

Modular heat treatment using nitriding and low-pressure carburising (part 2)

by **Gerald Hiller, Pierre Bertoni, Marco Jost, Olaf Irretier**

Vacuum heat treatment, and with it vacuum hardening, has become increasingly important in recent decades. In addition, low-pressure carburising (LPC) has been an alternative to the conventional carburising processes for more than 30 years. Its use, which was slowed down for a long time by technical and economic problems, has been further established in series production over the last 15 to 20 years. New considerations and applications now also bring together the nitriding and nitrocarburising processes with modular vacuum hardening technology. The three-part article represents the basic considerations of process and plant engineering in connection with the economic and environmental factors. Part 1 presented the plant technology (hp 3/2020). Part 2 now explains the basics of the heat treatment processes under consideration.

Vacuum heat treatment such as low-pressure carburising or brazing, but also nitriding and nitrocarburising of metallic components is determined by the parameters time, temperature, pressure, atmosphere and quenching or cooling. These process parameters can be adapted and optimised to the requirements in terms of improved component quality, energy efficiency and economic viability. Here, the industrial furnace technology has the decisive task of supporting the target values of the heat treatment process, i.e. the economic production of a component treated in a certain way from the point of view of suitability and possible applications as well as maximum service life.

PRINCIPLES OF THE HEAT TREATMENT PROCESSES UNDER CONSIDERATION

Nitriding and nitrocarburising

Surface and edge layer hardening are of high, value-adding importance for modern production. An increase in edge hardness offers the designer the possibility of minimising wear, decisively improving the performance of the components and reducing weight while maintaining the same performance. In practice, a number of thermochemical diffusion processes have become established to harden a wide variety of components made of different materials for a wide range of applications in mechanical and plant

engineering, automotive engineering, tool and gear construction. Among the most important thermochemical processes are case hardening and carbonitriding as well as nitriding and nitrocarburising. Although case hardening has by far the largest share of the market volume, nitriding processes have steadily increased in importance in recent years.

In the case of case hardening processes, the carbon content of the surface layer of the components is increased by carburising in a gas atmosphere or by means of vacuum technology (LPC) in order to be able to harden the materials in this area by quenching in liquid media or by means of high-pressure gas quenching. The hardening here is based on the mechanism of martensite formation. The carbon is interstitially dissolved in the microstructure above the A_{c3} temperature. During the subsequent quenching process, the martensite is formed by tilting the lattice structure from the face-centred cubic austenite to the body-centred cubic structure. Due to the relatively high quenching speed, the carbon does not have enough time to diffuse out of the lattice. The resulting distortion of the lattice structure leads to increased compressive residual stresses in the microstructure, which are the cause of the increase in hardness. On the other hand, it is not the formation of martensite but the mechanism of precipitation hardening that is responsible for the increase in hardness during nitriding. The hardness

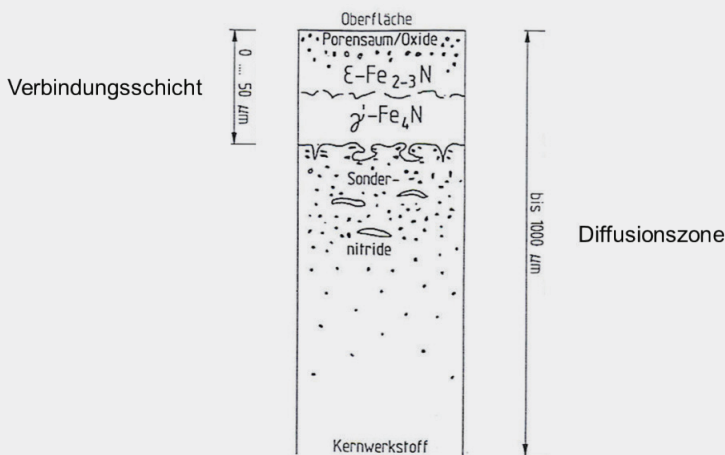


Fig. 1: Structure of the nitriding layer (W. Lerche)

carrier is not the carbon, but the nitrogen. Hardening is achieved by diffusion of nitrogen into the surface layer and subsequent nitride formation with the alloying elements of the steel, e.g. with aluminium, chromium, molybdenum, vanadium, manganese or silicon. The precipitation process of the nitrides and carbonitrides is further supported by the decreasing solubility of nitrogen during cooling.

