High Temperature Solution Nitriding of Stainless Steels; Current Status and Future Trends

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ABSTRACT
The present contribution seeks to provide an overview of the concepts of high temperature solution nitriding (HTSN) and the state of the art of the technology. It is shown how HTSN can be applied to different classes of stainless steels. New advances of HTSN are presented, in particular the combination of low temperature surface hardening, LTSH, with HTSN is addressed: HTSN is an excellent “pre-treatment” for LTSH for austenitic, duplex, ferritic and martensitic stainless steels. Examples of HTSN + LTSH of duplex and martensitic stainless steels are shown.

KEYWORD
HIGH TEMPERATURE SOLUTION NITRIDING; MARTENSITIC STAINLESS STEEL; DUPLEX STAINLESS STEEL; FERRITIC STAINLESS STEEL; EXPANDED AUSTENITE; LOW TEMPERATURE SURFACE HARDENING

INTRODUCTION
Stainless steels are used in many different applications owing to their favorable combination of properties, such as good corrosion resistance, strength and ductility. Different classes of stainless steel have been developed in order to meet different requirements, i.e. austenitic, duplex (ferritic and austenite), ferritic, martensitic and precipitation hardenable classes. One of the shortcomings of stainless steels is the lack of wear resistance and poor tribological behavior, e.g. they suffer from adhesive wear. In order to improve the (wear) performance of stainless steel thermochemical surface engineering can be applied. Historically, this has entailed conventional "ferritic nitriding", which relies on formation of chromium nitrides in the surface, albeit with drastic loss of corrosion resistance [1]. In the mid 1980s low temperature surface hardening (LTSH) based on carbon and/or nitrogen was developed [2,3]. LTSH is carried out at temperatures below, say, 450°C, for nitrogen and 520°C for carbon, and results in a supersaturated solid solution of carbon and/or nitrogen in austenite or martensite, i.e. expanded austenite and expanded martensite, respectively. This results in unaltered or even improved corrosion performance and a very high surface hardness, e.g. up to 1400-1500 HV, but the case depth is typically limited to, say, 20-30 µm. Moreover, LTSH is strongly influenced by the surface “condition” of the stainless steel, e.g. the presence of deformation martensite from machining etc. in an austenitic stainless steel is highly detrimental for the final corrosion performance of the treated part. In the beginning of the 1990s a new type of process was introduced by Berns [4,5], which in some ways resembles LTSH but in other ways is the immediate opposite. The process entails high temperatures and dissolution of nitrogen under equilibrium condition (at the processing temperature) and was coined high temperature solution nitriding (HTSN). Contrary, to LTSH, HTSN exploits existing knowledge of nitrogen solubility in stainless steels in a new way, whereas, the development of LTSH relied on the “discovery” of extreme supersaturation of nitrogen/carbon in stainless steel at low temperatures (see [6]). HTSN of stainless steel is in many aspects the “stainless” analogue to classical carburizing/case hardening of steels. The process involves the dissolution of nitrogen in stainless steel at temperatures above, say, 1050°C, from an atmosphere consisting of molecular nitrogen at a particular partial (or total) pressure. Austenitic, ferritic, duplex and martensitic stainless steels can all be high temperature solution nitrided. In general there are two different motivations for performing HTSN: i) to obtain a nitrogen-enriched austenitic case on austenitic, duplex and high Cr ferritic stainless steels for improved corrosion (and
cavitation erosion) performance, or ii) to obtain a nitrogen containing martensitic case on martensitic and low Cr ferritic stainless steels for improved wear, fatigue and corrosion performance. Hitherto, the HTSN process has been somewhat niche in industry owing, in part, to the high temperatures involved and in particular to the inherent challenges associated with the process and the resulting microstructures.

The present contribution gives an overview of the concepts and state of the art of HTSN for different classes of stainless steels and presents new developments in the optimization of the HTSN process. In particular, this includes the combination of HTSN and LTSH. Experimental details and background information are provided in the figure captions.

