Solution Nitriding

A Cost-Effective Case-Hardening Process for Stainless Steels
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June 10, 2008

Stainless steels are applied in various industries to take advantage of their corrosion resistance. Unfortunately, the most corrosion resistant are not very durable in wear or load-carrying applications. Producing a nitrogen-enriched surface layer with increased hardness and higher residual stress increases the wear resistance and load-carrying capability in addition to improving the resistance to cavitation, erosion and corrosion attack.

Carburizing and nitriding of highly alloyed stainless steels in the normal temperature region between 500 and 1000°C (930–1830°F) is not possible without considerable loss of corrosion resistance. The reason for this is the very low solubility of these steels for nitrogen and carbon in the respective temperature range. This leads to chromium carbide and chromium nitride precipitations, which destroy the passive chromium-oxide layer.

Carburizing in the range of 800–1150°C (1470–2100°F) leads to the formation of carbides of the type Cr23C6 or Cr7C3. Nitriding between 480 and 900°C (900–1650°F) produces nitrides of the type CrN and Cr2N.
A possibility to avoid chromium carbide or nitride precipitations is the lowering of the carburizing or nitriding temperature to values that do not permit their formation. This is the case for the temperature range between 350 and 400°C (660–750°F). The processes Kolsterising[1] and Nivox[2] make use of this temperature range and with process times of 30–60 hours produce case depths of 10-30 µm.

The production of much deeper cases is only possible with the development of the new solution-nitriding process called SolNit®. The theory and metallurgical and process fundamentals were developed by Professor H. Berns and his colleagues at the University of Bochum.[3] Ipsen’s part of the work was the upscaling and industrialization of the technology.[4] This process uses the capability of highly alloyed steels with especially high chromium, manganese and molybdenum content that exhibit an increasing solubility for nitrogen in the temperature range above 1050°C (1920°F). The influence of the chromium content on the solubility of carbon and nitrogen for the temperature of 1100°C (2010°F) is shown in Fig. 1.[4]

**Process Technology**

![Equilibrium Diagrams](image)

Fig. 2. Examples of equilibrium diagrams of two stainless steels [3]
The process technology of the SolNit solution-nitriding process is comparatively simple. The process gas used is nitrogen instead of the standard nitriding gas – ammonia. Nitrogen is usually a protective atmosphere and has no nitriding capability. But at temperatures above 1050°C (1920°F), the otherwise stable nitrogen molecule dissociates at metallic surfaces into atomic nitrogen. Despite the passive chromium-oxide layer at the surface of stainless steels, the dissociated atomic nitrogen is able to penetrate the surface and produce a nitrogen pickup.

The achieved surface nitrogen content depends on three factors, which are:
- Alloy content of the stainless steel
- Nitriding temperature
- Partial pressure of the nitrogen gas in the furnace

According to Sieverts’ law, the surface nitrogen content (NS) is proportional to the square root of the partial pressure of the nitrogen gas.

\[ NS \sim \sqrt{PN_2} \]

According to Fick’s second law, the depth of the nitrogen penetration into the steel, \( \delta N \), is proportional to the square root of the nitriding time.

\[ N \sim \sqrt{t} \]

In order to achieve the highest nitrogen surface concentration possible, the nitrogen solubility limit of the austenite for the respective stainless steel and the envisioned nitriding temperature needs to be known. This is calculated for each stainless steel using the Thermo-Calc program. The solubility limits of two different stainless steels are shown in the equilibrium diagrams of Fig. 2.[3]

Typical process data of the SolNit process are:
- Temperatures between 1050 and 1150°C (1920–2100°F)
- Nitrogen partial pressure between 0.1 and 2.0 bar
- Diffusion times of 15 minutes up to 4 hours
With this range of process data, case depths of 0.2–2.5 mm can be achieved. The surface hardness of solution-nitried martensitic stainless steels usually lies between 54 and 61 HRC. For austenitic or duplex (austenitic-ferritic) steels, it is in the range of 200–350 HV.

Even though the solution-nitriding cycle may take several hours, the consumption of nitrogen gas is practically zero. Thus, the SolNit process is the only thermo-chemical process with basically zero process-gas costs, beating all the other low-pressure and even plasma processes.

There are two basic solution-nitriding processes:
- SolNit-M (for martensitic stainless steels)
- SolNit-A (for austenitic and duplex steels)

An important step of the SolNit process is the quenching. Because the nitrogen solubility of the austenite of stainless steels decreases at lower temperatures, the quenching of the workpieces must be sufficiently fast in order to avoid the precipitation of chromium nitrides. Quenching in oil or high-pressure gas is therefore necessary.

Figure 3 shows the main solution-nitriding cycle for martensitic stainless steels. The quenching produces a nitrogen martensite with high residual (retained) austenite. A subsequent cryogenic treatment and a tempering at temperatures up to 450°C (840°F) effectively reduce the retained austenite.

Because of the high temperatures applied, some grain growth appears. If, for a certain application, the ductility of the hardened martensitic case is of vital importance, the grain growth can be eliminated by a double hardening. The hardness after hardening is close to 600 HV and increases to above 700 HV – about 60 HRc – after subzero treatment and tempering at 450°C (Fig. 4).[3]
The SolNit process for austenitic steels is much simpler consisting only of heating, nitriding and quenching. The grain growth also exists with austenitic steels, but it cannot be refined by a thermal process. With the two-phase austenitic-ferritic steels (duplex steels), hardly any grain growth is experienced. Despite a large nitrogen pickup of the austenitic steels, the hardness increase is comparatively small (Fig. 5). It nevertheless results in some amazing property improvements.

