Nitriding involves enriching the surface of ferrous parts with nitrogen via gas, salt bath, and plasma nitriding methods, resulting in a part having increased surface hardness, wear and corrosion resistance, and fatigue strength.

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The world is looking for better products produced at lower costs. Nitriding has been and continues to be one of the two main diffusion processes in the heat treating industry (carburizing is the other). To meet the more grueling environment that designs demand, nitriding practices and requirements have and continue to evolve.

Nitriding involves enriching a ferrous part’s surface with nitrogen and results in a part with increased surface hardness, wear and corrosion resistance, and fatigue strength. Nitriding has traditionally been accomplished using gas nitriding, salt bath nitriding, and plasma nitriding. The focus of this article is gas nitriding, which is commonly accomplished in a retort furnace in an ammonia, dissociated ammonia, hydrogen, and nitrogen atmosphere.

Nitriding Process Description
In nitriding, atomic nitrogen forms via a catalytic decomposition of ammonia (NH₃) on the metal surface of a work piece. This decomposition obeys the following reaction:

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

The rate that nitrogen diffuses into a part is dependent upon the processing temperature, the part’s alloy content, and amount of nitrogen that is available.

There are two common methods of gas nitriding. The first method is the so-called single stage nitriding. In this method, a work piece is heated to between 925 to 975°F (495 to 525°C) in an atmosphere which has an ammonia dissociation rate of between 15 and 30%. The resulting work piece contains a series of phases of progressively decreasing nitrogen content from the surface to the core. At a temperature above 850°F (450°C), nitrogen interstitially dissolves into a part until the concentration reaches 0.1%. Then, gamma prime (γ) nitride (Fe₄N) begins to form at grain boundaries with a nitrogen concentration of between 5.7 to 6.1%. When the nitrogen concentration exceeds 6%, a compact layer of γ nitride or compound layer begins to form on the part’s surface. As the process continues, new nitrides form in a diffusion zone below the compound or white layer and towards a part’s core.

The compound layer causes the resulting part to be brittle and could fail in service. For these reasons, it was in some cases desirable to minimize white layer thickness. This led to the development of the double stage or Floe process (U.S. Patent No.2,437,249). The first stage of the Floe process consists of heating a work piece to 925 to 975°F (495 to 525°C) and the ammonia dissociation rate is controlled to between 25 to 25%. During the second stage, the temperature can be maintained or raised to between 1,025 and 1,050°F (550 and 565°C). In addition, the dissociation rate is raised to between 75 and 80% by reducing the ammonia flow rate and diluting with nitrogen, dissociated ammonia or hydrogen. Keep in mind that raising the temperature during the second stage lowers the resulting case hardness, increases the case depth, and may lower the core hardness and effective case depth.

It is important to note that a work piece must be austenitized, hardened and tempered before beginning nitriding. Tempering is usually performed at 30°F (16°C) above the nitriding temperature to provide a stable core structure during nitriding. In

BeaverMatic nitriding furnace installation.
some materials, the case hardness reduces as the core hardness reduces.

**Fully Automated Nitriding Furnaces**

As is the case with all processing, it is desirable to minimize the cycle time. In nitriding, this can be accomplished by increasing the processing temperature and ammonia flowrate. However, in nitriding, higher processing temperatures and higher ammonia flowrates lead to an increase in the growth rate of the white layer. In some cases, it can be acceptable to have white layer on a resulting part. Since the white layer can be very hard and brittle, it may be desirable to minimize or completely eliminate it. This can be accomplished by controlling the nitriding potential during the nitriding process.

In contrast to the carburizing gas, the nitriding atmosphere is not in equilibrium since the ammonia flow rate is too high to allow it to fully dissociate to nitrogen and hydrogen during the process. For this reason, the furnaces exhaust gas consists of ammonia, nitrogen, and hydrogen. It is customary to use a burette to determine the percentage of ammonia dissociation. Ammonia is the only constituent that is soluble in water. A graduated burette filled with water can be used to measure the ammonia dissociation rate of the furnace exhaust gas. Since this method is not continuous and is manual, it introduces operator induced variability, which makes it difficult to repeat the process.

For this reason, work began on a new control parameter, nitriding potential as a means to reduce the white layer thickness or eliminate the white layer altogether. Nitriding potential, $K_n$, is based upon the partial pressure of the ammonia still present in a furnace (the amount of ammonia that has not yet dissociated) and the partial pressure of hydrogen ($H_2$) that has already dissociated from ammonia. $K_n$ is calculated as follows:

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

If we take $K_n$ as a value for nitride forming, we obtain the diagram developed by Lehrer. Although the Lehrer diagram only applies to pure iron, it can be used as a good approximation for steels that are not too highly alloyed.

Means of collecting the required data and calculating the nitriding potential have been introduced and implemented into current furnace technology. Integration of these devices along with smart flowmeters into control systems with recipe management systems and programmable logic controllers now enables a fully automated process and the results have shown to be repeatable.

Now that nitriding potential-control systems are more common and are proven, there have been specifications written that require nitriding potential control in critical applications where no white layer or a specific amount of white layer is required. This development has led to heat treating specifications like SAE International AMS 2759/10 to require control to specific nitriding potential values.

**Conclusion**

Equipment developments like sensors, computer control systems, and flow control devices have been proven invaluable for nitriding. These developments have increased the accuracy of the resulting work pieces and the ease of reproducing the final results.

**Bibliography**


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