



Liquid Ferritic Nitrocarburizing

by

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Introduction

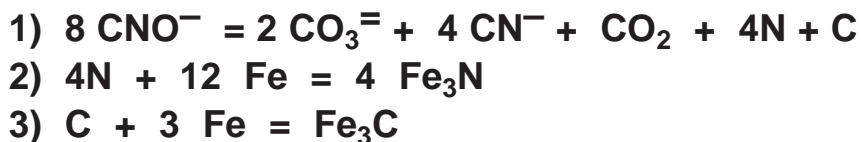
Ferritic nitrocarburizing is a thermochemical diffusion process whereby nitrogen and carbon are simultaneously introduced into the surface of ferrous metals to develop or enhance particular engineering properties and thus increase performance. The process is carried out in a liquid salt bath at a subcritical treatment temperature, typically 1075°F (580°C). The liquid salt is composed of a mixture of cyanates and carbonates of sodium and potassium and conforms to AMS 2753.

Liquid nitrocarburizing improves wear resistance, lubricity, fatigue strength, and corrosion resistance as a result of the presence of an iron nitride compound(s) formed at the surface, in addition to a zone of diffused nitrogen in solid solution with the base material, subjacent to the compound layer. Both of these zones are metallurgically discernible, each providing specific engineering properties.

Surface treatment at subcritical temperatures, using a bath of liquid salt as the source of nitrogen and carbon, has been known historically as “liquid nitriding” or “salt bath nitriding”. Although both terms are still used today, this process now falls under the generic classification “ferritic nitrocarburizing”, and is more precisely identified as “liquid nitrocarburizing”, or “liquid ferritic nitrocarburizing”.

Chemistry of Phase Development

Liquid salt baths obtain their source of nitrogen and carbon through use of sodium and potassium salts containing cyanates (CNO^-), in addition to carbonates. These non-cyanide salts are formulated to be very fluid at the processing temperature of 1075°F (580°C) and, most importantly, to generate a particular nitrogen and carbon activity within the operating bath, thus producing the desired epsilon iron nitride. A representative reaction is as follows:



As the ferrous component is immersed into the liquid bath, the above catalytic reaction occurs at the surface whereby the cyanate breaks down, releasing nitrogen and carbon. Referring to a characterization of this reaction, Figure 1, both elements diffuse into the ferrous surface causing a change in the element concentration at the surface and within the subjacent zone.

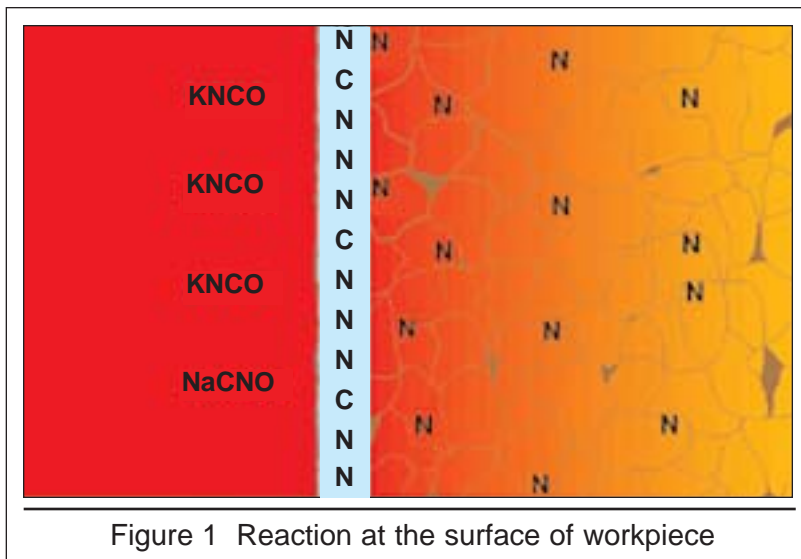


Figure 1 Reaction at the surface of workpiece

The quantitative results of the of the distribution of the diffused nitrogen and carbon are noted in Figure 2 for the outermost layer. The resulting concentrations of nitrogen and carbon at the surface are at a particular level to cause formation of a new phase at the processing temperature, i.e. a compound of iron and nitrogen/carbon. This compound layer consists predominantly of epsilon iron nitride, a phase generally identified as Fe₃N. A relatively small volume of gamma prime iron nitride, the stoichiometric compound Fe₄N, may also be present at the interface of the base metal and compound zone.

