

Application Bulletin

Introduction of the nitriding factor, K_N as the driving force for gas nitriding, provides for precise, continuous control. The traditional measurement of % dissociation provides an alternative parameter for checking the accuracy of the calculated K_N and in many cases, as the primary control parameter.

INTRODUCTION

The metallurgical processes of carburizing and nitriding have followed similar paths as the technology has advanced, and in a process of continuous evolution both procedures have progressed through similar developmental stages. Carburizing, early on, was conducted by packing the work pieces in a thick layer of carbon powder and raising them to temperatures conducive to diffusion of carbon into the work. While the process was effective, it was excessively slow, and difficult to control, so it progressed into a process utilizing a carbonaceous gas atmosphere. The only effective way of controlling this process was to establish a relationship between the enriching gas flow, and measurement of the carbon potential, using either periodic shim stock or dew point measurements. This technique persisted until the early seventies when the zirconia carbon sensor was first introduced. This device provided continuous measurement of the carbon potential, rather than the discontinuous measurements from shim stock or dew point. The measurement has been subsequently refined, by adjusting the sensor calibration using 3-gas (CO, CO₂ and CH₄) IR analyzers to calculate a more accurate carbon potential. The technique is currently applied to carbon control using continuous non-dispersive infrared analyzers, which measure continuously rather than periodically.

Nitriding has followed a similar path. The process provides several advantages for the alloys treated, such as high surface hardness, wear resistance, antigalling, good fatigue life, corrosion resistance and improved sag resistance at temperatures up to the nitriding temperatures. Since the early beginnings of gas nitriding, the % dissociated ammonia (PD) was considered the appropriate control parameter. This parameter is easily (but discontinuously) measured using the ammonia dissociation burette, which is calibrated directly in PD. In the 1990's, however, a new control parameter, the nitriding potential, was introduced. This parameter is defined by the equation

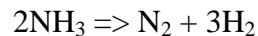
$$K_N = pNH_3/pH_2^{3/2}$$

It is now the specified control parameter for many industry material specifications.

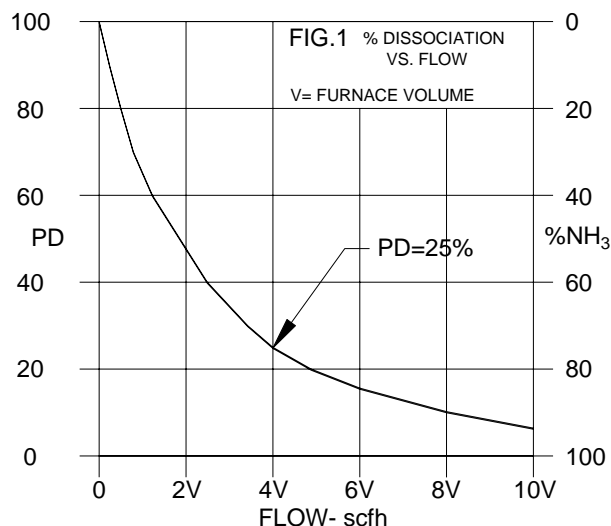
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THE TECHNOLOGY

When ammonia is introduced into a furnace, it dissociates according to the following reaction;



Although this reaction will ultimately go to completion, it is basically very slow. It has been determined that, if the furnace atmosphere is changed four times every hour, the amount that the ammonia is dissociated is 25% ±10%. An approximate relationship between ammonia flow rate and % dissociation is shown in Fig. 1. The general shape of the curve will vary with the particular nitriding furnace, and will also likely be affected by the size and surface area of the load. Fig. 1 also illustrates the basic relationship of ammonia concentration in the furnace atmosphere to the % dissociation, i.e. PD = 100 - %NH₃.



