sensors and computer controls.
3. Higher furnace capacity and lower cost.
4. Consistent and repeatable.
5. More environmentally friendly than liquid
6. Safer for operators and shop personnel

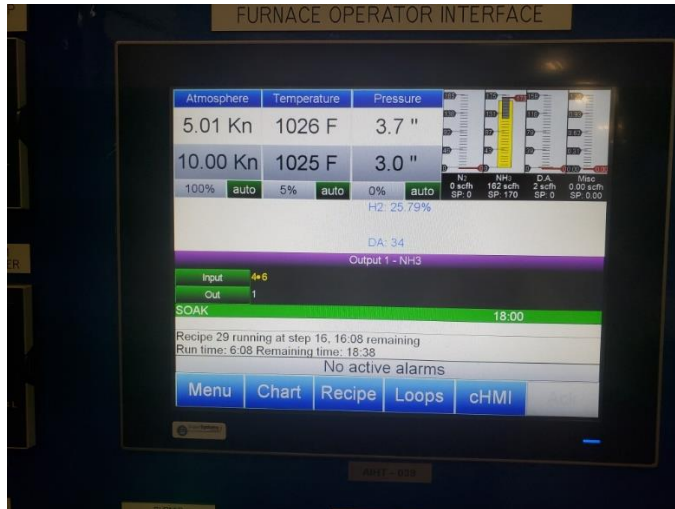
The adsorption step in gas nitriding is driven by two reactions, a gas exchange and a gas-solid reaction, which combine to place nascent nitrogen atoms on the surface of the steel. The rate at which these reactions occur is called the nitriding potential ( $K_N$ ), and can be calculated based on the flows of ammonia and hydrogen into and out of the furnace. Our furnaces monitor the  $K_N$  and adjust the gas flow rates to maintain the setpoint prescribed by one of our PhD metallurgists. Temperature is maintained in a similar way with thermocouples at various locations within the furnace.



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$$K_N \equiv \frac{P_{NH_3}}{P_{H_2}^{1.5}}$$



## Post-Oxidation Overview

An optional oxidation step can be performed following nitriding which produces a matte-black surface finish that masks any surface imperfections. The black color is the result of a high-temperature oxidation reaction on the surface of the steel, which forms Magnetite ( $Fe_3O_4$ ). This is similar to the process by which rust ( $Fe_2O_3$ ) forms at low temperatures, except that  $Fe_3O_4$  inhibits corrosion, and adheres to the nitrided surface to form a protective oxide. Oxynitriding, can be performed as a finishing step of a liquid, plasma, or gas nitriding process. Liquid nitriding often utilizes a post-oxidation step as part of a QPQ (quench-polish-quench) process, with the two quenches being post-oxidation steps. An intermediate blasting step is necessary to accommodate for the deterioration of the surface finish from the molten cyanide salts used in that process. A rust preventative oil (RPO) is also typically applied following the post-oxidation to enhance corrosion-resistance further. A thicker white layer may help to trap more RPO and thus improve-corrosion-resistance, but this may not be ideal for all situations.