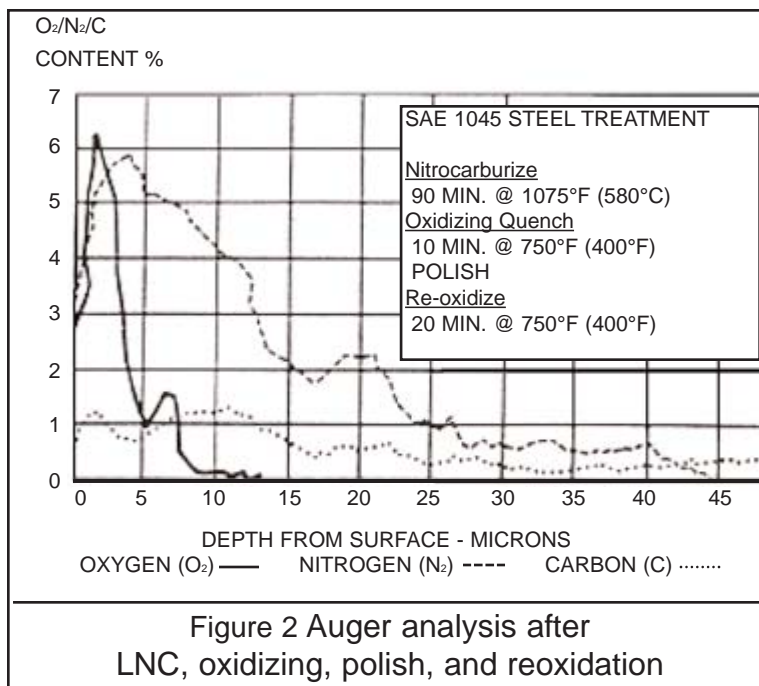


Figure 2 Auger analysis after LNC, oxidizing, polish, and reoxidation

In the zone subjacent to the compound layer, Figure 3, diffused nitrogen of lower concentration (less than 0.20% just beneath the compound zone) forms a solid solution with the base metal iron. This is termed the diffusion zone.

The physical characteristics of the microstructural layers resulting from processing are shown in the photomicrograph, Figure 4. In addition to displaying the compound zone and, in part, the diffusion zone (identified as iron nitride needles), the presence of microporosity is also apparent at the outermost surface. This is unique with ferritic nitrocarburizing, and varies in depth depending on materials and processing parameters. It has been demonstrated that microporosity enhances tribological properties, possibly by functioning as micro-reservoirs for lubricants.

