Nitriding steel: Nitrodur
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A speciality of Deutsche Edelstahlwerke

Whenever machines and components are subject to high surface stresses and dynamic loads, it is vitally important that special high-performance steel is used. Where high surface hardness and good fatigue strength are required and the material is also subjected to high temperatures, a material like our Nitrodur steel is an excellent choice. Nitrided surfaces maintain their hardness and strength at operating temperatures of up to approx. 500 °C - 550 °C.
Nitrodur is the brand name of the nitriding steel offered by Deutsche Edelstahlwerke, which is optimised for use at elevated temperatures. By varying the nitriding parameters, different hardness profiles and degrees of surface hardness can be achieved. One of the advantages compared to other methods, such as case hardening, is that there is less risk of deformation since no transformation process occurs when cooling down from the nitriding temperature.

The particularly high degree of purity and the homogeneity of the structure ensure consistent mechanical properties even for larger dimensions. Areas of hardness and toughness can be adjusted to the requirements of the particular component. Nitrodur steel offers an excellent degree of hot workability. The cold forming property and machinability depend on the analysis and type of structure. By adjusting the type of alloy and heat treatment, the material can also achieve optimal machinability.

The top quality of Nitrodur steel is achieved by a high level of process control, modern facilities for melting, secondary metallurgy, continuous casting, remelting*, hot working and heat treatment as well as advanced testing facilities. Deutsche Edelstahlwerke is able to deliver custom nitriding steel for any field of application and many different components.

Consult with one of our materials experts.

* Refer to our brochure “Remelting for highest standards” on our website www.dew-stahl.com for information on the function and details of the remelting process.
Our own steel production in our steelworks combined with additional remelting options form the basis for the purity and homogeneity of our nitriding steel. We achieve very defined properties as a result of precision alloying, process control and procedures for melting, forming and heat treatment. The steel is melted in 130-tonne electric arc furnaces. It is then metallurgically fine-tuned downstream in ladle furnaces of the same size. Depending on the steel grade and dimensions desired for the final product, the melted steel is cast via continuous casting or bloom casting procedures. For ingot casting, 50 different ingot mould formats from 600 kg to 40 tonnes are available.

Continuous casting is performed in a two-strand 475 mm x 340 mm vertical continuous casting facility or by means of a six-strand bow-type continuous caster in 138 mm, 150 mm and 265 mm formats. For the production of nitriding steel requiring particularly high levels of structural homogeneity, toughness, and purity, we use electroslag remelting furnaces (ESRs) and vacuum arc remelting furnaces (VARs).

In the ESU process, the slag absorbs non-metallic inclusions so that the remelted Nitrodur steel is free of macro inclusions. The improved microscopic cleanliness is due to desulphurisation and the resulting high level of sulphidic cleanliness as well as the reduced size and quantity of oxide inclusions.
The VAR remelting achieves the best possible microscopic oxidic cleanliness and the absence of macroscopic inclusions. Since this remelting process does not involve desulphurisation, it is important that the sulphur content is set to the lowest level possible before remelting in order to meet the requirements for sulphidic cleanliness. This method furthermore ensures the lowest possible gas content in the steel as well as a structure that is homogeneous and free of segregations.

**Hot Forming and Finishing**

The ingot or continuous casting products produced in the steelworks are hot formed according to the material. In a fully automatic programmed heating furnace, the ingots are preheated in an energy saving manner, and rolling plants produce semi-finished products, products in universal plate dimensions, bar steel > 22 mm Ø and wire > 5.5 mm Ø. For cross-sections > 250 mm Ø, a 30-MN forging press as well as one of the world’s largest and most efficient precision horizontal long forging machines (GFM RF 70) are provided. Another horizontal long forging machine (GFM SX 25) is available for smaller dimensions.

After the heat treatment of the hot-rolled products in continuous furnaces, the straightening of semi-finished products and steel bars in finishing lines with integrated fissure and ultrasound test procedures based on state-of-the-art technology takes place. Here, the test criteria are discussed with the customer.