High temperature solution nitriding

The basic idea behind HTSN can be illustrated by the use of a time temperature and transformation (TTT) diagram for a hypothetical austenitic stainless showing the lower stability limit of nitrogen rich austenite and the transformation of austenite into other phases, i.e. Cr₂N and CrN, see Fig. 1. Hence, it is analogous to classical TTT diagrams for Fe-C steels. At high temperatures austenite containing nitrogen is the thermodynamically stable phase; for increasing N contents in austenite the lower bound of the austenite stability range is shifted upwards (see also isopleths in the next section). It is in this region that nitrogen is introduced in the HTSN process, hence solution nitriding. At intermediate temperatures, say, at temperatures around 900°C, Cr₂N will form fast (firstly at grain boundaries and subsequently homogenously within the grains). Higher nitrogen contents and hence increasingly larger supersaturation during cooling will promote the formation of Cr₂N; this can be of the order of a few seconds. In the lower part of the TTT diagram formation of CrN occurs instead of Cr₂N. From the TTT diagram it is evident that in order to maintain nitrogen introduced by HTSN into solid solution, quenching is required to avoid formation of Cr₂N. Industrially, this is performed using high pressure gas quenching with N₂ (or Ar) with pressures up to 20 bars. At temperatures below, say 500-450°C formation of CrN is extremely sluggish as substitutional diffusion is largely suppressed. In this temperature regime low temperature surface hardening can be performed, which is associated with a large supersaturation, i.e. nitrogen contents in the range 4-8 wt%. It should be noted that such high nitrogen contents are not depicted in the schematic TTT diagram in Fig. 1.

The source of nitrogen at high temperature is molecular nitrogen, which normally is considered inert (for low-alloyed steel). Molecular nitrogen will dissociate on metallic surfaces at temperatures above, say, 750-800°C, forming atomic nitrogen. This occurs according to the following equilibrium:

\[ \frac{1}{2}N_2 = [N] \]

where the equilibrium constant of reaction 1 is written as:

\[ K_N = \frac{a_N}{\sqrt{p_{N_2}}} = \frac{f_{N,SN}}{p_{N_2}} = \frac{p_{N_2}}{p_{N_{2,0}}} \]

The activity coefficient, \( f_N \), relates the nitrogen activity, \( a_N \), to the atomic fraction of dissolved nitrogen in the solid state, \( x_N \); \( p_{N_{2,0}} \) is the reference pressure for the activity (usually 1 bar). In an iron-based alloy the activity coefficient will deviate from unity according to:

\[ \ln f_N = \ln f_{N,0} \sum_j \varepsilon_i \frac{x_i}{x_j} \]

where \( \varepsilon \) is the interaction parameter of nitrogen and the \( j \)th alloying element with atomic fraction \( x \).
Assuming equilibrium between nitrogen in the solid state and in the gas:

$$\mu_N^g = \mu_N^s$$ \hspace{1cm} [4]

it then follows:

$$\gamma_2 G^0_{N_2} - RT \ln p_{N_2} = G^0_N + RT \ln a_N$$ \hspace{1cm} [5]

After rewriting and substituting terms:

$$\ln x_N = \ln \left( \frac{p_{N_2}}{p_{N_2}^0} \right) - \frac{\Delta G^0}{RT} - \ln f_N$$ \hspace{1cm} [6]

Hence, it follows directly that the “process parameters” governing the nitrogen solubility in the stainless steel are partial (or total) pressure of nitrogen gas, $p_{N_2}$ and temperature, $T$. It follows straightforwardly from eq. 6 that increasing the pressure of $N_2$ leads to a higher nitrogen content in the solid state. For a fixed $p_{N_2}$ an increase in temperature results in a lower nitrogen concentration.

The chemical composition of steel also has a large influence on the amount of nitrogen that can be dissolved as expressed by the $\ln f_N$ term, which includes the interaction of nitrogen and alloying elements (cf. Eq. 3). A negative interaction parameter of an alloying element and nitrogen implies affinity between the elements, resulting in enhanced nitrogen solubility. Elements such as Cr, Mn, Mo will enhance the solubility while Ni will reduce the nitrogen solubility. Strong nitride formers such as Ti, V and Nb obviously have negative interaction parameters, but are not suitable for obtaining a solid solution of nitrogen in austenite. Due to the low solubility product of the corresponding nitrides they will form nitrides at low nitrogen concentrations. Cr is a key element in the process as it give rises to a significant nitrogen solubility in austenite at high temperatures, provided that the concentration of Cr is higher than, say, 9-10 wt%, i.e. stainless steels. As mentioned above, the quenching from the HTSN temperature relies on high pressure $N_2$; it follows directly from Eq. 6 that this procedure is problematic as the high $p_{N_2}$ in the (short) cooling stage strongly raises the nitrogen content (in the surface). Practically this implies that for a steel that is solution nitrided to a high nitrogen content (in the austenite region), relatively close to the maximum capacity, a strong propensity exists to form surface and grain boundary nitrides in the surface adjacent region. This is a combination of the high nitrogen content itself (cf. the shift of the “nose” of TTT diagram) and the $p_{N_2}$ in the quench that further enhances the nitrogen content. Hitherto, this problem has been largely overlooked and means that the full potential of the HTSN treatment has not (always) been realized: there is a fine line between improvement of corrosion properties and deterioration. A recent remedy to the problem is to use inert gas, viz. argon, in the quench state; this implies a $p_{N_2}$ equal to nil, thus avoiding the formation of detrimental surface nitrides [7]. In the following different classes of stainless steels will be discussed with respect to HTSN.
AUSTENITIC AND DUPLEX STAINLESS STEELS