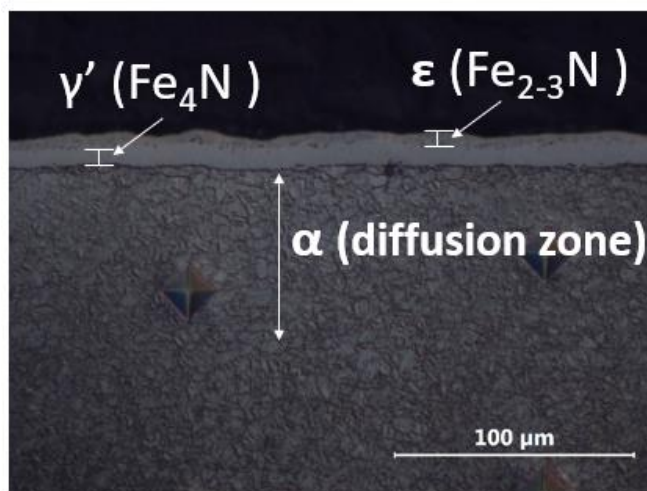
Gas Nitriding  
Post-Oxidation



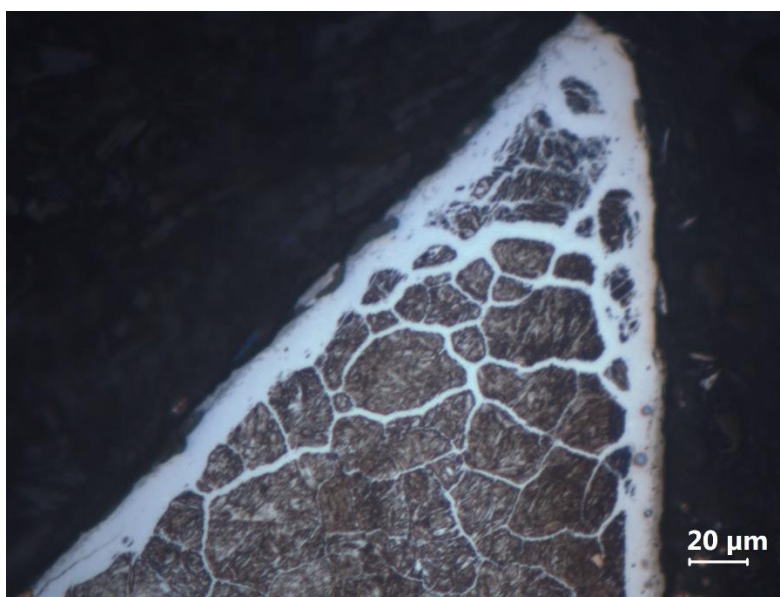
Standard  
Gas  
Nitriding

## White Layer Formation and Growth

The key difference between low temperature processes like gas nitriding and higher temperature processes like gas carburizing is that new phases can form with increasing nitrogen concentration. In gas nitriding a high nitrogen phase can be (and typically is) formed at the surface known as the white layer. The white layer is hard, with good wear-resistance and corrosion properties, but it is also porous and brittle and must be carefully managed. Excessive white layer growth can cause spalling or surface cracking, and is particularly prevalent at fine geometries like knife edges. Thin locations like edges experience growth of the white layer from two or more directions and can quickly start to form brittle spiderwebs where the white layer grew preferentially along existing grain boundaries. Nitride networks serve as initiation sites and propagation sites for cracks. “Too thick” is dependent on the alloy and application, but the typical range is 3-20 microns. Geometric areas like edges or corners are more prone to excessive white layer growth, as the nitrogen diffusion occurs from 2 or 3 directions as opposed to just one. It is also important to note that every alloy will grow white layer at slightly different rates due to chemical and microstructural differences. Nitriding potential can be carefully controlled to control white layer growth, solving one of the major flaws of conventional gas nitriding.



Composition of the white layer

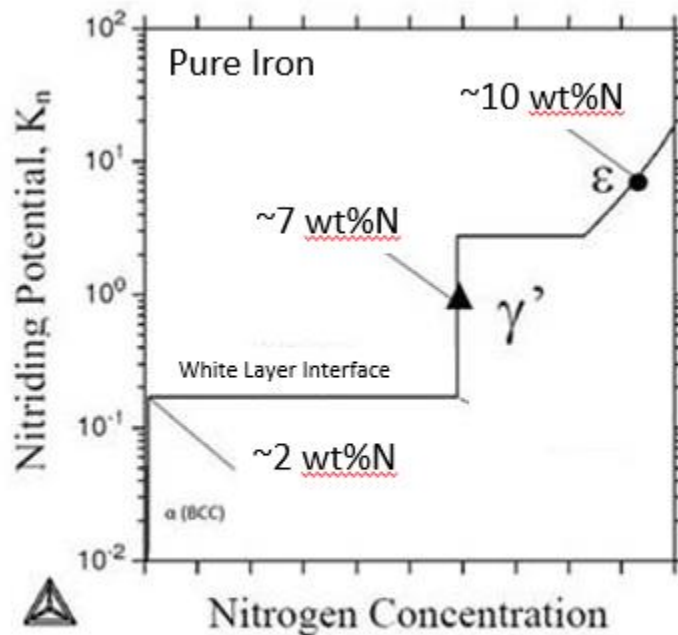


Nitride Networking at a sharp knife-edge.

