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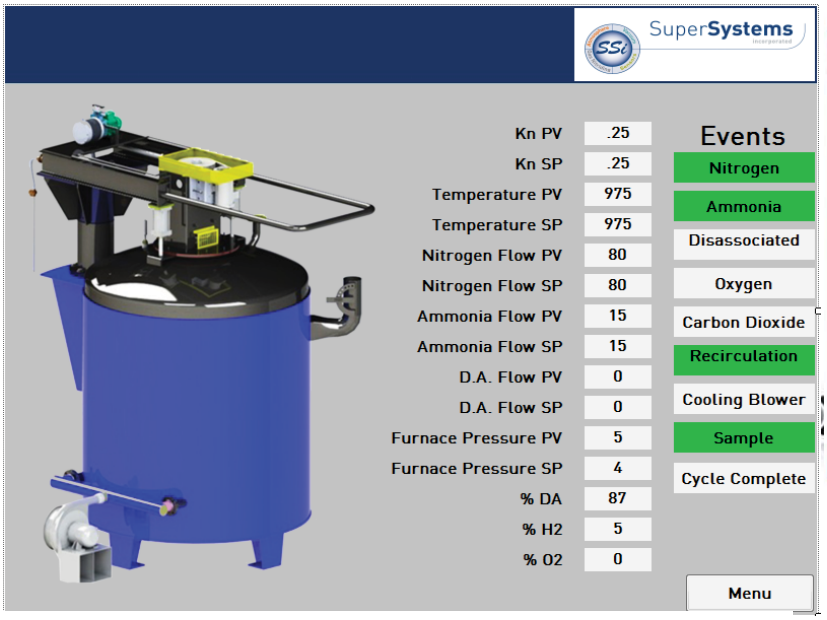

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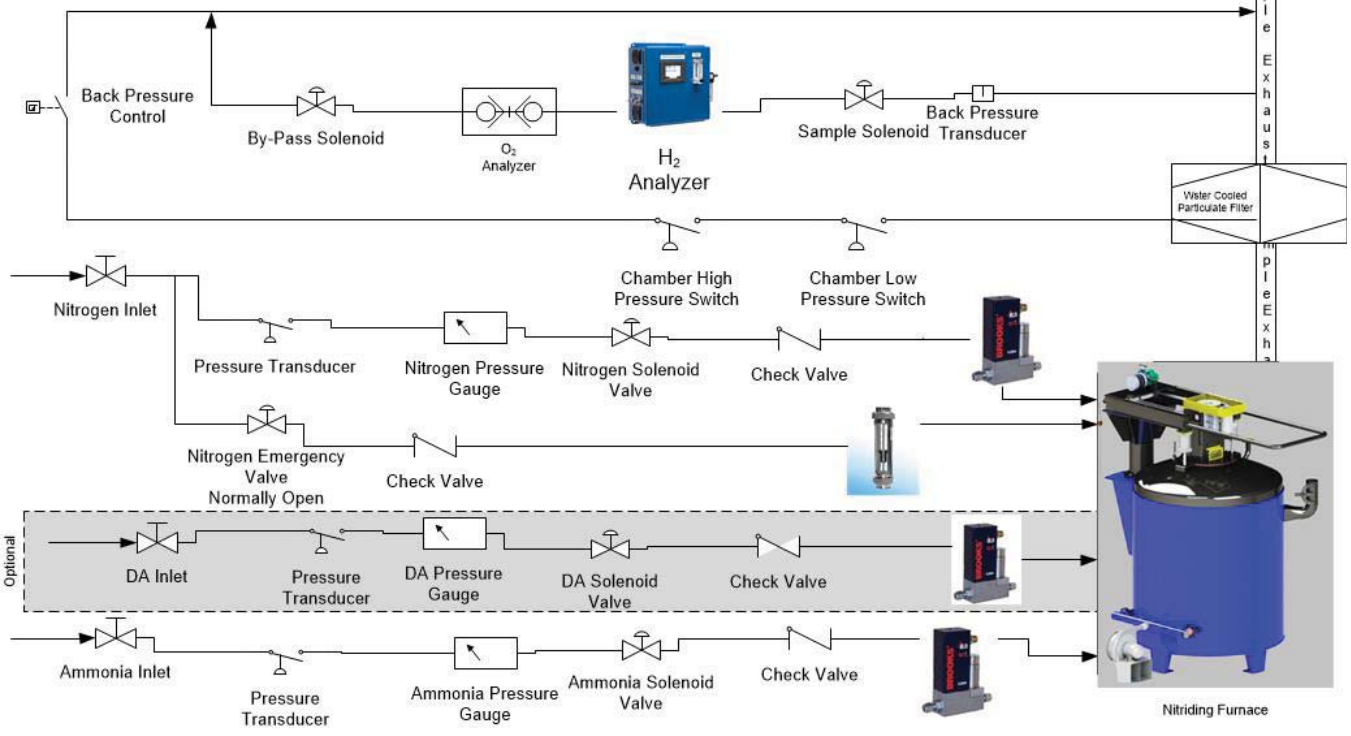