The isopleths of austenitic stainless steel AISI 316 and superduplex SAF 2507 are given in Fig. 2. From the figure it is clear that the composition strongly influences the stability range of austenite and affects the solubility of nitrogen in austenite (compare the two isopleths). Solution nitriding is typically carried out at temperatures of 1050°C and up to 1150-1175°C. For austenitic stainless steels nitrogen is introduced in a stable austenitic region and the nitrogen content is augmented. Isobars are shown for different pN₂ for AISI 316 and it is evident that a higher pN₂ increases the nitrogen content in the austenite region. It is also clear that the nitrogen solubility increases in austenite as a function of temperature, but will require higher pN₂ (for a fixed pN₂ the nitrogen content decreases with increasing temperature, cf. above).

For duplex stainless steels some of the same concepts apply as for austenitic stainless steels: a nitrogen stabilized austenitic case is desired. The difference is the core microstructure, which is still ferritic and austenitic for the duplex stainless steel; for austenitic stainless steels it remains austenitic. The introduction of nitrogen will stabilize the austenite, which is illustrated in the isopleth for the super-duplex stainless steel SAF 2507 shown in Fig. 2B. At the HTSN temperature, e.g. 1150°C, the material (without added nitrogen) is ferritic-austenitic, but when the nitrogen is introduced during HTSN, stable austenite is achieved due to the strong austenite stabilizing effect of nitrogen. The austenitic nitrogen-rich case formed has a relatively high content of nitrogen; for SAF2507 up to 1 wt% can be realized.

![Fig. 2. ThermoCalc. Isopleth for: A) austenitic stainless steel AISI 316 and B) super duplex stainless steel SAF2507. Isobars for several pN₂ are indicated in the figures.](image)

Obviously, such high nitrogen contents in solid solution give rise to an increase in hardness (cf. Fig. 3) and, more importantly, a significant improvement against localized corrosion as pitting and crevice corrosion can be obtained, provided that nitrogen stays in solid solution. The stabilization of austenite by interstitially dissolved nitrogen also entails redistribution of substitutional elements, which tend to partition in austenite and ferrite (ferrite formers Cr and Mo in ferrite and austenite stabilizers Ni and Mn in austenite). This redistribution takes time and chemical inhomogeneity on the substitutional lattice can be observed in the “youngest”, i.e. the deepest, part of the austenite case.

The microstructural evolution in HTSN for a duplex stainless steel is schematically depicted in Fig. 3. The initial duplex microstructure is maintained at the HTSN temperature and will only experience limited grain growth due to the impeding/interlocking effect of the dual phase microstructure. Nitrogen promotes formation of an austenitic case at the surface with a relatively high nitrogen content (cf. isopleth in Fig. 2B). The main effect of adding nitrogen to the austenite is strongly enhanced corrosion performance, provided that nitrogen stays in solid solution during processing. This is reflected by the pitting resistance equivalent number, PREN typically given as:

\[ \text{PREN} = \text{Cr} + 3.3\text{Mo} + 16\text{N} \]

Here it is obvious that dissolving up to 1 wt% N has a major effect on the PREN. In addition to localized corrosion resistance, also cavitation erosion performance can be improved by HTSN.
The combination of HTSN and LTSH has recently been introduced as a commercial process [8] and exploits the benefit of having a thick load bearing case with excellent corrosion properties (from HTSN) for the subsequent LTSH process. The concept and the resulting hardness depth profile of HTSN combined with LTSH are schematically shown in Fig. 3. The concept shown applies for both duplex and austenitic stainless steels; for the austenitic stainless steel no phase transformation occurs during any of the treatments.

![Schematic illustration of the microstructure of duplex stainless steel for HTSN and a combination of HTSN and LTSH.](image)

**Fig. 3.** A) Schematic illustration of the microstructure of duplex stainless steel for HTSN and a combination of HTSN and LTSH. B) Schematic hardness depth profile for HTSN and LTSH of duplex and austenitic stainless steel.

