



FUNDAMENTALS of SURFACE TECHNOLOGY



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EDITORIAL

Dear Reader

WOTech, with the products and services it offers, works to promote collaboration between developers, constructors, production engineers and technical experts along the entire process chain from basic materials and fabrication, all the way to final surface finishing. Key to this is a real understanding of the often complex interactions involved. Unlike mere journalists *We speak your language*. This English-language edition in this series covering the different aspects of finishing technology, offers a concise guide to various terms and an overview of the wide range of processes offered under the general heading of Surface Technology.

Best regards

The WOTech Team

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Iron and steel – Pure iron (Fe) is silvery white, but oxidises rapidly in moist air. The oxide layer (rust) flakes easily and is readily dissolved by diluted acids, but is resistant to alkaline solutions. The melting point of iron is at 1537 °C and the boiling point at 2750 °C. Pure iron occurs in the three forms of alpha, gamma and delta iron. In its chemical compounds, it is usually bivalent or trivalent (valences of +II to +VI occur).

These chemical properties and the magnetic properties of the iron are of great importance for its usage. The iron-carbon alloys containing 0.02 % to 2.06 % carbon (carbon steels), which are referred to as ‘steel’ or which are additionally alloyed with metallic or non-metallic components, are generally the most important metals used. The physical properties of iron alloys are greatly variable, and carbon is the most important alloying element, which significantly increases the strength and hardness, whilst decreasing the plasticity and flexibility.

The versatility of the steels as construction materials lies in the possibility of being able to change the properties of the steel over a wide range. In addition, the steels can be processed with all well-known manufacturing methods.

Steels can be classified in accordance with multiple criteria. The most common classification is according to the main quality classes (DIN EN 10020) in unalloyed steels (unalloyed quality and stainless steel), low-alloy steels (alloy quality and special steels) and high-alloy steels (e. g. stainless steels). In terms of different grades of basic carbon and stainless steels, the requirements play a decisive role in their performance characteristics.

In the basic or mass steels, their mechanical properties cannot be ensured by a heat treatment. The description system according to DIN EN 10027-1 is using a main tool for determining the intended use and the indication of the minimum consistency (e. g. yield strength).

Quality steels – Quality steels are non-alloyed or alloyed steels with specific requirements of their suitability for cold forming, their resistance to atmospheric corrosion or their electrical or magnetic properties. This is why they are usually intended to be used for a heat treatment. The content of elements other than iron, such as phosphorus and sulphur, is less than 0.045 %. Typical applications include the production of sheets, strips, tubes and other profiles.

Stainless steels – Stainless steels are non-alloyed or alloyed steels, and their properties are generally ensured by a heat treatment, such as quenching and tempering. They show a greater purity in terms of quality steels. Their phosphorus and sulphur content is below 0.035 %. Depending on the structure, they can be ferritic or austenitic. Their areas of application depend on the requirements, which can be, for example, in engines, automotive, nuclear power stations, climate technology, materials handling, water technology, food industry, plastics industry, furniture industry and medical technology.

Non-alloyed (general) steels – As per definition in DIN EN 10020, the non-alloyed steels must not exceed specific limit values on additional elements (*Table 1*).

Non-alloy construction steels cover, to a large extent, approximately 70 % of the world’s steel production. They are mainly offered in the cold worked condition or in conjunction with a stress relieved condition as thermoformed (hot-rolled), and are finding various applications in mechanical engineering, automotive, construction, civil engineering, bridge and building fabrication, tank construction and in marine and off-shore engineering.

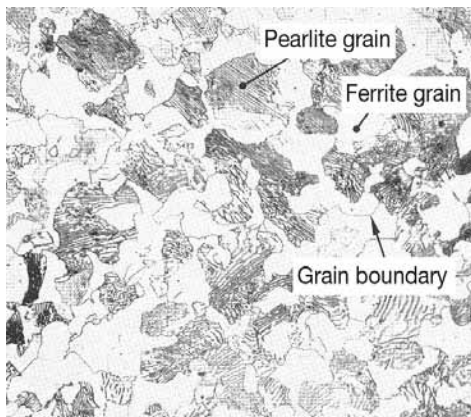
Table 1: Limits on additional elements

| Element | Content (%) |
|-----------------|-------------|
| Aluminium (Al) | 0.1 |
| Lead (Pb) | 0.4 |
| Boron (B) | 0.0008 |
| Bismuth (Bi) | 0.1 |
| Chrome (Cr) | 0.3 |
| Cobalt (Co) | 0.1 |
| Copper (Cu) | 0.4 |
| Molybdenum (Mo) | 0.08 |
| Nickel (Ni) | 0.3 |
| Niobium (Nb) | 0.05 |
| Selenium (Se) | 0.1 |
| Silicon (Si) | 0.5 |
| Tellurium (Te) | 0.1 |
| Titanium (Ti) | 0.05 |
| Tungsten (W) | 0.1 |
| Vanadium (V) | 0.1 |
| Zirconium (Zr) | 0.05 |

Non-alloy construction steels belong to the main grade of non-alloy quality steels. They are selected for their consistency or ability to weld, and for their resistance to brittle fracture. With their low carbon content and its ferritic-pearlitic structure, they differ in their mechanical characteristics and are standardised according to DIN EN 10025-2. The most important mechanical parameter is the minimum yield limit, which must be guaranteed. Their tensile strength is below 500 N/mm^2 . Weather resistant varieties include DIN EN 10025-5 (e. g. S235J2).

Non-alloy construction steels belong to the basic steels and are generally not intended for heat treatment. An exception, however, is the stress relieving between $550 \text{ }^\circ\text{C}$ to $650 \text{ }^\circ\text{C}$ and the normal glow in the temperature range of the structural transformation. They can be easily cold formed at room temperature, such as by bending, folding, beading and pressuring. Cold forming produces an increase in the internal stresses within the material. This leads to a cold solidification. In order to restore the mechanical properties (strength, ductility), a stress relieving may be necessary. In the temperature range of normal glow, a hot forming is usually possible. Construction steels are not universally suitable for welding. Reasons for example are: not specified de-oxidation, unspecified chemical composition or high carbon content. The weldability is also depending on the quality group and improves in the order of JR, J0, J2, K2. For example, a S275J2 is safer for being welded than is a S275JR.