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A Practical Approach to Controlling Gas Nitriding and FNC

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For most of its history, heat treating has been controlled manually. Operators would observe readings from gauges connected to sensors and, if changes to the atmosphere were needed, manually adjust heat, carbon or other outputs.

Fig. 2. Use of water burette in testing %DA

Over the last 30 years, technology has allowed heat treaters to automate those processes by using relay controls and intelligent process loop controllers that constantly monitor atmospheres and adjust outputs as needed. This kind of automation results in repeatability, traceability and higher quality at lower costs. In this paper, I will discuss different technologies used in the past and the application of new technologies used today, particularly in nitriding and ferritic nitrocarburizing.

Before discussing these technologies, it is important to establish definitions for nitriding and ferritic nitrocarburizing and related terms.

Definitions

Both nitriding and ferritic nitrocarburizing (FNC) are processes that use nitrogen and carbon to create case in steel that enhances wear resistance, corrosion resistance and anti-scuffing properties, all without distortion due to lower temperatures or rapid quenching.

Nitriding is a thermochemical treatment in which gaseous ammonia (NH_3) reacts at the surface of steel at temperatures needed to diffuse nitrogen (N_2) into iron. Temperature is controlled between 975-1050°F (524-566°C). The reaction of NH_3 with steel causes nascent nitrogen to diffuse into iron and create case.

Ferritic nitrocarburizing (FNC) involves two sets of reactions that occur simultaneously yet independently. The first reaction is nitriding, and the second is nitrocarburizing. Nitrocarburizing is a thermochemical treatment similar to nitriding in that it changes the properties of the metal. Nitrocarburizing, however, involves the addition of carbon at 1060°F (570°C) to produce a thin layer of iron carbonitride and nitrides, commonly referred to as "white layer" or "compound layer." The source of carbon can be natural gas, propane, endothermic gas or carbon dioxide (CO_2).

Dissociated ammonia (DA) is the result of splitting ammonia into the atoms of which it is made. The dissociated ammonia yields one atom of nitrogen and three atoms of hydrogen.

Nitriding potential (K_N) is a derived measurement of an atmosphere's potential to allow for the diffusion of nitrogen into a material – specifically, in this case, iron. K_N is mathematically defined in Equation 1.

$$K_N = pNH_3 / (pH_2)^{3/2} \quad \text{Eq. 1}$$

where p denotes partial pressure.

Traditional Control

Traditionally – and often still today – nitriding and FNC are controlled by temperature, time and flow. A metallurgical lab verifies the process, and process variables can be adjusted based on the results of the lab's analysis. Pressure in the furnace is controlled with a manual valve or oil bubbler (Fig. 1) where the gas passes through oil to create 1-4 inches of back pressure.