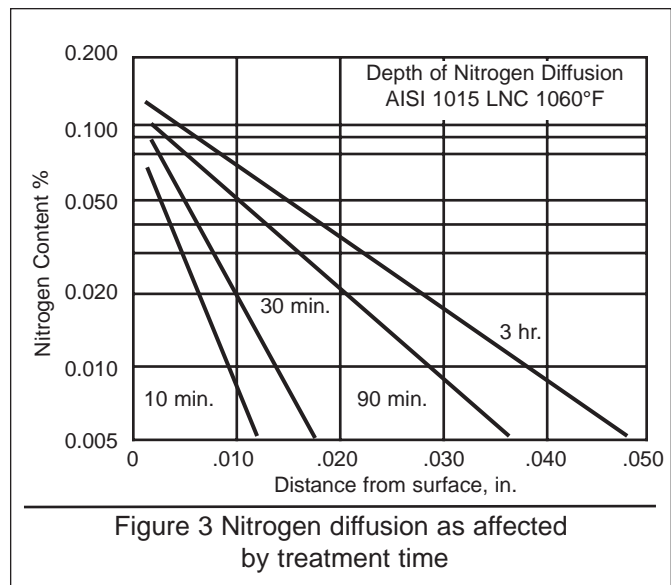


Figure 3 Nitrogen diffusion as affected by treatment time

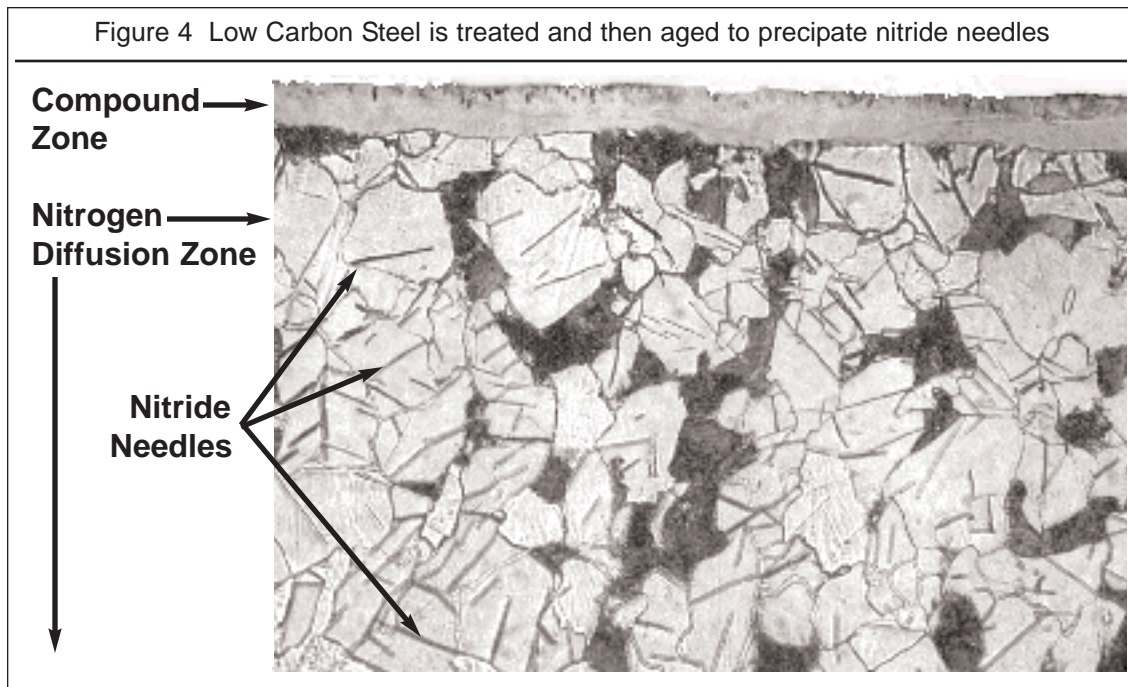


Figure 4 Low Carbon Steel is treated and then aged to precipitate nitride needles

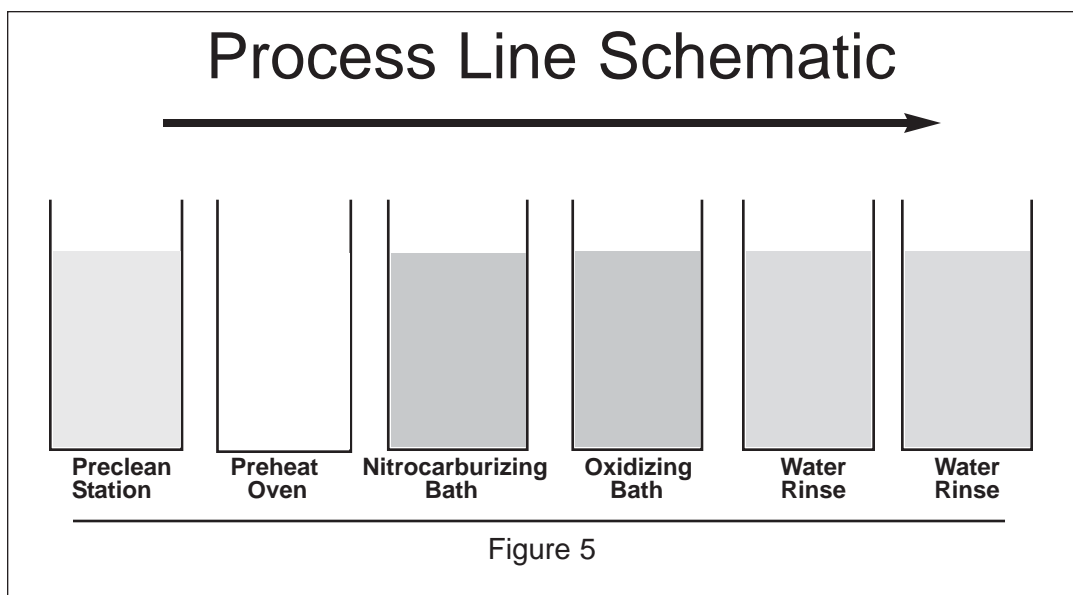
Dimensional Stability

Since processing is conducted at sub-critical temperatures, 1075°F (580°C), no thermally induced microstructural phase changes and accompanying volume changes occur. This permits the treated component to be cooled without drastic quenching, thus minimizing dimensional changes and distortion. Accordingly, components may be finished machined and/or ground prior to treatment. Any dimensional growth resulting from treatment is predictable and reproducible. Parts should be thermally stabilized prior to final machining, i.e. sufficiently tempered or stress relieved, typically at 1100°F minimum. Stampings and other parts with thin cross sections are well suited for processing because of the capability for dimensional stability and no distortion.

The Process

Referring to the schematic, Figure 5, the process begins with a preclean and preheat cycle, 750°F (400°C), to ensure that the parts are clean and dry. Also, a load of components that have been uniformly preheated will reduce thermal shock and permit more efficient recovery of the nitrocarburizing bath temperature.

The load is then transferred to the nitrocarburizing bath and held a predetermined period of dwell time, dependent on the required depth of compound layer. The parts are then quenched into an oxidizing salt bath at a lower temperature, typically 750°F (400°C), and held from 5 to 20 minutes. The reduced cooling rate resulting from intermediate quenching helps to mitigate thermally induced distortion.



After the oxidizing quench, parts are cooled to room temperature, rinsed, and if required, subjected to post treatment. This may include mechanical polishing if surface finish is of concern, or the quench-polish-quench treatment to develop maximum corrosion protection and/or enhance the cosmetic appearance. (The quench-polish-quench process is discussed in detail in another Nitromet Technology Update bulletin.)

Process Control

A most important factor in producing the desired monophasic epsilon iron nitride when nitrocarburizing, is to control the nitrogen and carbon activities of the processing environment. This is accomplished by monitoring and regulating the cyanate (CNO^-) concentration within the operating bath to 34%-38%. As more parts, and thus more iron, are put through the bath, cyanate content decreases until regeneration becomes necessary. Based on results of a standard titration analysis, an appropriate amount of an organic polymer regenerant is added, reacting with the carbonate in the bath and converting it to cyanate.

