The development of process sensors and computer control systems has proven to be valuable for nitriding programs, improving both nitriding and nitrocarburizing process consistency and repeatability.

Patrick Weymer
Ipsen Inc.
Cherry Valley, Ill.

**Member of ASM International and member, ASM Heat Treating Society**

In the past, gas nitriding and nitrocarburizing processes have been controlled using empirical calculations without any atmosphere process control. The generally accepted procedure to control the nitriding process was to adjust the flow rate of ammonia gas and other possible gas additions (endothermic gas, nitrogen, and CO₂), and occasionally to use an Orsat device to measure the amount of ammonia exhausted from the furnace. This procedure, for the most part, led to reproducible nitriding results, especially in processes using constant atmosphere flow rates. However, in pure nitriding and nitrocarburizing processes, deviations in the resulting part microstructure sometimes occurred for unknown reasons. The case depth on parts could be shallow in one load and could meet requirements in preceding and subsequent loads.

For this reason, work began ten years ago on the development of a reliable, continuous process control system capable of monitoring deviations in the gas atmosphere of the furnace.

In both nitriding and nitrocarburizing, atomic nitrogen forms via a catalytic decomposition of ammonia (NH₃) on the metal surface of a workpiece. This decomposition obeys the following reaction equation:

\[ \text{NH}_3 \rightarrow [\text{N}] + 3/2 \text{H}_2 \quad [1] \]

Nitriding reaction: This ammonia decomposition also takes place in the furnace atmosphere, only here it is molecular nitrogen that is formed, not atomic

\[ \text{NH}_3 \rightarrow 1/2 \text{N} + 3/2 \text{H}_2 \quad [2] \]

Atmosphere reaction: Different iron nitrides will form in the white layer depending on the amount of atomic nitrogen that is available to a part. At the heat treatment temperature for nitriding of approximately 975°F (525°C) and at a nitrogen concentration between 5.7 and 6.1%, the gamma prime (γ') cubic face-centered nitride (Fe₄N) is formed, while the epsilon (ε) hexagonally densest nitride (Fe₂.₃N) will form at a higher nitrogen content of between 7.8 and 11.3%.

However, while the concentration of atomic nitrogen can be used to determine the composition of the white layer, the so-called nitriding activity or nitriding potential (Kₙ) of the furnace atmosphere can also be used for this purpose. The higher the nitriding potential, the more nitrogen can be made available to the parts and the higher the nitriding effect.

\[ K_n = \frac{p(\text{NH}_3)}{p(\text{H}_2)^{3/2}} \quad [3] \]

The exponent in the denominator is due to factors from the chemical reaction equation. If we now take Kₙ as a value for nitride forming, we obtain the diagram developed by Lehrer (Fig. 1). Although the diagram
only applies to pure iron, it can be used as a good approximation for steels that are not too highly alloyed.

As can be seen in the $K_n$ potential equation, the data required to calculate $K_n$ includes:

- Quantity and composition of incoming process gases (mass flow controllers can be used to measure the incoming amount of each gas)
- Furnace pressure (a pressure sensor can be used)
- Hydrogen content present in the furnace (Ipsen’s HydroNit sensor can be installed in a furnace to provide an in-situ measurement of the hydrogen)

Ammonia is the only source of hydrogen when using only nitrogen and ammonia during nitriding. Thus, the measured hydrogen content can be calculated from the amount of ammonia that has decomposed. Subtracting the amount of ammonia gas in the furnace from the amount of incoming ammonia gas leaves the amount of ammonia that is still available for nitriding. This provides the data about the current composition of the gas in the furnace; that is, the ammonia remaining in the furnace still available for nitriding and the molecular hydrogen and nitrogen formed by the ammonia decomposition. The volume percentages and the internal furnace pressure are then used to calculate the partial pressure of the individual gases partial pressure required to calculate $K_n$.

If the incoming gas consists of both ammonia and hydrogen, then the amount of incoming hydrogen must also be deducted from the hydrogen measured by the HydroNit sensor prior to calculating the amount of ammonia still available for the reaction. The amount of nitrogen flowing into the furnace must also be taken into account when determining the partial pressures of the individual gases in the furnace.

Equation [3] can now be used to calculate the $K_n$ at any time during the process from the calculated partial pressures for hydrogen and ammonia. Knowing the current hydrogen level in the retort is absolutely essential for determining $K_n$. The HydroNit sensor continually makes such a measurement possible directly in the furnace atmosphere (Fig. 2).

**Sensor Particulars**

When using the HydroNit sensor, the furnace atmosphere is measured directly. This is in contrast to other sensors where the furnace atmosphere is pumped out of the furnace through hoses or pipes before reaching the sensor. The chemical and thermochemical reactions that occur in the gas as it travels from the furnace to the sensor can affect the measured value and can potentially invalidate the calculated $K_n$.