A water burette is used to test the percentage of dissociated ammonia, %DA (Fig. 2). NH_3 is 100% soluble in water and serves as a reliable way to measure the %DA with the remaining gas being composed of nitrogen and hydrogen. With this method, the furnace exhaust gas is passed through a vertical burette chamber and then sealed at the inlet and at the outlet. A valve is then opened at the top, where distilled water flows down and absorbs any unreacted NH_3. The water will stop flowing once the NH_3 is consumed.

The dissociation of the gas in the furnace can be determined based on the scale shown on the burette. Because of the water source, gas purging of the burette and operator interpretation of the water level, the measured %DA may vary from the actual %DA. Gas flows are controlled manually and adjusted based on metallurgical results and the burette reading. Purging of the vessel to eliminate O_2 is strictly based on time, which is determined by flow and furnace volume. All of these factors increase the chance of variability in results and reduce process repeatability.

Automated Control

Automated control for both nitriding and FNC processes is based on temperature, time and flow as well as measurement of hydrogen, oxygen, carbon monoxide (CO) and CO_2. In nitriding, hydrogen is the only variable that must be measured as a result of the reaction of NH_3 during dissociation. The reason for this is that there will be three corresponding

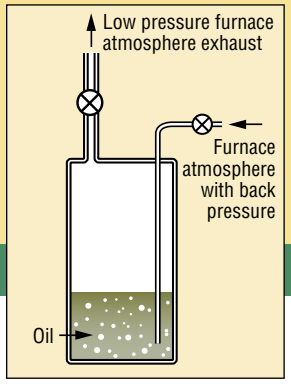

Fig. 1. Oil bubbler

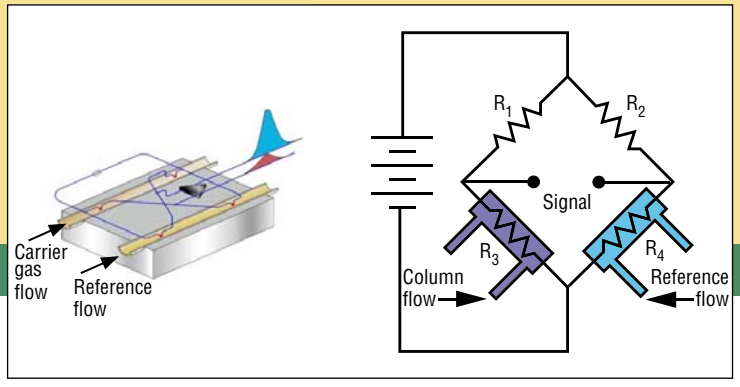

Fig. 3. Use of thermal-conductivity cell in measuring hydrogen

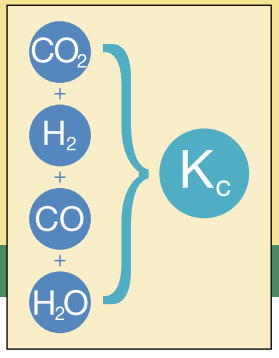

Fig. 4. Combination of gases for carbon activity

hydrogen atoms (Equation 2) for each nitrogen atom, both before and after this dissociation.

$$NH_3 \longleftrightarrow N+3H \qquad \text{Eq. 2}$$

Table 1 shows the relationship between specific values for %DA and K_N. When measuring hydrogen, the amount of nitrogen present is known. When an atmosphere contains 75% hydrogen and 25% nitrogen, full dissociation is achieved. A hydrogen concentration lower than 75% will result in unreacted NH_3. For example, an atmosphere with 50% DA (K_N of 2.18) and 37.5% hydrogen will yield a residual NH_3 of 50%.

Controlling a single- and dual-stage nitriding process is generally straightforward when NH_3 or dissociated NH_3 gas is utilized. Single- and dual-stage processes are controlled on the basis of temperature, time, flow control and the measurement of hydrogen. This process becomes more complicated when a diluent, such as nitrogen, is introduced. The purpose of using N_2 is to increase the %DA and lower the nitriding potential. When N_2 is provided from a source other than the NH_3 reaction, more nitrogen will be present in the atmosphere. Therefore, the N_2 (along with the NH_3) must be metered for the calculation to compensate for the presence of additional N_2 that is not a result of the catalytic reaction of NH_3.