Nitriding takes place at comparatively low temperatures below the Ac1 temperature. Usual nitriding temperatures are in the range of about 500 to 530 °C. The cooling rates are usually rather moderate (furnace cooling). Since the treatment is not accompanied by phase transformation and a sudden cooling (quenching) is usually avoided, no quenching distortion occurs. Nitriding is therefore a very low-distortion surface hardening process. Also, the danger of hardening cracks is not given by the missing quenching.

Table 1 summarises the properties of nitriding layers.

The nitrided, wear-resistant surface improves not only the wear resistance against abrasive and adhesive wear but also the sliding properties of the surface and the fatigue strength of the components. The surface hardness strongly depends on the material. For tempered and nitrided steels, normal hardness values are between 550 and 850 HV, depending on the tempering strength and alloy content, and for Al alloyed grades even over 1,000 HV.

Typical case hardening steels such as 16MnCr5 / 20MnCr5 or 18CrNiMo7-6 can also be nitrided very well due to the existing contents of nitride formers and reach quite high hardness values in the range of 700 to 800 HV. In the case of higher alloyed steels, e.g. some tool steels or stainless steels, hardness values of well over 1,000 HV are even achieved, depending on the chemical composition.

Nitriding layers are also permanently temperature resistant up to about 400 °C. The comparatively low treatment temperature, which on the one hand reduces distortion, has a negative effect on the treatment times and the adjustable hardening depths. Since the diffusion rate of nitrogen at the temperature level of nitriding treatments is comparatively low, the holding times are relatively long and the achievable nitriding hardness depths are limited. Usual holding times range from a few hours to several days.

Fig. 1 illustrates the structure of a nitriding layer.

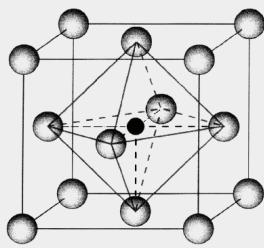
A nitriding layer consists of a compound layer on the surface, which is usually not more than 20 μm thick, and the diffusion zone in which the nitrides are deposited. The compound layer can consist of two phases with different properties. Classically, the so-called ε phase (Fe₂₋₃N) is formed towards the surface during nitriding, while the γ' phase (Fe₄N), which is lower in nitrogen, is formed towards the inside of the material. As the crystal structure and nitrogen content of the two phases are different, they also have different properties (**Fig. 2**).

The ε phase is significantly harder than γ' phase and has significantly better sliding properties. On the other hand, the γ' phase is much more ductile, which means, for example, that the crack tendency under load is comparatively lower. Today, it is possible to influence the thickness and the structure of the bonding layer in a defined manner via the control system and thus adapt it to the requirements of the component load.

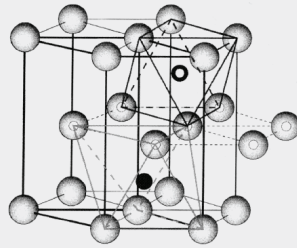
The nitriding hardness depth is accompanied by the nitrogen concentration profile or the formation of the diffusion zone, which is also called the precipitation zone. The adjustable nitriding hardness depth strongly depends on the material and is usually a few tenths to a maximum of 1 mm. Thus, for example, nitriding hardness depths in the range of 0.2 to 0.6 mm are set for quenched and tempered and nitriding steels depending on the requirements. The ductility of the nitriding layer, especially the compound