The sensor consists of a protective shield that is inserted into the retort (Fig. 3). This shield contains a measuring tube made of a material permeable to hydrogen only. Therefore, the result cannot be affected by cross-sensitivities from any other components of the furnace atmosphere.

The sensor is evacuated at the beginning of a heat treating process. During nitriding, the ammonia dissociation process causes a difference in hydrogen concentration and partial pressure between the furnace atmosphere and the interior of the measuring tube. This difference allows the hydrogen to diffuse through the wall and into the measuring tube. Diffusion continues until the concentrations and pressures equalize. That is, the pressure measured by the sensor is equal to the...
furnace atmosphere hydrogen partial pressure.

$K_n$ is calculated after the measurements are completed, and it can be used to control the heat treatment process. The nitriding potential can be programmed in the hold segment of a nitriding process recipe. When the hold segment is active, the programmer continuously compares the desired $K_n$ to the $K_n$ calculated from the data measured from the furnace atmosphere.

If the calculated $K_n$ is below the desired value, nitriding will not occur as expected. In this case, the hydrogen flow rate is reduced until the calculated $K_n$ matches the desired value. If reducing the hydrogen flow rate does not increase the calculated potential to match the desired potential, the ammonia supply flow rate can be increased.

If the calculated potential is higher than desired, the ammonia flow rate can be reduced until the desired value matches the actual value. However, if the ammonia is reduced to the minimum flow rate required to safely run the process and the nitriding potential is still higher than desired, the hydrogen flow rate can be increased. A schematic circuit for this type of control system is shown in Fig. 4.

**Benefits of Using the Sensor**

The use of the nitriding potential and a process management system to regulate the process significantly improves nitriding and nitrocarburizing process consistency and repeatability. The calculated $K_n$, atmosphere flow rates, furnace pressure, and temperature can be recorded. In the event that there is an issue with nitriding a load, the process data for that specific load can be compared to process data for previous loads to quickly identify any problems and to take in-process corrective action to prevent any adverse impact on heat treating results.

This is illustrated in examples showing laboratory results of loads run in nitriding and nitrocarburizing atmospheres with and without pre-oxidation.

Example No. 1: The following results are from a nitrided batch of ring gears (Fig. 5) made of 31CrMoV9V (equivalent to 1.8519). The treatment time was 70 hours at 960°F (515°C) with the $K_n$ controlled at approximately 4.

<table>
<thead>
<tr>
<th>Desired</th>
<th>Actual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface hardness, HV10</td>
<td>720-820</td>
</tr>
<tr>
<td>Case depth, mm</td>
<td>0.4-0.75</td>
</tr>
<tr>
<td>Max white layer thickness, μm</td>
<td>20</td>
</tr>
</tbody>
</table>

Figure 6 shows the white layer on the part surface.

Example No. 2: The following results are from nitrocarburizing differential pins (Fig. 7) made of 31CrMoV9V. The treatment time was 18 hours at 1000°F (540°C) with the $K_n$ controlled at approximately 3.

<table>
<thead>
<tr>
<th>Desired</th>
<th>Actual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface hardness, HV1</td>
<td>750-950</td>
</tr>
<tr>
<td>White layer thickness, μm</td>
<td>14-22</td>
</tr>
</tbody>
</table>
Figure 8 shows the white layer on the part surface.

Example No. 3: The following results are from nitrocarburizing internal geared wheels (Fig. 9) made of 42CrMo4 (equivalent to 1.7225). The treatment time was 5 hours at 1060°F (570°C) with the $K_n$ controlled at approximately 2.5.

<table>
<thead>
<tr>
<th>Desired</th>
<th>Actual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface hardness, HV10</td>
<td>550-650</td>
</tr>
<tr>
<td>Case depth, mm</td>
<td>0.4-0.55</td>
</tr>
<tr>
<td>White layer thickness, μm</td>
<td>8-35</td>
</tr>
</tbody>
</table>

Figure 10 shows the white layer on the part surface.

Example No. 4: The following results are from nitriding hubs (Figs. 11 and 12) made of 16MnCr5 (equivalent to 1.7131). The treatment time was 14 hours at 970°F (520°C) with the $K_n$ controlled at approximately 3.5.

<table>
<thead>
<tr>
<th>Desired</th>
<th>Actual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface hardness, HV1</td>
<td>550-750</td>
</tr>
<tr>
<td>Case depth, mm</td>
<td>0.30-0.60</td>
</tr>
</tbody>
</table>

The development of process sensors, such as the HydroNit, and computer control systems has proven to be invaluable for the nitriding process. Nitriding and nitrocarburizing process consistency and repeatability have improved considerably.

For more information: Patrick Weymer, Ipsen Inc., 984 Ipsen Rd., Cherry Valley, IL 61016; tel: 815-332-2539; e-mail: Patrick.weymer@ipsenusa.com; Web site: www.ipsenusa.com.