The need to ensure reliable nitriding and nitrocarburising treatments becomes increasingly important every year as equipment ages and tighter metallurgical requirements and full compliance to specification are demanded. In many instances, it’s possible to push existing equipment back into useful life with the application of new control and sensor technology. Using a solution-oriented approach, a selection of appropriate technologies can be identified based on process and specification requirements. This article examines control equipment and sensor technology upgrades that address the challenge.

STANDARDS

AMS 2759/6 (Nitriding)
Without proper control standards, the mechanical properties of parts may be completely different from one charge to another. The industry’s first attempt at nitriding specification was 25 years ago with the release of AMS 2759/6, based on control of ammonia dissociation via periodic burette measurement during the process (Fig. 1), the necessary adjustments being done manually.

AMS 2759/6 provisions include the following:

- Atmosphere control: Equipment shall be available to measure and maintain the dissociation of the process atmosphere in the retort within ±5% of the selected percent dissociation throughout the nitriding cycle.
- Ammonia dissociation: The ammonia gas dissociation shall be 15 to 35 percent for (single-stage) Class 2 and for the first stage of (two-stage) Class 1 (approximately 20 percent of total nitriding time). Ammonia dissociation for the second stage of Class 1 shall be 65 to 88 percent.

AMS 2759/10 (Nitriding)
A refinement to the earlier specification, AMS 2759/10, issued in 1999, allows the use of diluted atmospheres (i.e. nitrogen + ammonia). It also calls for “Automated Gaseous Nitriding Controlled by Nitriding Potential” Nitriding potential or $K_N$ determines the nitrogen concentration at a given temperature. This controlling parameter in nitriding is defined as:

$$K_N = \frac{p_{NH_3}}{p_{H_2}}^{3/2}$$

AMS 2759/10 provides the framework for process control using nitriding potential $K_N$ as a reference point. The Lehrer diagram (Fig. 2) illustrates the iron-nitrogen equilibrium at various temperatures and hydrogen/ammonia levels as defined by $K_N$. Note the relationship of $K_N$ to phase.

AMS 2759/10 classifies the nitriding processes described as follows:

- Class 0: No white layer permitted.
- Class 1: 0.0005inch (0.013mm) maximum white layer thickness permitted.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Class 0</th>
<th>Class 1</th>
<th>Class 2</th>
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This article is based on Pat Torok’s presentation at the CHTA-sponsored Surface Engineering & Heat Treatment Industry Conference in Stratford-upon-Avon UK on 16 October 2015.
Table 3. Ferritic nitrocarburising process parameters ensuring the formation of an epsilon-type compound layer with two ranges of porosity level. (From AMS 2759/12A)

<table>
<thead>
<tr>
<th>Material</th>
<th>Process temperature</th>
<th>Process time (hours)</th>
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<th>Porosity above 10% but not exceeding 50% of thickness of compound layer</th>
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<td>KN</td>
<td>KC</td>
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<td>Group 3***</td>
<td>1060</td>
<td>571</td>
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<td>1.82</td>
</tr>
</tbody>
</table>

*Group 1: HSLA, carbon steels    **Group 2: 4140, 4340, Nitralloy 135M    ***Group 3: Cast iron

**Fig.3: The elements of fully-automated process control of nitriding/nitrocarburising/post-oxidation, showing all the gas supply options.**

- Class 2: 0.001inch (0.025mm) maximum white layer thickness permitted.
- If no class is specified, Class 2 applies.
- Class 2 is not recommended for corrosion-resistant steels.

AMS2759/10 goes on to provide recommendations for various material types and nitriding classifications (Table 1). The specification also dictates permissible deviation from KN set point for both stages of the process.

**AMS 2759/12 (Nitrocarburising)**

Filling the gap for ferritic nitrocarburising came AMS 2759/12, “Gaseous Nitrocarburising, Automatically Controlled by Nitriding and Carburizing Potentials”. The aim of nitrocarburising is to build a compound layer on the surface of the workpiece, typically consisting of epsilon carbonitrides. In addition to the ammonia that is used in all nitriding processes, a carbon-bearing gas is also added. The carburising effect of the atmosphere, caused by the addition of CO or CO₂ or other gas containing these constituents, can be calculated.

The carburising potential K_C can be defined based on one or another of two reactions:
- the Boudoir reaction: \(2\text{CO} = \text{CO}_2 + \text{C}\), for which:
  \[ K_{CB} = \frac{p\text{CO}}{p\text{CO}_2} \]
- the water-gas shift reaction: \(\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2\), for which:
  \[ K_{CW} = \frac{p\text{CO} x p\text{H}_2}{p\text{H}_2\text{O}} \]

Note: \(K_{CB}\) and \(K_{CW}\) will not give the same numbers!

AMD 2759/12 establishes limits for the thickness of the compound layer for various materials (Table 2); it also indicates process values for \(K_N\) and \(K_C\) to ensure an epsilon-type compound layer with two ranges of porosity level in “Class 1” and “Class 2” ferritic nitrocarburising (Table 3).

**CONTROLLING THE POTENTIALS**

**Fig.3:** Illustrates the typical configuration of fully-automated process control and all the gas supply options. It comprises a controller with the capability of computing \(K_N\) or \(K_C\) for nitriding and nitrocarburising processes, electronic flow control of various gases, a hydrogen analyser, an oxygen probe for \(K_C\), measurement and an optional ammonia dissociator.