Table 1: Properties of nitriding layers

Nitriding layer	
Advantages	Disadvantages
High hardness and strength	Relatively thin layers
High fatigue strength	
Good sliding properties	Geringe Zähigkeit und hohe Empfindlichkeit bei Stoßbelastung
High temperature resistance	

 **γ' -Nitrid (Fe_4N)**

- kubisch-flächenzentriertes Gitter
- ferromagnetisch
- N-Löslichkeit 5,7-6,1 %N
- C-Löslichkeit < 0,2 %C
- weicher und zäher als ϵ

 **ϵ -Nitrid ($Fe_{2.3}N$)**

- hexagonale Gitterstruktur
- ferromagnetisch
- N-Löslichkeit 7,7-11,1 %N
- C-Löslichkeit 2-3 %C
- härter und spröder als γ'

Fig. 2: Crystal structure and properties of the ϵ phase ($Fe_{2.3}N$), towards the inside of the material the lower nitrogen γ' phase

layer, is relatively low. The sensitivity to impact and thermal shock is quite high, which increases the tendency to crack formation from the surface under appropriate stress.

Nitriding vs. nitrocarburising

The formation of the diffusion zone is primary in most applications during nitriding, since the resulting nitriding hardness depth as a supporting layer ensures wear protection. In many applications, nitriding attempts are made to minimise the formation of the compound layer and to keep it within narrow limits. This is especially true if the component is exposed to higher surface pressures during use. The attempt to nitride as little compound layer as possible is based on the low toughness of the compound layer. In order to achieve the highest possible ductility of the layer, the formation of a monophase γ' phase is often aimed for and at the same time the thickness of the compound layer is limited to, for example, max. 5 or 10 μm . In addition, the toughness properties in the diffusion zone can be optimised by increasing the cooling rate. The increase in the cooling rate is accompanied by finely dispersed nitride precipitation, which has a positive effect on the ductility of the layer.

One variant of nitriding is nitrocarburising. In nitrocarburising, a carbon donor gas such as CO_2 or CH_4 is added to the atmosphere in addition to the treatment gas ammonia (NH_3) to produce a wear-resistant compound layer. The treatment temperature of approx. 580 °C is higher than in nitriding. The holding times are usually only a few hours and are therefore often significantly shorter than with pure nitriding treatments. Nitrocarburising can therefore be a comparatively low-cost alternative to nitriding, provided

that the layer properties achieved are sufficient for the load profile of the component. While nitriding processes, as described above, usually focus on the formation of the diffusion zone, nitrocarburising usually focuses on the formation of the compound layer. The formation of the diffusion zone is often of secondary importance in nitrocarburising. The aim is the formation of a largely monophasic ϵ compound layer ($Fe_{2.3}N$), which has a high hardness, good sliding and corrosion protection properties. The thickness of the compound layer is adjustable within limits and is normally between 5 and 20 μm , depending on the application and material. Nitrocarburising processes are used for various reasons. They are used, for example, for components made of unalloyed steels (e.g. stampings) where, due to the lack of nitride formers, no significant increase in hardness can be achieved by nitriding treatment alone. In addition, nitrocarburising is always of interest when pure sliding wear occurs without high surface pressures under the operating conditions. Nitrocarburising can also be a good alternative to nitriding for very thin-walled components and components sensitive to distortion. In some applications, nitrocarburising is used not only to increase the hardness of the surface layer but also to improve the corrosion resistance. The corrosion resistance of the ϵ compound layer can be improved by a post-oxidation treatment.

Modern nitriding plants work during nitriding and nitrocarburising with a so-called nitriding characteristic number control on the basis of a hydrogen probe measurement, which determines the degree of decomposition of the ammonia in the treatment chamber of the plant and regulates the fresh gas supply of the treatment gases in a defined manner according to the corresponding specifications. With

the help of these controls, it is now possible to influence not only the nitriding hardness depth but also the structure of the nitriding layer, especially with regard to the thickness and phase structure of the compound layer, and to adjust it to the component stress in a defined manner depending on the requirements. Thus, the layer can be adapted to the wear protection requirements by a defined nitriding or nitrocarburising treatment.

