Improvement in Wear and Fatigue Properties of Structural Metals through Liquid Nitriding

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Aerated liquid nitriding is recommended to improve structural wear and fatigue. Treatment is performed at 1060°F (570°C), developing a wear resistant diffusion zone of epsilon iron nitride (Fe_3N) and iron carbide (Fe_3C). This zone varies from 0.0001 in. to 0.0009 in. (0.00025 cm to 0.0023 cm), dependent upon treatment time. The surface is ductile because of the absence of brittle Fe_2N. The low frictional coefficient produced is resistant to wear under rotational and vibrational conditions. Fatigue improvement up to 100% is common in structural materials since the surface strengthening overcomes notch effects. Nitrogen diffusion to a depth of 0.040 in. (0.102 cm) strengthens unnotched structures. Wear and fatigue data are documented in charts.

Compounds of Iron and Nitrogen

SURFACES developed from combinations of iron and nitrogen are moderately inert to most chemical reactions and, therefore, resistant to both fretting and atmospheric corrosion. The physical properties depend upon the atomic ratio of iron to nitrogen in the alloy. Molecular ratios of two parts iron to one part nitrogen as Fe_2N have good wear resistant characteristics but tend to be brittle.[1] The epsilon iron nitride ratio of Fe_3N has more ductility but also good wear resistance. A number of compounds are possible within the grouping of Fe_3N, each possessing its own characteristics. Likewise, each compound developed at a specific temperature and nitrogen potential can be identified by X-ray diffraction patterns. The soluble iron nitride (Fe_4N) occurs throughout the diffusion zone of liquid nitrided carbon steels.

Low-Temperature Liquid Nitriding

AMS 2755A defines an aerated low-temperature liquid nitriding process. The treatment involves a mixture of sodium cyanide (NaCN), potassium cyanide (KCN), sodium cyanate (NaCNO) and potassium cyanate (KCNO) in a molten bath operating in a temperature range of 1000° to 1060°F (538° to 570°C). Bath additions consist of a cyanide mixture added as required by chemical analysis. The cyanide is slowly oxidized in contact with aspirated air to form active cyanate compounds. Three percent of the bath is converted daily to form 2% of the mixed cyanate compounds. A controlled operating bath is maintained with a cyanide content between 45% and 50% and a cyanate content between 44% and 49%.

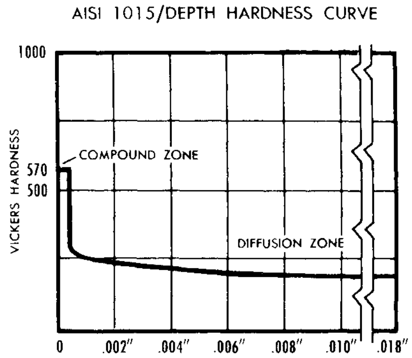

Fig. 1 Microhardness gradient in liquid nitrided plain carbon steels.

Metallurgical Effects

The wear resistant compound zone which is developed varies in depth from 0.0001 in. (0.00025 cm) in tool steels to 0.0009 in. (0.0023 cm) in stainless alloys. The typical depth developed in carbon and alloy steels is 0.0004 in. (0.0010 cm). This hardened compound zone is composed of epsilon iron nitride (Fe_3N) and iron carbide (Fe_3C) dispersed in an iron matrix. Converted hardness values of 55 to 60 Rockwell C can be measured throughout the diffusion zone in plain carbon and low alloy steels. The hardness traverse curve, Fig. 1, in plain carbon steels changes rather abruptly, indicating that the formation of nitrides and carbides is restricted to this outer layer.

Alloy steels develop an additional hardening effect from the formation of alloy nitrides throughout the diffusion zone and the hardness traverse has a more gradual slope, Fig. 2.

Internal strengthening of low temperature liquid nitrided steels is accomplished by the diffusion of nitrogen in the matrix. Total nitrogen diffusion can be determined by chemical analysis to a depth of 0.040 in. (0.10 cm).

A measurable diffusion zone can be determined microscopically in plain carbon steels by the needle-like precipitation developed after aging at 575°F (302°C), Fig. 3.