The **plain carbon steels** which are standardised according to their chemical composition, are described via a standard designation of primary and additional



Non-alloyed steel – metallographic finish

symbols. The main symbol C is the code letter for this type of steel. The subsequent number is the concentration of carbon multiplied by 100. A further requirement concerns the manganese content. It must not exceed 1 %. A steel with the description C40 has therefore $40/100 = 0.4 \%$ of carbon. The plain carbon steels are suitable for heat treatment, and therefore find their applications in the field of tool making.

Low-alloy steels – In this group of steels, the total proportion of alloying elements may not exceed 5 % and the manganese content is above 1 %. They usually have similar properties to the non-alloyed steels, but their mechanical properties can be significantly influenced by suitable heat treatment. In the designation system of this group of materials (DIN EN 10027-1), the chemical symbols of the alloying elements are listed in order of declining contents. The contents of carbon and the alloy elements are supplied with the factors in the *Table 2*.

Table 2: Factors for alloying elements

| Alloying elements | Factor |
|---------------------------------------|--------|
| Cr, Co, Mn, Ni, Si, W | 4 |
| Al, Cu, Mo, Ti, V, Be, Ta, Zr, Nb, Pb | 10 |
| C, N, P, S, Ce | 100 |
| B | 1000 |

A steel material with the label 40CrMo₄ is describing a low-alloy steel having the alloying elements chromium and molybdenum in the composition, is $40/100 = 0.4 \%$ of carbon, $4/4 = 1 \%$ chromium. The second element which is associated with molybdenum, does not have a number, since its proportion is far less than 1 %. This group includes, for example, the cutting steels, alloyed case-hardening steels, quenched and tempered steels, cold-work tool steels and spring steels.

High-alloy steel – In this steel group, the proportion of a group of the alloying elements (except carbon) is at least 5 %. The aim here is to achieve specific physical, chemical and mechanical properties by alloying certain elements. High-alloy steels are designated by the letter X. Here, the hundredfold carbon content is adjusted, which in turn follow the chemical symbols of the alloying elements in order of decreasing proportion. The following series of numbers indicate the

percentage amount of the main alloying elements. A steel material with the label X3CrNiMoV18-8 2 denotes a high alloy steel having the alloying elements chromium, nickel, molybdenum and vanadium in the composition with $3/100 = 0.03\%$ of carbon, 18% chromium, 8% nickel, 2% molybdenum and a small content of vanadium.

Heat-treatable steels – Heat-treatable steels are carbon and low alloy engineering steels with a carbon content between 0.20% and 0.70%, which are suitable for hardening, and in the quenched and tempered condition provide good toughness at a given tensile strength, or a significantly increased strength. They are mainly processed for dynamically high stressed components (e. g. gear shafts).

Case hardening steels – Case Hardening steels are unalloyed or alloyed (mainly Cr, Ni, Mo, Mn) engineering steels with a relatively low carbon content (0.1% to about 0.25%), whereby the surface layer is carburised prior to curing (0.7% to 0.90% C) or carbonitrided. Applications include components which need a tough core together with a wear-resistant surface.

Nitriding steels – Nitriding steels are alloy steels, which are particularly suitable for nitriding and nitrocarburising. They contain alloy elements such as Cr, Al, Mo, V, Ti and Nb, which tend to form nitrides and produce a surface layer with a high hardness.

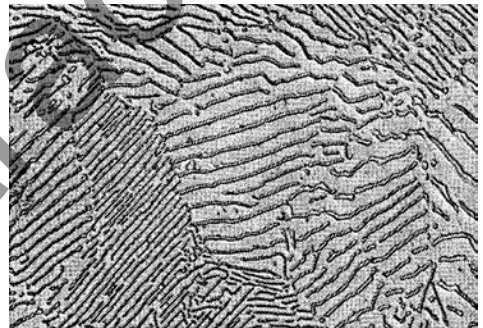
Free cutting steels – Free cutting steels are used for a cost-effective machining (for example turning or milling) and are used on high-speed machines. To evaluate the machineability, the four main evaluation parameters chip shape, surface finish, tool life and cutting force serve as indicators. For effective automation of the cutting process, free cutting steels need to offer the following advantages:

- Reduced tool wear (higher tool life) at the highest possible cutting speeds
- Low cutting forces to reduce tool wear and power consumption of the machine tool
- High surface quality
- Short brittle, well shovel-like shavings, low clamping force
- Avoidance of built-up edge

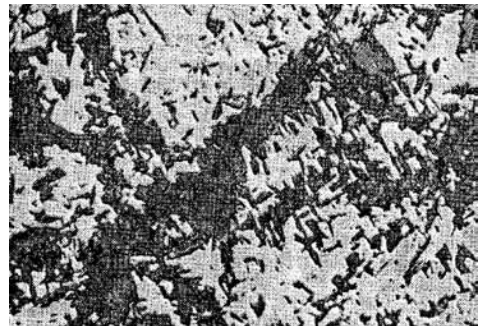
Stainless steels – In many industries, especially in the food, textile, pulp and paper, chemical, medical engineering and automotive, as well as in marine and

offshore engineering, stainless steels are required. The most important property of these steels is their chemical stability. The mechanical properties (e. g. strength, toughness) are of secondary importance.

