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NEW DEVELOPMENTS IN HIGH TEMPERATURE SOLUTION NITRIDING OF STAINLESS STEELS

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Abstract

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

Keywords

High temperature solution nitriding; martensitic stainless steel; austenitic stainless steel; duplex stainless steel; ferritic stainless steel; low temperature surface hardening; expanded austenite

1. Introduction

Stainless steels are used in many different applications owing to their favorable properties where corrosion resistance is - obviously - a key feature. Different classes of stainless steel have been developed in order to meet different requirements, i.e. austenitic, duplex (ferritic and austenitic), ferritic, martensitic and precipitation hardenable classes. One of the shortcomings of stainless steels is the lack of wear resistance and general poor tribological behavior, e.g. they suffer from galling/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]. More recently new methods were developed which entail formation of a supersaturated solid solution of nitrogen (and or carbon) in the stainless steel resulting in both increased hardness and unaltered or even improved corrosion resistance: 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 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-induced martensite in an austenitic stainless steel is highly detrimental for the final corrosion performance of the treated part [4]. In the beginning of the 1990s a new type of process was introduced by Berns [5,6] 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 conditions (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 [7]. 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 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 concepts of HTSN for different classes of stainless steels and presents new developments in the optimization of the HTSN process. This also includes the combination of HTSN and LTSH. Experimental details and background information are provided in the figure captions.

1.1. 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. Cr$_2$N and CrN, see Figure 1.

![Figure 1 Time-temperature-transformation diagram of hypothetical austenitic stainless steel containing different amounts of nitrogen.](image)

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, i.e solution nitriding. At intermediate temperatures, say, around 900°C, Cr$_2$N will form rapidly (firstly at grain boundaries and subsequently homogenously within grains). Higher nitrogen
contents and hence large supersaturation during cooling will promote the formation of Cr$_2$N; this transformation can be of the order of a few seconds. In the lower part of the TTT diagram formation of CrN occurs instead of Cr$_2$N. 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 Figure 1. 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 Cr$_2$N. Industrially, quenching is performed using high pressure gas quench with N$_2$ (or Ar) with pressures up to 20 bars.

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:

$$\frac{1}{2}N_2(g) = [N]_s$$  \[1\]

where the equilibrium constant of reaction 1 is written as:

$$K_N = \frac{a_N}{\sqrt{p_{N_2}^0}} \frac{p_{N_2}^0}{p_{N_2}}$$ \[2\]

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 (usually 1 bar). In an iron-based alloy the activity coefficient will deviate from unity according to:

$$\ln f_N = \ln f_N^0 \sum_j \varepsilon_j^{N} x_j$$ \[3\]

where $\varepsilon$ is the interaction parameter of nitrogen and the $j$ the alloying element with atomic fraction $x$.

Assuming equilibrium between nitrogen in the solid state and in the gas:

$$\mu_N^s = \mu_N^g$$ \[4\]

it then follows:

$$\frac{1}{2}G_{N_2}^0 - RT \ln p_{N_2} = G_N^0 + RT \ln a_N$$ \[5\]

After rewriting and substituting terms:

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

Hence, it follows directly that the “process parameters” governing the nitrogen solubility in the stainless steel are partial pressure of nitrogen gas, $p_{N_2}$ and temperature, $T$. It follows straightforwardly from Eq. 6 that increasing the partial pressure of N$_2$ leads to a higher nitrogen
content in the solid state. For a fixed pN₂ 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 it 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 gives rise 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 occurs in high pressure N₂; it follows directly from Eq. 6 that this procedure is problematic as the high pN₂ in the (short) cooling stage potentially can raise the nitrogen content in the surface region. Practically this implies that for a steel that is solution nitrided to a high nitrogen content (in the austenite region), relatively close to the solubility limit, a strong propensity to form surface and grain boundary nitrides exists 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 high pN₂ in the quench that further enhances the nitrogen content. Hitherto, this “problem” has largely been 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 of the material. A recent remedy to the problem is to use inert gas, viz. argon, in the quench state; this implies a pN₂ equal to nil, thus avoiding the formation of detrimental surface nitrides [8].