Metallurgical Results

The process may be performed on a number of ferrous based materials, ranging from carbon steels, low alloy steels, tool steels, to the stainless steels. Special “nitriding grades” respond well, but the presence of contained alloying elements is not required to produce a compound zone. Cast irons, gray iron, and nodular iron are also treatable by this diffusion process. The response to nitriding as measured by depths of compound zones and diffusion zones formed, and by the associated hardnesses of both zones, is directly related to the material composition. In general, with increase in carbon content and/or in the amount of alloying elements, the rate of diffusion decreases, thus resulting in shallower depths of nitrogen penetration, Figs. 6A and 6B. Diffusion rates are particularly sensitive to materials containing nitride forming elements, e.g. chromium and molybdenum.

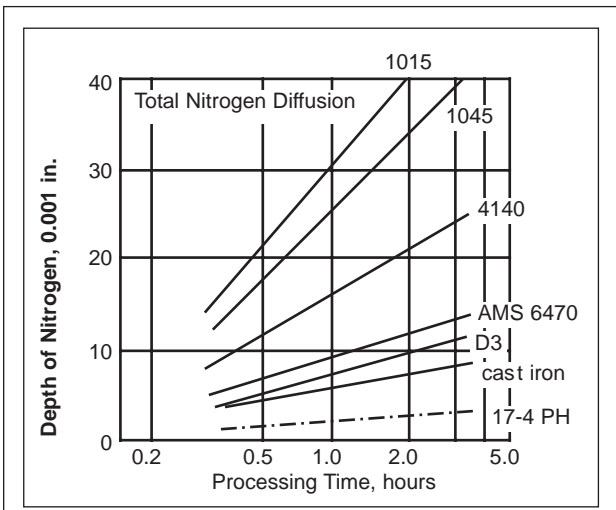


Figure 6A Influence of material on total depth of nitrogen diffusion

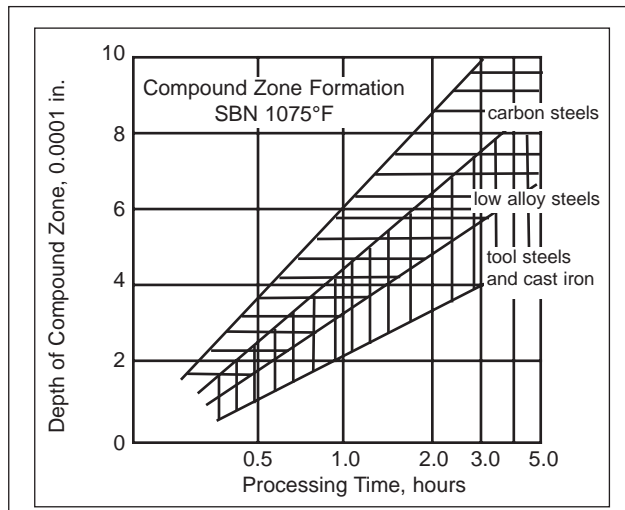


Figure 6B Influence of material on compound zone formation

Process time cycles are most often limited to 2 hours since diffusion rates decrease with time, and long cycles become increasingly non-productive. Typically, a compound zone depth of 0.0003 in. to 0.0008 in. would be produced in 90 minutes for carbon or low alloy steels with depths of diffusion zones ranging from 0.015 in. to 0.030 in. depending on material, Figures 7A, 7B, 8A, and 8B.

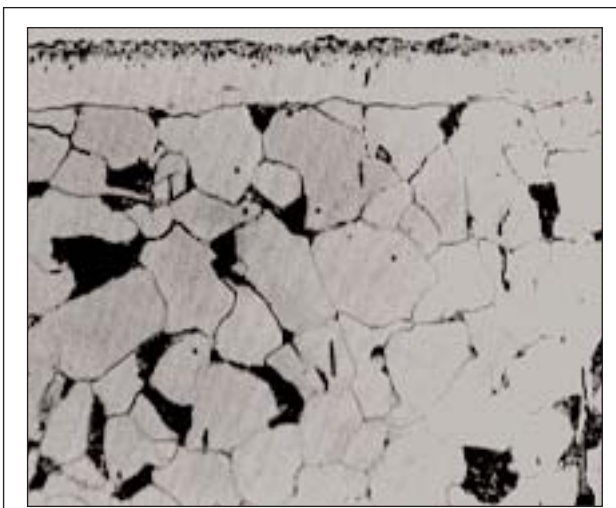


Figure 7A Low carbon steel, LNC treated 90 minutes, 1075°F
Original magnification 500X Nital etch