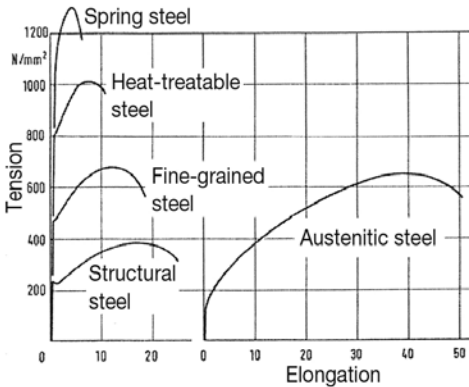
More than 80 years ago, it was discovered that chromium significantly improves the corrosion resistance at a certain concentration in the steel. The first stainless steel with 18% chromium and 8% nickel was designed by Maurer and Strauss at Krupp, under the trade name **V2A** in 1912, and patented. With the addition of further alloying elements, many new stainless steels had been developed with optimised properties. The steels are commonly known by trade or brand names, such as V4A, Stainless Steel or Chromargan. The common use of the term “stainless steel” for stainless steels, however, is incorrect, because this designation is according to DIN EN 10020 and is used for a wider classification.



Texture picture – rough lamellar pearlit of C80-steel – magnification = 500:1



Texture picture – steel with 0.98% carbon, heat-treated with austenite formation in advanced state



Stress-strain diagram of different kind of steels

The good corrosion resistance of stainless steels is due to the presence of a dense, tough, firmly adhering and very thin (about 1 nm to 20 nm) oxide layer, or adsorptive bound oxygen layer on the steel surface. It is formed on the surface in the presence of oxygen, with chromium contents over 12 %. Since these oxide or oxygen layers prevent the dissolution of the metal ions, the steel is passive from an electrochemical point of view. Accordingly, these protective layers are also referred to as “passive layers”. A violation results immediately in a re-passivation in the presence of oxygen. In addition, other metals such as aluminium, titanium, nickel, chromium and copper also form in similar corrosion performance, significantly enhancing the protective layers.

Stainless steels can lose their corrosion resistance under certain conditions. This is the case, for example, at an increased surface roughness, since no closed passive film can be formed, or if the chromium is not homogeneously distributed in the crystal lattice of the iron (for example, by chromium carbide after welding). A particularly dangerous form of corrosion is pitting corrosion, which is also referred to as a grain disintegration intergranular corrosion, or as stress corrosion cracking.

The stainless steels are divided according to their structural composition, and thus their functional properties, into ferritic and semi-ferritic chromium steels (C < 0.1 %, Cr 12-30 %), martensitic chromium steels (C 0.15 to 1.2 %, Cr 12-18 %) austenitic chromium-nickel steels (C < 0.15 %, Cr 16-28 %, 6-32 % Ni) austenitic and ferritic stainless steels (C < 0.05 %, Cr 21-29 %, Ni 4-7 %).

The advantages of austenitic Cr-Ni steels, as compared to other stainless steel groups, lie in their excellent corrosion resistance (except for stress corrosion cracking), their excellent plastic deformability and their good strength, even at very low temperatures. The required chromium content of more than 12 % would lead to a predominantly ferritic microstructure. To form an austenitic structure, with its widely differing characteristics from the other types of steel properties, austenite-stabilising alloying elements must be added in certain concentrations. Nickel is particularly well suited for this purpose as a strong austenite former. By lowering the passivation it additionally improves the corrosion resistance to acids. The fcc lattice of Cr-Ni steels has a very good plastic deformability, with elongations up to 50 %. They are thus at least twice as high as compared to other types of steel.

Influence of alloying elements – Steel properties are influenced by the manufacturing processes and desired undesirable alloying elements, and by accompanying elements. Desirable elements offer specific mechanical and chemical properties to the steel, such as high strength or toughness, good forming and machining properties, as well as corrosion resistance and wear resistance. However, some accompanying elements can degrade these properties in an undesirable manner. (Table 3).

Aluminium and aluminium alloys – Aluminium is a lightweight metal with a density of 2.7 kg/dm³, a melting point of 660.2 °C and an electrical conductivity of 27.7 m/(Ω mm²). The strength properties are far lower than those of the steels. Pure aluminium reaches a tensile strength of up to 50 MPa, a 0.2-proof stress of up to 25 MPa and a maximum elongation to break of 45 %.

With the addition of alloying elements such as magnesium, manganese, molybdenum, silicon, titanium, zirconium, beryllium, chromium, iron, copper or zinc, the mechanical and chemical properties can be greatly improved. As a starting material, pure aluminium is used with a purity of 99.5 % in most cases. Even small additions of alloying elements, have a strong influence on the properties of pure aluminium. For example, they increase the strength and hardness, without adversely affecting the good ductility. For example, the 0.2-proof strength can be increased to 450 MPa in the aluminium alloy AlZn1, 5MgCu of 40 MPa (at Al99,5).

Cleaning of metal – During manufacturing production processes of metal components, various lubricants and cutting fluids are used; these materials can be water-soluble (aqueous cooling emulsions) or water insoluble (oils and greases) compounds. These materials can leave residues on the components. In addition to this metals react with oxygen from the air to form surface oxides, depending on the metal. The oxides form a porous or dense cover film on the surface of the component. A common example is rust on ferrous materials. These surface contaminants will interfere with any subsequent metal or organic coating materials, as they prevent the adhesion of the coating or cause locally imperfections. These surface layers can also interfere with the manufacturing assembly operations or can affect the performance or function of completed machines. For these reasons, metallic components must often be cleaned before a further processing – sometimes even within the process chain for the production of components. For the cleaning process, the cleaning agent must be matched to the particular material to be removed and the base material. For example a weak aqueous detergent solution can be used to remove water-soluble substances. Water-insoluble oils and greases can be removed by organic solvents, these however need closed loop cleaning systems. The cleaning effect is accelerated by the use of heat or ultrasound. Oxide surface layers can be removed using acids or alkalis. Often the removal of oxide layers is referred to as pickling. In all cases a metallic bright surface will arise when surfaces are cleaned properly.

Degrease – During the processing of materials, particularly in the handling and processing of metals, oils and greases are used. They serve, for example, to protect the metal surface against oxidation and corrosion. They are also used in mechanical forming operations by improving the sliding of the work piece surface on the tool surface. This is particularly important in the case of metallic tools, for example, bending tools: without lubrication scoring or seizure can take place leading to partial welding at high loads. Oils and greases left on the metal surface will prevent good adhesion between the base material and coating. This applies in principle to any kind of coating – electro-deposition, painting, PVD coating. Oils and grease will harden during extended exposure to light or heat, or burn when exposed to higher temperatures. The remaining residue can interfere with or hinder further processing of the base material. For these reasons,

materials must be thoroughly degreased in any case before a coating.

