

# Nitriding steels: Nitrodur

DEUTSCHE EDELSTAHLWERKE

Providing special steel solutions



## Nitriding steels: Nitrodur

Nitrodur –  
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 steels are used. Premium materials, like one of our Nitrodur steels, is an excellent choice for applications in which the material is subjected to high temperatures and where high surface hardness and good fatigue strength are required. Nitrided surfaces maintain their hardness and strength up to operating temperatures of approx. 500 to 550° C.

**Nitrodur** is the brand name of the family of nitriding steels that Deutsche Edelstahlwerke offers 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 steels offer an excellent degree of hot workability. Cold formability and machinability are

dependent on the analysis and the type of structure. By adjusting the type of alloy and heat treatment, the material can also achieve optimal machinability.

The high quality of Nitrodur steels 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 non-destructive testing facilities. Deutsche Edelstahlwerke is able to deliver a custom nitriding steel for any field of application and many different components.

**Consult with one of our materials experts.**



## State of the art

### Our expertise in steel production means security for you

Steel production facilities in both of our steelworks combined with additional re-melting options, is the basis for the purity and homogeneity of our nitriding steels. We achieve very clearly defined properties as a result of precise specifications, process control and procedures for melting, forming and heat treatment. The steels are melted in 130 ton electric arc furnaces. Then they go through metallurgical fine-tuning 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 t are available. Continuous casting is performed in a two-strand 475 x 340 mm vertical continuous casting facility or by means of a six-strand bow-type continuous caster in the sizes 138 mm and 265 mm. For tool steels requiring particularly high levels of structural homogeneity, toughness, and purity, we use electroslag remelting furnaces (ESRs) and vacuum arc remelting furnaces (VARs).

#### Electroslag Remelting

During electroslag remelting (ESR), a process that involves alternating current, a cast or forged consumable electrode is immersed in molten slag which serves as an electrical resistor. The material to be remelted drips through the slag from the end of the electrode and forms the new block in the water-cooled mould. The heat dissipation allows the solidification to be directed towards the longitudinal axis of the block. The remelting slag serves multiple purposes in this procedure. It generates the necessary heat, initiates chemical reactions such as desulphurisation and protects the molten bath of the newly formed block from oxidation.

In addition, the slag has a high capacity for non-metallic inclusions, which results in remelted material which is then 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.

#### Vacuum Arc Remelting

Vacuum arc remelting (VAR) is a procedure that involves the remelting of cast or forged consumable electrodes in a vacuum. A molten bath is created under vacuum by means of an arc in a copper pan that serves as the opposite pole for the remelting electrode and is connected to a DC power source via power contacts. In a continuous process, a new block is formed drop by drop from the liquefied electrode material. In the VAR method, the steel is refined because the oxygen released in the steel reacts with the carbon in the molten mass as a result of the vacuum. This leads to an optimal degree of 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 homogenous and free of segregations.

#### Hot Forming and Finishing

The ingot or continuous casting products produced in the steelworks are fed into the blooming mill via computer-controlled rotating hearth furnace and rolled into semi-finished products, bar steel or products in universal plate dimensions. An intermediate reheating furnace located after the first forming unit, facilitates rolling in very narrow temperature ranges, which allows even critical high-alloy steels to be rolled. Modern finishing lines are available for straightening semi-finished products and steel bars, where the interior quality and surface properties are examined and dimensions and identity are checked. Forging as a way of hot forming is performed in a 45 MN press, a 33 MN press and one of the world's largest and most efficient precision long forging machines (GFM RF 70). This machine can

forge products in dimensions up to approx. 550 mm in diameter. A horizontal long forging machine is available for smaller dimensions.