**Mechanical Processing**

Deutsche Edelstahlwerke not only offers the optimal material in various product forms, but also rough-machined and ready-to-use components. Our customers have access to the extensive expertise of our employees and our modern processing systems. Rolled or forged steel bars as well as round pipe blanks up to 300 mm can be peeled, pressure-polished or bevelled after straightening. In Krefeld, Germany, rotation-symmetric parts with unit weights of up to 20 tonnes are manufactured in conventional and state-of-the-art CNC lathes and grinding machines. The focus of our production is on shafts, cylinders and continuous casting guiding rollers.
Nitrodur –
Hardness and precision for increased safety

Plastic Processing
During injection, pressing and extruding, the cylinders, pistons, worm gears, injection nozzles and other components are exposed to high mechanical and thermal stress (working temperature up to 500 °C). A consistently high level of hardness must be maintained to ensure an even degree of precision in the products to be manufactured. Nitrodur meets these requirements.

Gear Manufacturing
In power plant operation, rolls, gear wheels and pinions with external and internal gear systems manufactured from Nitrodur steel achieve greater operational reliability and longer service life. Nitrodur steel is also particularly suited for situations in which components cannot be reworked after heat treatment due to their geometry or small dimensions. Nitriding increases the surface hardness without resulting in severe distortion.
Engine Construction
Since engines, for example racing engines, are subject to extreme stresses, particularly thermal, the use of special Nitrodur steel is recommended for crankshafts, connecting rods, piston pins, cylinders, cylinder liners and drive chains.

General Mechanical Engineering
Nitrodur steel is suitable for any application in mechanical engineering that requires reliable operation and precise functioning under high temperatures. This includes the manufacture of pump drive shafts, timing chains, pistons for hydraulic controls, worm shafts and gears, spindles, straightening rolls, super-heated steam valves, valve guides and valve seats.

Toolmaking
For precision parts and tools operating under elevated operating temperatures, Nitrodur guarantees that the geometry of the components, such as calibrating rollers, calibration rings, thread gauges, plug gauges, gear wheels and piston rods, remains stable.

Machine Tool Construction
Nitrodur steel guarantees a long service life, reliable functioning and consistently high precision for machine tools, such as spindles, guide rails, grinding and drilling equipment as well as milling machines and lathes.
Nitrodur –
the nitriding steel by Deutsche Edelstahlwerke

Surface treatment is used whenever a component must feature a ductile core and a higher hardness on the surface, combined with inherent compressive stress to increase the wear resistance and vibration resistance. In addition to the chemical procedure of selective surface hardening and the thermo-chemical procedure of case hardening, the thermo-chemical procedure of nitriding is particularly important.

Definition of Nitriding
According to DIN EN 10052:1994-01, nitriding is defined as the thermo-chemical treatment of a workpiece in order to enrich the surface layer with nitrogen. Carbo-nitriding involves enriching the surface layer with nitrogen and carbon.

Principle of Nitriding
The purpose of nitriding is to increase the surface hardness. The process of nitriding takes advantage of the low solubility of nitrogen in the ferritic crystal structure to promote the precipitation of iron nitrides or alloy nitrides. With a nitrogen content of a few percent, a nitride layer that is mostly cohesive (connecting layer) forms on the surface. This layer is connected to a diffusion zone, in which the precipitated nitrides are evenly distributed in the steel matrix and which results in hardening, particularly for alloyed steel. Since nitrogen lowers the gamma/alpha transformation temperature of iron down to 590 °C, the nitriding temperatures are generally below this temperature. The lower limit for the nitriding temperature is 350 °C, because below this temperature, nitrogen diffusion does not occur at a rate that can be exploited technologically or economically. As temperatures decrease, the necessary nitriding time to reach a given depth of hardness increases. The depth of nitriding hardness may reach 500 μm with maximum hardness levels of > 1000 HV. Since warming up and cooling down occurs slowly and the basic structure does not undergo any transformation or change in volume, there is only a low risk of deformation.