Advanced process technologies during the production of high quality products, for example in the field of precision engineering, may include several degreasing operations during the manufacturing process. This is carried out to facilitate the best possible mechanical processing of materials or the fitting of parts into intermediate assemblies. For the degreasing organic solvents such as methanol and other alcohols (for weak impurities), acetone, benzene, methylene chloride, trichlorethylene, or trichloroethane (for heavy impurities) are very effective. However due to the adverse effect of the organic solvents towards the health of living organisms or the environmental effects such as the destruction of ozone layer in the atmosphere, the use of solvents is restricted or they have to be used in totally enclosed or emission-free systems. As an alternative to organic solvents, aqueous cleaning agents are increasingly being used. These however have the disadvantage of reduced cleaning effect and the risk of causing corrosion of metal surfaces.

Immersion degreasing – In immersion degreasing the parts to be cleaned are immersed in the degreasing agent and left there for a certain time. The immersion duration depends on the degree of contamination of the components surface. The cleaning effect of a degreasing agent can be improved if the temperature is raised. In the case of the use of organic solvents, however, the exposure of operators to the solvents vapours has to be taken into account (occupational health and safety, environmental protection). In aqueous degreasers, the corrosive effect on metals must be considered. Usually aqueous degreasing solutions will have inhibitors added that suppress or reduce corrosive attack.

Vapour degreasing – Cleaning by vapour degreasing involves the parts to be cleaned being placed in a closed system above a degreasing solvent heated to just below its boiling point. The space above the liquid is highly enriched with the vapour of the degreasing solvent. The solvent condenses on the surface to be cleaned; this produces an effective and rapid cleaning action. This is very intense due to the high temperature and the solvent vapour will be clean. The oils and greases removed from the component will accumulate in the liquid phase. This prevents redistribution of the contaminants on the surface when the parts are removed from the degreasing system.

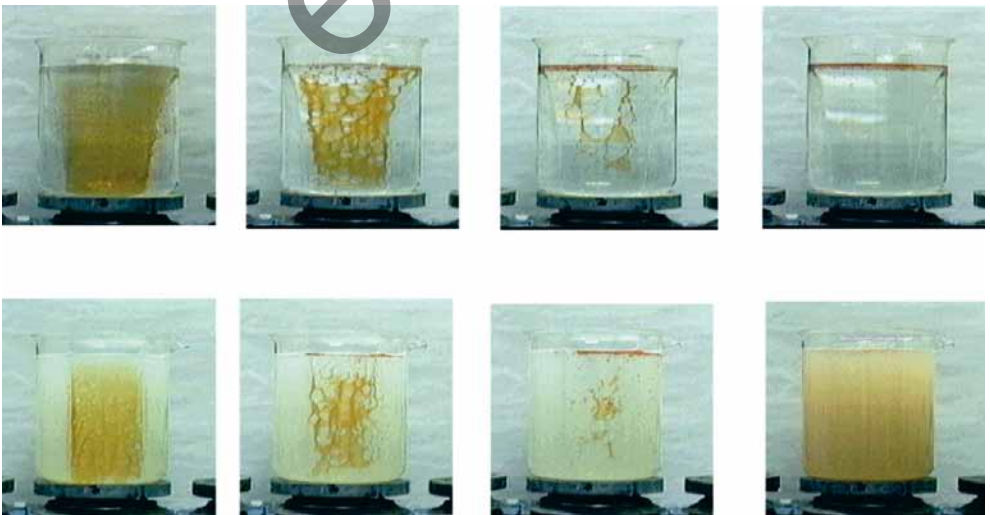
Solvent degreasing – The degreasing with solvents is a very efficient method for the removal of oils and fats, preferably of metal surfaces. The solvents used can be hydrocarbons, chlorinated hydrocarbons or modified alcohols. Nowadays, the cleaning is being carried out almost exclusively in completely closed systems using increased medium temperature. The systems include devices for the treatment of the cleaning medium and separating the removed oils and greases. In addition, the equipment is designed to be explosion proof.

Aqueous degreaser – In electroplating process the use of aqueous degreasing is common practice. In general, the degreasing solutions are based on low to high strength alkaline solutions of sodium or potassium hydroxide. In addition, they contain oil and grease binding additives. Degreasing is often carried out in several stages depending on the degree of contamination. In so-called soak cleaning degreasing is carried out in an alkaline solution at a temperature of 50 °C to 70 °C. In the second stage, an electrolytic degreasing is performed. In this case, the metal to be cleaned is connected anodically or cathodically using low voltage direct current. In the case of the anodic circuit oxygen is generated, in the cathodic circuit, hydrogen is generated by the water being electrolytically split up. The gas evolution lifts off adhering dirt from the surface. The cleaning solutions can contain

emulsifying or de-emulsifying additives. With the addition of emulsifiers, the detached oils and greases are dispersed and held in the solution as very small droplets (emulsified). De-emulsifiers lead to the formation of larger conglomerates of oil and grease, which float to the surface, are usually removed via an oil separator from the degreasing solution. When using aqueous degreasing it is essential that the concentration of detached oils and grease is not too high, as otherwise redispersion can take place when removing the parts from the cleaner. Any residues of alkaline degreasing solution can be removed by immersion in a dilute acid (usually sulphuric acid), this process is called pickling.

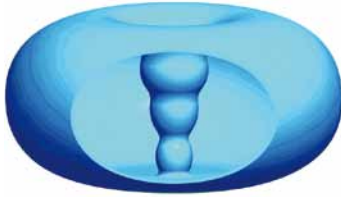
Ultrasound – Ultrasound is used as a cleaning process for almost a century and has become established in a variety of applications in manufacturing. The process enables the efficient, material-friendly and rapid removal of particulate contamination, for example, particles, chips and dust, and of filmic residues, for example by machining media such as oils and emulsions. The process works for parts with complex geometries as well as hard to reach areas such as blind holes, crevices or undercuts. The use of Ultrasound also means that the use of cleaning chemicals can be reduced.