#### Mechanical Processing

Deutsche Edelstahlwerke not only offers an optimal material in different product forms but also rough-machined and ready-to-use components. Our customers have access to extensive expertise and modern processing systems. Rolled or forged steel bars as well as round pipe blanks up to 300 mm can be peeled, pressure-polished or chamfered after straightening. In Krefeld, Germany, rotation-symmetric parts with unit weights of up to 20 tons are manufactured in conventional and modern 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 intruding, the cylinders, piston, worm gears, injection nozzles and other components are exposed to high degrees of stress. Even during increased working temperatures up to approx. 500° C, a consistently high level of hardness must be maintained in order 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 improved systems manufactured from Nitrodur achieve reliability and longer service lives. Nitrodur steels are also particularly suited for situations in which components cannot

be reworked after heat treatment due to their geometry or small dimensions. This is because 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 stresses, the use of special Nitrodur steels is recommended for crank-shafts, connecting rods, pistons gears, cylinders, cylinder liners and driving chains.

### General Mechanical Engineering

Nitrodur steels are suitable for any application in mechanical engineering that requires reliable operation and precise functioning even for 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 steels guarantee 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 is to feature a ductile core and a higher hardness on the surface combined with compressive residual stress to increase 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. This procedure generally involves special nitriding steels, which are produced under the trade name Nitrodur at Deutsche Edelstahlwerke.

### 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 enrich the surface layer of a workpiece with nitrogen in order to increase the hardness in the surface. 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 steels. 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 considered to be 350° C, because below this temperature, nitrogen diffusion does not occur on a rate

that can be exploited technologically or economically. As temperatures decrease, the nitriding time necessary 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 Steels

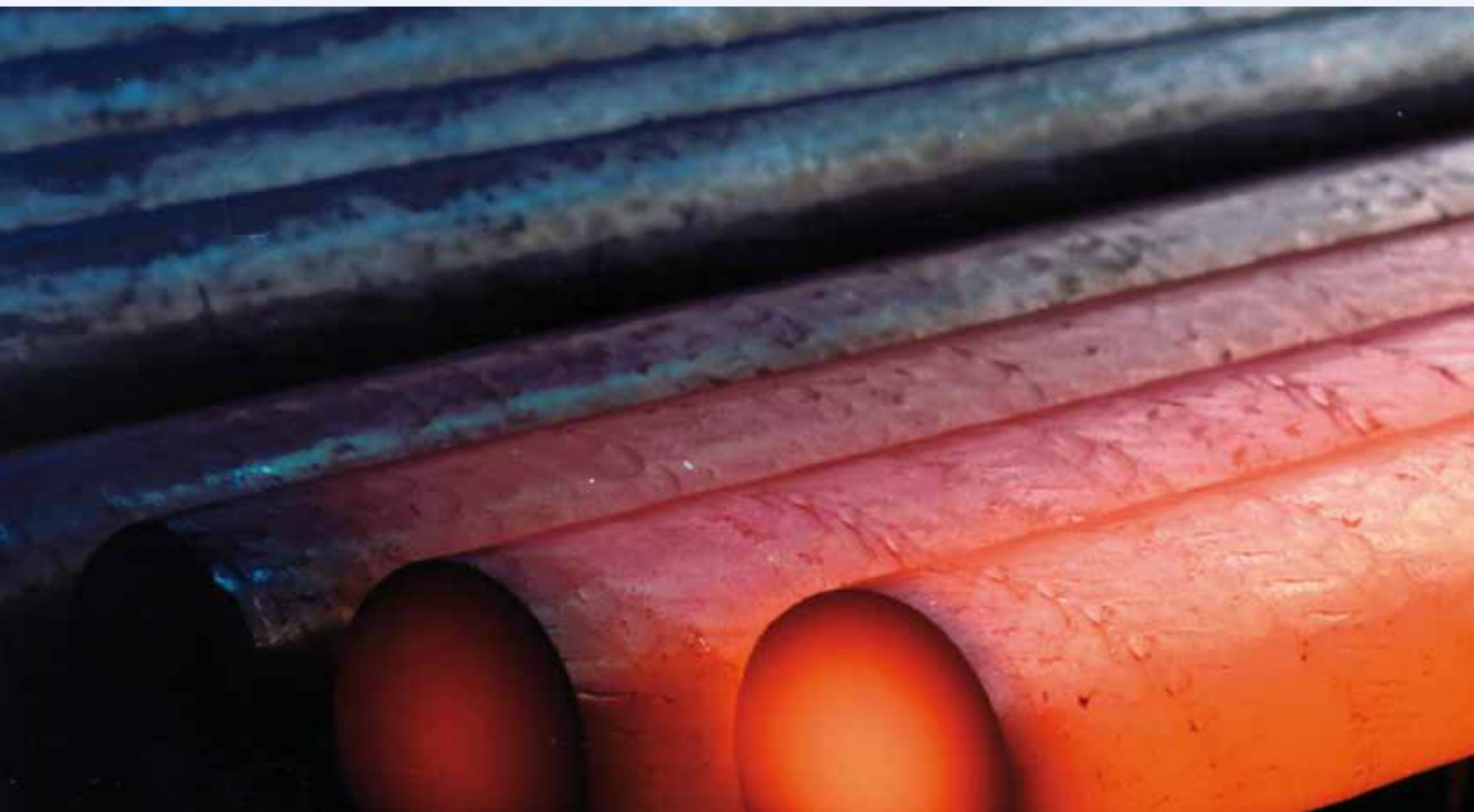
The material of choice is generally a nitriding steel according to DIN EN 10085: 2001/7, alloyed steels with nitride-forming elements. Nitrided steels are primarily available in the soft-annealed (A) or tempered (QT) condition.