Why not measure NH_3 instead of hydrogen for the nitriding process? The answer is simple. NH_3 must be measured with infrared technology and cannot be reliably used in the calculation due to the non-dispersive infrared (NDIR) frequency range and zero drift associated with it. Gases such as CH_4, CO_2 and CO have a more measurable frequency range that provides accurate and repeatable results when using NDIR. Hydrogen is highly conductive and easily measured using thermal-conductivity technology.

Thermal conductivity – the measure of a gas's ability to conduct heat – is cost-effective and extremely stable. Recalibration, though not frequently needed, can be easily performed. Hydrogen is seven times more conductive than air and will transfer more heat when present, meaning that the sensor will require more energy. The thermal-conductivity cell measures the energy required to maintain a specific temperature and accurately calculates hydrogen (Fig. 3). It is important to note that the temperature at which the thermal-conductivity cell operates must be below that of the temperature of dissociation of NH_3. Many hydrogen cells operate at temperatures above 900°F (773°C).

Oxygen sensors are used to verify purging of the vessel. Electronic flow meters, with feedback, allow for automatic adjustment of NH_3, DA and N_2 gases based on the calculated K_N as a result of the measured hydrogen. This shortens purge time and reduces the amount of nitrogen used in the process.

FNC is similar to nitriding but with the addition of a carbon-bearing gas. When controlling FNC, hydrogen is one of a number of variables that must be considered. With the use of CO_2 (common in pit-type furnaces), there is a reaction with hydrogen that produces CO to create carbon activity (K_C; Equation 3).

$$K_C = p(CO_2)\ p(H_2) / p(CO)\ p(H_2O) \qquad \text{Eq. 3}$$

Where p denotes partial pressure.

Also, endothermic gas is commonly used in batch-type furnaces that have 40% H_2, 20% CO and small amounts of CO_2 (Fig. 4). With the addition of these gases, K_C must be controlled in addition to K_N to provide the needed metallurgical reaction of nitriding and nitrocarburizing.

CO and CO_2 are both measured reliably with infrared technology (Fig. 5). It must be noted that the infrared cell technology must be compatible with NH_3 and water

Table 1. Relationship of percentage dissociated ammonia (%DA) to nitriding potential (K_N)

% dissociated ammonia	K_N
1.33	986.67
2.67	344.13
6.67	83.48
13.33	27.41
20.00	13.77
26.67	8.20
33.33	5.33
40.00	3.65
46.67	2.58
50.00	2.18
53.33	1.84
60.00	1.33
66.67	0.94
73.33	0.65
80.00	0.43
86.67	0.25
93.00	0.11
100.00	0.00

