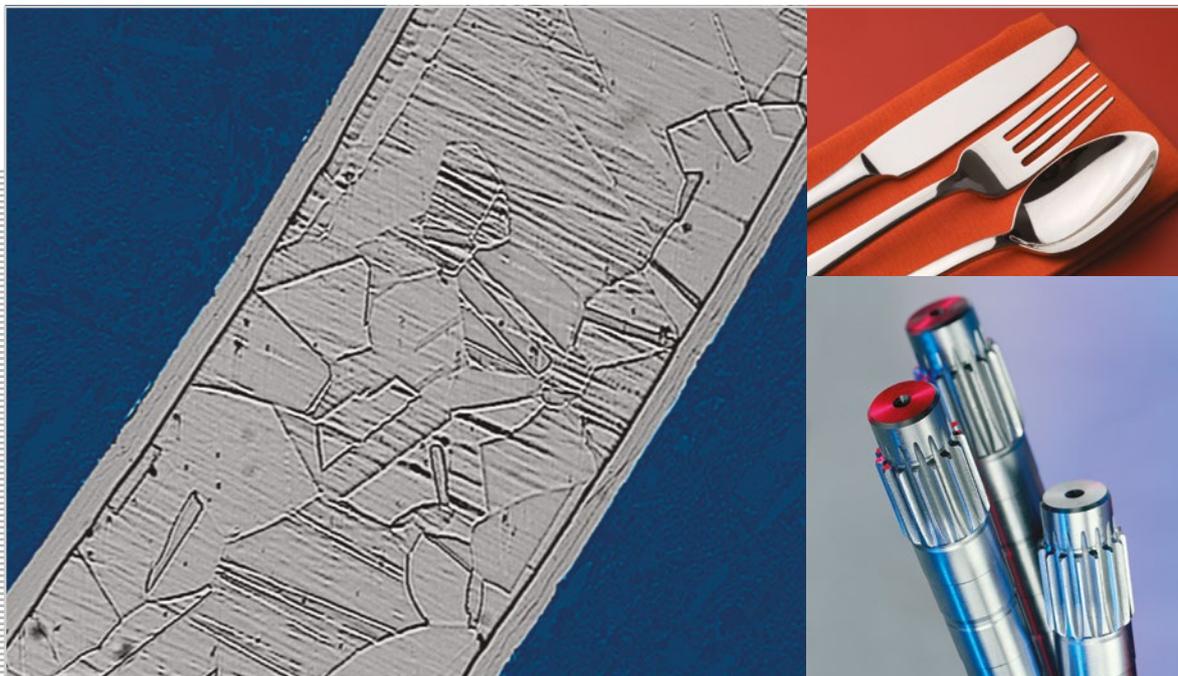


Surface Hardening of Stainless Steels



Euro Inox

Euro Inox is the European market development association for stainless steel. Members of Euro Inox include:

- European stainless steel producers;
- national stainless steel development associations;
- development associations of the alloying element industries.

The prime objectives of Euro Inox are to create awareness of the unique properties of stainless steel and to further its use in existing applications and in new markets. To achieve these objectives, Euro Inox organises conferences and seminars and issues guidance in printed and electronic form, to enable architects, designers, specifiers, fabricators and end users to become more familiar with the material. Euro Inox also supports technical and market research.

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1 Introduction

Scratch resistance of the surface is often requested for high-visibility applications.



Stainless steel is widely used in applications in which corrosion resistance is of high importance. In many end-uses, the material is also expected to have a hard, scratch-resistant surface. When improved wear resistance is required, surface engineering provides solutions. Industrially proven processes are available that improve surface hardness, scratch and wear resistance.

Properties most often expected from surface hardening [1, 2]:

- scratch resistance
- surface hardness above 900 HV_{0.05}
- unchanged corrosion resistance
- reduced friction coefficient
- no dimensional change
- minimal or no change in visual appearance
- no cracking or flaking of the hardened layer
- minimal or no change in surface roughness
- no pre-treatment
- no post-treatment
- enhanced lifetime and reduced downtime and costs
- weldability
- suppression of fretting/galling (adhesion)

Surface hardening provides surfaces for different consumer products and ensures that stainless home appliances, household objects, cutlery and highly exposed objects maintain their pleasing appearance and durability. It is also necessary in industrial applications where exceptional wear resistance combined with corrosion resistance are needed. A wide range of such applications can be found in [1, 2, 3, 4, 5]:

- consumer goods
- household appliances
- food and beverage industry
- mobile devices
- industrial fluid handling
- industrial and consumer fasteners
- valve and pump parts
- medical applications
- marine applications
- automotive components
- axis and rotating parts

Surface hardening can be used in many different areas, from building and architecture to the food and beverage industry. Photo: Heat & Surface Treatment, Eindhoven (NL)



2 Principle

Surface hardening includes a wide variety of techniques. Most often it is used to improve the wear resistance of parts without affecting the softer, tough base material necessary to resist impact occurring during operation.

Wear involves the physical removal of material from a solid object. It can be divided into three categories: abrasive, adhesive and fatigue wear.

Abrasive wear is when two surfaces rub together and the harder surface grinds away the softer. It can be characterized by a rough appearance. Often, work hardening of the surface can occur.

Adhesive wear, like abrasive wear, is caused by loaded surfaces rubbing together. With adhesive wear, high localized temperatures are created by friction at the tips of opposing asperities on rubbing surfaces. These tips can deform and “weld” together, due to localized temperatures. They either break and fall away as debris or are cold-welded together.

Fatigue wear occurs whenever a surface is subjected to repeated high-stress load. Wear rates are less affected by temperature than is corrosion [6].

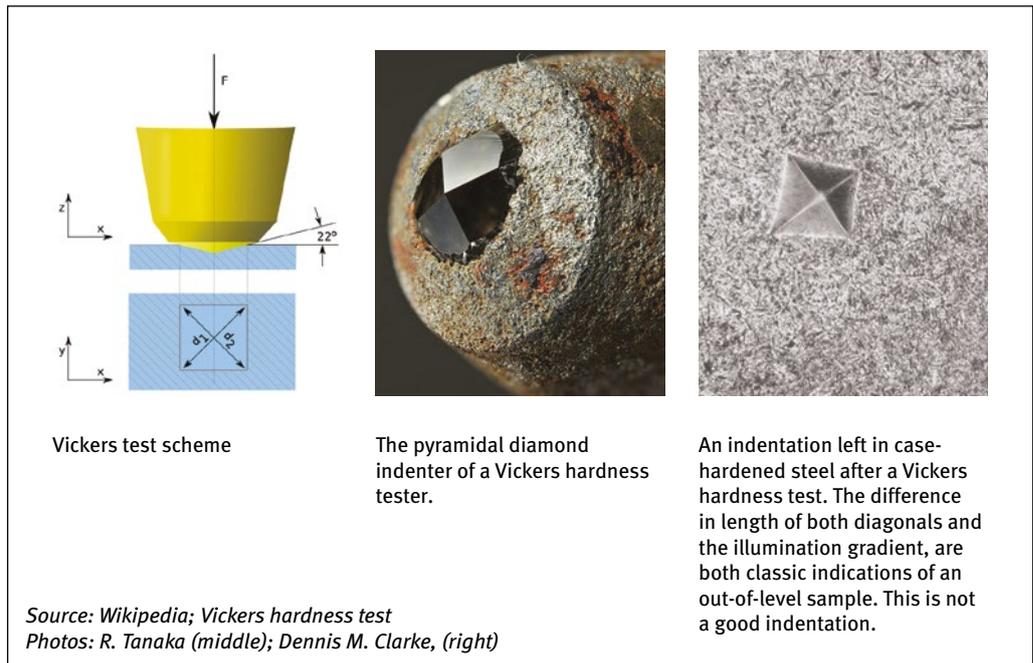
There are three distinctly different approaches to the various surface-hardening methods [7]:

1. Thermochemical diffusion methods, which modify the chemical composition of the surface with hardening species such as carbon, nitrogen and boron. Diffusion methods allow effective hardening of the entire surface. They can be used for both single parts and batches.
2. Applied energy or thermal methods, which do not modify the chemical composition of the surface but rather improve properties by altering the surface structure – that is they produce a quench-hardened surface, without additional alloying species. They can be used to harden the entire surface or only part of it (selective surface-hardening).
3. Surface coating or surface-modification methods, which involve the intentional build-up of a new layer on the steel substrate.

Various process methods for the surface hardening of steels are shown in Table 1. These long-established techniques are continually improved and remain among the most widely applied ones. This publication discusses the most important surface-hardening methods used on stainless steels (marked in italics in the following table).

Table 1. Process methods for the surface hardening of steels [7]

Diffusion methods	Coating and surface modification
<i>Carburising</i>	Hard chromium plating
<i>Nitriding</i>	Electroless nickel plating
<i>Nitrocarburising</i>	Thermal spraying
Carbonitriding	Weld hardfacing
<i>Boriding or boronising</i>	Chemical vapour deposition
Thermal diffusion process	Physical vapour deposition ¹
Applied energy methods	Ion implantation
Flame hardening	Laser surface processing
<i>Induction hardening</i>	
Laser-beam hardening	
Electron-beam hardening	



¹ Physical vapour deposition is discussed in the Euro Inox publication *Colouring Stainless Steel, Materials and Applications Series, Volume 16*, http://www.euro-inox.org/pdf/map/ColouringStainlessSteel_EN.pdf

3 Thermochemical diffusion methods

Traditional thermochemical treatment on stainless steel is associated with a loss of corrosion resistance as nitrogen and carbon react with chromium to form carbides/nitrides, thus withdrawing chromium from solid solution. In the case of stainless steels, hardening by thermochemical treatment has been considered bad practice or a compromise between corrosion proper-

ties and tribological properties [8]. Some recently developed processes, in contrast, do not diminish the corrosion resistance of stainless steels.

Table 2. Typical characteristics of thermochemical diffusion treatments for stainless steels [7, 8]

Process	Name of case	Process temperature °C	Typical case depth µm	Case hardness HV	Process characteristics
Nitriding/Carburising/Nitrocarburising					
Gas	Diffused nitrogen and/or carbon compounds	380–600	10–200	750–1600	Hardest cases from nitriding steels, low distortion, bulk batches possible, flexibility, high repeatability, low distortion; however, nitriding can produce brittle layers
Ion	Diffused nitrogen and/or carbon compounds	380–600	10–200	750–1600	Close case control, good controllability of layer formation, suitable for large parts, local treatment possible, good process control, high equipment cost
Other					
Boriding or boronising	Diffused boron, boron compounds	700–1000	10–50	1500 to over 2800	Produces a hard diffusion layer, high process temperature can cause distortion, possible loss of corrosion resistance



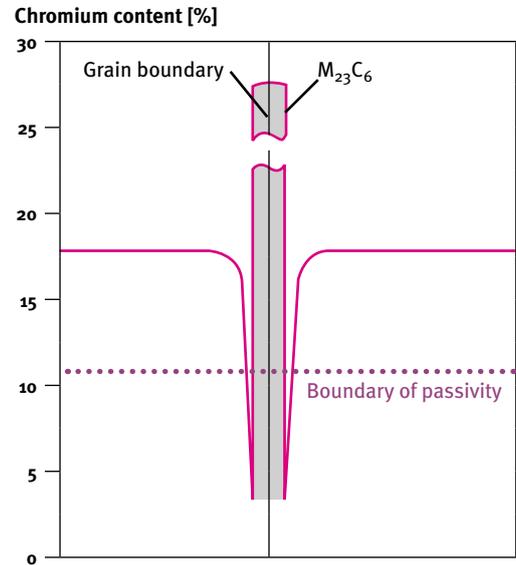
Photo: Heat & Surface Treatment, Eindhoven (NL)

3.1 Carburising

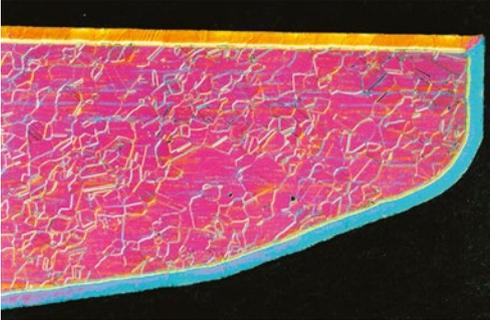
Stainless steels can be carburised to improve surface hardness and resistance to galling. During the carburising process, the carbon atoms diffuse through the surface at high temperatures and have the affinity to react with the chromium present in stainless steels. They can form chromium carbide (Cr_{23}C_6). This process is known as sensitisation. Some chromium could therefore be lost and eventually corrosion resistance reduced. Conventional carburising has mostly been replaced by nitridation, which does not incur problems of sensitisation [10].

Sensitisation occurs when the material is heated to the 600–800 °C temperature range. At these temperatures, chromium and carbon diffuse to the grain boundaries to form type Cr_{23}C_6 chromium carbides. As the carbides form, chromium is depleted from the base material but is considerably increased at the grain boundaries. In areas with a low chromium level, the chromium content is below that of the bulk alloy, making these areas susceptible to corrosion.

Some industrially proven processes work at lower temperatures. They have a hardening effect without affecting the original corrosion resistance - providing the base material is of good quality. No coating is applied to the surface, but a carbon-rich (up to 2–3 % weight rate) diffusion zone is produced from the surface inwards, with excellent toughness and no risk of delamination or peeling. It is low-temperature carburising, at a diffusion temperature below 450 °C. The process



increases the surface hardness of most austenitic stainless steels to a level of about 1000–1200 $\text{HV}_{0.05}$, which is about five times the original hardness. High compressive stresses are formed on the surface, due to interstitial solution of carbon atoms. All austenitic stainless steels can be hardened using this process. The process has also been successfully applied to duplex and precipitation hardening stainless steel grades. Materials to be treated by low-temperature carburising should be in the solution annealed condition. Sharp edges, the inside of bores and gaps present no limitation to the process [4, 11, 12, 13].



Uniform hardening of sharp edges can be achieved with a carburised layer. Photo: Bodycote Hardiff, Düsseldorf (D)

3.2 Gas nitriding

Gas nitriding is a case-hardening process whereby nitrogen is introduced into the surface by holding the steel at a suitable temperature in contact with a nitrogenous gas, usually ammonia. Quenching is not required for the production of hard case. The nitriding temperature for most steels is between 500 °C and 550 °C. Although nitriding, similarly to carburising, adversely affects corrosion resistance, it increases surface hardness and provides a lower coefficient of friction, thus improving abrasion resistance. Before being gas nitrided, austenitic stainless steels and ferritic steels should be annealed and relieved of machining stresses (as recommended also before carburising). Normal annealing treatments generally employed to obtain maximum corrosion resistance are usually adequate. Martensitic steels should be in the quenched-and-tempered condition² [9].

Alloying elements such as chromium and molybdenum are beneficial in nitriding, since they form nitrides that are stable at nitriding temperatures. Because of their chromium content, all stainless steels can be nitrided to some degree [9]. However, the high chromium content of some stainless steels makes them more difficult to nitride. This is because chromium forms a passive layer on the stainless steel surface, which has to be removed before nitriding. Once the passive film is broken down (by dry honing, wet blasting, pickling, chemical reduction in a reducing atmosphere, submersion in molten salts or one of several proprietary processes), nitriding is effective. The positive side of this is usually a high surface-hardness value. Other alloying elements, such as nickel, copper and manganese, have little if any effect on nitriding characteristics [7]. Nitridable stainless steels are:

- **Martensitic stainless steels.** The hardenable martensitic stainless steels are capable of providing high core strength to support the nitrided case. Hardening, followed by tempering at a temperature at least 15 °C higher than the nitriding temperature, should precede the nitriding operation.
- **Austenitic stainless steels.** Austenitic stainless steels are the most difficult to nitride. Nevertheless most can be successfully nitrided [9]. If nitrided, parts must be in the annealed condition, to prevent flaking or blistering of the nitrided

² More information on specific heat treatment conditions of different stainless steels can be found in the Euro Inox publication *Stainless Steels: Tables of Fabrication Parameters, Materials and Applications Series, Volume 17*, http://www.euro-inox.org/pdf/map/Tables_Fabrication_Parameters_EN.pdf

case. Stabilised or low-carbon grades are recommended for nitriding, for the obvious reason that the nitriding temperature of approximately 540 °C is in the sensitising range. The nitrided case that can be achieved on austenitic grades is very thin and seldom above 0.125 mm. In addition, it seriously impairs resistance to corrosion in most media. Nitriding austenitic stainless steels is therefore only carried out for highly specialised applications – for example, when the material must be non-magnetic and still have an abrasion-resistant surface [14].

- **Ferritic stainless steels.** Ferritic stainless steel grades are non-hardenable by conventional heat treatment methods. However, the grades on which surface hardening can be successfully applied include 1.4016 (430) and 1.4749 (446).
- **Precipitation-hardening stainless steels.** Steel grades such as 1.4542, 1.4548 (17-4 PH), 1.4564, 1.4568 (17-7 PH), 1.4545 (15-5 PH), 1.4980 (A-286) can be successfully nitrided.

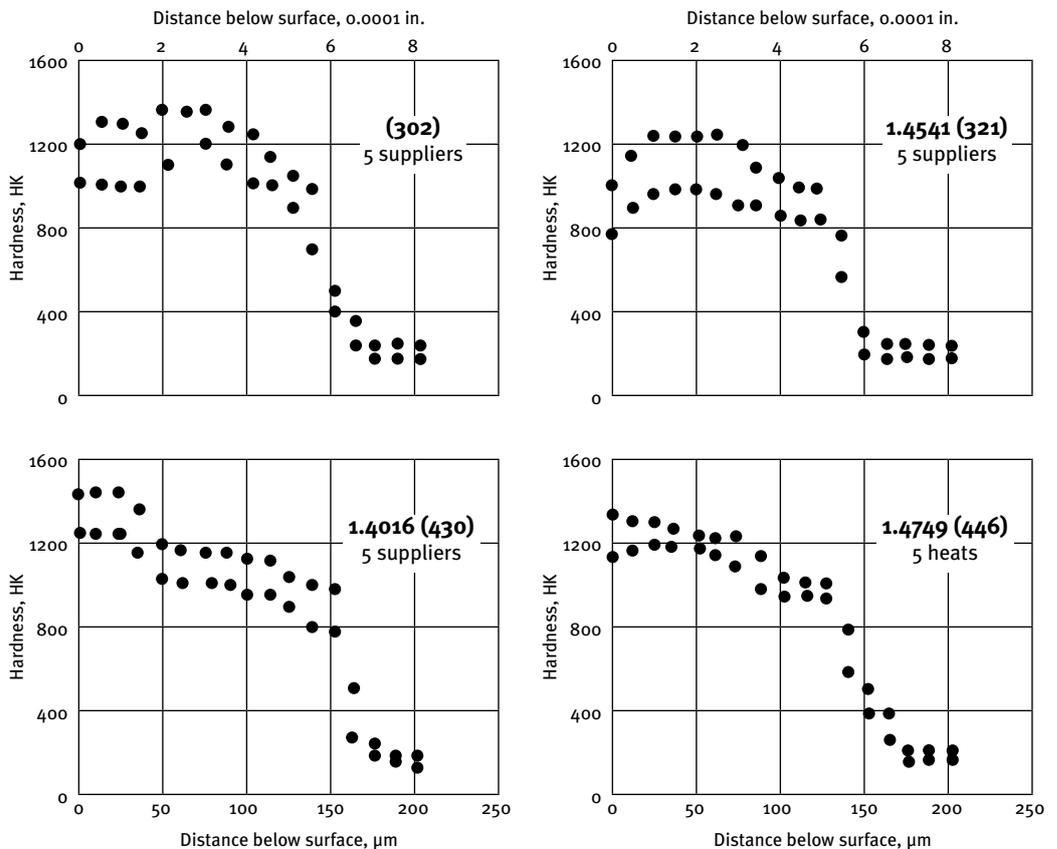


Figure 1. Hardness related to case depth for four stainless steels that were annealed prior to nitriding. The annealing temperature was 1065 °C for steel grades 302 and 1.4541 (321), 980 °C for steel grade 1.4016 (430) and 900 °C for steel grade 1.4749 (446). Hardness is measured in Knoop values [9].

Table 3. Surface hardness ranges and case depth for some corrosion-resistant and acid-resistant steels [7]

Steel designation			Hardness HV	Nitride hardness depth mm
EN Number	EN Name	Approximate AISI/ASTM		
1.4028	X30Cr13	420	950–1200	0.2 max.
1.4104	X14CrMoS17	-	950–1200	0.2 max.
1.4112	X90CrMoV18	440 B	950–1200	0.2 max.
1.4117	X38CrMoV15	-	950–1200	0.2 max.
1.4301	X5CrNi18-10	304	950–1600	0.2 max.
1.4305	X10CrNiS18-9	303	950–1600	0.2 max.
1.4401	X5CrNiMo17-12-2	316	950–1600	0.2 max.
1.4535	X90CrCoMoV17	-	950–1600	0.2 max.

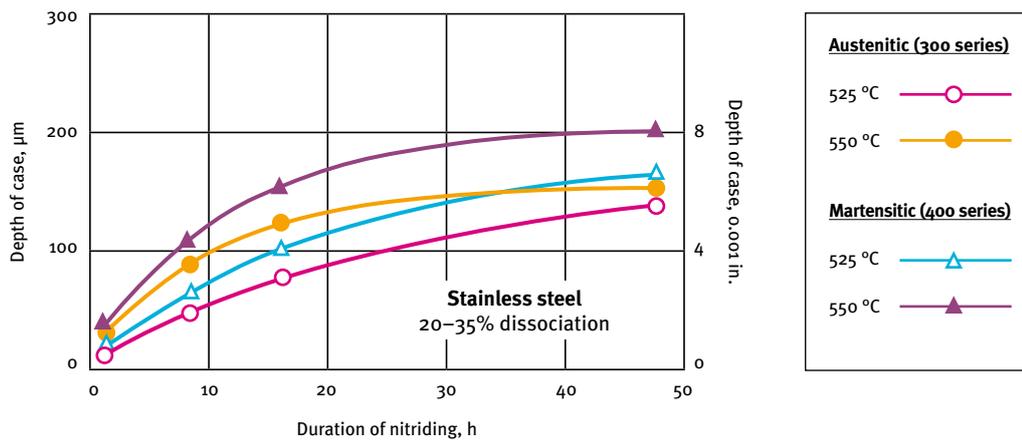


Figure 2. Comparison of the nitriding characteristics of austenitic (300 series) and martensitic (400 series) stainless steels, single-stage nitride at 525 °C and 550 °C [9]

3.3 Plasma (ion) nitriding and liquid nitriding

Plasma (or ion) nitriding is a method of surface hardening that uses glow-discharge technology to introduce elemental nitrogen to the surface of a metal part, for subsequent diffusion into the material. In a vacuum, high-voltage electrical energy is used to form plasma, through which nitrogen ions are accelerated to impinge on the workpiece. This ion bombardment heats the workpiece, cleans the surface and provides active nitrogen. It actually avoids the need to remove the passive layer, as this is removed by sputtering prior to the nitriding phase. Ion nitriding provides better control of case chemistry and uniformity and has other advantages, such as lower part distortion than conventional gas nitriding. For most ferrous alloys, the diffusion zone formed by nitriding cannot be seen in a metallographic image, because the coherent precipitates are generally not large enough to resolve. In stainless steels, the chromium level is high enough for extensive nitride formation, which can be seen in etched

cross-sections [9]. However, it should be noted that the presence of chromium nitrides is also an indicator of reduced corrosion resistance. This process is particularly suitable for stainless steels.

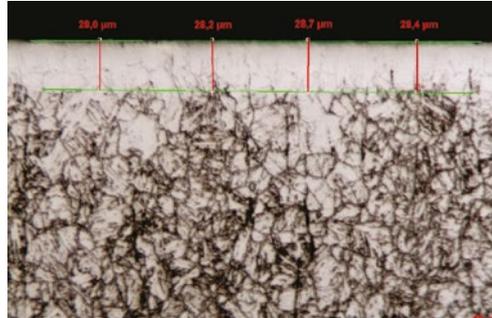
Liquid nitriding is performed at temperatures above 500 °C in a molten, nitrogen-bearing, fused-salt bath containing either cyanides or cyanates. Cyanide-free liquid nitriding salt compositions have also been introduced. However, in the active bath, a small amount of cyanide, generally up to 5 %, is produced as part of the reaction. This is a relatively low concentration and these compositions have gained widespread acceptance within the heat-treating industry because they contribute substantially to the alleviation of a potential source of pollution. Liquid nitriding treatments result in some loss of corrosion resistance because the formation of nitrides and carbides depletes adjacent matrix areas. Corrosion data based on weight loss indicates that in some cases liquid-nitrided stainless steels face some loss of corrosion resistance. However, these materials remain largely superior to untreated carbon and low-alloy steels [9].

In stainless steel cutlery, surface hardening is available as an option to improve wear resistance. Photo: WMF, Geislingen (D)



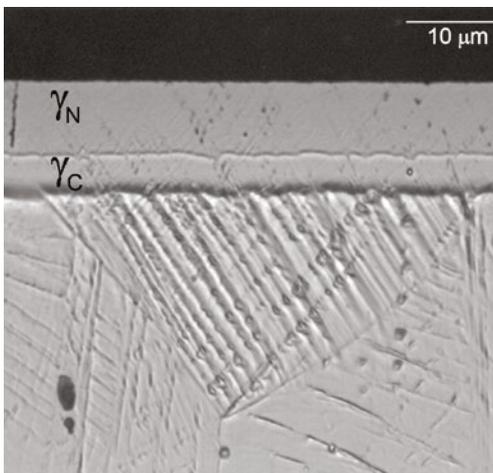
3.4 Nitrocarburising

Some gas-based and plasma-based processes dissolve carbon and/or nitrogen atoms in the surface region of the material. Dissolution of carbon and nitrogen atoms is possible due to their smaller size compared to the alloy metal atoms. As in the previously described processes, the surface hardening results not in a coating but in a surface zone with a high concentration of carbon and/or nitrogen [1, 2, 3]. Large amounts of atomic nitrogen and/or carbon dissolve in stainless steel at temperatures below approximately 400–500 °C, expanding the original microstructure. The thickness of the zone is approximately 20–40 μm. Expanded austenite surfaces are four to eight times harder than those of the base material. Along with the increase in hardness and wear resistance, corrosion resistance is fully maintained [15, 16].

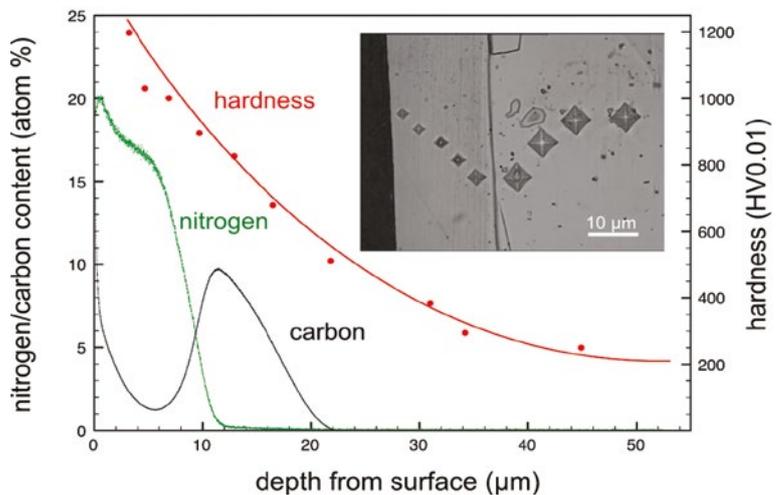


Cross-section of low-temperature nitrocarburised precipitation-hardening stainless steel. Photo: Bodycote Hardiff, Düsseldorf (D)

The outer zone is richer in nitrogen and the inner one in carbon. The thickness of each zone can be influenced by gas composition – i.e. by modifying the nitrogen and carbon content in the gas. The combinations of thickness of each zone allow different material properties to be achieved. Gas-based and plasma-based processes enable nitriding, carburising or nitrocarburising to be employed, depending on requirements.



Cross section of nitrocarburised stainless steel (left), depth profile (right). Photo: Expanite, Hillerød (DK)



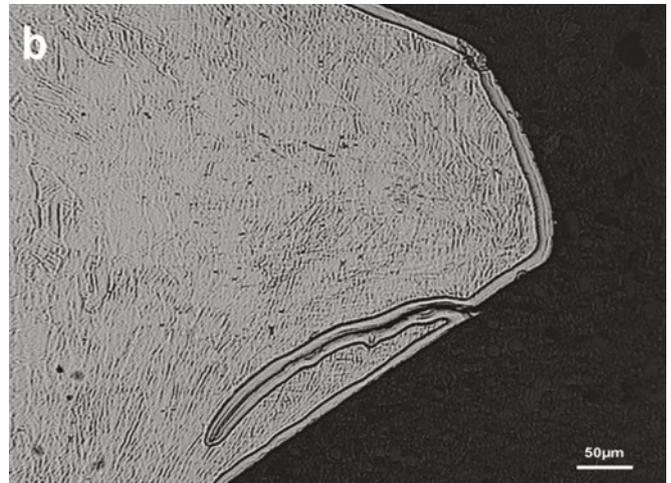
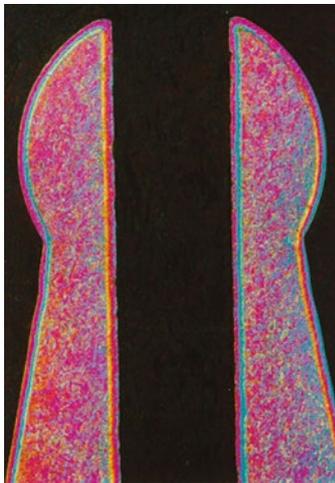
Surface hardening can be used also on the objects like watch cases. Photo: Askania, Berlin (D)



It is also possible to nitrocarburise martensitic stainless steels. Grade 1.4057 (431), treated for 75 minutes, yielded a case approximately 20 μm thick with a surface hardness higher than 1800 HV. Depending on other process parameters, the hardened zone can be tailored – i.e. it is possible to obtain expanded austenite, however, the principle can also be applied to martensitic and precipitation hardening grades. As a consequence of the very high surface hardness, the surface is virtually scratchproof [15]. Expanded austenite is a metastable phase

and tends to decompose upon prolonged exposure to higher temperatures [16]. Nitrocarburising should not be confused with carbonitriding, which is a higher temperature process used for low-carbon steels.

Nitrocarburising can also be successfully applied in small bores and even in very small cavities. Photos: Bodycote Hardiff, Düsseldorf (D) left and Expanite, Hillerød (DK) right



3.5 Boriding or boronising

Boriding or boronising is a thermochemical process in which boron atoms are diffused into the surface of a workpiece to form complex borides with the base metal. It is a diffusion-controlled process. In addition to nickel, titanium, cobalt alloys and cemented carbides, nearly any ferrous material can be boronised. It should be noted that the diffusion rate slows down with higher-alloyed steels.

Because of their high hardness, boronised steels are extremely resistant to abrasion and their service life can be significantly increased. The process uses boronising agents such as powders, granulates of various grain sizes and pastes, which are commercially available. The diffusion layer thickness is in a range of 20–200 μm depth, depending on the requirements of the parts. In the case of austenitic stainless steels, layers are much thinner. Due to the similar thermal expansion coeffi-

cient, boronised steel parts can be vacuum hardened afterwards to achieve the desired mechanical properties of the base material. The process temperature for boronising depends on the material grade and lies between 700 °C and 1000 °C. To minimize distortion, a stress-relieving treatment can be carried out after machining and prior to boronising. Other heat treatments before boronising, such as quench-hardening, should not be performed, since the boronising process removes the results of a pre-heat treatment [5, 17]. Where dimensional accuracy (exactness of fit) is paramount, the workpiece must be undersized during manufacturing, since the boride layer will add 20–30 % of its thickness to the size of the part [5]. Because of the process temperature in the range of 700–1000 °C, unwanted precipitates (sigma phase) are, however, possible.

Table 4. Proven applications for boronised steels [7]

Steel designation			Applications
EN Number	EN Name	Approximate AISI/ASTM	
-	-	302	Screw cases, bushes
1.4401	X5CrNiMo17-12-2	316	Perforated or slotted-hole screens, parts for the textile and rubber industries
1.4006	X12Cr13	410	Valve components, fittings
1.4031	X39Cr13	420	Valve components, plunger rods, fittings, guides, parts for chemical plants

4 Applied energy methods

Surface hardening by applied energy includes conventional thermal treatments such as induction hardening and flame hardening and high-energy treatments, such as laser or electron beams. All these methods can be classified as thermal treatments without chemistry changes. The modification of the surface is done by austenitising the steel followed by fast cooling, which leads to the formation of martensite. The entire surface of the application can be treated, or only a part of it. When the heating is done locally, the treatment is called selective surface hardening [7].

4.1 Induction hardening

The induction hardening process is used to increase wear resistance, surface hardness and fatigue life through the creation of a hardened surface layer, while maintaining an unaffected core microstructure. The parts to be heat-treated are placed inside a copper coil then heated above their transformation temperature by applying an alternating current to the coil. The alternating current in the coil induces an alternating magnetic field within the workpiece, which

causes the outer surface of the part to heat to a temperature within or above the transformation range. The process is followed by immediate quenching. It is an electromagnetic process, using a copper inductor coil fed a current at a specific frequency and power level.

Only martensitic stainless steels can be hardened using this process. Induction hardening is favoured for components subjected to heavy loading, especially parts that experience torsional loading and surfaces that experience impact forces. Typical applications of induction-hardening include gears, shafts, spindles – mostly symmetrical parts [18].

Table 5. Induction-hardenable stainless steels and their approximate induction austenitising temperatures

Steel designation			Carbon, in mass %	Austenitising temperature °C
EN Number	EN Name	Approximate AISI/ASTM		
1.4005	X12CrS13	416	< 0.15	1065
1.4021 1.4028 1.4031 1.4034	X20Cr13 X30Cr13 X39Cr13 X46Cr13	420	> 0.15	1065
1.4125	X105CrMo17	440C	0.95–1.20	1065

5 Costs

Cost must be weighed against the performance required from the surface-treatment system. A low-cost surface treatment that fails to perform its function is a wasted expense. Unfortunately, it is nearly impossible to give absolute comparative costs for different surface-engineering options. Probably the most important factor concerning the cost of producing a wear-resistant surface on a part is part quantity. Treating many parts usually allows economies in treatment and finishing. Another consideration when assessing surface-treatment costs is part size. There are critical sizes for each surface-treatment process above which the cost of obtaining the treatment may be high. Other factors to be considered are:

- the time required for a given surface treatment
- fixturing, masking and inspection costs
- final finishing costs
- material costs
- energy costs
- labour costs
- environment-related costs (for example, disposal of spent solutions)
- expected service life

Because of these various factors, it is difficult to compare costs with a high degree of accuracy [7].



Surface hardening can also be applied to complex parts with recess areas. Photo: Heat & Surface Treatment, Eindhoven (NL)

6 Summary

There are several processes by which the surface of stainless steels can be successfully hardened [19]. These processes not only improve the hardness of the surface but also increase the material's scratch and wear resistance. Such surfaces are also used in applications where galling is an issue or cutting edges are required (for example, in medical equipment). All processes showed in this publication are based on altering the original surface without an additional layer being applied, which might peel or wear off.

It is common belief that surface-hardening techniques diminish the original corrosion resistance of stainless steels. The latest techniques developed show that this is no longer the case and that corrosion resistance can be retained. Services are available from specialised companies, some of them offer also plug-and-play technologies.



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