### 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 on the surface of the component (grain boundaries and nodes at which several grains meet). 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. Along with the nitride forming alloy elements, nitrides form and disperse submicroscopically in the matrix.



### Composition of a Nitride Layer

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 increases

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.

### Depth of Nitriding Hardness

The depth of nitriding hardness is a characteristic value for the thickness of the nitride layer 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.

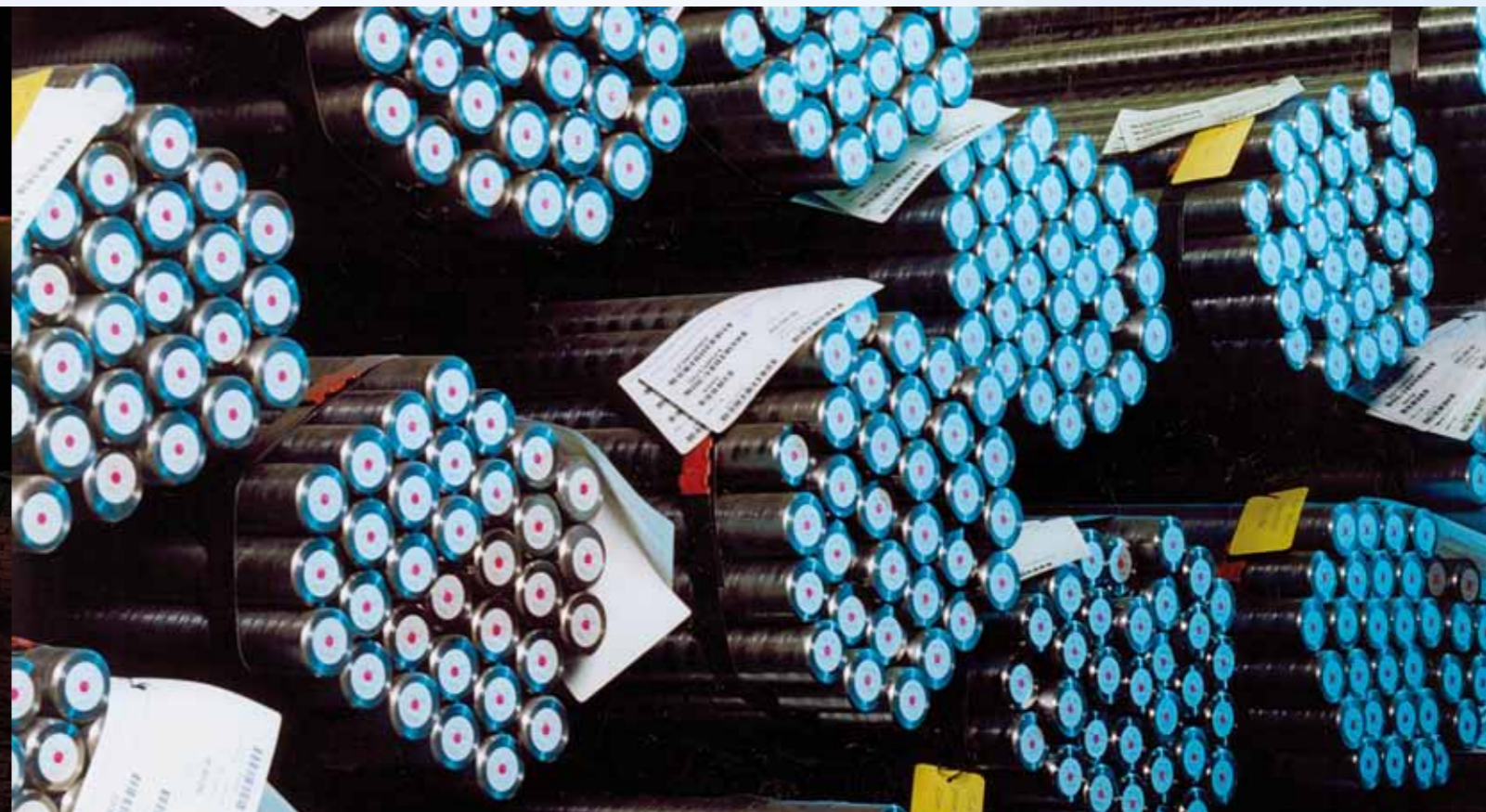
### Effect of the Tempering Temperature

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

Out 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 upon 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 alloy 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 higher risk of cracking during mechanical stressing.



Since 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 nitrided steels:

The more homogenous 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 a base material (the nitriding steel), the higher 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.