The sound waves are produced by a generator which converts the normal mains electricity frequency of 50 Hertz to 60 Hertz into high frequency vibrations.



Effect of de-emulsifying (upper row) and emulsifying degreasing agents

(Photo: SurTec)



The cleaning effect of ultrasound is based on cavitation: the lower the ultrasonic frequency the greater the cavitation bubbles and the energy released by them (Photo: Bandelin)

The electromagnetic vibrations are then converted by acoustic transducers into mechanical vibrations of the same frequency and transferred to a cleaning fluid. If the oscillations in the cleaning fluid meet a solid surface it causes cavitation at the surface. This is because of the high intensity of the alternating sound pressure during the rarefaction phase of the oscillation the forces between liquid molecules are overcome causing millions of microscopic bubbles. In the subsequent pressure phase, the cavitation bubbles become unstable, collapsing in on themselves (implode) and produce hydraulic shocks with significant energy densities that trigger in the liquid micro-currents. If they hit a surface, they remove the dirt and loosely adhering solid particles. An advantage of this intensive surface

treatment is the reduction of the cleaning time by up to 90 % compared to a pure immersion treatment in the same cleaning solution.

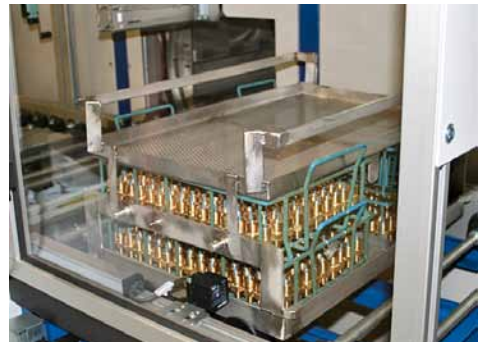
Such transducers are available as rod, submersible and plate transducers. An alternative are ultrasound units that work with individual elements. For elimination of water-based (polar) impurities such as cooling and lubricating emulsions, polishing pastes, additives, salts, metal particles and other solids usually aqueous cleaners are used. They are available as a pH neutral, alkaline and acidic media.



Cleaning system for using solvents and aqueous media as well as ultrasound (Photo: EMO)



The most commonly used transducer systems in the industrial parts cleaning are rod and submersible transducers (Photo: Weber Ultrasonics)



To ensure an optimal cleaning result by the sound waves the parts must be easily accessible (Photo: Dürr Ecoclean)

A criterion for the successful use of ultrasonic cleaning is the frequency. In general, the lower the frequency, the greater the cavitation bubbles and the energy released by them. This means a low frequency on the one hand leads to a large cleaning effect on the surface, on the other hand, this reduces the ability to penetrate component features such as bores and holes. This means that for workpieces with a complex geometry and/or high cleanliness requirements ultrasound is used at different frequencies. Multi or mixed frequency systems are available in which the cleaning liquid can be sonically agitated with multiple frequencies, for example 25 kilohertz and 40 kilohertz. The resulting mixing of large and small cavitation bubbles gives optimal cleaning of the complex geometries. This enables the creation of effective space-saving cleaning systems.

The cleaning result is influenced by the number and positioning of the transducer elements in the cleaning solution. In order to ensure a sufficient cleaning effect, usually 8 W to 10 W ultrasonic power per litre cleaning solution volume is required. This means that an output power of 800 W to 1000 W is required in a cleaning tank with 100 liters of volume.

The sound waves propagate from sound-emitting surface in the liquid as longitudinal waves. Due to interference this results in regions of low and enhanced sonic zones. The arrangement of transducer elements therefore has a great influence on the cleaning result. If for example transducer elements are only attached to the bottom of the cleaning tank, the sound propagates vertically to the surface of the cleaning medium and is reflected back to the bottom of the tank. This has implications for the cleaning parts with cavities and blind holes. If these contain trapped air bubbles, these will act as barriers preventing the propagation and the ultrasound result in preventing cleaning taking place. It is therefore important to ensure that all cavities are filled with cleaning fluid. For this purpose, the parts should be oscillated or rotated in the cleaning medium. Some ultrasonic generators have a sweep function for frequency modulation, this gives a more uniform distribution of the ultrasonic oscillation in the cleaning liquid.

Next to air, cleaning baskets which are completely closed or consist of perforated metal can also have an unfavourable effect on the cleaning. Ideal workpiece carriers and baskets are constructed from stainless round wire. They allow both the ultrasound and the cleaning medium to be transmitted from all sides.



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Metal deposition – The concept of metal deposition is generally used to describe the electrochemical production of metallic coatings. Electrochemical deposition is divided into electrodeposition using an external electrical circuit, and electroless deposition or chemical metal deposition.

In addition to the electrochemical metal deposition some other forms of physical deposition exist, for example, by immersion in liquid metal (hot-dip galvanizing, dip tinning), various types of mechanical applying coatings by burnishing, cladding or the vacuum evaporation (PVD coatings).

By using the metal deposition, it is possible to change or improve the properties of the base material. One of the major requirements today is to increase the corrosion resistance of materials, particularly useful for ferrous materials. Another interesting feature is to increase the wear resistance, which is possible especially by the deposition of chromium or nickel-phosphorus. Finally, the deposition of multiple layers from nickel-chromium, or from noble metals such as gold, palladium or silver, offers the possibility to change the colour and the tactile feel of a surface. Colour and the tactile feel of a surface are especially important in the automotive sector in the coating of plastic parts for the interior of vehicles.

Electroplating – Electroplating means the conversion of dissolved metal to the solid metal by the use of an applied electric current. Electroplating is carried out in most cases from an aqueous solution of a metal salt – such as nickel chloride, nickel sulfate, copper sulfate, and zinc chloride. In addition to the dissolved metal salt, the aqueous solution contains additional substances depending on the type of metal deposition. Brightening agents, for example, are added for the production of smooth and bright metal layers, conductivity salts to improve the electrical conductivity of the aqueous solution.