In the following different classes of stainless steels will be discussed with respect to HTSN.

2. Austenitic & duplex stainless steels

The isopleths of 3 different hypothetical austenitic stainless steels, with a composition close to AISI 316, are given in Figure 2. From the isopleths it is clear that the composition strongly influences the stability range of austenite and affects the solubility of nitrogen in austenite. HTSN is typically carried out at temperatures from 1050°C and up to 1150-1175°C; for the 16Cr alloy depicted in Figure 2 the material is stable austenitic up to 1235°C whereas the 20Cr alloy will be duplex in the same temperature interval. When nitrogen is introduced to the surface nitrogen stabilized austenite is obtained. Substitution of Ni with Mn is seen to increase the solubility of nitrogen in austenite and for a fixed pN₂ increase the nitrogen content, see Figure 2B. Commercial stainless steels, such as AISI 304 and AISI 316 will normally be stable austenitic at the applied HTSN temperature. Isobars are shown for different pN₂ and for the different isopleths for the alloys. Here it is evident that a higher pN₂ increases the nitrogen content - and the nitrogen content in austenite. 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).
The microstructural evolution in HTSN for an austenitic stainless steel is schematically depicted in Figure 3A. The initial austenitic microstructure is maintained at the HTSN temperature (although cold worked parts will recrystallize) and will experience grain growth. Concomitantly, nitrogen is dissolved in the austenitic surface leading to typical nitrogen contents in the range 0.1 - 1.0 wt% (see also isopleths and solubility of nitrogen in austenite in Figure 2). For most technical parts the high temperatures are associated with loss of strength due to removal of cold work, but this can to a large degree be compensated by the solid-solution hardening by nitrogen in the nitrogen rich austenite case. Moreover, the grain hardening effect (Hall-Petch relationship) becomes more prominent with increasing nitrogen alloying in austenite, which further mitigates the loss of strength by removal of cold work. The main effect of adding nitrogen to austenite is strongly enhanced corrosion performance, provided that nitrogen remains in solid solution during processing! Also cavitation erosion performance can be improved by HTSN. Another benefit is that nitrogen alloying does not have a negative impact on the ductility of the material.

The combination of HTSN and LTSH has recently been introduced as a commercial process [9] and exploits the benefit of having a thick load bearing case with excellent corrosion properties and without the presence of deformation-induced martensite (from cold working); the presence of deformation-induced martensite is highly detrimental for LTSH processes. The
concept is schematically shown for an austenitic stainless steel in Figure 3A and the resulting hardness depth profile of HTSN combined with LTSH is schematically shown in Figure 3B.

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. This concept is illustrated in Figure 4.

Figure 4 Schematic illustration of solution nitriding of duplex stainless steel. The surface is transformed into a case of nitrogen stabilized austenite. See schematic hardness depth profile in Figure 3.

The introduction of nitrogen will stabilize the austenite, which is also clear from the isopleth for the duplex stainless steel SAF2205 shown in Figure 5. At the HTSN temperature, e.g. 1150°C, the material without added nitrogen is ferritic-austenitic, but when 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 SAF2205 up to 1 wt% can be realized. Obviously, such high nitrogen contents in solid solution give rise to an increase in hardness (cf. Figure 3B) 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 interstitial 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 compositional inhomogeneity on the substitutional lattice can be observed in “youngest” part of the austenite case.