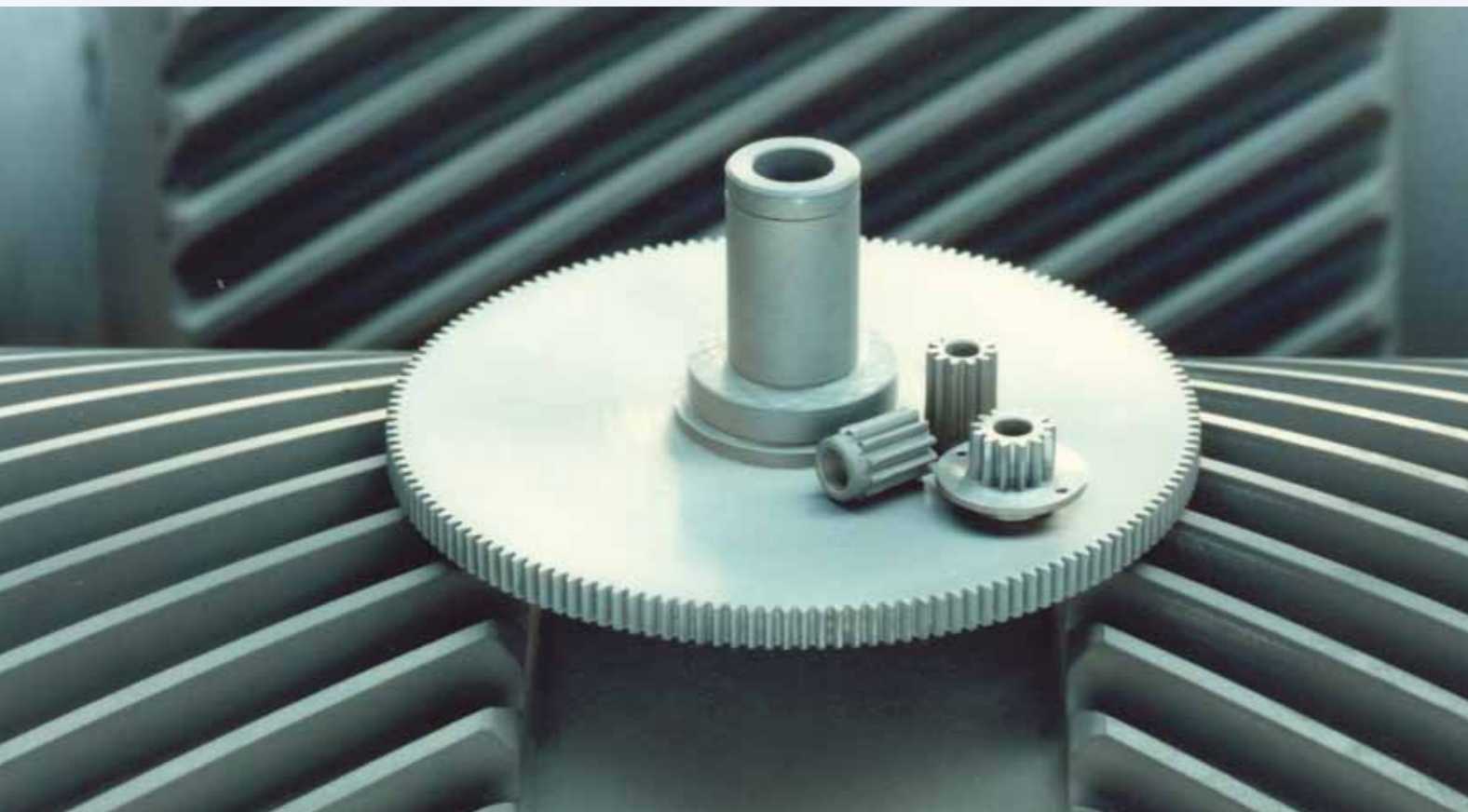
## Materials Overview, Chemical Composition and Properties of Common Nitriding Steels

Material	Code designation	Material no.	C	Mn	Cr	Mo	Ni	V	Al
Nitrodur 8515	31CrMo12	1.8515	0,31	0,6	3,0	0,4	-	-	-
Nitrodur 8519	31CrMoC9	1.8519	0,31	0,6	2,5	0,2	-	0,15	-
Nitrodur 8550	34CrAlNi7-10	1.8550	0,34	0,6	1,7	0,2	1,0	-	1,0
Nitrodur 8509	41CrAlMo7-10	1.8509	0,41	0,6	1,7	0,3	-	-	1,0
Nitrodur 8507	34CrAlMo5-10	1.8507	0,34	0,6	1,2	0,2	-	-	1,0
Nitrodur 8522	33CrMoV12-9	1.8522	0,32	0,5	3,0	0,9	-	0,20	-
Nitrodur 8523	40CrMoV13-9	1.8523	0,40	0,6	3,3	1,0	-	0,20	-
Nitrodur 8524*	8CrMo16*	1.8524*	0,08	1,1	3,9	0,5	0,3	-	-

\*Material not standardised (see: Bosch Rexroth company standard ZF 93008-110:2008-01-28); all other materials: EN 10085: July 2001.