CASE HARDENING AND LOW-PRESSURE CARBURISING

Case hardening is a thermochemical heat treatment process which consists of the sub-steps or processes of (1) carburising, (2) hardening by quenching the components and (3) final tempering of a steel component in order to improve or increase the component properties and here in particular the surface hardness by martensite formation.

The aim of case hardening is to achieve a soft and originally ductile core with a comparatively hard component surface. The combination of soft core and hard surface is achieved by a thermochemical treatment process, carburising. Further objectives of the process are the improvement of the mechanical properties, e.g. by increasing the wear resistance or improving the bending fatigue strength.

During case hardening, the workpiece is exposed to a carburising medium (solid, liquid or gaseous) in an industrial furnace for a certain period of time and at a correspondingly high treatment temperature. The diffusion of the carbon caused by the thermal process, i.e. the exchange of carbon atoms in the steel atom lattice, enriches the surface layer with carbon so that a carbon depth curve is formed in accordance with the diffusion laws, which decreases towards the core and maintains its original basic carbon content below a limit value – the carburisation depth – in accordance with the alloy composition. The characteristic values set during carburisation according to the carbon depth curve are carburisation depth and marginal carbon content. The carburisation depth and the marginal carbon content are adjusted according to the process and the desired component properties and geometry and are generally between 0.1 and 5.0 mm (AT) or 0.5 to 0.8 mass % carbon. According to DIN EN 10052, the carburising depth is defined as the edge distance from the carburised workpiece surface at which the carbon content has reached the specified limit value of usually $C = 0.35\%$. For the practitioner, the rough estimation/formula of thumb applies here that carburisation over a period of 4 h at 930 °C results in a carburisation depth of about 1 mm.

The carburisation process of the steel takes place in accordance with the carbon concentration in the so-called austenite phase, i.e. a lattice structure (face-centred cubic

of the steel in which there is a high diffusion rate of the carbon atoms with additional high carbon solubility in the steel. This is given according to the iron-carbon diagram above the austenite transformation point (Ac3) at temperatures between 880 and 950 °C (see also in Edition 1 "Fundamentals and Applications of Heat Treatment and Hardening Processes/M. Jost" in the PROZESSWÄRME issue 1/2018).

As a rule, so-called case hardening steels are used, i.e. unalloyed or low-alloy steels with a carbon content of 0.10 to 0.20 % (e.g. 16MnCr5, 20MnCr5, 17CrNiMo6). With this relatively low carbon content, these steels cannot achieve martensitic hardness and significant increase in strength without appropriate insertion in a carbon-containing atmosphere and subsequent quenching. By case hardening these steels, a component can then be obtained which has a high toughness in the core, a high hardness in the edge area and thus high resistance to wear.

At temperatures of more than 950 °C to about 1,050 °C, this is referred to as high-temperature carburising, a process that is currently the focus of attention with regard to minimising process times and thus improving economic efficiency.

The carburisation of components is carried out in a medium or atmosphere with the property of releasing carbon into the component via the surface of the workpiece. According to Fick's second law of diffusion, it is therefore necessary that there is a difference in concentration in the carbon-releasing medium compared to the surface to be enriched with carbon. Carburising processes are powder or granular carburising (solid), salt bath carburising (liquid) and gas carburising (gaseous). Carburising in vacuum or under pressure with or without plasma support (low-pressure carburising) is the most innovative of the carburising processes.

In addition, it can make sense in terms of component and application technology that only certain areas should be case hardened and thus initially only partially carburised. In salt bath carburising, this process is relatively simple by partial immersion, i.e. not complete immersion in the molten salt. With gas carburising, on the other hand, partial carburising can only be achieved by covering the areas that are not to be carburised, e.g. by applying a covering or hardness protection paste. It can also be useful to avoid carburisation in threads in order to avoid embrittlement of the thread.