Nitriding Steel
The material of choice is generally nitriding steel according to DIN EN 10085: 2001-07. This is an alloyed steel with nitride-forming elements. Nitrided steel is primarily available in the soft-annealed (A) or tempered (QT) condition.

Formation of a Nitride Layer
The nitrogen is transferred from the surrounding medium in the following steps:
» adsorption of nitrogen atoms
  on the surface of the component,
» absorption of nitrogen atoms
  by the component surface,
» diffusion of the nitrogen atoms
  along the grain boundaries and
  within the grains.

Nitrides form around seed points (grain boundaries and nodes at which several grains meet) on the surface of the component. As the nitrogen concentration and nitriding time increase, the nitrides grow deeper and expand laterally into the grains until a closed layer has been formed. The resulting nitrides disperse submicroscopically in the matrix.
**Composition of a Nitride Layer**
The external connecting layer influences the corrosion and wear characteristics. It is almost unavoidable that this layer displays a certain degree of porosity. This is due to a recombination to molecular nitrogen in energetically suitable spots, such as grain boundaries, in the connecting layer. The connecting layer may be brittle with a tendency to chip and is therefore removed by means of grinding in some cases. The adjacent diffusion zone affects strength characteristics (fatigue resistance) and the resistance against rolling wear and abrasion. The composition of nitride layers may be modified significantly by adapting nitriding conditions and systematically selecting materials. The transition from the hardness of the diffusion zone to the core hardness of the base material is fluid, which, unlike surface layers, reduces the risk of chipping during mechanical stressing. Nitride layers are also heat resistant up to approx. 550 °C.

**Effect of the Tempering Temperature**
As the tempering temperature increases, the amount of Cr and Mo carbides increases as well. This reduces the precipitation of nitrides and results in a lower increase in hardness. The nitriding temperature should be below the tempering temperature in order to keep the core hardness from decreasing.

**Effect of the Alloying Elements**
Of the nitride forming elements aluminium, chromium, vanadium and molybdenum, the elements chromium and aluminium particularly affect surface hardness. However, 1% aluminium results in a higher increase in hardness than 3% chromium, and it is independent of the carbon content of the steel, since aluminium does not form carbides and is therefore fully available for nitride formation. Lower contents of molybdenum and vanadium improve the tempering resistance and reduce sensitivity to temper embrittlement.

The higher surface hardness, which is caused by the additional alloying elements, results in a lower tendency to adhere to a wear partner and in increased abrasion resistance. However, the increased surface hardness also leads to a greater risk of cracking during mechanical stressing.

**Depth of Nitriding Hardness**
The depth of nitriding hardness is a characteristic value for the thickness of the nitride layer (Nht) as defined in DIN 50190-3:1979-03. It describes the vertical distance from the surface to the point at which the hardness is still 50 HV higher than the core hardness.
As the deformability of the nitrided component not only depends on the thin, hard nitride layer but also on the chemical composition and structure of the base material, the following is true for all kinds of nitrided steel: The more homogeneous and fine-grained the structure is, the better the nitriding result. However, generally, the tempered initial state (QT) is preferred over the annealed state (A).

Steel grades containing aluminium form more aluminium oxides that deteriorate the microscopic, oxidic level of purity and prevent the diffusion of nitrogen into the component surface if the precipitation occurs on the surface of the component.