Wear Properties

The wear resistance of low temperature liquid nitrided surfaces results from a dispersion of iron nitride (Fe_3N) and iron carbide

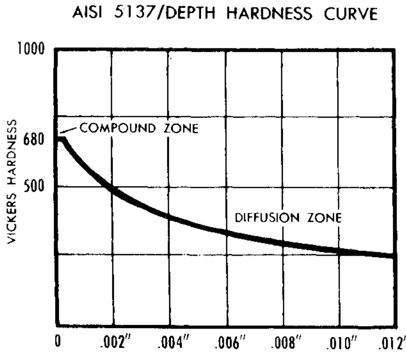

Fig. 2 Microhardness gradient in liquid nitrided alloy steels.

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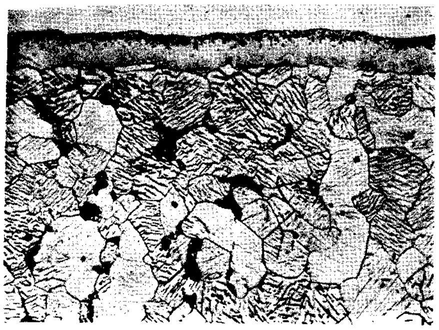

Fig. 3 Fe_4N needles developed after aging at 575°F – 302°C (500X).

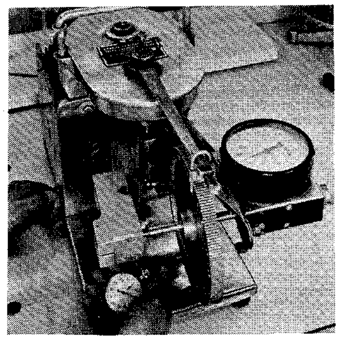

Fig. 5 Faville-LeVally test machine.

(Fe_3C) throughout the 0.0004 in. (0.0010 cm) of compound zone developed. Laboratory tests on an Amsler test machine indicate that treated surfaces have better or superior wear resistant properties than carburized and hardened, gas nitrided, hard chromium plated or carbonitrided surfaces. A graphical presentation of two of these wear tests is shown in Fig. 4. The wear resistant properties of the surface are independent of prior heat treatment except where core support is a factor. The information developed has been responsible for production nitriding of cylinder liners, gears, hydraulic valves, spools, castings, and engine valves.

The Faville-LeVally test machine, Fig. 5, is frequently used in testing surface wear properties. Although it is normally employed as a laboratory test for lubricants, it is also suitable as an indicator of nonlubricated surfaces including galling and frictional properties. The roughened low carbon Falex pin shown in Fig. 6 is typical of the failure expected in untreated surfaces. Contrastingly, the low-temperature liquid nitrided pin of the same composition has failed in a manner typical of a lubricated or low frictional surface.

Endurance Properties

Fatigue values of structural components are dramatically improved through liquid nitriding. The 0.0004 in. (0.0010 cm) compound zone, in conjunction with nitrogen diffusion to a depth of 0.040 in. (0.10 cm), has resulted in improvements of 80% to 100% in low carbon and medium carbon steels, Table 1.

Endurance failures in notched structures originate in the area of highest stress concentration at the notch, Point A, Fig. 7, and strengthening of the surface is of prime importance. The load stress curve is developed from test bars subjected to maximum loading without failure after 10^7 cycles. At all points, except A, the load stress is well below the critical stress curve of the low temperature liquid nitrided SAE 1045 steel.

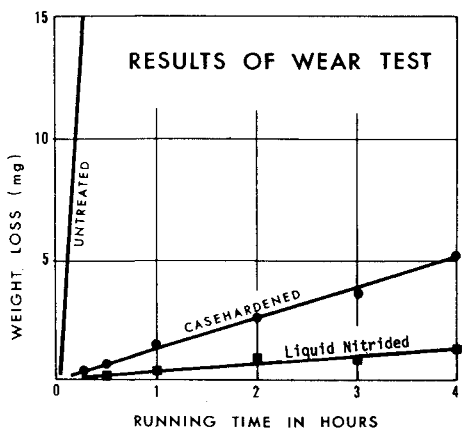

Fig. 4 Wear test comparison of untreated, case hardened and liquid nitrided carbon steel.