The deposition of metal is carried out by the positively charged metal ions – e. g. twice positively charged nickel ions (Ni^{2+}) or twice positively charged copper ions (Cu^{2+}). These are reduced at the cathode electrode to the pure metal. In order to complete the electrical circuit, a second electrode (anode) is situated in the same container to which the reverse process takes place. Metal ions are formed at the the

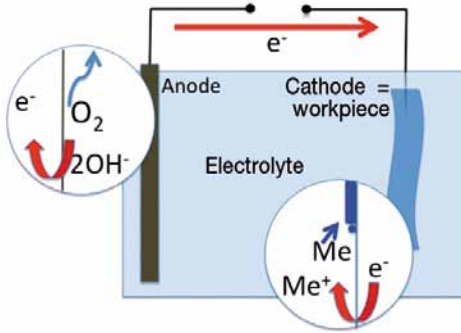
anode by removal of electron: Nickel metal will become nickel ions (Ni^{2+}).

For this process, direct current is used in most cases. The magnitude of the current depends on the size of the surface which is coated with a galvanic deposited metal layer. Depending on the type and characteristics of the deposited metal, the current densities (current per unit area) vary between 0.1 A/dm² and up to 100 A/dm²; in exceptional cases lower or higher values can be used. This results in deposition rates ranging from 0.1 microns per minute and up to 10 microns per minute. Differences arise mainly due to different charge states of the metal ions used (depending on metal this can be between one and up to six elementary charges) as well as the proportion of undesirable side reactions; in the case of electroplating this is the evolution of hydrogen.

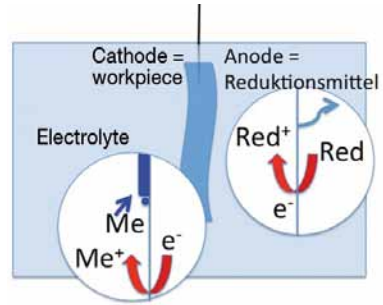
The electroplating is characterised, among other things, by the fact that a wide variety of metal combinations of base material and coating can be used, thus, different additional properties can be imparted in the base material. Furthermore, the metal layers can relatively evenly be applied onto all areas which are in contact with the aqueous solutions (deposition electrolytes). At points with higher field strength (corners, edges, points), more metal is deposited in many types of electrolytes. The result leads to differences in the layer thickness, this needs to be considered for parts with small fitting tolerances.

A major advantage of galvanic metal deposition is the extremely efficient and economical use of metals. With minimal amounts of metal a base material is given a determined property. For example, iron materials are protected against corrosion by electrolytic zinc coatings with thicknesses between 10 microns and 15 microns. A component with a surface area of 1 m² consumes only 107 g of zinc at a thickness of the zinc coating of 15 microns. (Note: 1000 micron = 1 mm). The process can be designed to prevent loss of zinc metal from effluent discharges. With the help of special masking techniques, in almost all electroplating processes, the layers can also be partially applied where they have to perform their functions.

Chemical metal deposition – Chemical metal deposition or electroless deposition is the conversion of dissolved metal to the solid metal without the use of an applied electric current. In this case, the



The principle of electroplating



The principle of chemical metal deposition

electric charges come from reducing agent which is also dissolved in the aqueous solution and is thereby oxidized, while the metal ions are reduced by gaining the electric charges into metal. The reduction of the metal ions takes place on the surface to be coated of the solid body and leads to the formation of a metal layer. The metal reduction occurs in all areas of the coated solid body with equal speed, as long as sufficient amounts of metal ions and reducing agents are present, i. e. as long as there is flow of the aqueous solution (electrolyte) over the surface

of the solid body. Layers of nickel or nickel-phosphorus, copper and gold can be produced by chemical metal deposition. The deposition rates are in the chemical metal deposition at about 10 microns/hour to 20 micrometres/hour, considerably slower than in the galvanic metal deposition. As such, the layer thickness over the entire area to be coated solid has a uniform thickness and therefore the geometric shape is maintained. Due to the slower deposition rate, the thickness of the metal layer can be precisely controlled within very narrow limits. Thus, the metal deposition is perfectly adequate for the exact coating surfaces with tightest tolerances.



Shut-off ball valve, chemical deposited with nickel
(Source: AHC)

A special variant is the metal deposition in the immersion coating process. Metals differ in their electrochemical behavior, this is measure of the metals relative reactivity. Copper and precious metals are among the more noble metals (less reactive). If a less noble metal such as zinc or iron will be immersed in a solution containing, for example, copper, silver or gold, then the basic material will dissolve and the surface will be covered with copper, silver or gold. The process will end as soon as the entire surface will be covered with the noble metal coating. However, the layers produced with this method are very thin with significantly less than 0.1 microns. This technique is used in the electronic manufacture for the production of intermediate layers or contact surfaces.

Aluminium – Aluminium is one of the most reactive metals, while in use it behaves like a relatively non-reactive metal. This is because aluminium in contact with atmospheric oxygen, will be instantaneously coated with a dense and very stable oxide layer.

The reactivity of metallic aluminum is so high that the aluminum oxidation takes place, for example, in water or an aqueous solution in which the metal can react with the dissolved oxygen or with the oxygen of the water molecule. However, this reaction depends on the acidity (pH value) of an aqueous solution.

Although aluminum salts (e. g. aluminum chloride) can be dissolved in water, but when passing a current flow between an anode and a metal to be coated as the cathode, there will be no aluminum deposition, because the hydrogen ions (H^+ or correct H_3O^+) in the aqueous solution will be reduced much more easily than the available aluminum ions (Al^{3+}). From aqueous solutions containing aluminum ions, hydrogen is evolved exclusively. The aluminum deposition will only be successful if aluminum salts will be present in a non-aqueous solution, or for example, an anhydrous organic solvent or the recent availability of ionic liquids.