The white layer is not typically seen with a standard microhardness survey due to how thin the layer is but understanding how it forms is key to controlling the nitriding process. The white layer is predominantly the result of  $\epsilon$  ( $Fe_{2-3}N$ ) and  $\gamma'$  ( $Fe_4N$ ) stability at high nitrogen concentrations. The growth and composition of the white layer is dependent on the nitriding potential in the furnace and the time spent at that potential, and can be predicted and controlled with our automated nitriding furnaces. The most common process used to control the white layer thickness is the Floe process, which uses a first stage at high nitriding potentials to grow the white layer, and a longer second stage at lower



nitriding potentials to achieve the target case depth with minimal white layer growth. Depending on the nitriding potential set, the near surface can either be composed of  $\epsilon$  ( $\text{Fe}_{2-3}\text{N}$ ),  $\gamma'$  ( $\text{Fe}_4\text{N}$ ) or a two phase region of the two. Typical gas nitriding of alloy steels prescribes a nitriding potential in the  $\epsilon$  region during the first stage to drive white layer growth, and a nitriding potential near the bottom end of the  $\gamma'$  region to maintain the white layer thickness.

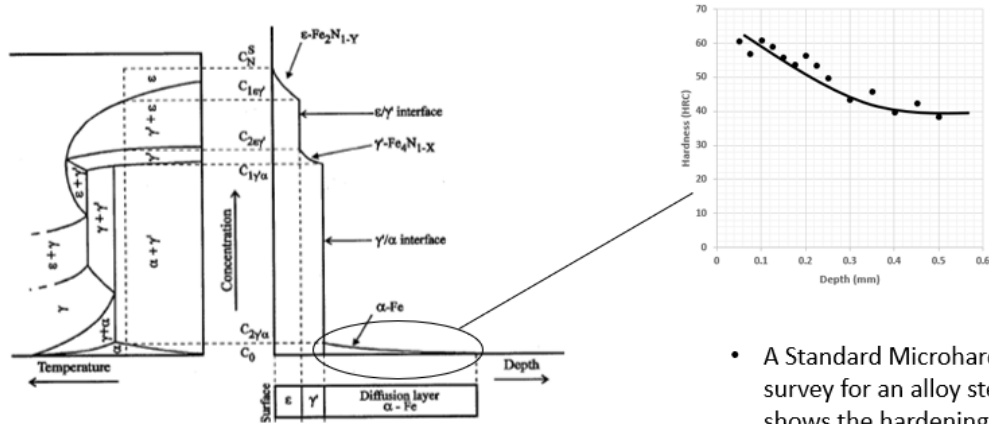


Yang, Mei. "Nitriding-fundamentals, modeling and process optimization." (2012).

Because of the presence of the white layer, the case depth is not very dependent on the nitriding potential in the furnace. This is because diffusion rates within the white layer are extremely low, and the  $\gamma'$ - $\alpha$  interface doesn't move much (<20microns over the entire process). Because the solubility for nitrogen in bcc iron is set for a given temperature and alloy combination, the effective surface concentration in the diffusion zone is fixed. The key takeaway is that case depth is minimally altered by the nitriding potential in the furnace and that case depth and white layer can be controlled independently as the white layer has three degrees of freedom (time, temperature, nitriding potential), while the case depth only has two (time, temperature). The last important note is that the surface hardness cannot be meaningfully changed with nitriding potential as is possible in the carburizing



process.