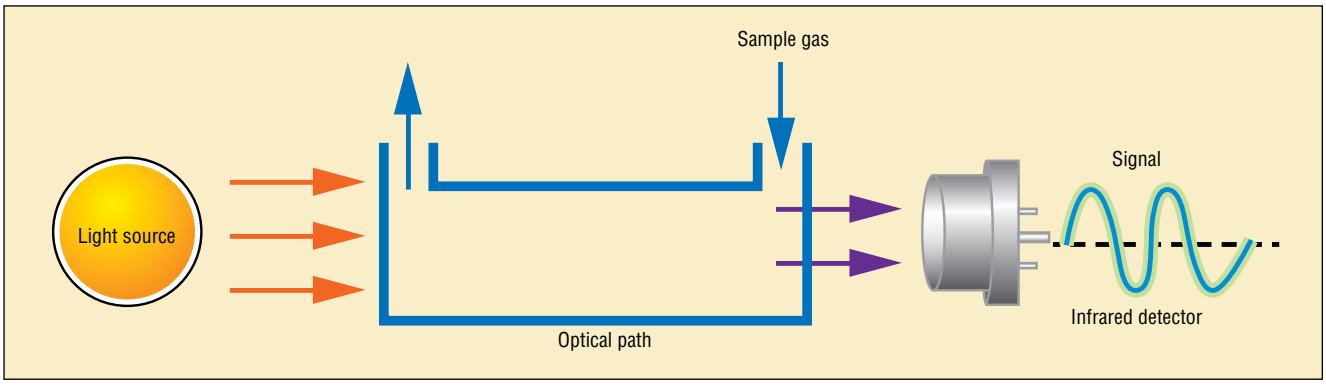

Fig. 5. Infrared measurement of a gas

for the FNC process. Oxygen is measured using zirconia or lambda-probe technology. As with nitriding, it is important to meter the gas flows when using nitrogen and any other diluents. When using endothermic gas with 40% hydrogen present, it is important to meter and compensate for the gas flow and hydrogen content. With these variables being considered, K_N and K_C are calculated to allow for more precise control of the nitrogen and carbon compound layer.

Nitriding and FNC processes are often based on an Aerospace Material Specification (AMS) requirement. Using FNC as an example, AMS 2759/12A is commonly used. It is possible to define the material, group and class. Table 2 allows for the determination of the desired K_N and K_C based on the required epsilon layer and allowable porosity.

Challenges of Automated Control

Automating the nitriding and FNC processes brings new challenges that require specific technical expertise. In many industries, there is often a misconception that automation removes the need for any manual intervention. This is not the case with most automation technologies. In fact, automation typically requires a more educated intervention. For example, sample lines and filters to the H_2 analyzer and oxygen cell must be maintained on a regular basis. Calibration of the instrumentation and analyzers must be completed at manufacturer-required intervals. Instrument certifications must be current and on record.

In addition, the mechanical assembly of the system must take into account the need for filtration and ease of maintenance. For example, sample systems must be supplied with drip legs in order to remove any moisture that might be generated during the pre-oxidation process. When nitriding stainless steel and using a pre-activation process, filtration and heat tracing must be included in the exhaust piping. Lines and filters must be cleaned for each run. Filtration systems should be designed with pressure indication and automatic bypass modes. FNC processes are more challenging due to the formation of ammonium carbonate in the exhaust.

Table 2. Process parameters for required epsilon layer and allowed porosity

Material	Process temperature		Process time (hours)	Class 1 Not exceeding 15% of thickness of white layer				Class 2 Above 10% but not exceeding 50% of thickness of white layer			
				K_N		K_C		K_N		K_C	
	°F	°C		min	max	min	max	min	max	min	max
Group 1*	1040 1075	560 579	3-6 2-5	2.13 1.50	2.41 1.60	0.57 1.10	0.69 1.22	2.48 1.68	2.68 1.78	0.49 0.86	0.54 0.94
Group 2**	980	527	6-30	4.51	5.55	0.16	0.24	6.03	7.10	0.09	0.13
Group 3***	1060	571	3-10	1.82	2.10	0.76	0.99	2.22	2.64	0.48	0.68

Temperatures shown are not firm requirements. Once a temperature is selected, however, both potential values shall be within specified limits for the given temperatures.
*Group 1: HLSA, carbon steels • **Group 2: 4140, 4340, Nitralloy 135M • ***Group 3: Cast iron

Benefits of Automation

Automating a nitriding or FNC process brings with it many distinct advantages. With the automated control of temperature, gas flows, K_N, K_C, supply pressure and back pressure comes the ability to generate alarms and, more recently, notify operators and others of alarm conditions electronically. Automation allows for alarms on such events as temperature deviation, K_N deviation, flow deviation, low or high back-pressure, and bypass mode. Today, electronic notification is available in the form of computer-automated e-mail and text messaging. Just as important, the process requires no human intervention once started unless an alarm condition arises. Secure, remote access to the process from anywhere in the world is now available.

Process automation allows heat treaters to generate and maintain historical records, reduce the consumption of gas and make decisions that ultimately provide a more repeatable process with higher quality results. **IH**

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