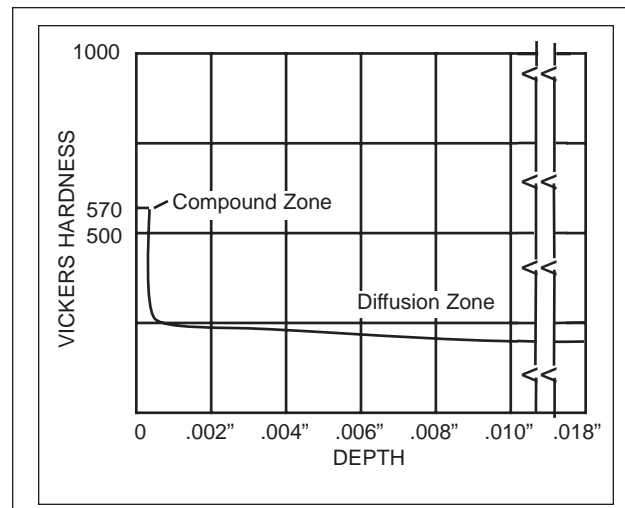


Figure 7B Traverse hardness, AISI 1015 steel, LNC treated 2 hours, 1060°F



Figure 8A SAE 5115, chrome-manganese low carbon steel, LNC treated 90 minutes, 1075°F
Original magnification 500X Nital etch

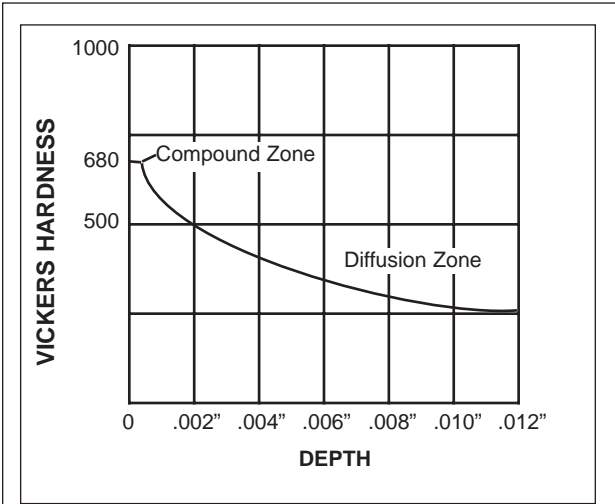


Figure 8B Traverse hardness, AISI 5137 steel. LNC treated 2 hours, 1060°F

Compound zones depth requirements, and associated time cycles, for tool steels depend on the application. High speed cutting tools require a very thin compound layer and thus are treated for only 10-20 minutes at reduced temperature, 1000°F, to maintain base material hardness. This provides resistance to chip welding at the cutting edge.

Liquid nitrocarburizing also benefits die casting dies, Figure 9, by reducing heat checking, soldering, and diffusion and wear from molten metals. Cycle time for H series die steels may require 2 hours to achieve the desired properties. Also, treatment of stamping dies increase performance by reducing galling and seizing, Figure 10.

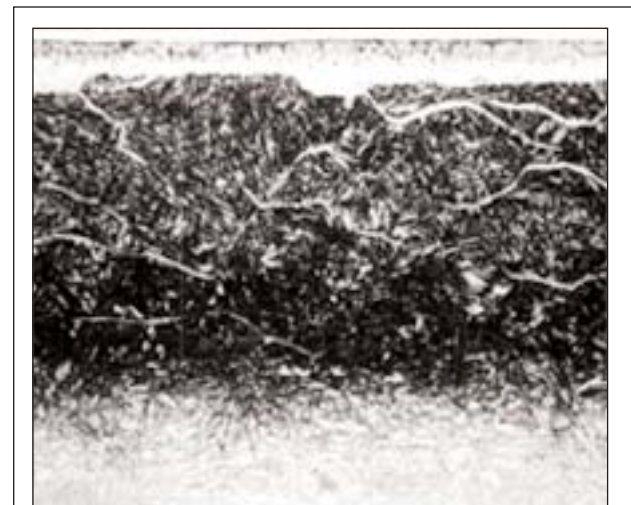


Figure 9 H-13 die steel, LNC treated 2 hours 1075°F
Original magnification 500X Nital etch

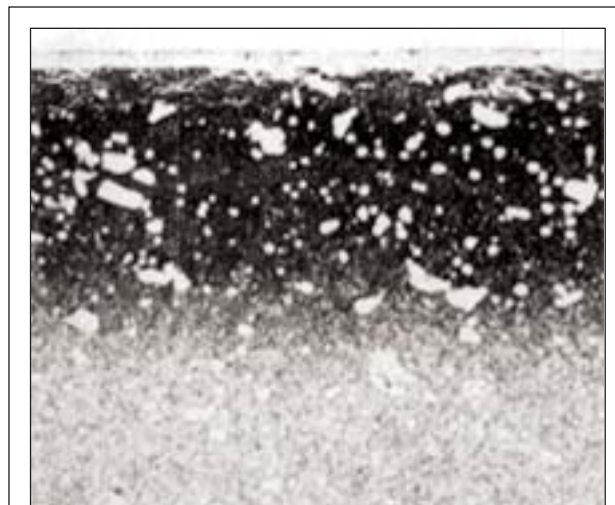


Figure 10 D-2 tool steel, LNC treated 90 minutes 1075°F
Original magnification 500X Nital etch

Stainless steels are treated primarily to introduce wear resistance and anti-galling properties. While developing these properties, there could be significant degradation of the stainless (corrosion resistant) qualities of the material which should be considered when specifying any nitrocarburizing process. Stainless steels respond quickly to diffused nitrogen, developing an extremely hard compound zone of complex nitrides, Figure 11A. Zone depths of 0.001 in. may be developed within 1 hour, with depth of diffusion layer of only 0.003 in., Figure 11B.