- A Standard Microhardness survey for an alloy steel only shows the hardening in the diffusion zone

Yang, Mei. "Nitriding-fundamentals, modeling and process optimization." (2012).

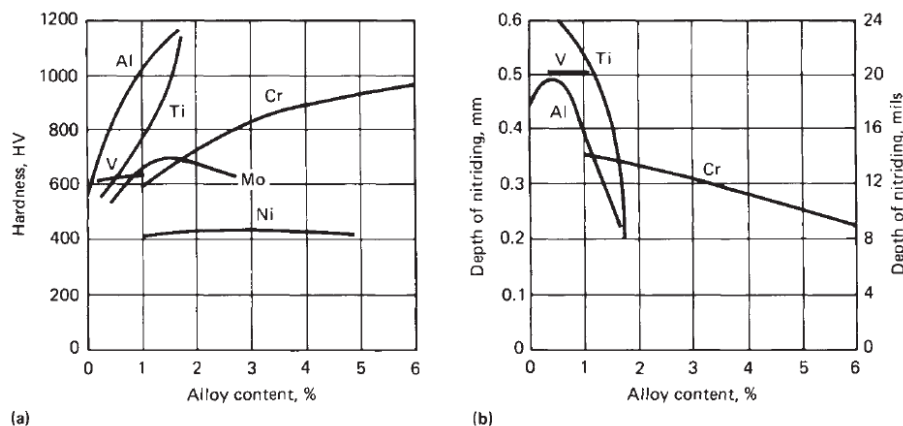
Relationship between Fe-N phase diagram, Nitrogen Concentration profile following nitriding, and microhardness testing.

## Factors affecting Case Depth and Hardness

Nitriding case hardness and depth are dependent on 3 major factors:

- Alloy Chemistry and Tempering Condition
- Processing Time
- Processing Temperature

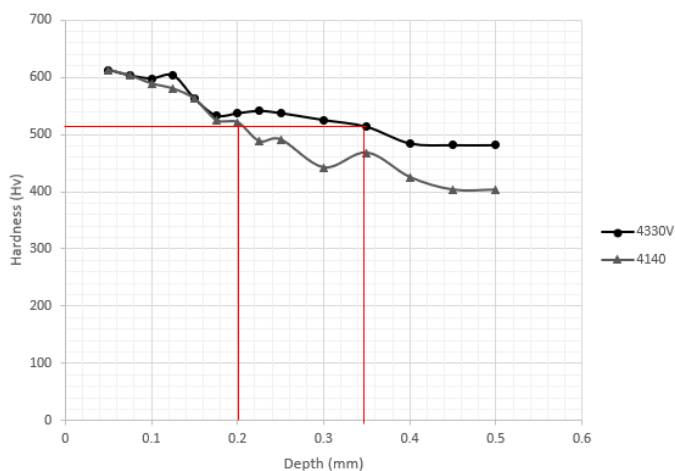
Each alloy will have a different nitriding response due to its chemistry. The hardening response of nitriding is dictated by the minor alloying elements (nitride formers) within the alloy. The major nitride formers are Al, Ti, V, and Cr. Increasing the amount of nitride-forming elements will increase the hardness of the case, but will also decrease the achievable case depth. Interstitial elements such as carbon also tend to slow the diffusion of nitriding, reducing the case depth.



Relationship between alloying elements and achievable nitriding hardness/ case depth. Steels which don't contain a lot of nitride-forming elements are limited in terms of the hardening potential with nitriding.

Dossett, J., and G. E. Totten. "Introduction to surface hardening of steels." *ASM Handbook 4* (2013): 389-398.

Different alloys nitride at different rates, and can result in a difference in case depth. The difference in case depth for various alloys is more apparent at deeper depths as over longer processing times. For example, 4330V alloy steel material can have nearly double the case depth of a 4140 alloy for the same processing conditions. This makes it more difficult to run multiple materials at the same time for deeper cases, and makes some materials less economical than others.



