Carbonitriding of Fasteners

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Carbonitriding is an excellent choice for low-carbon fastener materials that require a uniform, but shallow case with good wear properties.

One of the most common case hardening heat treatments for fasteners is that of gas carbonitriding. Carburizing is a modified form of the carburizing process and is not a form of nitriding. In this process, both carbon (C) and nitrogen (N) are introduced into the surface of the steel by introducing ammonia (NH₃) as well as a hydrocarbon enriching gas into the furnace atmosphere in order to add nitrogen to the carburized case as it is being produced (Figure 1).

The Carbonitriding Process

Typically, carbonitriding is done at a lower temperature than carburizing—between 1300°F and 1650°F (700°C and 900°C)—and for a shorter time. Combine this with the fact that nitrogen inhibits the diffusion of carbon, and what generally results is a shallower case than is typical for carburized parts. A carbonitrided case is usually between 0.003” and 0.030” (0.075 and 0.75 mm) deep.

It is important to note that a common contributor to nonuniform case depths is to begin the ammonia addition before the load is stabilized at temperature. This mistake often occurs in batch furnaces that start gas additions as soon as the set point recovers, or in continuous furnaces where the parts are not up to temperature. It’s better to introduce a time delay so that the entire load reaches temperature. Remember, too, that when the ammonia addition ends, desorption of nitrogen begins.

The temperature range for carbonitriding is not arbitrary. At higher austenitizing temperatures, the thermal decomposition of ammonia is too rapid, limiting nitrogen availability. At lower temperatures, a brittle structure is formed. Also, operating furnaces below 1400°F (760°C) can pose a safety concern.

Over the years, carbonitriding has been known by many names, including “dry cyaniding”, “gas cyaniding”, “nicarbting” and “nitrocarburizing”. Today, nitrocarburizing is used to describe another type of case hardening process.

Nitrogen Content of the Case

The nitrogen in carbonitrided steel enhances hardenability and makes it possible to form martensite in plain carbon and low-alloy steels that initially have low hardenability. Examples include AISI/SAE 1018, 12L14 and 1117 that can be transformed in the case to martensite due to the lowering of the critical cooling rate required to transform the steel. The nitrides formed contribute to a high surface hardness.

Carbonitrided steels cover a broad cross section including those in the AISI 10xx, 11xx, 12xx, 13xx, 15xx, 40xx, 41xx, 46xx, 51xx, 61xx, 86xx and 87xx series. Carbon contents up to about 0.25% are typical. However, many steels in these same series with carbon contents as high as 0.50% are carbonitrided to case depths up to about 0.010” (0.3 mm).

Nitrogen, like carbon, manganese and nickel, is an austenite stabilizer, so retained austenite is a concern after quenching. Lowering the ammonia percentage will reduce the amount of retained austenite and should be done if decreases in hardness or wear resistance can be tolerated. Another consequence of too-high nitrogen is the formation of voids or porosity. In general, the nitrogen content at the surface should be no greater than 0.40%.

A common carbonitriding variation is to introduce ammonia near the end of the carburizing cycle. This introduction is typically done 15 to 30 minutes before the load is quenched. Any loss of hardenability that might occur due to internal (or intergranular) oxidation is partially offset by the nitrogen absorption.

Temper Resistance

Several other points are worth mentioning. The nitrogen in the carbonitrided case increases the steel’s resistance to softening on tempering, just like some alloying elements do. In other words, the greater the nitrogen content, the greater the resistance to softening. This is why higher tempering temperatures, up to 440°F (225°C), are often used on carbonitrided parts.

The resistance to tempering manifests itself in improved wear resistance. Carbonitrided gears for example often exhibit better wear properties than carburized gears. In addition, many shallow-case, thin-section parts made of
unalloyed steel such as die-cutting punches, can be used without tempering.

Case depth is a function of time at temperature (as seen in Figure 2). The data collected in Figure 2 shows considerable spread and is represented as a band width, explained by the original authors as, “not at all surprising due to differences in definitions of case depth and methods of measuring it, lack of precise knowledge of the length of time for which a given part is actually at the furnace temperature and the effect of variation of heating-up time.”

During carbonitriding, nitrogen is added in the form of ammonia since the dissociation (or breakdown) of ammonia will produce atomic (or nascent) nitrogen as opposed to molecular nitrogen. Atomic nitrogen will combine to form molecular nitrogen, but if the dissociation occurs at the surface of the steel, the nascent nitrogen can diffuse into the steel simultaneously with carbon (Figure 3).

Carbonitriding is usually carried out in the temperature range of 1475°F to 1650°F (800°C to 900°C), but temperatures as low as 1300°F (700°C) are sometimes used (Figure 4). The optimum range appears to be between 1550°F to 1600°F (845°C to 870°C). Penetration rates are up to 50% faster than carburizing. For example, carbonitriding at 1560°F (850°C) and carburizing at 1650°F (900°C) produce about the same case depth in the same amount of time.

Since carbonitriding is typically done at lower temperatures and for shorter times than gas carburizing, it produces shallower, but harder case depths (Figure 5 on next page), usually no greater than about 0.030" maximum. Carbonitrided fasteners are typically mounted (Figure 6a on next page) and etched (Figure 6b on next page) to reveal their case depth pattern and microstructure.

Reasons for shallower case depths in carbonitrided parts include the following:

- Carbonitriding is generally done at lower temperatures and for shorter times than gas carburizing.
- The nitrogen addition is less readily controlled than the carbon addition. This leads to an excess of nitrogen in the steel and consequently to high levels of retained...
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austenite. Increased porosity may occur when cycle times are too long.

Carbonitriding like carburizing is utilized primarily to produce a hard, wear-resistant case. This case has higher hardenability than a carburized case. Consequently, carbonitriding creates a harder case on low-carbon or low-alloy steels.

Specific advantages of carbonitriding for fasteners compared to carburizing are as follows:

• A carbonitrided case has better hardenability due to the addition of nitrogen into the surface layer.
• A more rapid enrichment in carbon that results in a shorter treatment time at lower temperature.
• A better resistance to wear and to softening (at elevated service temperatures).
• Better fatigue properties (i.e., higher fatigue limits) than carburized parts.
• Lower cost of operation due to the lower temperatures and shorter time cycles involved.

Summing Up

Carbonitriding is an excellent choice for low-carbon fastener materials that require a uniform, but shallow case with good wear properties.

In general, heat treaters performing these processes have a great deal of experience and the practical know-how in controlling their time, temperature and furnace atmospheres to achieve the required case depths. Now you have a better idea of how they do their work.

To learn more about carbonitriding of fasteners, visit the website listed below.

www.heat-treat-doctor.com

References:

3 Hancock, P. F., Modern Case Hardening Processes, Iron and Steel, 1956.
6 Key-to-Metals (www.keytometals.com).