Figure 11A 304 stainless, steel,
LNC treated 90 minutes 1075°F
Original magnification 500X Complex etchant

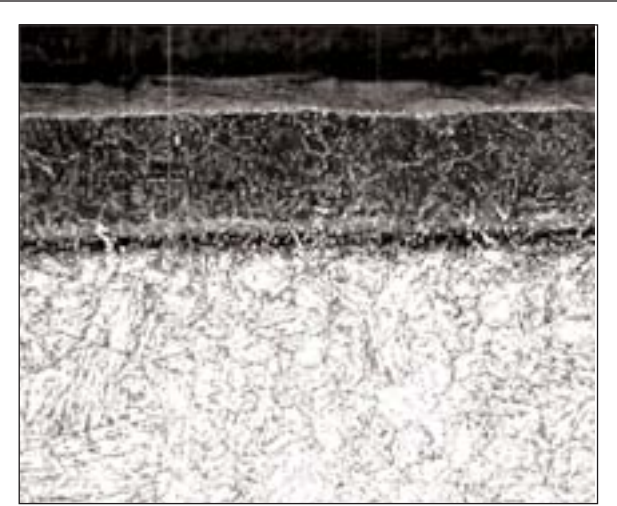


Figure 11B 17-4 PH stainless steel
LNC treated 60 minutes 1075°F
Original magnification 500X Complex etchant

Cast irons also respond to nitrocarburizing but at a somewhat reduced rate. Cycle times of 90 to 120 minutes are normally specified to generate compound zone depths of 0.0003 in. to 0.0008 in. and diffusion zones to 0.015 in. Both gray iron, Figure 12, and nodular iron, Figure 13, are generally treated to improve wear resistance and increase fatigue strength.



Figure 12 Gray iron
LNC treated 2 hours 1075°F
Original magnification 500X Nital etch

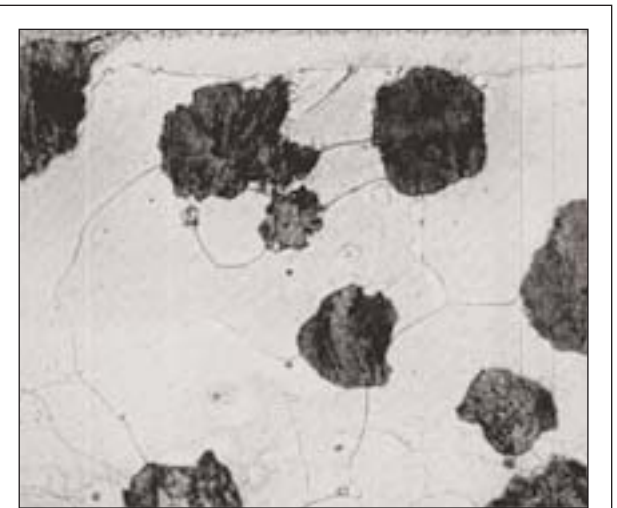
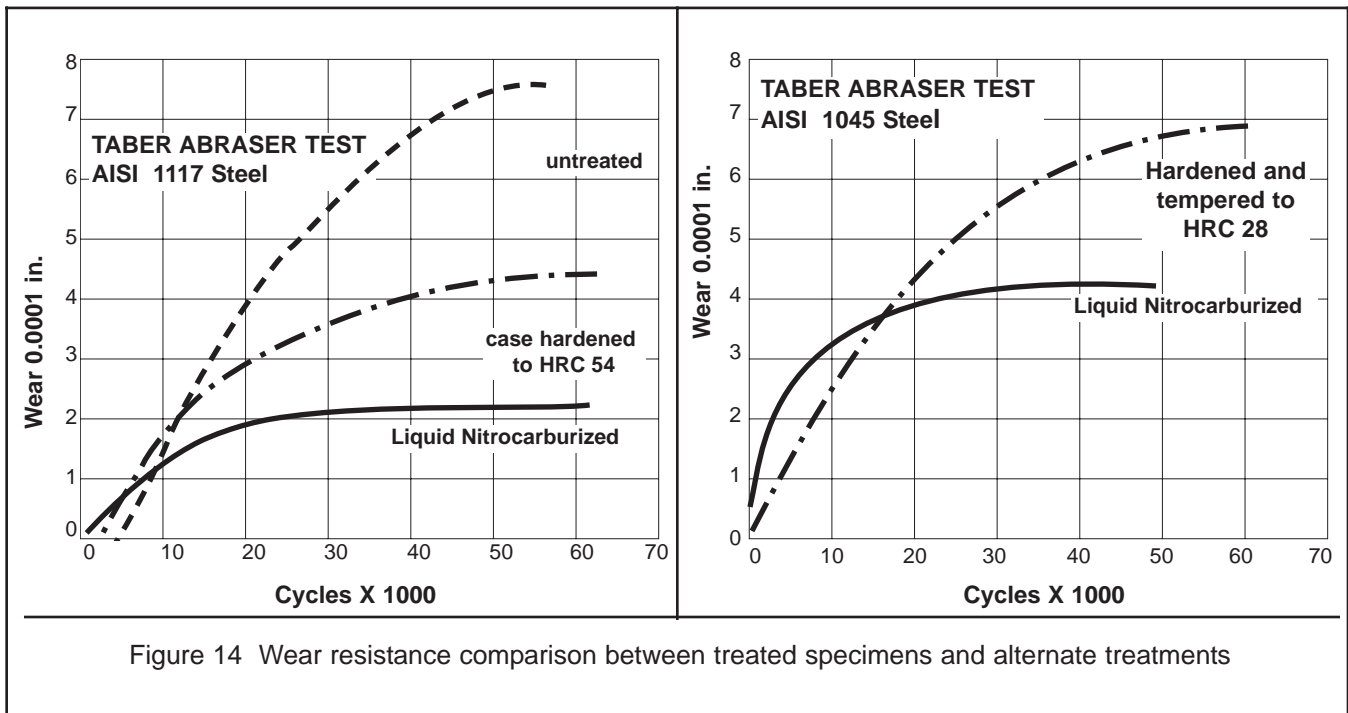