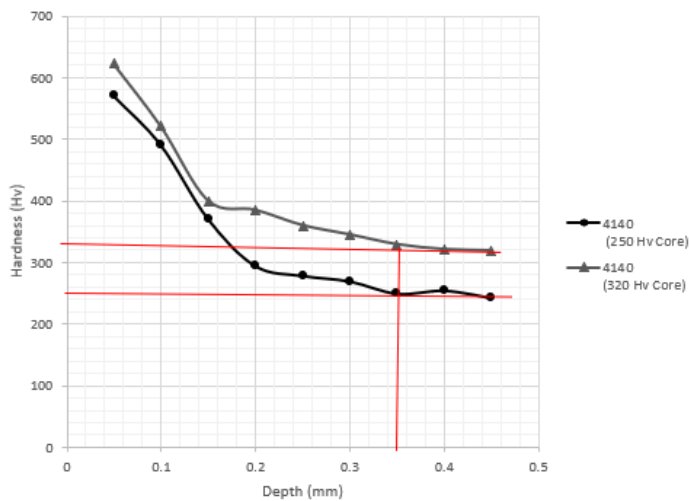
Hardness as a Function of Depth for 4140 and 4330V alloys nitrided concurrently. Effective case depth for 4140 is 0.2mm (0.008"), while 4330V is almost 2x deeper at 0.35mm (0.014")

The tempering condition of the material is also a key factor that can affect both the hardness and the depth of the case. The actual diffusivity of nitrogen in the material seems fairly consistent as the metallurgical case depth (return to base material hardness) is roughly the same. The difference between





the two is the extent of hardening possible as there are more residual stresses created in a harder matrix. Using an effective case depth definition such as 40 HRC can cause discrepancies in the case depth reported. Additionally, it may become difficult to meet surface hardness requirements, as the base material chemistry and condition are the major factors affecting surface hardness, as modifying processing parameters has minimal effect.

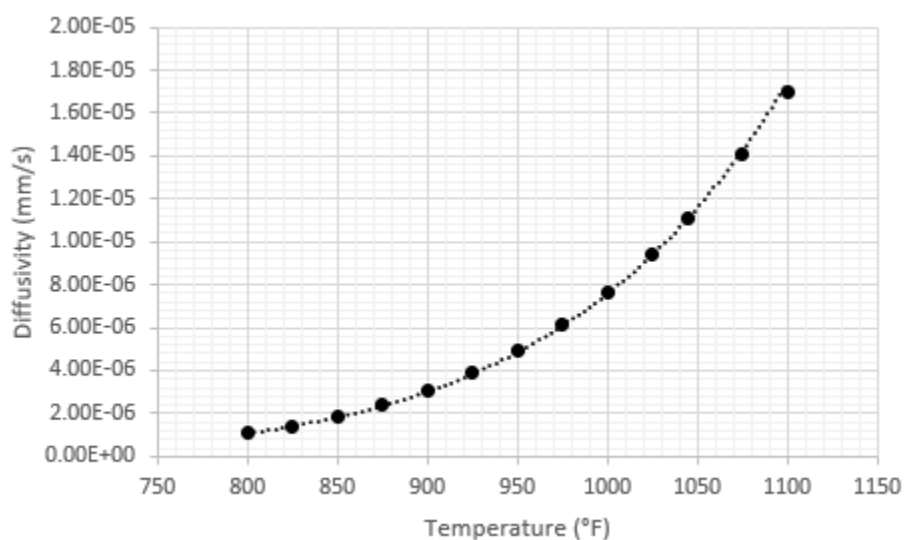
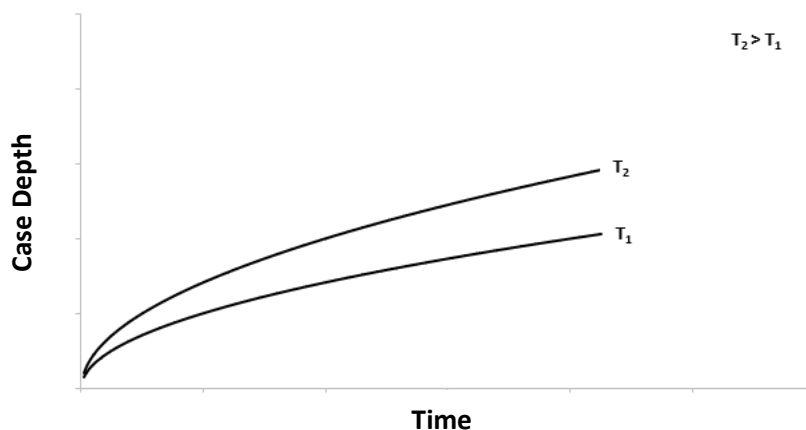