Table 1 Expected range of improvement in fatigue properties of liquid nitrided ferrous materials over normally hardened structures

Low carbon steels	80–100%
Medium carbon steels	60–80%
Stainless steels	25–35%
Low carbon, chrome manganese steels	25–35%
Chrome alloy, medium carbon steels	20–30%
Cast irons	20–80%

The high nitrogen and iron carbide content of the compound zone imparts sufficient surface strength to overcome load stress concentrations at a properly designed notch. Higher operating loads are thus possible with existing designs. Alternatively, new structures can be reduced in mass, effecting substantial savings in material and operating weight.

In unnotched structures, Fig. 8, the load induced shear stress curve intersects the critical stress curve well below the surface which has been strengthened by low temperature liquid nitriding. Fatigue fracture is liable to occur at Point B, and increased treatment times would shift this point to the right, automatically increasing the maximum allowable load stress.

Carbon resists nitrogen penetration and, therefore, the fatigue improvement is lower as carbon concentration increases. Alloy elements also resist nitrogen penetration and, frequently, nitrided carbon steels can surpass treated alloy steels in endurance values. Maximum improvements in endurance limit can be developed in medium carbon and low alloy steel unnotched fabrications because of higher concentrations of nitrogen in the diffusion zone.

Corrosion Resistance

The effect of low-temperature liquid nitriding on the corrosion resistance of structural materials is dependent upon the composition of the material. Stainless alloys will have a slightly lower resistance to atmospheric corrosion after nitriding because of the restriction of that part of the alloy content which is

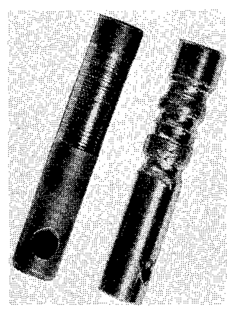

Fig. 6 Falex pins after testing.

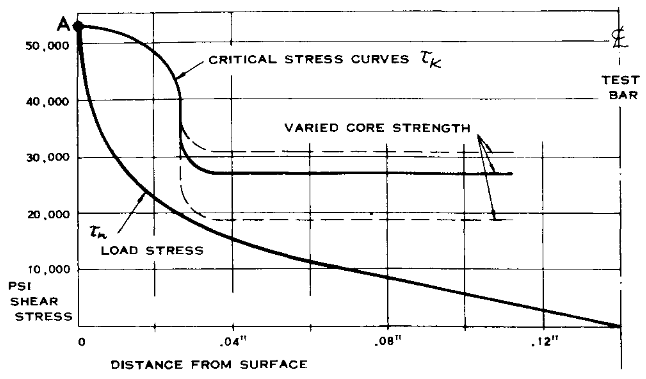

Fig. 7 Stress patterns in notched structures.[2]

combined with nitrogen and carbon. The corrosion resistance of carbon steels and cast iron, contrastingly, is upgraded with the low temperature liquid nitriding process.

Alloys of iron and nitrogen are relatively inert to normal oxidizing conditions. This same property is also effective in preventing fretting corrosion, a frequent source of mechanical failures. Low temperature liquid nitrided carbon steel has been substituted for stainless steel structures with little loss in corrosion resistance and substantial improvement in fatigue and wear properties.

The ability of a liquid nitrided surface to resist corrosion and the low coefficient of friction developed suggests some special applications for the process. Rotational movement under non-lubricating conditions is a distinct possibility. Frequently, lubricants are not permitted because of temperature and atmospheric conditions or because of possible contamination.

Design Factors

To obtain full advantage from the low-temperature liquid nitriding process, certain design changes must be incorporated. Dimensions which include allowances for changes resulting from metallurgical transformations and thermal effects should be adjusted to correlate with the minimum geometrical effects expected. The temperature of liquid nitriding is subcritical and, therefore, no metallurgical changes are experienced in properly hardened and drawn material. This permits designing more closely to tolerances, eliminating excessive final grinding stock. In addition, distortion is minimized, further eliminating allowances for final finishing. Low-temperature liquid nitrided sections are preferably rough machined, stress relieved at 1100°F (593°C), and final machined and heat treated. Dimensional changes are normally within 0.0001 in. to 0.0003 in. (0.00025 cm to 0.00076 cm) and are reproducible and allowable.