Figure 13 Ferritic nodular iron
LNC treated 90 minutes 1075°F
Original magnification 500X Nital etch

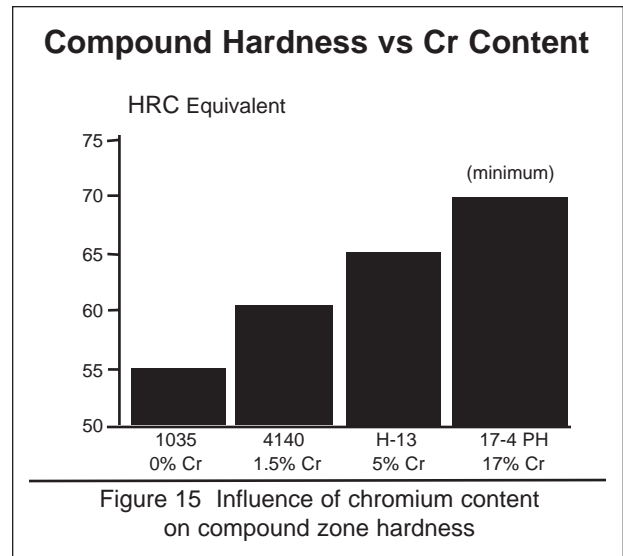
Engineering Properties

The end result of nitrocarburizing is the formation of two distinct layers of nitrogen bearing microstructures. The outermost layer identified as the compound zone, and the subjacent interior layer is called the diffusion zone. Each of the zones contribute to improving performance by enhancing specific engineering properties, i.e. wear resistance, lubricity, corrosion resistance, and fatigue strength. From these, other benefits in performance are realized, e.g. excellent running properties, anti-galling and anti-seizing characteristics, and reduced tendency for fretting corrosion.

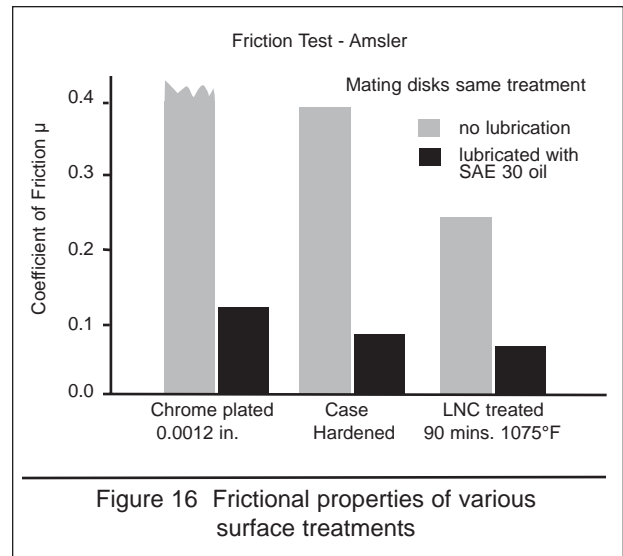


Wear resistance is perhaps the most significant property resulting from treatment. The ability of the compound zone to resist wear is dependent on the type of wear system, specifically whether it is adhesive or abrasive wear. Adhesive wear occurs when two components are in relative motion in an essentially abrasive free environment. Under these conditions, the intrinsic physical characteristics of the compound zone, i.e. hardness and lubricity, notably improve the sliding and running behavior and consequently, increase the resistance to adhesive wear, Figure 14. The phase composition of the compound zone that demonstrates the best wear resistance consists predominantly of epsilon nitride phase (monophase preferred) with a very small amount of gamma prime phase.