**Fig.4:** (a) Ammonia flow versus \(K_N\); (b) Ammonia / dissociated ammonia flow versus \(K_N\).
**Nitriding**

Let’s take the simplest case: one process gas: ammonia. The required control elements are electronic flow control of ammonia, hydrogen analyser for determining $K_n$, and a controller that has the capability to compute and control $K_n$. Nitriding potential is controlled by modulating ammonia flow (Fig. 4a). When low $K_n$ set points are desired, furnace flow and pressure may too low. This problem can be solved by the addition of dissociated ammonia (Fig. 4b).

The other advantage of this control scheme is that it is possible to obtain very low $K_n$ values which are necessary for low, or no, white layer. If dissociated ammonia is not available, dilution with nitrogen will definitely solve the furnace pressure problem. This approach introduces two other problems: the transfer coefficient of nitrogen is affected and there is a problem with the $K_n$ calculation. Atmosphere dilution of 3:1 lowers the nitrogen transfer coefficient by a factor of 5 at constant $K_n$ (Fig. 5).

Diluting ammonia with nitrogen will reduce $K_n$ down to a certain minimum, determined by the availability of ammonia. When there are not enough ammonia molecules in the atmosphere, $K_n$ will go up.

**Nitrocarburising**

Carbon and nitriding potentials are inter-related. An adjustment of one potential requires the adjustment of the other. Per AMS 2759/12, selected pairs of $K_n$ and $K_C$ are always aiming to achieve epsilon carbonitrides with defined percentages of nitrogen and carbon in the compound layer (Fig. 6).

Nitrocarburising is typically aiming for a compound layer of Fe$_2$N or Fe$_3$N iron nitrides of high hardness, increasing corrosion resistance and lowering the coefficient of friction.

By defining the weight percentages of carbon and nitrogen in the compound layer, porosity and corrosion resistance can be controlled. The micrographs in Fig. 7 illustrate results from different wt% nitrogen and wt% carbon. Pitting potential also increases with total wt% of carbon and nitrogen greater than 8.5% in the compound layer (Fig. 8).

$CO_2$ may be used as the carbon-bearing gas in the nitrocarburising process. However, using $CO_2$ as the only carburising gas forces a reversed behaviour of the control loop, as increasing $CO_2$ results in a lower $K_C$. Remember, too much $CO_2$ can be decarburising.

Endothermic gas as the carbon-bearing addition enables high $K_C$. A lower $K_C$ can be achieved by adding $CO_2$ or air. However, the disadvantage in this case is that the high hydrogen content in endo hinders high nitriding potentials.

Fig. 9 shows carbon potential for the various gases. Note that, with endo, we end up with very high carbon potentials. Therefore it is advisable to have the “gas” and the “brake”. This can be done with a combination of endo and $CO_2$ or air.

**Fig. 5:** Effect of nitrogen dilution on transfer coefficient, $k_3$. (570°C, $K_n = 1$)

**Fig. 6:** Defined nitriding and carburising potentials.

**Fig. 8:** Pitting potential with increased total nitrogen and carbon concentrations.

**Fig. 7:** Compound layer porosity with various carbon and nitrogen contents.

**Fig. 9:** Various carburising gas choices.

**Fig. 10:** Control behaviour in a real nitrocarburising process (570°C, 4hours). The controller is able to react to varying process conditions so that both potentials ($K_n = 1$; $K_{CB} = 0.3$) are kept constant.
One of the challenges for control is the speed of reaction of the control system. Nitrocarburising cycles are short compared with nitriding durations. Atmosphere potentials must be established at the very beginning of the cycle to achieve the desired compound layer composition. Potentials must be controlled to achieve the desired epsilon phase. This includes heat up and cool down (Fig. 10).

Relative transfer times are affected by process pressure. The nitrogen uptake can be expressed as a function of the hydrogen partial pressure. There is a six-fold increase in transfer time from a H₂ partial pressure of 0.09 bar to 0.33 bar (Table 4).

**Post oxidation**

Post oxidation is very effective way to promote corrosion resistance. Control gases are H₂O or N₂O vs. NH₃ or H₂. Control and measurement can be achieved with the use of an oxygen probe. A 13µm epsilon compound layer with an additional magnetite oxide layer provides four times better corrosion resistance than 40µm chrome plating. Using the signal of the oxygen probe enables a controlled post-oxidation process aiming for best corrosion resistance.

**FULLY-AUTOMATED PROCESS CONTROL**

Atmosphere must be analysed continuously. The system must be capable of calculating Kₘ, Kₜ, and Kₜ, and of adjusting gas flows to maintain the process set points.

Elements of the system are: a programmable controller that can calculate potentials and interface with sensors, electronic flowmeters and temperature control devices. The controller should also be able to store a large number of process recipes, have logging capability, for data analysis, and a webserver for easy maintenance and reporting (Fig. 11a).

Electronic flowmeters should be accurate, with precise calibration curves such as polynomial fits, and feature modern communications that will eliminate analog signal error such as Ethernet or Modbus/TCP. They should also be easy to maintain and feature a built-in webserver (Fig. 11b).

Hydrogen measurement demands built-in precise temperature control of the measuring cell and accurate continuously-variable flow control. It is also imperative that this device has extremely low drift and polynomial calibration (Fig. 11c).

For nitrocarburising and post oxidation, an oxygen sensor that is operational at process temperatures is a necessity. The electrode impedance must remain below 50kohms in order to produce a reliable signal. The sensor design must also accommodate high dewpoints during parts of the cycle without resulting in sensor damage (Fig. 11d).

**SUMMARY**

Sensor and control technology exists to ensure process control that is compliant with specifications such as AMS 2750, AMS 2759 and CQI-9. This technology also features sensor and control components that are reliable enough to take full recipe control of the process. A technology upgrade to an existing furnace will add years of service and performance to equipment that might have been underutilised.

**BIBLIOGRAPHY**


**FURTHER INFORMATION**

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