The microstructures of SAF2507 solution nitrided at 1150°C for 1 and 4 hours at a partial pressure of nitrogen of 0.5 bar are shown in Fig. 4. The development of a nitrogen stabilized case is evident and the core still consists of ferrite and austenite. Due to the presence of both phases grain growth in the duplex part (core) of the material is largely hindered; grain growth does occur in nitrogen stabilized case. However, after 4 hours of treatment it is obvious that the grains are slightly larger than for the 1 hour treatment, but compared to single phase materials general grain growth is largely prevented. The applied partial pressure of 0.5 bar slightly exceeds the limit for nitrogen solubility and should lead to formation of Cr2N (cf. Fig. 2B), but this is not observed with LOM even after 4 hours treatment. This can be attributed to the dynamic situation present for the growing layer where the equilibrium nitrogen content is not realized due to continued inward transport of nitrogen and/or slow surfaces kinetics leading to flux controlled growth. As schematically shown above, HTSN treated duplex materials can be combined with LTSH, enabling formation of expanded austenite in the outermost surface of the nitrogen stabilized austenite case. However, care must be taken to avoid "475°C embrittlement" as a consequence of the thermal impact of the LTSH treatment. Low temperature surface hardening by gaseous nitriding after HTSN (condition Fig 4A) is shown in Fig. 4C &D. Two different nitriding potentials were applied, giving rise to formation of expanded austenite. For the highest nitriding potential (Fig. 4C) the expanded austenite layer becomes relatively brittle, which is reflected by the tendency for cracking (partly due to sample preparation). The SEM micrograph in Fig. 4D shows a uniform layer of expanded austenite, which has a reduced nitrogen content. The applied temperature of 420°C is considered low enough to avoid significant 475°C embrittlement (loss of impact toughness). The hardness of the outermost surface is around 1400 HV. The nitrogen content in the expanded austenite case can easily exceed, say, 5-6 wt% nitrogen. Such high loads of nitrogen in solid solution give a large increase in wear resistance, but also has a major impact on the corrosion performance; the PREN equation above suggests a dramatic increase in PREN. However, the PREN equation has not been validated for such high N concentrations.
HTSN of martensitic and ferritic (including ferritic/martensitic) stainless steels is somewhat different from austenitic and duplex stainless steel. Instead of forming a case of nitrogen stabilized austenite the purpose is to form a case of nitrogen containing martensite. Hence, the attainable surface hardness is significantly higher than for the austenitic and duplex stainless steels.

For the martensitic stainless steels the materials are fully austenitic at the HTSN temperature, which is slightly higher than the typically recommended austenitisation temperature, due to the presence of carbon. Nitrogen is added to austenite similarly to the concept of austenitic stainless steels. Upon cooling, the case is ideally transformed into nitrogen-containing martensite and the core becomes the usual carbon-containing martensite. The concept is visualized in Fig. 5A. The process is normally associated with grain growth, leading to large austenite grains prior to quenching. However, the presence of primary (stable) carbides can prevent grain growth to a certain extent. In order to refine the grain structure a second hardening cycle (HTSN treatment) can be carried out which essentially is a re-austenitization followed by quenching. There is a limit to the amount of nitrogen that can be added to the material, because nitrogen will lower the martensite start temperature, Ms. Hence, the amount of nitrogen that can be added to a material depends strongly on the composition of the alloy. For high-carbon or high-chromium and medium- to low-carbon martensitic
stainless steels only minor amounts of nitrogen can be added. The consequence of adding too much nitrogen is the stabilization of relatively soft retained austenite, such that it cannot be transformed into martensite. This situation is also shown in Fig. 5, where too much nitrogen is added to the surface and results in a low Ms temperature. In principle, the surface can be fully austenitic at room temperature; this is actually the outcome if solution nitriding is performed on high chromium ferritic stainless steels. For martensitic stainless steel this, to some extent, curtails the use of the HTSN process, especially for the high-alloyed materials (C & Cr). Cryogenic treatment can partially mitigate the problem [10]. Also dedicated heat treatment procedures can partly overcome the problem of high fractions of retained austenite, i.e. special tempering procedures.

For medium chromium ferritic stainless steels the core remains stable ferrite during HTSN and the introduction of nitrogen to the surface brings about a transformation of ferrite into austenite due to the austenite stabilizing effect of nitrogen. Hence, an austenite case develops which will transform to nitrogen martensite upon cooling; a schematic illustration of a hardness depth profile compared to a martensic stainless steel is shown in Fig. 5B. Ferrite will experience significant grain growth in the core and will be softer than the martensitic stainless steel. However, the nitrogen-containing case on ferrite can be relatively hard, but typically not as hard as the nitrogen- and carbon-containing case obtained for carbon-containing martensitic grades.