The deposition of aluminum has been known for 60 years and has been patented as Sigal process in 1973 by Siemens AG. The organic solvents used for this purpose, however, are easily flammable and react adversely when in contact with water. The deposition must, therefore, take place in the absence of air and water in completely enclosed systems. In addition, the aluminum layers only adhere on base materials that have thoroughly degreased and pickled; both operations usually being carried out in aqueous media and counteract the necessary anhydrous process. The scale of the effort needed for the safe operation of the process has so far prevented the profitable deposition of aluminum from organic solvents.

Currently, the aluminum deposition is carried out for special requirements on small parts in a laboratory scale. The usually matt, high-purity aluminum layers exhibit very good corrosion behavior and can be anodised and dyed with conventional methods. In addition, since the layers are very ductile, even thicker layers in the range of 50 micrometers and more can be produced which are mechanically deformable. In addition to aluminum, aluminum-magnesium-layers can be produced from aprotic solvents.

The deposition of aluminum from ionic liquids is currently in development. Since the currently available ionic liquids dissolve only a small concentration of aluminum salts, the deposition rate is low. The great advantage of ionic liquids is seen in the fact that they

can be used under normal atmosphere. Also here, next to pure aluminum, alloys can be deposited.

Chromium – The electrodeposition of chromium is one of the most important processes for the production of technical and decorative surfaces. Only in an electroplated state chrome has the very advantageous properties of corrosion resistance, good gloss, high reflectivity and very high hardness. In addition, the deposition of chromium results of very simply constructed electrolytes with only very limited amounts of additives, resulting in the high reliability of the galvanic deposition of chromium both for decorative applications as polished chrome as well as for functional applications as hard chrome. The disadvantages of chromium plating are the use of carcinogenic hexavalent chromium (Cr^{6+}) compounds and environmentally harmful wetting agents. These are also the reasons that the galvanic chrome plating is presently being discussed in the context of the european chemicals regulation REACh. On the other hand it must be emphasized, that in accordance with the applicable policies which have been existing for many years with regards to environmental and occupational safety, no dangers by galvanic chromium plating are resulting. It is required to wear the usual protective clothing and the use of extractors with washing facilities and the use of rinsing devices.

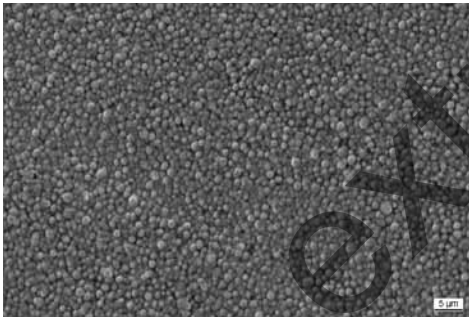
Decorative chromium coatings are generally deposited on nickel layers with thicknesses between 0.2 micron and 1 micron. Especially in the plumbing



Roll: hard chrome coated and mechanically polished to high gloss
(Photo: LKS)

Table Properties of chromium layers

| Parameter | Hard chromium | Decorative chromium |
|---------------------------------|--|-------------------------------|
| Thickness | up to a few millimeters | < 1 μm |
| Colour | initial state after deposition matt silver after mechanical machining high glossy | high glossy |
| Hardness | state after deposition approx. 600 HV–approx. 1250 HV annealed (> 600 °C) approx. 400 HV–approx. 700 HV | approx. 600 HV–1100 HV |
| Coefficient of friction | 0,12 (chromium/chromium) 0,17 (chromium/steel) 0,05 (bright chromium/bronze) | |
| Modulus of elasticity (E-Modul) | approx. 120 kN/mm ² –230 kN/mm ² | |
| Tensile strength | 130 N/mm ² –500 N/mm ² | |
| Coefficient of linear expansion | 6–9 (20 °C/500 °C) | |
| Corrosion resistance | very good in many climates; but: vulnerable to calcium chloride | very good in many climates |



Scanning microscopic image of a structured chromium layer (Photo: GWC)

industry, furniture industry, or on parts inside the vehicle decorative chromium coatings are used without further coatings; they are characterised by good reflectivity, their bright metallic surface and good scratch and abrasion resistance. Furthermore, chrome surfaces are difficult to wet, making them easy to clean. In part, decorative chrome surfaces also receive an additional finish, for example, on spectacle frames, whereby an additional selective coloring and selective printing will be possible. Parts in the vehicle interior can be chrome plated because the surfaces reflect the light very well and the parts are easy to be seen in very low light conditions. For

decorative layers, electrolytes based on the health-safe chromium(III) can be used. However, these chrome layers have a slightly grayer shade and a significantly lower hardness and wear resistance.

The second major area of electroplated chromium deposition is that of hard chrome plating. Hard chromium layers serve as wear and corrosion protection of heavily stressed base materials, primarily of steel, and are, for example, essential for hydraulic parts, rollers for the paper industry and metal processing and tool parts for textile production. The deposition of hard chromium layers is also carried out by electrolyte on the basis of hexavalent chromium, with modified operating parameters. The layer thicknesses produced depend on the load in terms of wear and corrosion environment, and whether the surface will need to be further processed, for example, by grinding and mechanically polishing. Usual layer thicknesses are between about 20 microns and more than 1000 microns.

In particular, if the applied chromium layers will be mechanically grounded and polished, then higher thicknesses (e. g. more than 100 microns) are useful. With thicker chromium layers (greater than about 50 microns) it is to be expected that the roughness increases or even nodules may arise on edges. If in such thick chromium coatings a low roughness (high

flatness) is required for use, then the mechanical grinding and polishing may be unavoidable.

To a considerable extent, the high hardness of chromium layers is mainly due to the incorporation of hydrogen formed during galvanic chromium deposition. Due to the hydrogen incorporation, the layers display internal stresses which lead to cracking. This allows the existing stresses to be reduced, without the properties of the chromium coating suffering in terms of mechanical stresses. If in addition to a high hardness and wear resistance, a good corrosion resistance is demanded, then the deposition is controlled in the way that produces multilayers. This means that cracks do not extend through the entire chromium layer, but stop at the interface between two chrome layers. Thus, an outside corrosion medium cannot fully penetrate to the base material. The corrosion resistance of the layer will thereby be increased.

