



## HTPro: Low-temperature Surface Hardening of Stainless Steel

Christiansen, Thomas Lundin; Somers, Marcel A. J.

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# LOW-TEMPERATURE SURFACE HARDENING OF STAINLESS STEEL

LOW-TEMPERATURE SURFACE HARDENING OF STAINLESS STEEL PROVIDES THE REQUIRED PERFORMANCE PROPERTIES WITHOUT AFFECTING CORROSION RESISTANCE.

Thomas L. Christiansen and Marcel A.J. Somers  
Technical University of Denmark, Lyngby

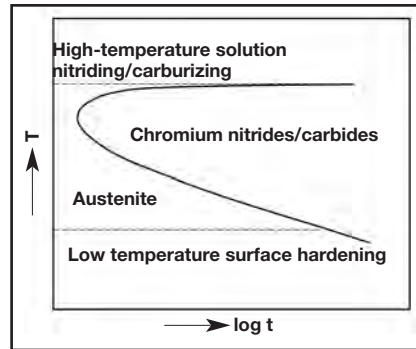
Stainless steels rely on the presence of chromium in solid solution, which allows the development and maintenance of a passive layer at the surface. Nitriding, carburizing, and nitrocarburizing are generally not considered good practice, because processing in the conventional temperature range between 490° and 950°C leads to chromium nitride and chromium carbide precipitation. While this provides a hardening effect, it is highly detrimental to corrosion properties. Since the mid-1980s, several processes were developed that enable low-temperature surface hardening of stainless steel at temperatures below 440°C.

The first deliberate surface hardening of stainless steel was achieved by a process known today as Kolsterizing<sup>[1]</sup>, a method ostensibly inspired by corrosion phenomena observed in liquid-metal fast breeder reactors<sup>[2,3]</sup>. About the same time, seminal work by Zhang and Bell<sup>[4]</sup> on plasma nitriding of stainless steel was published. Throughout the 80s and 90s, the development of low-temperature surface hardening of stainless steel relied largely on plasma-based techniques, while in the past 10 years in particular, gaseous processing was developed and commercialized.

This article describes fundamental and technological aspects of low-temperature surface hardening (LTSH) of stainless steel. The results shown are taken from the authors' research during the past 15 years.

## LTSH principles

The TTT diagram in Fig. 1 demonstrates the combination of allowable treatment time at low temperature before precipitation of Cr-based nitrides or carbides occurs. In this temperature range, carbon, interstitially dissolved nitrogen and carbon can diffuse over a relatively long distance, while substitutional dissolved metallic elements can be considered stationary. Consequently, nitride or carbide development



**Fig. 1** — TTT diagram of austenite with a high nitrogen or carbon content. A low-temperature treatment of long duration or a high temperature treatment (>1050°C) combined with fast cooling can be applied to prevent development of chromium nitrides/carbides.

proceeds so slowly that a nitrogen or carbon rich case free of chromium-nitrides/carbides develops. In the early days of LTSH, the case produced was considered a new phase, dubbed the S phase<sup>[4]</sup>. Recent research shows that no new phase develops, but rather LTSH of austenitic stainless steels produces a case that is essentially a solid solution of high amounts of nitrogen and/or carbon in austenite where interstitial atoms group around chromium atoms<sup>[5-7]</sup>. Therefore, it is incorrect to refer to the case produced as S phase; expanded austenite is preferred.

The hardening effect that occurs by dissolving nitrogen and carbon at low temperature in stainless steel is not due to nitride or carbide formation. Rather, solution of high amounts of interstitial atoms in the austenite lattice provides effective hardening.

## Process technology and applications

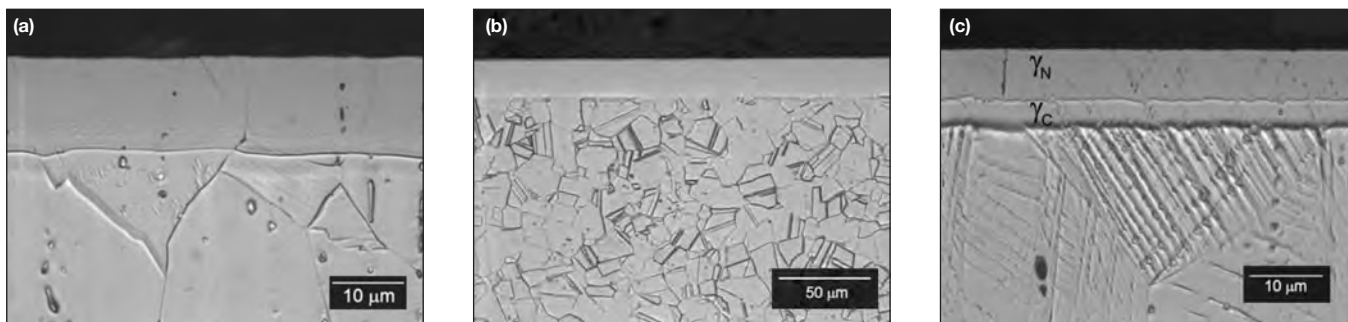
Plasma processes, apart from the proprietary Kolsterizing process, have a unique advantage over gaseous processing, because surface activation (removal of the passive film through sputtering) is an inherent step of such treatments. The (temporary) removal of the passive layer is

necessary to allow surface penetration of nitrogen and carbon from the nitriding/carburizing atmosphere.