**Property Enhancement**

With austenitic and austenitic-ferritic steels, the elevated surface nitrogen content, which can range up to 0.9 wt.%, can yield a pronounced corrosion-resistance improvement, reduced coefficient of friction and a reduction of the fretting tendency of the treated components.

The increased strength of the surface layer as depicted by a hardness increase of 50–150 HV results in an improved resistance to wear, cavitation and erosion. This has proven effective with components of fluid machines.

With martensitic stainless steels, the increased surface nitrogen content (without chromium-rich precipitations) also yields an increased corrosion resistance. The multiple increase of the surface strength by the formation of nitrogen martensite produces:
- A pronounced higher surface hardness
- A largely improved corrosion resistance
- Compressional stresses in the surface layer
- An increased fatigue strength
- A largely increased resistance to cavitation and erosion attack
- A pronounced increase of hot strength

These enhanced surface properties yield a large application range for martensitic stainless steels treated by the SolNit-M process for components of...
For both martensitic and austenitic stainless steels, the solution of nitrogen atoms in the chrome-oxide passive layer increases the stability of this layer. This reduces the passive current density in sulphuric acid and the resistance to salt-spray test and seawater for martensitic stainless steels significantly. SolNit-A-treated austenitic steels show an especially strong resistance to the attack of sulphuric acid.

**Installation Technology**

![Scheme of the single-chamber vacuum furnace TurboTreater® with high-pressure gas-quenching capability](image)

The high temperature – above 1050°C (1920°F) – used by the SolNit process and the nitrogen partial pressure, which can go as low as 0.1 bar, call for the usage of a vacuum furnace. Cold-wall vacuum furnaces with graphite hot chambers are the preferred choice. They are specially adapted to overcome the passivation problems connected with stainless steels.[4]

The quenching of the SolNit-treated components can be done directly in the vacuum furnace without a movement of the load by usage of the high-pressure gas-quenching technology. Single-chamber vacuum furnaces with high-pressure gas-quenching systems such as TurboTreater® (Fig. 6) and Turbo2Treater as well as VUTK are used for this process.

**Applications**
Stainless steels are mainly used in the following applications:

- Chemical industry
- Textile industry
- Food industry
- Machine building
- Architecture
- Household appliances
- Medicine

Within these fields, the following components have shown excellent behavior after SolNit treatment:

- Tools for plastic processing machines
- Components of gearboxes
- Bearings of jet turbines
- Pumps and valves of fluid machines
- Surgical instruments
- Cutlery
- Implants
- Sanitary accessories
- Membranes

Out of this large variety, three applications of the industrial utilization of the SolNit process are discussed.[5]
Figure 7 shows gear wheels with a diameter of 130 mm (5.12 inches) and a module of 2.5 produced from the material X15C13 (AISI 416). The SolNit-M treatment at 1100°C (2010°F) with a nitriding time of 60 minutes produced a nitriding depth of 0.6 mm. After a cryogenic treatment at -40°C (-40°F) and a subsequent temper at 150°C (300°F), the surface-hardness values reach 50 HRC with core hardness of 46 HRC.

Figure 8 shows nozzles made from the material X14CrMoS17 (AISI 429F). They are treated at 1150°C (2100°F), subzero treated at -80°C (-112°F) and tempered at 150°C (300°F). Surface hardness is about 655 HV10, and the nitriding depth is roughly 0.7 mm (0.028 inches). The uniformity of the nitriding effect of the SolNit process can be very well documented as the results of full production loads of these nozzles show. The small injection holes in these nozzles have a diameter of only 0.3 mm, and all surface areas of the nozzles also in the small injection holes show an extremely uniform deep nitriding.

Figure 9 shows regulating membranes made from the austenitic steel DIN 1.4435 (AISI 317). They are used in valves for food-processing machines. They formerly were solution annealed and chromium coated, but their lifetime was not satisfactory. Using a SolNit-A-treatment increased the lifetime of these parts substantially. A 2.5-hour treatment at 1100°C (2010°F) produces a surface hardness of about 230 HV and a core hardness of 150 HV. The depth of nitriding is about 0.8 mm (0.031 inches).
The newly developed solution-nitriding process for stainless steels produces a high nitrogen-containing surface layer at elevated temperatures. It is also the first process capable of producing deep cases of up to 2.5 mm (0.1 inches) on stainless steels.

There are basically two different process technologies used depending on the type of stainless steel. For austenitic or partially austenitic (duplex) steels, the process cycle consists of nitriding and quenching only, whereas for martensitic stainless steels a subzero treatment and a temper are added.

Producing a nitrogen-enriched surface layer with increased hardness and higher residual stress increases the wear resistance and load-carrying capability in addition to improving the resistance to cavitation, erosion and corrosion attack.

The solution-nitriding process requires clean and tight vacuum furnaces. It is non-toxic, non-explosive, works with zero process-gas flow and therefore produces no wastes. This new process improves the utilization of stainless steels and largely improves the performance of components manufactured from them.
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References