Material no.	Rm* [MPa]	Rp <sub>0,2</sub> *[MPa]	Av (RT) [J]	Core hardness	Core toughness	Achievable surface hardness	Polishability
1.8515	880 - 1230	min. 675	min. 25	++	+	+	+
1.8519	850 - 1300	min. 650	min. 25	++	+	+	+
1.8550	800 - 1100	min. 600	min. 30	+	++	++	-
1.8509	800 - 1150	min. 600	min. 25	+	+	++	-
1.8507	800 - 1000**	min. 600**	min. 35**	+	+++	++	-
1.8522	900 - 1350	min. 700	min. 30	+++****	++	0****	+
1.8523	800 - 1150	min. 625	min. 25	++****	+	0****	+
1.8524	800 - 1000	min. 700	min. 40***	++****	++++	++****	+

\* Values for longitudinal dimension  $16 \text{ mm} \leq d \leq 250 \text{ mm}$ ; confirmable values depend on diameter.  
 \*\*Only for dimensions  $16 \text{ mm} \leq d \leq 70 \text{ mm}$ . \*\*\*Av (-40°C) = min. 40 J \*\*\*\* 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  $450^{\circ}\text{C} \leq T \leq 590^{\circ}\text{C}$ . 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,  $\text{NH}_3$  is added to the fresh gas, which dilutes the  $\text{NH}_3$  content. In the so called oxi-nitriding process, oxygen, generally in the form of air, is used to intensify the nitriding process. 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  $\text{CO}$  and  $\text{CO}_2$ , 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

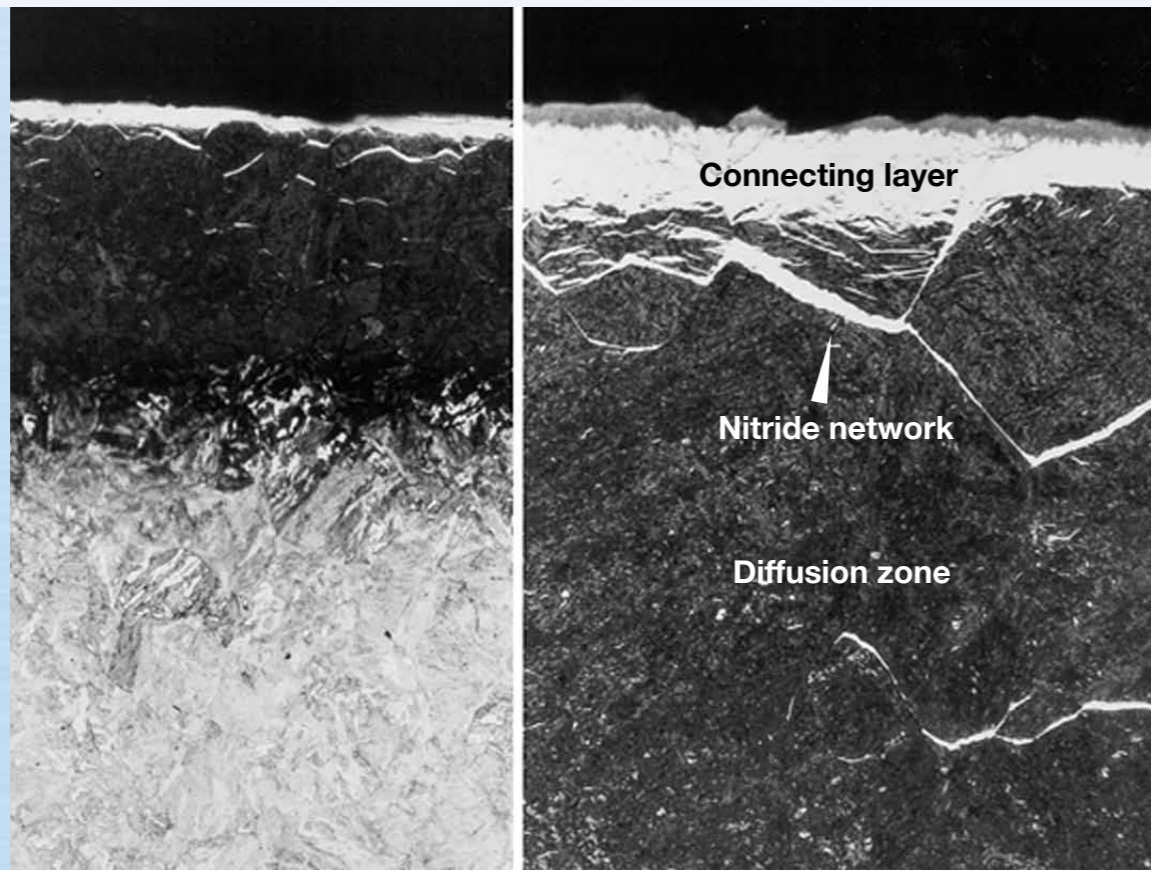
wear characteristics because sulphur is deposited in the connecting layer, it is seldomly used in Germany. Unlike other methods, gas nitriding and gas-carbo-nitriding can achieve a variety of different structures, connecting layer thicknesses and nitriding hardness depths. The batch setup of the product to be nitrided 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.