Gaseous processing enables the highest flexibility, as well as straightforward monitoring and control. For a long time, it appeared that gaseous processing of stainless steel was possible only by in-situ removal of the passive layer in aggressive halogenides<sup>[8,9]</sup>, or after ex-situ deposition of a metal layer promoting dissociation of the gas components and protecting the surface against (re)passivation during storage and treatment<sup>[10,11]</sup>. Later, robust gaseous treatments were developed based on gas mixtures that can both remove the passive layer and provide the nitrogen/carbon to the stainless steel surface<sup>[12-14]</sup>. Expanite, a company co-founded by the authors and Thomas Strabo Hummelshøj, works exclusively with gas mixtures that have this dual ability.

Figure 2a shows the case produced during gaseous nitriding of austenitic stainless steel. The corresponding nitrogen content profile, hardness, and residual stress level are shown in Fig. 3. Dissolution of a huge amount of nitrogen leads to an appreciable increase in surface hardness and high compressive residual stresses, which arise due to austenite lattice expansion in the nitrated case. High surface hardness contributes to improved wear and galling performance, while residual stress enhances fatigue performance. During nitriding of austenitic stainless steel, an almost featureless case develops at the surface (Fig. 2a), indicating that the zone is more difficult to dissolve by the etching reagent than the unaffected austenite.

Similar results are obtained with carburizing (Fig. 2b), although less carbon can be dissolved resulting in lower increase in hardness and residual stress. The choice of nitriding or carburizing depends on the application, as both processes have advan-



**Fig. 2** — Cross sections of (a) AISI 316 after nitriding at 445°C for 22 h in a gas mixture containing 60%  $\text{NH}_3$  and 40%  $\text{H}_2$ , (b) AISI 316 carburized in acetylene at 520°C for 3 h (the transition from core to hardened case is more diffuse than for nitriding), and (c) cold-worked AISI 304 nitrocarburized at 420°C for 19 h (the nitrocarburized case is subdivided in a zone of nitrogen-expanded austenite and a zone of carbon-expanded austenite below).

tages. For example, dissolved nitrogen has a positive effect on corrosion resistance (e.g., pitting). Carburizing produces an advantageous shallow case-core transition because the affinity of chromium for carbon is not as high as for nitrogen. By comparison, nitriding yields a relatively sharp case-core transition. A gradual transition in hardness/composition can be tailored by adopting gaseous nitrocarburizing or the two-stage process of carburizing followed by nitriding<sup>[15]</sup>. These processes produce a hardened case consisting of a hard zone of nitrogen-expanded austenite and a zone of carbon-expanded austenite underneath (Fig. 2c).

For the case of heavy surface loading, austenite load bearing capacity should be enhanced further. The simplest solution is to prolong the duration of the nitriding/nitrocarburizing treatment. However, this enhances the risk for precipitation of chromium nitrides and associated loss of corrosion resistance. In such demanding applications, the low-temperature surface hardening treatment can be preceded by a high-temperature solution nitriding treatment<sup>[16]</sup>, which dissolves a relatively low amount of nitrogen into austenite up to a depth of several millimeters. Cooling from the solution nitriding temperature should be done carefully to prevent development of chromium nitride ( $\text{Cr}_2\text{N}$  or  $\text{CrN}$ ) precipitation (see Fig. 1).

Alloy grades other than austenitic stainless steels can be treated. Most stainless steel types including austenitic, ferritic, duplex, martensitic, and precipitation-hardening (PH) grades can develop a surface case of nitrogen and/or carbon-expanded austenite by undergoing gaseous nitriding, carburizing, and nitrocarburizing treatments. Expanded austenite can also be formed in other types of (similar) alloy systems, such as many Ni-base alloys. For example, Ni-

base superalloys such as the Nimonic series can be nitrided, but low temperatures (360–400°C) are required to suppress formation of unwanted  $\text{CrN}$ <sup>[17]</sup>. Also, martensitic and austenitic PH steels can be nitrided and simultaneously bulk hardened<sup>[18, 19]</sup>.

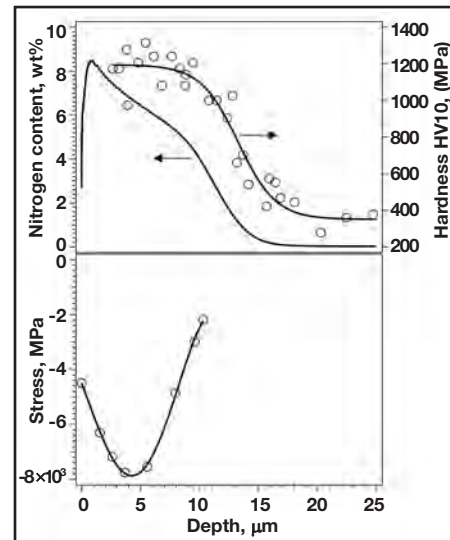
### Summary and outlook

Surface hardening of stainless steel can be achieved by low temperature nitriding, carburizing, and nitrocarburizing by transformation of the surface into nitrogen and/or carbon-expanded austenite. Gaseous processing provides a high degree of tailorability of the hard surface case enabling tailoring of materials properties, and therefore, performance. Most stainless steels and similar alloy systems can be surface hardened by means of gaseous processing.

Today's stainless steel alloys treated using LTSH are designed for purposes other than surface hardening. New stainless steel alloys with compositions tailored for optimal LTSH will further expand the applicability of low-temperature surface hardening. **HTPRO**

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**Fig. 3** — Nitrogen content, hardness, and residual stress in AISI 316 after nitriding at 445°C for 22 h in a gas mixture containing 60%  $\text{NH}_3$  and 40%  $\text{H}_2$ .

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**For more information:** Marcel A.J. Somers, Prof. and Section Head – DTU Mechanical Engineering, Technical University of Denmark, Produktionstorvet Bldg. 425, 2800 Kgs. Lyngby, Denmark; somers@mek.dtu.dk; www.mek.dtu.dk.