The higher the alloy content of the nitriding steel, the greater the surface hardness that can be achieved. The compressive residual stress in the nitrided surface layer also increases, which leads to higher fatigue strength. This, however, also reduces the depth of nitriding hardness that can be achieved because the alloying elements impair diffusion of the nitrogen into the interior of the component.
## CHEMICAL COMPOSITION
IN ACCORDANCE WITH DIN EN 10085:2001-07

<table>
<thead>
<tr>
<th>Material</th>
<th>Code designation</th>
<th>Material no.</th>
<th>C</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>V</th>
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<tbody>
<tr>
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<td>min. 0.28</td>
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*Material is not standardised (see: Bosch Rexroth company standard ZN 93008-110: 2013-03-28)

## MECHANICAL PROPERTIES
IN THE TEMPERED STATE

### Material Properties

<table>
<thead>
<tr>
<th>Material</th>
<th>16 ≤ d ≤ 40 mm</th>
<th>40 &lt; d ≤ 100 mm</th>
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<tbody>
<tr>
<td></td>
<td>Rm in MPa</td>
<td>Rp0,2 in MPa</td>
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<tr>
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<tr>
<td>Nitrodur 8519</td>
<td>1100 - 1300</td>
<td>min. 900</td>
</tr>
<tr>
<td>Nitrodur 8550</td>
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<tr>
<td>Nitrodur 8509</td>
<td>950 - 1150</td>
<td>min. 750</td>
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<tr>
<td>Nitrodur 8507**</td>
<td>800 - 1000</td>
<td>min. 600</td>
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<td>1150 - 1350</td>
<td>min. 950</td>
</tr>
<tr>
<td>Nitrodur 8523</td>
<td>950 - 1150</td>
<td>min. 750</td>
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** Only for dimensions d ≤ 70 mm

### Material Properties

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<th>160 &lt; d ≤ 250 mm</th>
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<td>Rm in MPa</td>
<td>Rp0,2 in MPa</td>
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<td>min. 700</td>
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<td>800 - 1000</td>
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<td>850 - 1050</td>
<td>min. 670</td>
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<td>-</td>
</tr>
<tr>
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<td>min. 750</td>
</tr>
<tr>
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<td>min. 700</td>
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### GENERAL PROPERTIES

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<th>Achievable surface hardness</th>
<th>Polishability</th>
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<td>+</td>
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<td>+</td>
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<td>+++**</td>
<td>+++</td>
<td>+***</td>
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</tbody>
</table>

*** Empirical values
Thermo-Chemical Process of Nitriding

Gas-Nitriding and Gas-Carbo-Nitriding

The normal temperature range for gas-nitriding and gas-carbo-nitriding is $450 \ °C \leq T \leq 590 \ °C$. The crucial factor in gas-nitriding of the component is the release of diffusible N by means of a gradual reduction of ammonia and its absorption in the surface of the component. In some cases, NH$_3$ is added to the fresh gas, which dilutes the NH$_3$ content. In the so-called oxi-nitriding process, oxygen, generally in the form of air, is used to intensify the nitriding process. The oxi-carbo-nitriding is used to treat passivated surfaces. For gas-carbo-nitriding, diffusible carbon is added. It is generally added in the form of CO and CO$_2$, either pure or as part of a gaseous mixture (e.g. endogas or exogas).

In gas sulphonitriding, sulphur or hydrogen sulphide is added to the ammonia. Though the process leads to better wear characteristics because sulphur is deposited in the connecting layer, it is seldom used. Unlike other methods, gas-nitriding and gas-carbo-nitriding can achieve a variety of different structures, connecting layer thicknesses and nitriding hardness depths. The structure setup of the nitride product can be adjusted to the component shape. The methods are suitable for large and small parts. Please note that special safety precautions must be met due to the use of flammable gases.

Excessive nitriding may lead to a more pronounced connecting layer and the formation of a nitride network around the grain boundaries. This increases brittleness and thus also the risk of chipping.
Plasma-Nitriding and Carbo-Nitriding
Plasma-nitriding and carbo-nitriding are performed at temperatures between 350 °C and 590 °C. Positively charged ions strike the component that acts as a cathode at high velocities in front of the furnace wall (anode). In the beginning, this ion bombardment causes the component surface to be cleansed (sputtering), thus allowing passive layers to be removed. Then it is heated and the component surface is nitrided. Pulsed discharges increase the uniformity in the batch and lower the energy transfer in the plant. Placing a negative active screen between the positive furnace wall and the negative components leads to glow discharge on the screen. In high-alloy materials, nitriding is uniform and passivating layers can be removed even without sputtering. This method is also called ASPN (active screen plasma nitriding).