### Plasma Nitriding and Carbo-nitriding

Plasma nitriding and carbo-nitriding is performed at temperatures between  $350$  and  $590^{\circ}\text{C}$ . 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 of specialty steels 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  $\text{N}_{\text{Ht}}$ ). 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.

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.



### Salt Bath Carbo-nitriding

Treatment generally lasts between 30 and 120 minutes at  $570^{\circ}\text{C} \leq T \leq 590^{\circ}\text{C}$ . 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 easily be washed off. Salt bath carbo-nitriding is performed in the following treatment steps:

- **Precleaning**

(Spray wash with alkaline cleaning agents and rinse)

- **Preheating**

(Preheat components for 30 to 120 minutes in a recirculating furnace at  $350$  to  $400^{\circ}\text{C}$  depending on the thickness of the component)

- **Carbo-nitriding**

(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 steels, the cooling speed does not affect the nitrogen solution state of alloyed steels because hard submicroscopic nitrides are already deposited during carbo-nitriding with the nitride forming alloy elements. The choice of 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 hole bores.)

The key advantage of this method is that the process is not very susceptible to fluctuations and requires only few parameters to be adjusted. It can be used to treat practically any steel grade and cast iron. The batch setup hardly impacts the treatment results, which means that batches can be loaded densely without detrimental effects.

The method can, however, not be used for pure nitriding without carbon diffusion. 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  $\text{NH}_3$  solutions as well as nitriding / carbo-nitriding in fluid bed reactors. The focus of current research is on microcutting 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.



### **Gas Nitriding and Pulsed Plasma Nitriding**

Deutsche Edelstahlwerke not only produces Nitrodur nitriding steels created according to exact requirements, but also offers the option of treating the manufactured components in our hardening facility Härterei Technik GmbH in Lüdenscheid and Stuttgart, where they undergo a thermo-chemical heat treatment process, gas nitriding and pulsed plasma nitriding.

Both locations offer gas nitriding, carbonitriding and carbo-nitriding in temperature ranges for short-term and long-term nitriding for batch dimensions of 900 x 600 x 600 mm (length x width x height).

Plasma nitriding for round batch dimensions up to 1200 x 1900 mm is offered at both locations.