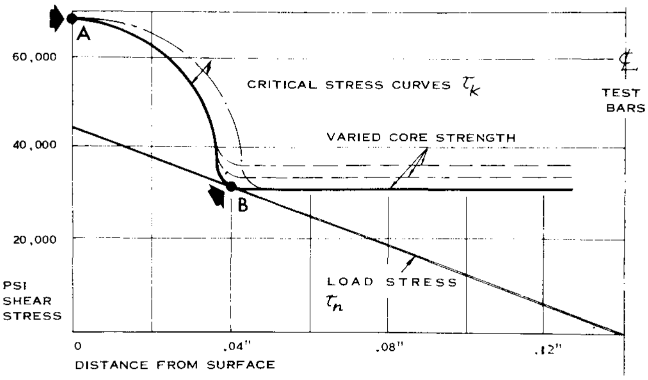

Fig. 8 Stress patterns in unnotched structures.

Material and Energy Factors

Measurable economic advantages can be realized with low-temperature liquid nitriding. The single-step treatment which improves wear properties, endurance values, and corrosion resistance is attractive from a designer's point of view. In addition, the lower processing temperature involved, 1060°F (570°C), compared to 1550°F (843°C) for carbonitriding, or 1700°F (927°C) for carburizing, effects substantial savings in fuel requirements. The energy shortage which will be experienced in the United States during 1974 threatens to be a major factor in manufacturing operations during the next decade. The 10 to 1 comparison between gas requirements for carbonitriding and low temperature liquid nitriding indicated in Table 2 could be of prime importance in volume production operations.

Table 2 Comparison of energy requirements for low-temperature liquid nitriding and carbonitriding

	Low-temperature liquid nitriding	Carbonitriding
Material	Carbon steel	Carbon steel
Load size	1500 lb	1500 lb
Gas requirements:		
Preheat	200 ft^3	Not required
Furnace firing	270 ft^3	2400 ft^3
Endothermic generator	Not required	1500 ft^3
Tempering furnace	Not required	1400 ft^3
	470 ft^3	5300 ft^3

Post treatments are not required after low-temperature liquid nitriding, resulting in additional savings in processing energy. Structures are normally finished to final dimensions prior to heat treatment. Surface finish changes are not measurable and are only apparent because of a change in reflectivity after treatment.

The cooling rate following low-temperature liquid nitriding is of little importance in practically all situations. There is some slight difference in the maximum endurance values obtainable in unnotched carbon steels that are slow cooled, but generally the improvement is sufficient to make this negligible. Slow cooling, combined with the low temperature of operation and the lack of metallurgical changes, permits closer tolerances on final machining operations. Substantial energy savings result from the elimination of grinding and honing which are normally required to restore geometry after hardening. Low temperature liquid nitriding produces minimum size and distortion effects and, therefore, final finishing after heat treatment is not required.

Summary

Low-temperature liquid nitriding offers a method of heat treatment which is rapid and capable of upgrading the performance characteristics of ferrous materials. Design factors include the possibility of making parts lighter, effecting over-all weight savings in engine and frame structures. All applications involving wear and endurance properties can be considered with the possibility of replacing higher temperature heat treatment processes. Substantial savings in energy and finishing costs may be realized. The process has distinct advantages in most applications where endurance properties and wear characteristics are of prime importance. It is limited where unit loads are sufficiently high to crush the thin nitrided case with its minimum core strength.

References

[1] Komura, Sh., "Spring Steel Wire Treated by Tufftriding Process," *Wire and Wire Products*, Vol. 40, No. 4, April 1965.

[2] Müller, J., "Influence of Core Structure and Strength on the Fatigue Resistance of Tufftride Processed Rotating Bend Test Bars," presented at the 1962 National Metal Congress, New York.