The advantage of treatment in plasma is that the layer composition can be optimised (e.g. thin connecting layers with high Nht). The treatment is easy to reproduce and results in minimal changes in dimension. Compared to nitriding in gas or salt baths, it results in the lowest level of coarseness. Component charging, however, requires exact definitions and plasma cannot enter crevices smaller than 0.6 to 0.8 mm.
Salt Bath Carbo-Nitriding
Treatment generally lasts between 30 min and 120 min at $570 \, ^\circ C \leq T \leq 590 \, ^\circ C$. The components are immersed in molten salt baths and then quenched in water. The resulting layers improve fatigue strength and are very resistant against adhesive and abrasive wear. If the components are then quenched in an oxidising molten salt bath or treated in an oxidising medium, corrosion resistance increases significantly. Salt containing nitrogen must be present in the molten salt bath and the salt should be soluble in water so that it can be easily washed off.

Salt bath carbo-nitriding is performed in the following treatment steps:

» **Precleaning**
  Spray washer with alkaline cleaning agents and “rinse”

» **Preheating**
  Preheat components for 30 to 120 minutes in a recirculating furnace at 350 °C to 400 °C (depending on the thickness of the component)

» **Carbo-Nitriding**
  The process begins immediately after immersion in the molten salt bath. A closed connecting layer forms after only several minutes (very high nitrogen content).

» **Cool down / Oxidising**
  Unlike with non-alloy steel, the cooling speed does not affect the nitrogen solution state of alloyed steel because hard sub-microscopic nitrides are already deposited during carbo-nitriding with the nitride forming alloying elements. The choice of the cooling method is made based on the component’s tendency to crack and deform, its chemical composition and the desired layer properties.

» **Washing**
  Elaborate for deep blind bore holes

The key advantage of this method is that the process is not very susceptible to fluctuations and requires only a few parameters to be adjusted.

The batch setup barely impacts the treatment results, which means that batches can be loaded densely without detrimental effects.

However, the method cannot be used for pure nitriding without carbon diffusion. In addition, partial treatment due to lack of suitable means of insulation against nitrogen absorption in the molten salt baths is also only possible to a limited extent. The ratio of connecting layer thickness to diffusion depth can only be adjusted to a certain degree as well.
Newer Special Methods
In addition to the methods described previously, there are also special methods that will not be described in further detail here because they do not yet play a significant role in the industry. This includes powder carbo-nitriding, nitriding in aqueous NH₃ solutions as well as nitriding/carbo-nitriding in fluid bed reactors.

The research is based, among other things, on the microcutting of gas-carbo-nitriding steel with diamond tools to obtain visual surface qualities. To date, microcutting has not been suitable for commercial use due to the extreme wear on diamond tools. The creation of thicker, low-pore connecting layers has been used as a starting point.
Gas-Nitriding and Pulsed-Plasma-Nitriding
Deutsche Edelstahlwerke not only produces Nitrodur nitriding steel created according to exact requirements, but also offers the option of treating the manufactured components in our hardening facilities, where they undergo a thermo-chemical heat treatment process, gas-nitriding and pulsed-plasma-nitriding. The gas-nitriding, gas-carbo-nitriding and carbo-nitriding are carried out at a temperature range of short-term and long-term nitriding for batch dimensions (length x width x height) of 900 x 600 x 600 mm.

Plasma-nitriding is offered for batch dimensions around 1200 x 1900 mm and around 800 x 1300 mm. The facilities of Deutsche Edelstahlwerke allow for the production of steel within diameter ranges of 5.5 to 900 mm Ø.
Deutsche Edelstahlwerke not only produces high-grade construction steel but also stainless steel and tool steel that can also be nitried to a certain extent.

Our specialist departments are happy to assist and provide you with further information at any time.
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