Examples of the microstructures of HTSN treated martensitic stainless steel AISI 410 and AISI 420 are shown in Fig. 6A & B and the resulting hardness depth profiles in Fig. 7A. In both steels a nitrogen containing martensitic case has formed after HTSN and the core consists of carbon martensite. The case depths for both materials after HTSN are approximately 200-250 µm. The carbon contents in the two steels are clearly reflected in the obtained core hardness; a significantly higher value is obtained in AISI 420 which has the highest carbon content. The gradient in the nitrogen content is reflected in the gradual transition of the microstructure from the surface into the bulk. For the AISI 410 the hardness depth profile has a smooth transition from a surface hardness of 680-690 HV to a core hardness of approximately 470 HV. The higher carbon AISI 420 does not exhibit the same characteristic profile; the surface hardness is only marginally higher than the core – 760HV versus approximately 700HV. The HTSN process brings about introduction of some amounts of retained austenite in the surface region, which counteracts the hardening effect obtained from a higher interstitial content. After an appropriate cryogenic treatment procedure and/or after tempering the profile can be altered/tailored [10].

Figure. 5. A) Schematic illustration of the microstructure of HTSN of martensitic stainless steel. B) Schematic illustration of possible hardness depth profiles after HTSN of martensitic and ferritic stainless steel.
As already mentioned above, HTSN can be combined with LTSH, which is also possible for martensitic stainless steels; examples of this are shown in Fig.6C & D for the two steels. The LTSH (nitriding) process for AISI 410 results in formation of 35-40 µm thick case consisting of expanded martensite with a hardness reaching 1400 HV at the surface, see hardness profiles in Fig. 7B. The hardened case from the LTSH treatment is shallower for AISI 420; here a case of 25-30 µm is obtained. The difference in LTSH behavior can be attributed to the change in microstructure and composition. The LTSH treatment also functions as tempering of the martensite formed from cooling after the HTSN treatment. The impact of the LTSH treatment on the AISI 410 and AISI 420 in terms of tempering response is different. For the AISI 410 the specific LTSH treatment leads to a slight increase in hardness in the nitrogen containing sub-surface (to a depth of 200-250 µm) and in the nitrogen-free core of the material (not shown in Fig. 7B). This behavior can be attributed to secondary hardening, i.e. formation of chromium (carbo-)nitrides/carbides. The secondary hardening effect is more pronounced for the nitrogen-rich martensite subsurface where a significant increase is observed after LTSH (thermal impact). This provides high load bearing capacity for the outmost hard case formed from low temperature nitriding. The AISI 420 experiences a minute reduction in hardness both in the nitrogen containing sub-surface (from HTSN) and in the carbon containing core.

It is also a possibility to temper the material prior to LTSH e.g. at a temperature higher than LTSH temperature. The combination of a very hard surface zone consisting of expanded martensite with nitrogen in solid solution supported by a thick case of hard nitrogen-rich martensite provides highly improved wear and corrosion performance. The incorporation of nitrogen by high and low temperature processes also gives rise to the formation of compressive residual stresses, which are beneficial for the fatigue performance of the material.
SUMMARY AND OUTLOOK

HTSN of stainless steels has hitherto played a niche role, but is gaining ground as an industrial process, which can be applied to improve the performance of most classes of stainless steels. For austenitic stainless steels nitrogen can be incorporated and lead to a further stabilization of the austenite such as the steel remains fully austenitic (non-magnetic) during (severe) deformation. It also strongly enhances the resistance of the steel against localized corrosion. The application of HTSN could also play a major role for 3D printed austenitic stainless steel parts, where the large diffusion depth of nitrogen can be used to impart the steel with strength and enhanced corrosion resistance whilst homogenizing the microstructure. For duplex stainless steels further improvements in corrosion performance can be achieved due to the possibility of having very high contents of nitrogen in solid solution in austenite. Moreover, the concept also implies that the core structure can have the mechanical benefit from the duplex structure while the case is fully austenitic. The full benefit of improved corrosion performance can be gained upon quenching in inert gas instead of nitrogen. The analogy to classical case hardening (carburizing) of non-stainless materials is evident for ferritic and martensitic stainless steels: essentially HTSN can be considered the “stainless” version of this process. Designing the nitrogen load in the case combined with optimized sub-zero treatment and tempering can lead to highly improved materials performance. The possibility of combining LTSH (carburizing, nitriding and nitrocarburising) with HTSN can give properties that so far have not been possible in stainless steels, as for example very high wear- and corrosion resistance combined with high load-bearing capacity and high endurance limit. In particular, for martensitic stainless steels high hardness from expanded martensite supported by a thick zone of nitrogen containing martensite is intriguing. It is anticipated that HTSN will gain more and more ground as a surface and bulk engineering process for stainless steels.

REFERENCES