In order to achieve the martensitic hardening desired during case hardening, it is necessary to quench a component after carburisation above the so-called critical cooling rate. The critical cooling rate depends on the material composition, i.e. the alloy of the steel used. When the so-called lower critical cooling rate is exceeded, martensite is formed for the first time. When the upper critical cooling rate is

reached, the resulting hardening structure consists of about 99 % martensite. The transformation into the martensitic hardening structure begins when the martensite starting temperature is reached and ends when the martensite-finishing temperature is reached.

At carbon concentrations of more than 0.6 %, so-called retained austenite must always be expected during hardening, since the martensite-finish temperature in these components is below room temperature and therefore the austenite cannot be completely converted into martensite. The further transformation of the retained austenite can and should be achieved by so-called deep-freezing, as otherwise this transformation may occur with a time delay and often unintentionally and uncontrollably in the later installation state. The transformation of retained austenite is associated with an increase in volume and thus significant stresses in the component, which can lead to dimensional and shape changes and ultimately to cracks and component failure.

This quenching process can be carried out in various media. On the one hand, water can be used as quenching medium, which is usually supplemented with appropriate chemical additives to suppress the surface tension of the water and thus the occurrence of the so-called Leidenfrost phenomenon (insulating steam skin on the component surface during quenching). Other quenching media are oil, salt bath, aqueous polymer solutions, air or gases such as nitrogen (N₂) or argon (Ar) (vacuum hardening). However, the most common process is quenching in oil.

After the quenching process, the steel is very hard (spring or glass hard) and brittle and is generally not suitable for technical applications. Therefore, after quenching, a further annealing process, the so-called tempering, is necessary in which the edge of the component is adjusted to the desired properties such as hardness, tensile strength or toughness. In principle, it can be stated that the hardness decreases, and the toughness increases with increasing tempering temperature.

Depending on the chemical composition of the alloys, tempering is carried out in a temperature range from 100 to 350 °C, and up to 600 °C for high-alloy steels. Some higher alloyed tool steels are not repeatedly tempered in order to achieve an increase in hardness by forming the secondary hardness maximum.

Case hardening vs. low-pressure carburising

Low-pressure carburising in vacuum furnaces offers a number of advantages such as the prevention of oxidation, improved carburising uniformity and reproducibility, reduction of metallurgical tolerances such as carburising depth and hardness control in the component core. In addition, low-pressure carburising is in line with

environmental standards and significantly reduces CO₂ emissions.

The reaction kinetics of low-pressure carburising are higher than those of conventional atmospheric carburising, which is based on a CO/CO₂ equilibrium. Since the low-pressure carburising process is operated without carbon potential control, in situ atmospheric control is unnecessary and the process is therefore easier. In addition, the process temperature is higher than in atmospheric carburising and can reach up to 1,050 °C. The cycle time can thus be significantly reduced by up to 50 % according to the diffusion kinetics.

*** Translated with www.DeepL.com/Translator (free version) ***

In the final part 3, the economic and environmental factors are examined in more detail.

AUTHORS



Gerald Hiller
ECM GmbH
Offenbach-Waldhof, Germany
+49 (0)69 / 667788-065
g.hiller@ecmtech-gmbh.de



Pierre Bertoni
ECM Technologies
Grenoble, France
+33 (0)476 / 4965-60
p.bertoni@ecmtech.fr



Dipl.-Ing. **Marco Jost**
IBW Dr. Irretier GmbH
Düsseldorf, Germany
+49 (0)177 / 23595-36
marco.jost@ibw-irretier.de



Dr.-Ing. **Olaf Irretier**
IBW Dr. Irretier GmbH
Kleve, Germany
+49 (0)2821 / 71539-48
olaf.irretier@ibw-irretier.de