Nitriding has historically been conducted as either a single-stage or a double stage process using anhydrous ammonia. Temperatures in the single stage process range from about 925°F to 975°F, and dissociation from 15% to 30%. The first stage normally lasts for a period of 4 to 10 hours. The process creates an intense layer at the work surface, which is known as the white nitride layer. This layer is rich in dissolved nitrogen and nitrides. When the two-stage process, known also as the Floe process (U.S. Patent 2,437,249) is used, it has the advantage of widening and modifying the intensity of the white layer. The second stage may proceed at the same temperature as the first stage, or may be raised to from 1025°F to 1050°F. The second stage PD is increased to 65% to 80% which allows the further diffusion of white layer components toward the core. This PD may be achieved by reducing ammonia flow rate, or by adding a diluent such as nitrogen, dissociated ammonia or hydrogen, in order to ensure adequate positive flow. The nitriding process is carried out by the catalytic generation of nascent (monatomic) nitrogen at the

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surface of ferrous alloys. The nascent nitrogen diffuses into the surface and exists as either dissolved nitrogen or as iron nitrides such as the γ' phase (Fe_4N) or the ϵ phase ($\text{Fe}_{1.2}\text{N}$). There are several alloying elements in alloy steels that also contribute to the favorable characteristics provided by nitriding. Notable are aluminum, chromium, molybdenum, tungsten and vanadium, all of which form nitrides that are stable at nitriding temperatures.

In addition to microscopic cross section evaluation of work samples, effective processes are often evaluated by plotting hardness profiles with depth. Because these profiles are significantly affected by the core hardness, the work should be pre-tempered (before nitriding) at the lowest possible temperature, usually 30°F to 50°F above the nitriding temperature.

PROCESSING

Metallurgists have developed proprietary recipes for a large variety of products, tailored to suit their requirements for these products. An extensive list of these recipes is provided in the ASM Handbook, Vol. 4, Heat Treating, March 2001. Single stage processes vary in time from 8 hrs to 48 hrs. Two stage processes vary in time between 42 and 127 hours, with the second stage time being between 2 and 5 times the first stage time.

An aerospace industry standard was published in 1999, SAE Aerospace Material Standard AMS2759/10, which stipulates control with the K_N nitriding potential as the primary control parameter. This standard specifies three classes of processes. Class 0- has no white layer, Class 1- 0.0005" maximum white layer and Class 2- 0.001" maximum white layer. Nitriding potentials for all classes range from 4 to 15 for the first stage. They range from 0.2 to 0.8 for the second stage of Class 0, from 0.4 to 2.6 for the second stage of Class 1 and from 1.2 to 5.5 for the second stage of Class 2. Treatment times are not stipulated.

This specification provides a brief description of essential controls for nitriding processes:

- 1) Pressure controls: To maintain a positive retort pressure (e.g.-1" H₂O).
- 2) Nitriding atmosphere: Control, maintain and record composition of the feed gasses and the nitriding potential K_N .
- 3) Atmosphere flow rate controls: Control flow rates to maintain the nitriding potential and
- 4) Shutdown and alarms: Capable of safety shutdown in the event of system malfunctions.

Super Systems nitriding control systems meet this specification. SSi control systems also provide cascade temperature controls, and sufficient memory for 300 twelve-step programs.

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SUMMARY

Nitriding control by % dissociation will continue to be a significant portion of the nitriding market place. The introduction of the nitriding potential, K_N presents a viable alternative, but there is insufficient data on effectiveness of the two parameters to make a judgment about which is preferable. Super Systems addresses this paradox by providing both parameters as a feature of all systems. As with carbon control, where %C is calculated from the measurement of oxygen, both nitriding control parameters (PD and K_N) are precisely calculated by an SSi proprietary analytical technique.

It is important to note that, unlike in carburizing, the gases used in gas nitriding are extremely pure, and accordingly the calculations used in nitriding process control are stable, and reproducible.

The importance of superior temperature control has been demonstrated, and is related to the fact that retort temperature will have a significant effect on % dissociation. A change in retort temperature will cause a change in the PD curve displayed in Fig. 1. This characteristic is addressed by the provision of advanced cascade temperature controls in SSi nitriding systems.