The effective case depth for materials can differ depending on the tempering condition, even though the actual diffusivity is relatively constant.

Nitriding is a diffusion process, and is dictated by time and temperature. Longer processing times have deeper case depths, but the increase in depth diminishes with processing time. A generic relationship between case depth ( $x$ ), diffusivity ( $D$ ), and time ( $t$ ) is  $x \propto \sqrt{Dt}$ . In other words, in order to double the case depth a 4x increase in the processing time is required. Some case depths are unachievable in a reasonable timeframe. For example, increasing the case depth from 0.008" to 0.011" using a 50HRC definition on 4140 requires 2.5 days longer in the furnace, which will increase costs and lead times substantially. The diffusivity is dependent on the alloy, and on the processing temperature. Higher processing temperatures allow for shorter processing times; however, an upper limit will exist as nitriding temperatures must be 25-50°F below final tempering temperature to ensure base material properties like yield strength don't change substantially. The general relationship between diffusivity and temperature is:

$$D = D_0 e^{-\frac{Q_0}{RT}}$$

The intrinsic diffusivity,  $D_0$ , and activation energy,  $Q_0$ , are material constants, and  $R$  represents the ideal gas constant. This means that a 10% increase in operating temperature can have an upwards of 50% decrease on processing time. At AIHT, we have optimized our recipes so that we can pass the savings on to you.



Relationship between Temperature and Diffusivity for Pure Iron. Estimated using material coefficients from Porter, David A., Kenneth E. Easterling, and Mohamed Sherif. Phase transformations in metals and alloys (Revised Reprint). CRC press, 2009.

## Distortion

While distortion in nitriding is minimal, understanding how parts distort can be important for some applications with tight tolerances.

There are three basic causes of distortion during nitriding.

1. Growth of the surface layer due to the addition of nitrogen atoms. The amount of growth is proportional to the case depth, and will occur outward from any surface exposed to a nitriding atmosphere (OD increase, ID decrease).

2. Stress relief due to processing temperatures. While processing temperatures are relatively low, there is a possibility of residual stresses imparted during forming or machining to cause a distortion in thin-walled components.
3. Tempering during nitriding. If parts aren't tempered before nitriding, or if the nitriding temperatures exceed the tempering temperatures the material can grow or shrink depending on the alloy as the metallurgy evolves. This is of greater concern during liquid nitriding where processing temperatures are typically higher.

Since tempering is typically done prior to nitriding, this is unlikely to be a concern, but should be considered for stainless steels. Stress relief is difficult to account for, but is a low-risk, and is best accounted for through trials. A stress-relief step before final machining can help limit the amount of residual stresses within the component. Growth typically accounts for the majority of the dimensional change in alloy steels, and is directly related to the case depth achieved. For deep case treatments on steels with high diffusivity (4330V), the planar growth was measured 0.00048" as measured with a CMM before and after treatment.

Process	Case Depth in. (mm)	Radial Growth of Nitrided Layer (x10 <sup>-3</sup> in.)
Liquid	0.009 (0.25)	0.18
Gas (Thin-Case)	0.005 (0.125)	0.08
Gas (Deep Case)	0.022 (0.55)	0.48