The microstructures of SAF2205 solution nitrided at 1150°C for 1 hour at two different partial pressures of nitrogen, pN₂ = 0.5 and 0.7, are given in Figure 6. The isobars are also indicated in Figure 5; 0.5 bar is within the austenite phase field, whereas 0.7 exceeds the limit for nitrogen solubility and should lead to formation of Cr₂N. From Figure 6 the nitrogen stabilized case is evident and the core still consists of ferrite and austenite. Due to the presence of two phases, grain growth in the duplex part of the material is largely hindered; grain growth does occur in the single phase austenite region (hardened case). Even for the high pN₂ of 0.7 bar there are no signs of Cr₂N formation in the surface region, as predicted from Figure 5. 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.
Figure 5 ThermoCalc. Isoplets for duplex stainless steel SAF2205. Isobars for two different partial pressures of nitrogen, $p_{N_2}=0.5$ and 0.7 are indicated in the figure.

Electrochemical polarization measurements in chloride containing solution show highly improved corrosion performance of the HTSN treated SAF2205 (not shown).

As for austenitic stainless steels the HTSN treated duplex materials can be combined with LTSH, i.e. 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.

Figure 6 LOM SAF 2205 duplex stainless steel solution nitrided for 1 hour at 1150°C. A) $p_{N_2}=0.5$ bar. B) $p_{N_2}=0.7$ bar. From [10].

3. Martensitic and ferritic stainless steels

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 Figure 7A. The process is normally associated with grain growth, leading to relatively 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. This poses a restriction as the nitrogen that can be added to the 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, that cannot be transformed into martensite, although cryogenic treatment can, to some extent, mitigate this problem [11].

For 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 martensitic stainless steel is shown in Figure 7B. The ferritic material 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.

![Figure 7 A) Schematic illustration of the microstructure of HTSN of martensitic stainless steel. B) Schematic illustration of (idealized) hardness depth profiles of HTSN of martensitic and ferritic stainless steel.](image)

An example of the microstructure of HTSN treated martensitic stainless steel AISI 410 is shown in Figure 8A, where a nitrogen containing martensitic case has formed and the core consists of carbon martensite. The gradient in the nitrogen content is reflected in the gradual transition of the microstructure, i.e. the nitrogen containing part etches less severely due to improved corrosion performance. As already mentioned above, HTSN can be combined with LTSH, which is also possible for martensitic stainless steels; such an example is shown in Figure 8B.
The LTSH (nitriding) process results in formation of 35-40 µm thick case (atop the pre-existing HTSN case) consisting of expanded martensite with a hardness reaching 1400 HV at the surface; see hardness profiles of the HTSN and HTSN+LTSH treatment in Figure 9. The LTSH treatment also functions as tempering of the martensite formed from the HTSN treatment. For the specific LTSH treatment shown in Figure 9 the thermal impact leads to a slight increase in hardness in the core of the material (without nitrogen), which can be attributed to secondary hardening. The secondary hardening effect is more pronounced for the nitrogen rich martensite (from HTSN) 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. It is also possible to temper the material prior to LTSH at a temperature higher than the 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 leads to formation of compressive residual stresses, which are beneficial for the fatigue performance of the material.

**Figure 8** Light optical microscopy of surface hardened AISI 410. HTSN: 1110°; \( pN_2 = 3 \text{ bar for 10 minutes} \) followed by \( pN_2 = 2 \text{ bar for 10 min}. \) LTSH: gaseous nitriding in flowing \( NH_3 \) for 30 hours at 390°C. A) HTSN; Kalling’s reagent. B) HTSN+ LTSN, Vilella’s etchant.

**Figure 9** Hardness depth profiles of surface hardened AISI 410. See corresponding micrographs and process conditions in Figure 8.
4. Summary and outlook

HTSN of stainless steels has hitherto experienced a niche role, but is gaining ground as an industrial process that 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, hence the steel remains fully austenitic (and 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 could be used to add strength whilst homogenizing the material. 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 corrosion performance from nitrogen in solid solution 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 achievable in stainless steels, as for example very high wear- and corrosion resistance combined with high load bearing capacity and high endurance limit. It is thus anticipated that HTSN will gain more and more ground in industry in the years to come.

References: