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Gas Nitriding

Related terms:

Residual Stress, Carburizing, Nitriding, Ammonia, Nitrogen, Hardness, Plasma Nitriding, Expanded Austenite, Nitriding Process

Laser Machining and Surface Treatment

P. Schaaf, … D. Höche, in Comprehensive Materials Processing, 2014

9.13.2.1 Gas Nitriding

Gas nitriding, together with carbonitriding or nitrocarburization, if a carbon-delivering medium is also added, are the most used industrial processes. Millions of tons per year (43) are treated this way and many efforts are made for their optimization (44,45). Although the thermodynamics of the reactions are well described, the exact mechanisms during gas nitriding are still not fully understood. The practical control of the process is still based on the empirical and theoretical results developed in the 1930s (46,47). Gas nitriding uses ammonia or ammonia–hydrogen mixtures to enhance the nitrogen activity. Ammonia easily dissociates into gaseous nitrogen and hydrogen according to the chemical equilibrium.

ZeroFlow gas nitriding of steels

L. Maldzinski, J. Tacikowski, in Thermochemical Surface Engineering of Steels, 2015

Abstract

Gas nitriding using the ZeroFlow method is discussed in this chapter. This method was created on the basis of thermodynamical, kinetic and technological research on the nitriding of steel. The process is carried out using pure ammonia and regulation of the flow, and hence the chemical composition of the atmosphere in the retort, which in turn regulates the growth kinetics of the nitrided layer. ZeroFlow nitriding enables the precise creation of nitrided layers in terms of the required phase structure, thickness of existing layers and character of nitrogen concentration and hardness. ZeroFlow nitriding is characterized by an ammonia consumption that is several times lower than in other currently used processes for controlled nitriding. As a consequence several times lower emission of exhaust gases to the atmosphere is achieved. Furnaces equipped with ZeroFlow nitriding technology require simpler and cheaper exhaust gas regulation and control systems. Industrial experience of nitriding machine and automotive parts and tools using this method has confirmed its advantages.

Surface Engineering Processes

K.G. Swift, J.D. Booker, in Manufacturing Process Selection Handbook, 2013

Process Variations

- Gas Nitriding: the part is heated in dry ammonia gas (NH_3) at temperatures up to 530°C. The nitrogen dissociates, resulting in atomic nitrogen diffusing into the part surface. Slow process taking up to 80 hours, which is more suited to low volumes.

- Salt Bath Nitriding: preheated part is immersed in a bath of molten salts of sodium cyanide at a temperature of up to 570°C. For low volumes due to long treatment times.

- Plasma Nitriding: part is made the cathode and the reactor wall is the anode. Positively charged nitrogen ions from a plasma bombard the part, causing nitrogen to be absorbed into the surface. Lower temperature process down to 340°C caused by ion bombardment on part. Good process control of thickness treatment and faster process more suitable for highly complex parts.

- Nitrocarburising: nitrogen and carbon diffused into the surface using gas, salt bath or plasma technologies. Higher temperature process variant at 570°C and achieves only small depths of treatment in low carbon steels and cast irons.

Scratching of Materials and Applications

A.P. Tschiptschin, ... D.M. Lopez, in Tribology and Interface Engineering Series, 2006

CONCLUSIONS

1 - High temperature gas nitriding strongly improves the scratch resistance of UNS S30403 austenitic SS. Increasing the nitrogen content in solid solution up to 0.5 wt-% leads to an increase in the specific energy from 1770 to 3540 J/g. This can be attributed to the strong hardening effect of nitrogen in solid solution, which does not affect work hardening and toughness significantly.

2 - A linear correlation between the mass loss rate during vibratory cavitation, measured in a previous work, and the machinability (inverse of the specific energy) of high temperature gas nitrided UNS S30403 austenitic SS was observed.

3 - The single pass scratch test is suitable to assess the performance of case hardened HTGN SS, submitted to dynamic contact and cutting stress allowing to measure the abrasion resistance and to estimate the cavitation erosion resistance of these steels.

Process technologies for thermochemical surface engineering

K.-M. Winter, ... D. Koshel, in Thermochemical Surface Engineering of Steels, 2015

3.14 Fluidised bed nitriding
3.14.1 General description
From the technological point of view, nitriding and ferritic nitrocarburising in a fluidised bed are essentially equivalent to all other types of gas nitriding processes. The major difference is the use of a furnace designed for a fluidised bed filled with particles.

3.14.2 Equipment

Fluidised bed furnaces (see Figure 3.35) can be adapted to many heat-treatment processes such as neutral hardening, tempering, carburising and nitriding. The range of temperatures is very wide, up to 1040°C. There are different types of fluidised bed furnaces: those that are externally gas-fired and electrically heated are common, but for some applications furnaces with submerged combustion are used. In nitriding applications (as well as oxinitriding and ferritic nitrocarburising) the most common furnaces are externally heated. This type of vessel is fitted with a refractory alloy retort. The process gas is supplied through a diffuser plate in the bottom of the furnace, below the work rack support. The retort is partially filled with a bed of dry, fine particles, usually aluminium oxide
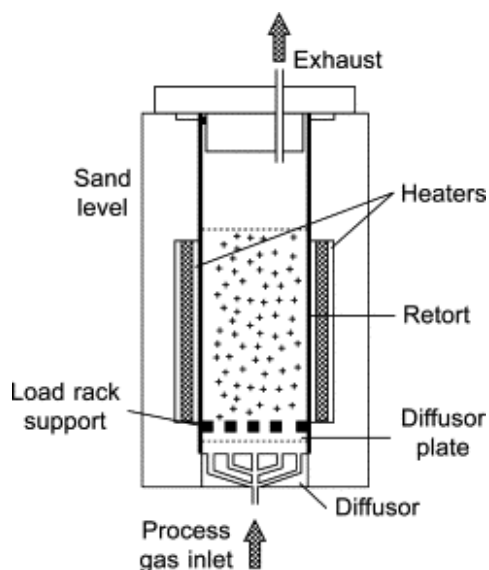

Figure 3.35. Schematic drawing of a fluidised bed furnace.

During the operation, gas is introduced through the bottom diffusion plate. As it moves upward through the fine particles, the bed unlocks and starts to behave like a fluid, and as the gas velocity increases, the degree of fluidisation becomes smoother. Past a certain velocity, bubbles start to appear and the surface of the 'bed' becomes heterogeneous and liquid-like. Fluidisation is influenced by the uniformity of the gas flow, the constant pressure drop through the vessel, and the particle size. The minimum fluidisation velocity (μ_{mf}) can be approximated to a function of the square of the particle diameter (d) and a linear function of particle mass (p), or $\mu_{mf} \approx d^2 p$ (Sagon-King, 1991).

The principle of nitriding (and ferritic nitrocarburising) of components in a fluidised bed furnace is the same as for gas nitriding/ferritic nitrocarburising. The process gas is ammonia (as well as nitrogen, and any carbon-carrier gas that may be used for ferritic nitrocarburising) and is introduced through the diffuser to achieve fluidisation and nitrided parts.

The inherent advantage of fluidised bed furnaces is their flexibility (in terms of different process capabilities) and simplicity, as well as a high efficiency of heat transfer; the coefficient of heat transfer is usually between 120 and 1200 W/m^2 (Sagon-King, 1991). The nature of the fluidised bed also limits the need for the extended nitrogen purges that are necessary in gas nitriding furnaces.

On the other hand, fluidised bed furnaces also have several drawbacks. One of them is de-fluidisation: horizontal fluidisation is weaker at lower nitriding temperatures, and in denser loads, or on parts with complex geometry that will not allow easy gas flow, the fluidised bed can locally 'collapse'. The resulting layer of

particles may then insulate the treated surface from the process gas. The second drawback is usually related to gas flows necessary to obtain minimum <u>fluidisation velocities</u>. Typically, the gas flow cannot be decreased below a certain minimum, potentially causing the resultant nitriding atmospheres to be overly aggressive, with low dissociation rates (or high nitriding potential). This control limit means that the fluidised bed furnace is suitable mainly for shorter processes, or for specifications that do not require deep-case nitriding with limited white layers. Minimum fluidisation gas flows also have an impact on high ammonia consumption and emissions.

3.14.3 Media

The parts are exposed to an ammonia or ammonia–nitrogen atmosphere. However, with the ammonia dissociating at nitriding temperatures, and with already dissociated ammonia or hydrogen injected for control purposes, the process atmosphere will always also contain a certain amount of hydrogen.

3.14.4 Process parameters

As in gaseous nitriding, the determinant process parameters are:

- temperature
- nitriding potential k_N or dissociation rate D, depending on specification
- time.

In addition, the control system has to provide

- minimum gas flow to obtain fluidisation velocities.

3.14.5 Measuring devices

As in gaseous nitriding, the typical measuring devices for fluidised bed nitriding are ammonia or hydrogen analysers. For further information, see Section 3.6.

3.14.6 Process set-up

Process set-up is also identical to that for gaseous nitriding, except that the furnace technology does not allow for a vacuum purge.

Tribology

Edward H. Smith, ... (Section 9.10), in <u>Mechanical Engineer's Reference Book (Twelfth Edition)</u>, 1994

9.9.7.7 Thermochemical treatments

These treatments involve the diffusion of carbon, nitrogen and, less usually, <u>chromium</u> or <u>boron</u>. The most common thermochemical treatments are <u>carburizing</u>, <u>carbonitriding</u>, nitrocarburizing and gas <u>nitriding</u>. The factors involved in the selection of a thermochemical treatment are too numerous to go into in detail here, but it is possible to make generalizations about this form of palliative.

This category of treatments is designed to increase surface hardness. In general, the adhesive and <u>abrasive</u> resistance improve with increased surface hardness. The most effective treatment against <u>fretting wear</u> is therefore likely to be the one producing the largest increase in hardness. However, the effect of the treatment on the <u>friction coefficient</u> must not be ignored. For instance, on En32 steel, liquid nitrocarburizing using the Cassel Sulfinuz process reduced the friction coefficient in slow linear sliding from 0.8 down to 0.2.[124]Clearly, for displacement controlled <u>fretting</u>, reduced frictional traction will enhance the effectiveness of the palliative. However, in a force controlled situation the reduction in friction may negate the benefits.

By virtue of the compressive stresses developed in the outer surface layers the fatigue strength of steel is normally enhanced by thermochemical treatments. As a general principle, any process which increases the normal fatigue strength of the steel, providing it is not accompanied by a significant increase in friction coefficient, will improve the fretting fatigue performance. The process giving rise to the greatest increase in normal fatigue strength is likely to provide the largest improvement in fretting performance.

Thermal Engineering of Steel Alloy Systems

H.-J. Spies, A. Dalke, in Comprehensive Materials Processing, 2014

12.14.3.4 Corrosion Behavior

In the early nineteenth century, it was already known that iron nitrides are characterized by an increased resistance against neutral and alkaline media. The increase of the corrosion resistance of components made of iron and steel by means of gas nitriding was the subject of many patents at the beginning of the twentieth century. However, the application of nitriding for improving the corrosion resistance of components had still been a niche technology in the leading industrial nations for a long time. Only the Soviet Union industrially used the technologies of gas and salt bath nitriding for corrosion protection in a broad extent since the 1930s. It was known, for example, that ε-nitride layers showed a considerably better resistance against sea water compared to compound layers consisting of γ'-nitrides. Weathering tests in different climates proved the unchanged appearance of ε-nitride layers after a removal time of about 1 year.

Intensive research work within the last 40 years consistently proved the increased resistance of compound layers against neutral salt solutions and atmospheric corrosion. This is particularly valid in the case of their resistance against pitting corrosion caused by chloride ions. The corrosion resistance of compound layers is defined by its phase constitution and its chemical composition. An illustration of the broad property range of variably generated compound layers is given in Figure 54 and Table 8. As it can be seen, the corrosion resistance increases in the order of γ'-nitride, ε-nitride, and ε-carbonitride. The resistance of ε-nitride layers is significantly defined by the height of the nitrogen content (see Table 9). ε-Carbonitride layers obtaining a nitrogen and carbon concentration of about 8.6% show an optimal pitting corrosion resistance (65).
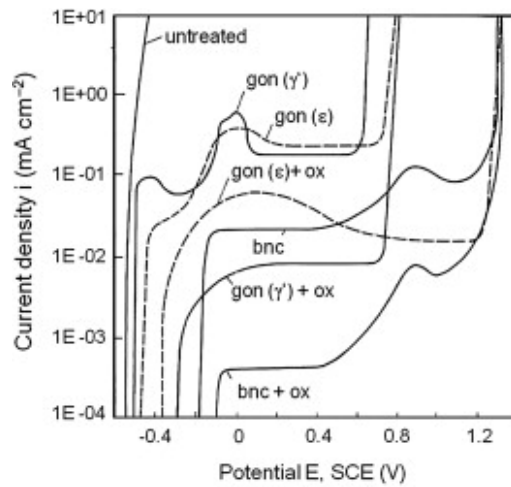
Figure 54. Potentiodynamic anodic current density/potential curves of differently treated samples of steel 20MnCr5, 0.9 M NaCl-electrolyte; gon: gas oxinitrided, bnc: bath nitrocarburized, ox: post-oxidized.

Reproduced from Ebersbach, U.; Friedrich, S.; Nghia, T.; Spies, H.-J. Elektrochemische Korrosionsuntersuchungen an gasoxinitriertem und salzbadnitrocarburiertem Stahl in Abhängigkeit vom Aufbau der Nitrierschicht. *Härterei-Tech. Mitt.* **1991**, *46*, 339–349.

Table 8. Layer structure and corrosion behavior, extended

Layer parameter		Salt-spray test[a]	Immersion test[b] (mg Fe/100 ml)	Corrosion potential[c] E_{cor}, SCE (mv)	Passive current density[c] ($\mu A\ cm^{-2}$)	Pitting potential[c] E_{pit}, SCE (mv)
Thickness (µm)	Structure					
10–14	γ′	8	143.0	−490 to −510	180	580–605
	γ′ – oxidized	23	4.6	−280 to −300	200	700–765
	ε(γ′)	8	3.3	−320 to −370	100	550–670
	ε(γ′) – oxidized	35	1.4	−190 to −210	10–20	1000–1200[e]
20–25	ε(γ′) – oxidized	43	0.7	–	10–20	1000–1200[e]
13–15	ε(C)[d]	–	–	−250 to −320	10–20	1240–1300[e]
13–15	ε(C) – oxidized	–	–	−170 to −210	0.1–3.4	1220–1280[e]
40	Hard chromium	8	2.5	–	0.02	620–740

a

    Test cycles up to first corrosion; cycles: 8 h: 35 °C, 0.5% NaCl pH = 6.5–7.2; 16 h: 20 °C, relative humidity, 75%.

b

Test solution after Machu-Schiffmann: 50 g l^{-1} NaCl; 10 ml l^{-1} glacial acetic acid; 5 g l^{-1} 30% H_2O_2 solution; pH = 3, test duration: 4 h.

c

Electrolyte: 0.9 M NaCl.

d

ε(C): ε-carbonitride.

e

Transpassivation potential E_t.

Reproduced from Ebersbach, U.; Friedrich, S.; Nghia, T.; Spies, H.-J. Elektrochemische Korrosionsuntersuchungen an gasoxinitriertem und salzbadnitrocarburiertem Stahl in Abhängigkeit vom Aufbau der Nitrierschicht. *Härterei-Tech. Mitt.* **1991**, *46*, 339–349.

Table 9. Electrochemical behavior of ε-nitride layers in dependence from nitrogen concentration, pure iron, layer thickness: 9–11 μm

Layer	Nitrogen concentration, wt.%	Pitting potential[a] E_{pit}, mV	Passive current density[a], mA cm^{-2}
ε(γ′) – 7%N	7.2	640–700	0.1
ε(γ′) – 7%N-oxidised	8.9	1150–1200[b]	0.01–0.02
ε(γ′) – 9%N	9.2	1200–1350[b]	0.01–0.02

a

Electrolyte: 0.9 M NaCl.

b

Transpassivation potential E_t.

Reproduced from Winkler, H. P.; Spies, H.-J.; Schubert, T. Korrosionsverhalten nitrierter Eisenwerkstoffe. In Freiberger Forschungshefte; pp 49–54. Leipzig.

The corrosion resistance of nitrided cases can be additionally improved by means of oxidation after nitriding (Table 8). Oxidized nitrided cases considerably exceed the corrosion resistance of hard chromium cases and today, they are widely used as a substitute of such layers (*67–70*).

Depending on the applied treatment technology, the corrosion behavior of oxidized compound layers can differ significantly. It is considerably defined by the composition of the compound layers beneath the oxide layer and the structure of the oxide layer.

An oxidation at temperatures below 500 °C and times between 0.5 h and 1.5 h has been established. Under these conditions, the nitrogen, which is displaced from the near-surface areas, enriches, e.g., beneath the oxide layer. Thereby, the enriched layer reaches depths of about 8–9 μm depending on the oxidation conditions. This ensures satisfying corrosion resistances also in the case of layer wear due to an interaction of tribological and chemical loads (*67*). The results of investigations on the resistance of an oxidized compound layer against pitting corrosion, shown in Figure 55, confirm this conclusion. The pitting corrosion potential considerably decreases first after a layer removal of more than 8 μm.
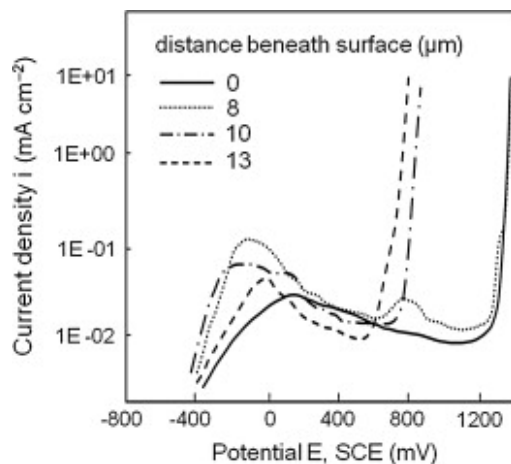
Figure 55. Change of potentiodynamic anodic current density/potential curves of nitrided and post-oxidized steel S355 with increasing distance from the surface; compound layer thickness 20 μm; 0.9 M NaCl electrolyte.

Reproduced from Winkler, H. P.; Spies, H.-J.; Schubert, T. Korrosionsverhalten nitrierter Eisenwerkstoffe. In Freiberger Forschungshefte; pp 49–54. Leipzig.

An example of the chemical composition and the microstructure of an oxidized compound layer exhibiting a high corrosion resistance is depicted in the SEM micrograph in Figure 56. The compound layer mainly consists of ε-phase, in the lower areas of a nearly pore free ε-carbonitride etched dark grey and, in the near-surface areas, it consists of the light grey ε-nitride (Figure 56(a)). Tracks of γ′-nitride appear in the lower regions of the layer, identifiable on the white, nonetched areas. The critical value of the sum of nitrogen and carbon content being in the range of 8.6% is first underrun in a surface distance of 12.5 μm (Figure 56(b)).
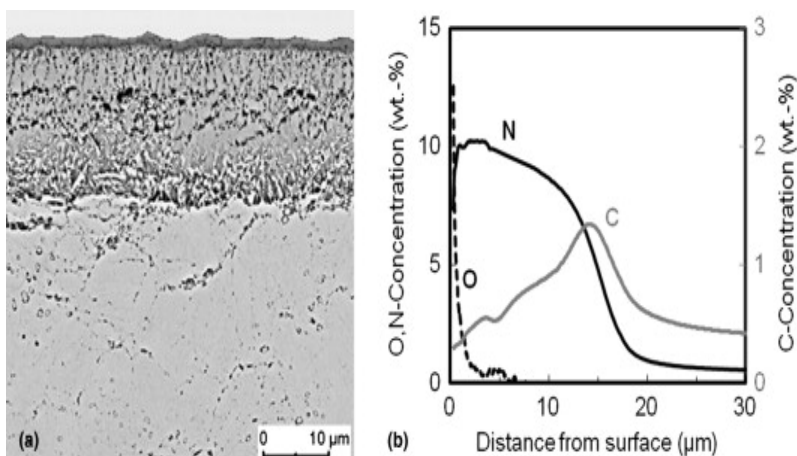

Figure 56. Gas nitrocarburized and oxidized compound layer of steel 42CrMo4: (a) microstructure, etchant: alkaline sodium picrate solution and (b) concentration profile.

Besides the resistance against pitting corrosion, the uniform corrosion behavior matters to describe the comprehensive corrosion behavior of nitrided cases. It can be specified by the free corrosion potential E_{cor} and free corrosion current i_{cor}. For the characterization of the uniform corrosion behavior, the reciprocal polarization resistance R_p^{-1} is often used (68). The reciprocal polarization resistance, measured in the vicinity of the free corrosion potential, is inversely proportional to the free corrosion current. As shown in Table 8, there are clear differences between the free corrosion potentials of γ′- and ε-compound layers. Starting from γ′-nitride layers

to oxidized layers and ε-nitride layers to ε-carbonitride layers, the free corrosion potential is shifted in the noble direction.

The reciprocal polarization resistance provides the possibility of precisely characterizing the corrosion behavior of the ε-phase with dependence on their chemical composition described by the concentration ratio [C]/[N + C]. The results of investigations on low-alloyed steels, which have been differently nitrocarburized, are shown in Figure 57. As a results out of it ε-carbonitrides of the concentration range of [C]/[N + C] = 0.02–0.2 exhibit a considerably better corrosion behavior. The reciprocal polarization resistance decreases about more than 1 order of magnitude. Pure ε-nitrides und ε-carbonitrides containing high carbon contents show considerably worse uniform corrosion behavior.

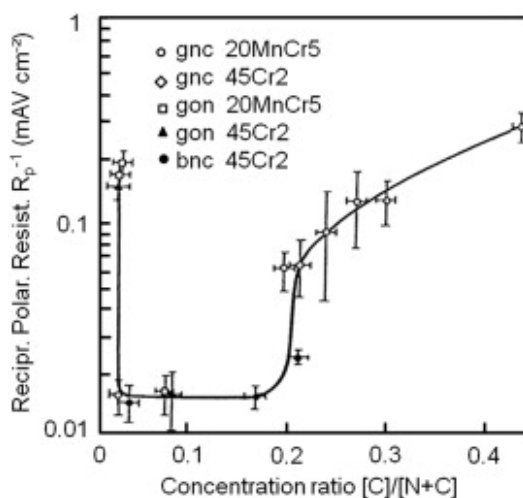Figure 57. Reciprocal polarization resistance of nitrided and nitrocarburized samples in dependence on the concentration ratio [C/C + N] in the ε-phase, steels: 20MnCr5 and 45Cr2; 0.9 M NaCl electrolyte, gnc: gas nitrocarburized, gon: gas oxinitrided, bnc: bath nitrocarburized.

Reproduced from Ebersbach, U.; Friedrich, S.; Nghia, T. Structure and Corrosions Behavior of Nitride Layers. In *Proc. Surf. Eng*; DGM Informges: Bremen, 1993; pp 299–304.

Compound layers also exhibit an increased resistance against the attack of molten metals. Again, this property can be improved by means of a subsequent oxidation. This has been proved by investigations on samples of the steel X38CrMoV5-1 nitrided differently. Thereby, the mass of the samples lost after a 4 h attack of molten aluminum at 735 °C was determined. Due to a nitriding with generating a compound layer the mass lost determined on non-nitrided samples decreased on the average of 580 mg cm^{-2} to 85 mg cm^{-2}. An oxidation of the compound layer results in a further decrease of the mass lost to 32 mg cm^{-2}.

The development of processes for generating oxidized carbonitrided layers started from the development of the Q and QPQ process in the 1980s (70). Nearly at the same time the NITROTEC process was developed in Great Britain (43). The QPQ process, developed out of the tuff <u>nitride</u> Q process, consists of a salt bath <u>nitrocarburizing</u> treatment with an oxidizing <u>quenching</u> followed by a polishing step and a requenching in an oxidizing atmosphere. In the NITROTEC process, gas nitrocarburizing is followed by oil quenching, post-oxidizing, and <u>impregnation</u> with a corrosion-inhibiting <u>sealant</u> protection. Also, recent investigations proved that a polymer post-impregnation treatment definitively increases the corrosion resistance of oxinitrided steels (71,72).

For the generation of oxidized carbonitrided layers having optimal corrosion behavior, a multitude of process variants are available today. Besides the bath

nitrocarburization, gas nitrocarburization and plasma nitrocarburization are also used. Due to the development of the controlled nitriding, it is possible today, for all three processes, to generate ε-carbonitride layers having a high corrosion resistance by means of adjusting the defined nitrogen and carbon contents.

On austenitic and ferritic stainless steels, no compound layer is generally formed under normal nitriding conditions. The bonding of chromium within the precipitation layer results in a breakdown of its corrosion resistance. A possibility of improving the tribological load capacity of these steels by simultaneously keeping the excellent corrosion resistance offers a nitriding or carburizing treatment at temperatures below 450 °C. The formation of precipitates causing a depletion of chromium in the matrix is strongly impeded in this temperature range. Depending on temperature and time of this low-temperature treatment, the nitrogen or carbon within the case remain, dissolved. A strongly dilated austenite, an expanded austenite (γ_N or γ_C), is generated, which is distinguished by a high hardness and high compressive residual stresses(73).

An illustration of the influence of the treatment conditions on the corrosion behavior of stainless austenitic steels conveys the results of electrochemical investigations shown in Figures 58 and 59. The pitting corrosion behavior in aqueous 0.5 M NaCl solutions and the passivation behavior in dilute H_2SO_4 solutions (0.05 M) have been characterized by means of potentiodynamic measurements using a potential feed rate of 0.2 V h^{-1} (NaCl) and 1.8 V h^{-1} (H_2SO_4), respectively.
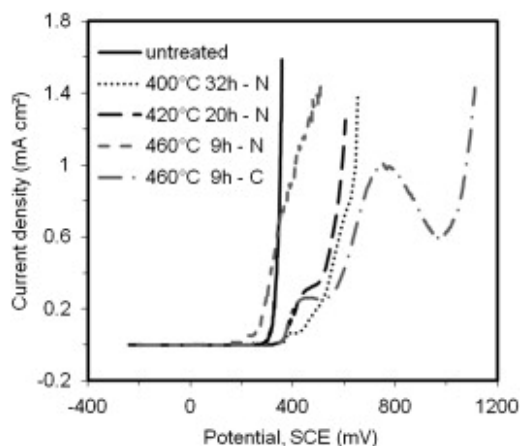

Figure 58. Anodic polarization curves of differently treated samples of steel X2CrNiMo17-12-2; 0.9 M NaCl-electrolyte, N: nitrided, C: carburized.

Figure 59. Anodic polarization curves of differently treated samples of steel X2CrNiMo17-12-2; 0.05 M H_2SO_4 electrolyte. N: nitrided, C: carburized.

Reproduced from Spies, H.-J.; Bell, T.; Kolozsvary, Z. Thermochemical Surface Treatment of Stainless Steels at Low Temperatures. *Härterei-Tech. Mitt.* **2010**, *65*, 11–21.
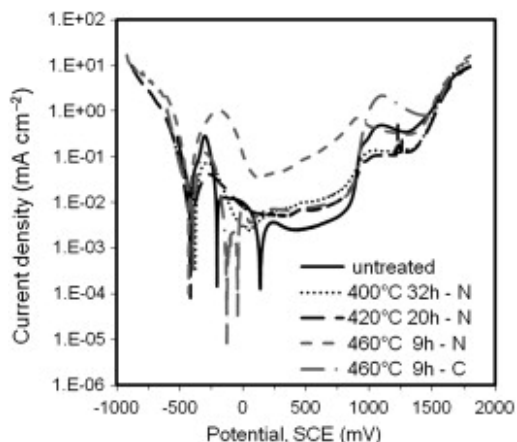
As can be seen in Figure 58, the resistance against pitting corrosion is considerably increased by means of nitriding as well as carburization. Only the nitriding treatment applying 9 h at 460 °C resulted in a decrease of the pitting corrosion potential within the less noble areas. For this treatment condition, metallographic investigations showed the formation of chromium nitride precipitates at grain boundaries within the near-surface regions. In contrast, layers generated by means of carburization under comparable treatment conditions have been free of precipitation. This is evidence of the higher thermal stability of the expanded carbon austenite as described in the literature several times (75).

In contrast to pitting corrosion, the passivation behavior is not changed by a low-temperature nitriding treatment at 400–420 °C compared to the initial condition (Figure 59). This is clear evidence for the formation of a single-phase, precipitation-free surface layer. The chromium depletion within the region near the grain boundaries caused by the precipitation of chromium nitrides during the nitriding treatment of 460 °C for 9 h considerably influences the developing of the current density potential curve. Being characteristic for a starting intercrystalline corrosion, the current density for passivation and the current density within the passive region clearly increase. In contrast, between the profiles of the current density potential curve obtained on a carburized sample, treated at 460 °C for 9 h, and the initial condition nearly no difference exists. So, also the passivation behavior confirms the higher thermal stability of the expanded austenite.

Due to the attractive possibilities for improving the tribological load capacity of stainless steels without losing their corrosion resistance, the low-temperature nitriding treatment of these steels have been the subject of intensive research work for the last 20 years. Based on deepened knowledge concerning the thermal stability of expanded austenite, the work resulted in the development of industrially used treatment processes.

An overview of the characteristics of nitriding, carburizing, and nitrocarburizing processes at low temperatures is given in Table 10. The duplex layers generated by means of nitrocarburizing and the combination of carburization and nitriding, respectively, exhibit the high surface hardness of nitrided cases as well as the high thickness and the smooth hardness profile of carburized layers. Thus, they combine the advantages of nitriding and carburizing. Varying the carbon supply and the temperature and time, respectively, of the single processes for a sequential treatment and the variation of nitrogen and carbon potential during a duplex treatment, respectively, modifies their structural constitution within broad limits

(74). Hence, for numerous applications, such layers provide optimal solutions. Between layers with equal compositions, which are generated by means of different processes, no fundamental differences exist.

Table 10. Characteristics of low-temperature nitriding, carburizing, and nitrocarburizing according to Bell and Sun, extended

Features	Process		
	Nitriding	Carburizing	Nitrocarburizing
Temperature, °C	300–450	300–520	300–450
Layer thickness, μm	2–15	5–45	5–30
Layer uniformity	Good	Very good	Very good
Layer structure	Precipitation-free expanded austenite		
Corrosion resistance	Good	Good	Good
Surface hardness, HV0.05	1400–1600	900–1100	1400–1600
Hardness profile	Abrupt	Gradual	Gradual
Wear resistance	Very good	Good	Very good
Layer toughness	Poor	Very good	Good
Load-bearing capacity	Low	High	High

Reproduced from Bell, T.; Sun, Y. Low Temperature Plasma Nitriding and Carburizing of Austenitic Stainless Steels. In *Stainless Steel 2000, Proc. Int. Sem. Osaka/Japan, 2000*; Maney Publ: London, 2001; pp 275–288.

# Evolution of microstructure in ferrous and non-ferrous materials

H. Danninger, ... S. Strobl, in Advances in Powder Metallurgy, 2013

### 11.3.5 Sintered steels: effect of heat treatment

Sintered steels can be heat treated in the same way as wrought steels when considering their special features. The open pores cause problems when quenching in an oil or salt bath, being filled with the quench media, and during gas carburizing or nitriding, resulting in a tendency to 'through treatment', that is carburizing or nitriding of the cores. On the other hand, overheating is not a problem owing to the grain growth inhibiting effect of the pores.

Sintered steel parts are frequently sinter hardened, by blowing cold gas onto them immediately upon leaving the sintering zone of the furnace. If the alloy composition is suitably selected, fully martensitic microstructures are obtained, as shown in Fig. 20. Since the cooling rates obtained with sinter hardening are barely > 3 K s^{-1}, air hardening behaviour is required, which means sufficient amounts of Cr, Mo, Ni and Cu, with the combination of Mo + Cu or Cr + Cu being particularly effective. Tempering or at least stress relieving is usually done after sinter hardening. Generally, sinter hardening is more economical than separate heat

treatment and also results in cleaner parts without oil; the penalty is the higher alloy element content necessary.
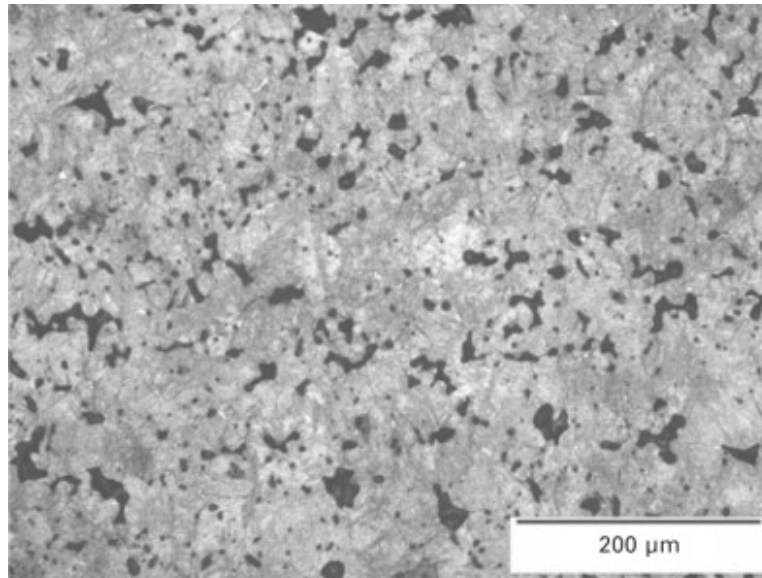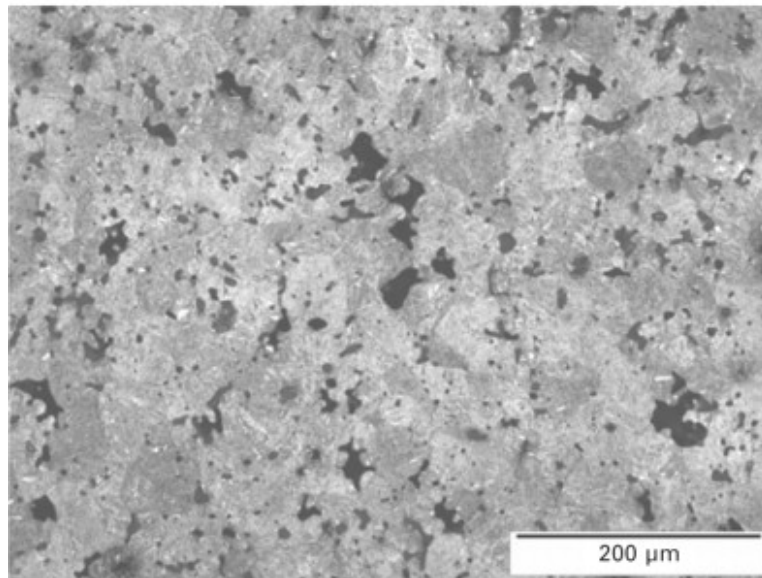

11.20. Microstructures of sinter hardened Cr–Mo prealloyed steels:[28] (a) as gas quenched, (b) gas quenched and tempered at 180 °C.

Quench and temper treatments are frequently done as induction hardening of the surface and subsurface zone, which is the standard procedure, for example for sprockets: In Fig. 21, for a typical sintered steel, the hardened martensitic surface zone is shown compared to the non-hardened ferritic– pearlitic core. Rapid austenitizing is followed by emulsion quenching, which results in hard surfaces and reasonably tough cores, although the process has to be done properly to avoid quench cracks.
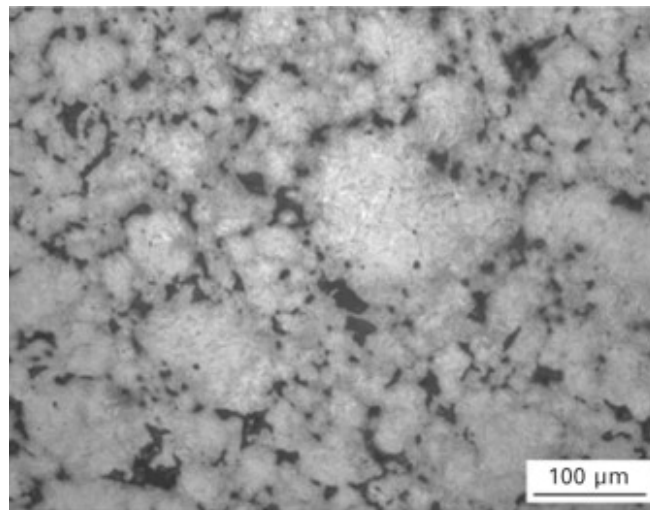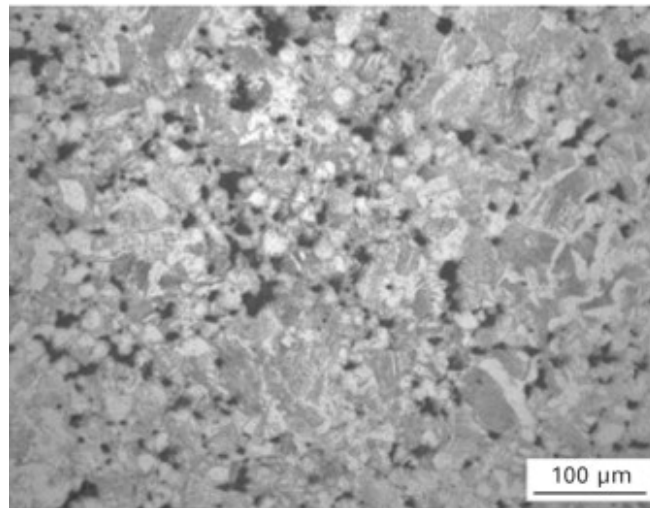
11.21. Induction hardened sprockets from Cu alloyed sintered steel: (a) induction hardened surface zone, (b) base material.

The most popular way of obtaining hard surfaces and tough cores is, however, thermochemical treatment by carburizing, carbonitriding or nitriding. In case of parts with homogeneous porosity, the problem of through carburizing can at least be alleviated by adapting the parameters; for surface densified parts, it is however extremely difficult to obtain well carburized densified areas without overcarburizing the non-densified surfaces. Here, either plasma carburizing or low pressure carburizing combined with high pressure gas quenching are alternatives, in particular LP carburizing has been shown to be suited to surface densified PM gears.[29] Since both processes use oxygen-free carbon carriers – CH_4 and C_2H_2 or C_3H_8, respectively – they are also applicable for Cr alloyed sintered steels and do not suffer from the oxidation problems encountered with gas carburizing using CO–H_2 mixes. Microstructures of carburized parts are shown in Fig. 22.
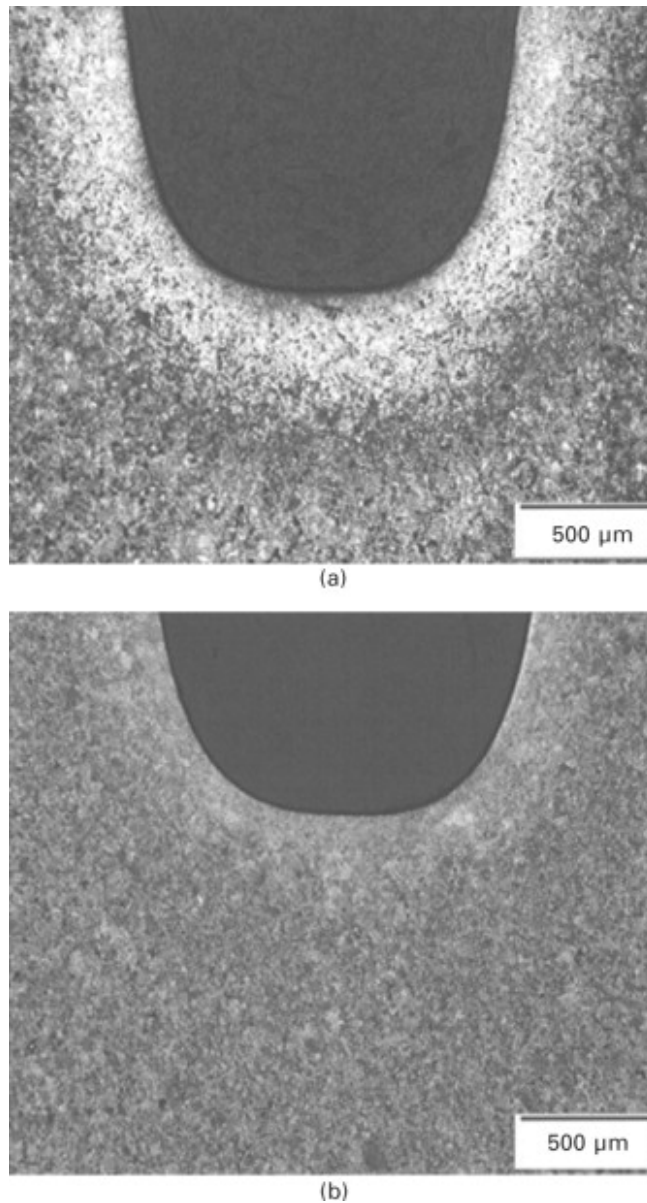
11.22. Microstructures of surface densified sintered steel gears, differently carburized: (a) low pressure carburized, (b) standard gas carburized.

For nitriding, standard gas nitriding tends to result in through nitriding, with pronounced expansion; therefore, plasma nitriding is the method of choice here, which limits the nitriding effect on the surface. Mo prealloyed steels are particularly well suited here, and more recently Cr and Cr–Mo prealloyed steels have also been used.[30] In general, chemically homogeneous prealloyed steel grades are better suited to thermochemical treatments than heterogeneous ones prepared from mixed or diffusion bonded powders.

Materials, properties and selection

Leslie M. Wyatt, ... (Section 7.10), in Mechanical Engineer's Reference Book (Twelfth Edition), 1994

7.3.11.4 Nitriding
Nitriding may be achieved by heating steel in a cyanide bath or an atmosphere of gaseous nitrogen at 510–565°C. The steel component is heat treated and finish

machined before nitriding

Liquid nitriding uses a bath of sodium and potassium cyanides, or sodium cyanide and sodium carbonate. The bath is pre-aged for a week to convert about a third of the cyanide into cyanate. Two variants of the process are liquid pressure nitriding in which liquid anhydrous ammonia is piped into the bath under a pressure of 1–30 atm, and aerated bath nitriding in which measured amounts of air are pumped through the molten bath. All the processes provide excellent results, depth and hardness of case being the same as obtained from gas nitriding. Unlike gas nitriding, carbon steels can be liquid nitrided and the case produced on tool steels is tougher and lower in nitrogen than a gas-nitrided case. On the other hand, liquid nitriding uses a highly poisonous liquid bath at a high temperature and the process may take as long as 72 hours. It is really only suitable for small components.

Gas nitriding is achieved by introducing nitrogen into the surface of a steel by holding the metal at between 510°C and 565°C in contact with a nitrogenous gas, usually ammonia. A brittle nitrogen-rich surface layer known as the 'white nitride layer' which may have to be removed by grinding or lapping is produced. There are two processes: single- and double-stage nitriding.

In the single-stage process a temperature between 496°C and 524°C is used and about 22% of the ammonia dissociates. This process produces a brittle white layer at the surface. The first stage of the double-stage process is the same as the single stage but, following this, the ammonia is catalytically dissociated to about 80% and the temperature increased above 524°C. Less ammonia is used in the double-stage compared with the single-stage process and the brittle white layer is reduced in depth and is softer and more ductile. Process times are in the order of 72 hours.

Gas nitriding can only be used if the steel contains an alloying element such as aluminium, chromium, vanadium or molybdenum that forms a stable nitride at nitriding temperatures. The film produced by nitriding carbon steels is extremely brittle and spalls readily. In general, stainless steels, hot-work die steels containing 5% chromium and medium-carbon chromium containing low-alloy steels have been gas nitrided. High-speed steels have been liquid nitrided.

There are also a number of steels listed in AISI/SAE or BS 970 (or having the name 'Nitralloy') to which 1% aluminium has been added to make the steel suited for gas nitriding. AISI 7140 (BS 970 905 M39) is typical.

Nitriding can produce case hardnesses up to 75 Rockwell C depending on the steel. This hardness persists for about 0.125 mm but depths of case with hardness above 60 Rockwell of 0.8 mm may be produced.

The relatively thin case compared with other methods of case hardening make it customary to use fairly strong core material. For ferritic steels a UTS between 850 and 1400 MPa is usual. Typical components nitrided are gears, bushings, seals, camshaft journals and other bearings, and dies - in fact all components which are subject to wear. In spite of their relatively low hardness, austenitic stainless steel components are nitrided to prevent seizure and wear, particularly at high temperatures. Two considerations apply.

First, stainless steels must be depassivated by mechanical or chemical removal of the chromic oxide film before nitriding. Second, nitriding decreases corrosion resistance by replacing the chromic oxide film by a chromium nitride film and should not be employed when corrosion resistance is of paramount importance.

Ion implantation is achieved by bombarding the surface of a steel with charged ions, usually nitrogen when the object is to harden the surface. The cost is high, the quantity of nitrogen implanted small, and it can only be carried out by a laboratory which has an accelerator such as AERE. It is used for special applications which will probably increase in number.

Fatigue failure of metallic biomaterials

M. Niinomi, in Metals for Biomedical Devices, 2010

Fatigue strength and surface hardening treatment

The S–N curves of titanium alloys such as Ti–6Al–4 V ELI and TNTZ subjected to nitriding are shown in Fig. 5.13 (Akahori et al., 2008). In this figure, $TNTZ_{ST}$, $TNTZ_{1123NP}$, $TNTZ_{1223NP}$, $Ti64_{ST}$, $Ti64_{1123NP}$ indicate TNTZ subjected to solution treatment and gas nitriding at 1123 K and 1223 K, and Ti–6Al–4 V ELI subjected to solution treatment and gas nitriding at 1123 K and 1223 K, respectively. The fatigue strengths of TNTZ and Ti–6Al–4 V ELI are lowered by nitriding. The hard layers, TiN or Ti_2N, formed on the surface of both alloys, are brittle, leading to easy fatigue crack initiation. The intensity of the TiN peak has been found to increase with the nitriding temperature by XRD analysis. The Vickers hardness near the specimen surface of nitrided Ti–6Al–4 V ELI has been reported to be greater than that of TNTZ.
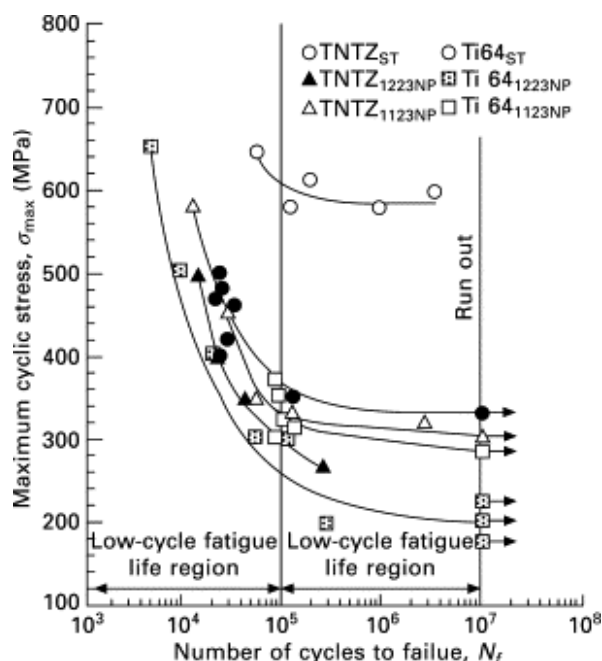
5.13. S–N curves of TNTZ and Ti 64 subjected to solution treatment and nitriding process.

The run out, which is the maximum cyclic stress that can be applied without causing fracture after 10^7 cycles, of $TNTZ_{1123NP}$ was around 300 MPa and it is nearly equal to that of $Ti64_{1123NP}$, although the tensile strength of $TNTZ_{1123NP}$ was around 200 MPa lower than that of $Ti64_{1123NP}$. This value was slightly lower than that of $TNTZ_{ST}$. The fatigue crack seems to be more easily initiated when the brittle nitrided layer (TiN or Ti_2N), is thicker as is slightly the case with nitrided Ti–6Al–4 V ELI compared to nitrided TNTZ. Particularly, the elastic modulus of TiN is two or more times higher than that of the matrix (Yan et al., 2001). Thus, the TiN layer of nitrided TNTZ and Ti–6Al–4 V ELI is severely deformed under cyclic loading, wherein localized fatigue deformation could take place. This seems to result in brittle cracking and shortening of crack initiation life, in particular, with nitrided Ti–6Al–4 V ELI which has a relatively high Vickers hardness and thicker nitride- and nitrogen-rich layers. In addition, the notch factor (run out of smooth specimen/run out of notch specimen), which indicates the notch sensitivity, of aged TNTZ

decreases with an increase in the volume fraction of the β phase, and it is lower than that of annealed Ti–6Al4V ELI with an equiaxed β structure (Akahori *et al.*, 2008). From these points of view, it follows that by the nitriding process, the plain fatigue strength of TNTZ is not as degraded as compared to that of Ti–6Al4V ELI.