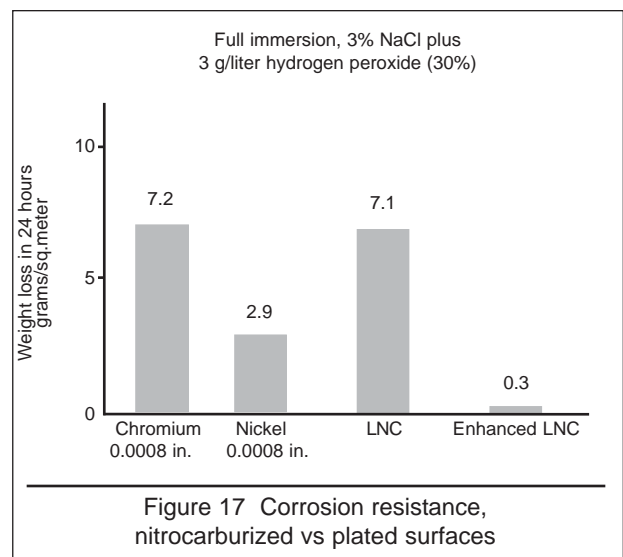
Resistance to abrasive wear is dependent on the relative hardnesses of the abrading substance and of the compound zone. For unalloyed carbon steels, the compound zone hardness is equivalent to approximately HRC 55, thus providing only short time resistance to abrasants of higher hardness. One method of increasing hardness, and thus abrasive wear resistance, is to increase the content of nitride forming elements, viz. chromium, of the base material. Referring to Figure 15., progressive increases in chromium from zero (carbon steel) to 17% (stainless steel) result in a corresponding increase in hardness up to HRC (equiv.) 70 minimum.



The other engineering property that influences resistance to adhesive wear is lubricity. The compound zone has an inherent low coefficient of friction, Figure 16, and functions as a solid film lubricant by providing a non-metallic interface between mating surfaces. Applications that are thus benefitted include forming tools, extrusion dies, and sliding and rotating systems that rely on good running properties.



An increase in corrosion resistance also results from processing, most notably with the quench, polish, quench process, Figure 17. Since the total nitrocarburizing process includes quenching the treated component directly from the nitrocarburizing bath into the oxidizing salt bath, the compound zone absorbs a small amount of oxygen. This produces a level of corrosion protection equivalent to that resulting from 20 micron depth of chrome plating, and for many applications may be sufficient.



Fatigue strength under bending and torsional loading develops as a result of the nitrogen present in the diffusion zone, and particularly the amount in solid solution. Improvement in fatigue strength occurs in a range of materials, Table 1, and in varying degrees. Low carbon steels with relatively low strength, display the greatest increase, 80% to 100%, whereas the higher alloy steels and cast irons show from 20% to 80% improvement in strength.

Table 1: Improvement in Fatigue Strength	
<i>Alloy Treated</i>	<i>Fatigue Strength Improvement</i>
Low Carbon Steels	80% - 100%
Medium Carbon Steels	60% - 80%
Stainless Steels	25% - 35%
Chrome/Manganese (low carbon) Steels	25% - 35%
Chrome Alloy (medium carbon) Steels	20% - 30%
Cast Irons	20% - 80%

Regarding results for unalloyed steels, the rate of cooling from the nitrocarburizing bath (1075°F) influences the degree of strengthening. If the part is rapidly quenched to room temperature, the nitrogen will be retained in solid solution, thus maximizing the strengthening effect. However, if the part is slow cooled at a rate that permits the nitrogen to precipitate out of solid solution, the increase in strengthening will be reduced about 20%. This diminishing effect of slow cooling on fatigue strengthening does not occur with alloy grades.

Conclusion

Liquid nitrocarburizing is an effective and economical means to enhance performance of engineered components made of ferrous metals. This primer should serve as a starting point for metallurgists, technicians, engineers, and anyone with interest in product improvement through surface engineering. Additional technical documents addressing more detailed aspects of the process and applications are available as "Technology Updates" from the Nitromet Division of Kolene Corporation.

About this **Technology Update**:

The purpose of this Technology Update - "Liquid Ferritic Nitrocarburizing" - is to inform and educate those who specify, purchase, and/or evaluate Nitromet's nitrocarburizing processes.

It is authored by James R. Easterday, P.E. and is designed to provide you with the basic nitriding process theory and benefits. Other Technology Updates in this series are more specific in nature, and build on the basics presented in this document.

If you should have any questions about the content of this document or wish to discuss a particular application for nitrocarburizing, please contact the Nitromet Division of Kolene Corporation.

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