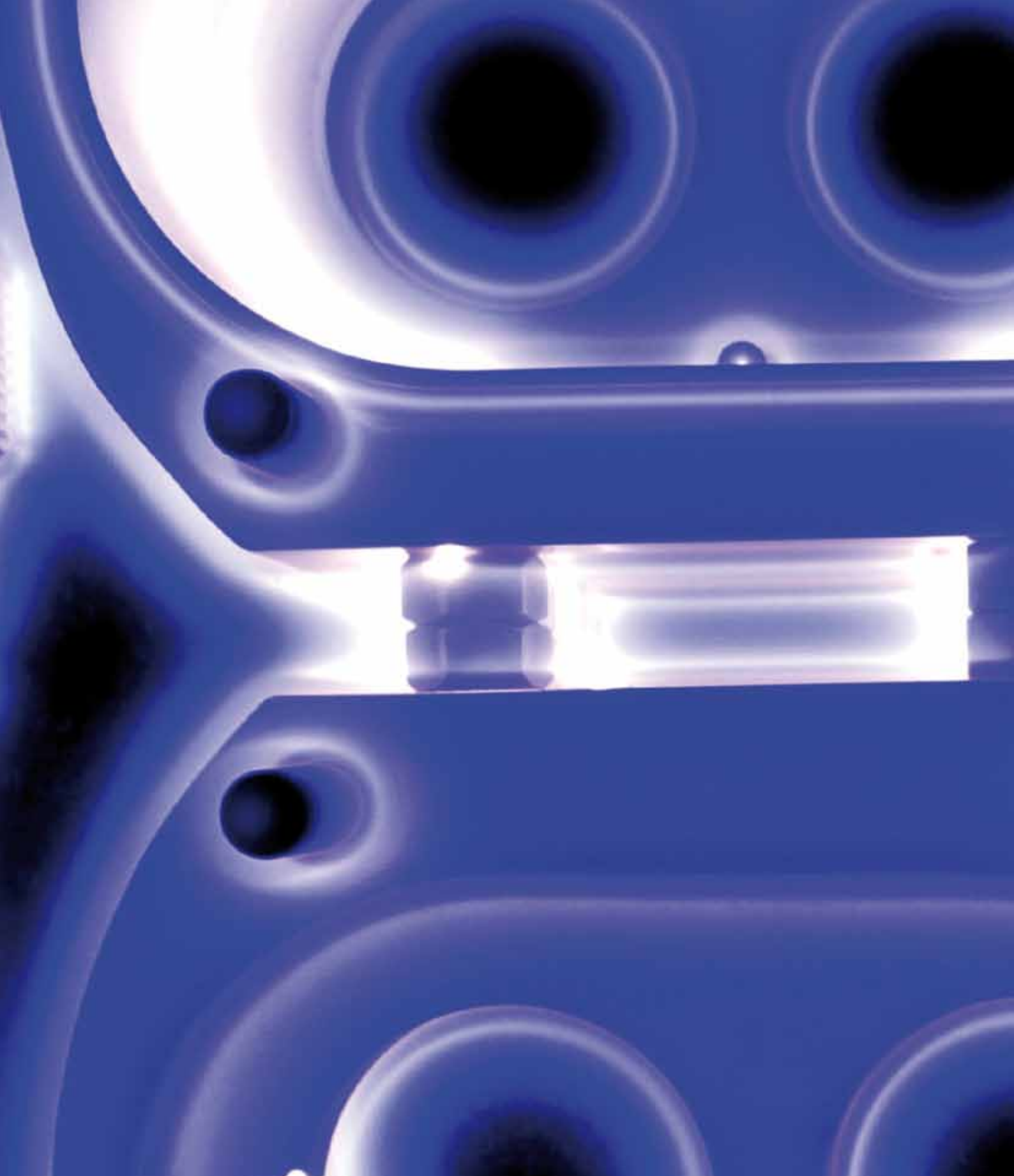
The facilities of Deutsche Edelstahlwerke allow for the production of steel within diameter ranges of 5.5 to 1,200 mm. Deutsche Edelstahlwerke GmbH not only produces high-grade construction steels but also stainless, acid and heat-resistant steels and tool steels that can also be nitrided to a certain extent.

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

### **General note (liability)**

Information about the quality or usability of materials or products is for descriptive purposes only. Confirmations in relation to the existence of certain characteristics or with reference to a certain application always require a special written agreement. Printing errors, omissions and changes excepted.





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