Chromium consists of a good corrosion resistance, because in contact with air it forms a very stable chromium oxide and the metal will become passive. After that, it behaves like a precious metal. If cracks or pores will occur in a decorative chromium layer (use decorative system for iron substrates), an attack of the nickel or iron materials by the corrosive medium starts. In the case of decorative chromium, which usually have thicknesses of less than 1 micron, the corrosion attack of the base material can be reduced by the deliberate production of so-called micro-cracked chromium layers. Professionals with electroplating knowledge can optimise the structure of

the layer system. For high mechanical and corrosive requirements, for example, combinations of chemically deposited nickel layers (high hardness) and hard chrome coatings have proven successful (high hardness and high corrosion resistance).

For parts which are coated in high numbers (e. g. piston rods for shock absorbers), it is possible to use special tooling, rotationally symmetrical parts to be coated with micrometer accuracy. Thereby, a final mechanical finishing process by grinding or polishing is not required. Due to the method, this technology is also allowing a very high deposition rate and is therefore especially economical. The deposition rate can be increased by a factor of 10 or more, depending on the procedure

Another speciality is the production of defined surface structures, such as spherical shaped indentations in the range of a few micrometers. Such layers are characterised by a special wetting behaviour, which is why they are especially used for printing rollers or in rolling mills for sheet metal processing, the so-called temper rolling.

Iron – Iron is always deposited when the metal is required in a high purity. The layers consist (depending on the type of electrolyte) of up to 99.996 % of iron. They are malleable, but not corrosion and oxidation resistant. For this reason they are only suitable for technical purposes and should be provided with an additional corrosion protection. Since the layers are low stressed and ductile, they can be deposited at a high thickness and will be used, for example, for repair purposes or for the electroforming.

Table: Properties of gold layers

| <i>Alloy metal</i> | <i>Gold content</i> | <i>Hardness</i> | <i>Colour</i> |
|--------------------|---------------------|-----------------|------------------------|
| - | 99,9–99,99 % | 70–90 HV | yellow |
| Arsenic | 99,9 % | 250 HV | yellow |
| Cobalt or nickel | 99,5–99,9 % | 140–220 HV | yellow |
| Cobalt or nickel | 99,7–99,8 % | 150–180 HV | yellow |
| Nickel or indium | 95,5–98,5 % | 200–270 HV | pale yellow |
| Cobalt | 93–99 % | 220 HV | brown-yellow |
| Silver | 75–95 % | 115–140 HV | green-yellow to yellow |
| Silver, copper | 70 % | 370 HV | pale reddish |
| Copper, cadmium | 66–75 % | 260–300 HV | reddish |
| Silver | 58 % | 220 HV | light yellow |



Parts for the electrical engineering coated with gold
(Photo: IMO)

Gold – The electrical and chemical deposition of gold and gold alloys is one of the most economically attractive methods of electroplating, because the character of the noble metal can already be achieved with a thickness of a few microns. The first commercial processes have been patented in 1840. The deposition itself is still predominantly taking place of cyanide compounds, since cyanide is one of the most stable water-soluble gold salts. Alternatively, sulphite gold compounds are in use, but which lead to the chemical reduction of gold when in contact with air and, thus, produce unwanted gold deposits on the inside of the coating or storage tanks. Since pure gold is very soft, gold alloys are predominantly deposited with significantly higher hardness. With the so-called hard gold layers, already with very small amounts (0.1 % to 0.5 %), for example, on nickel, indium and cobalt, the layer hardness can be increased from about 70 HV to 90 HV for unalloyed gold up to about 150 HV to 220 HV for gold alloys. Another reason for the increased use of gold alloys is the possible saving in gold. Up to a proportion of gold of approximately 85 %, the layers have the typical gold colour. With lower gold content, a reddish (copper-coloured) or white colour will result, depending on

the alloy component. As with metallurgical alloys, also electroplated alloys can be mixed with many alloying metals in almost any concentration. Thereby, the good corrosion and oxidation resistance is being maintained for almost all gold alloys. Nickel, cobalt, indium, palladium, silver, copper or iron are used as alloying partners for electroplating gold. The use of cadmium, arsenic or thallium is avoided as far as possible, although no health concerns of these alloys are known. The applied thicknesses of the gold films are ranging from 50 nm for the electrical/electronics up to a few millimeters for the electroforming.

Especially for use in electronics and electrical engineering, gold is not only electroplated, but deposited with electroless and reductive electrolytes. In the reductive depositing electrolyte, the base material (e. g. an electrodeposited nickel layer) will be dissolved when immersed in the electrolyte. The thereby released electric charges will reduce the dissolved gold in the electrolyte and cover the nickel surface. Once the entire surface is covered with gold, the deposition ends, in which case available gold layer thicknesses of a few 10 nanometers will occur. Hereby, in order to guarantee the property of gold, a good wetting by solder or welding materials (bonding in electronics) is being used. In the electroless gold deposition, a reducing agent is located in the electrolyte, which leads to the reduction of the dissolved gold. With this method, gold layer thicknesses up to about 1 micron will be achieved. Both processes are relatively slow, so the gold layer thickness can be adequately controlled, however, only in good conduct or an exact observance of the operating parameters (concentration of gold and reducing agent, temperature, electrolyte movement).

Copper – Copper and copper alloys are electrically and chemically deposited in order to exploit their good electrical conductivity and corrosion resistance. In addition, it is possible to smooth a

Table: Properties of electroplated copper

| Parameter | Copper, high-purity | Copper with additives | Copper-zinc | Copper-tin |
|------------------|---------------------------|---------------------------|----------------------------|------------|
| Tensile strength | 120–150 N/mm ² | 200–540 N/mm ² | 900–1100 N/mm ² | |
| Ductility | 11–15 % | 1–40 % | | |
| Hardness | 120–135 HV | 40–350 HV | 100–600 HV | 200–600 HV |

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micro-rough surface by a copper plating and, thus, to produce a glossy surface. To take advantage of the good electrical conductivity, high purity copper is usually deposited from the electrolyte with no or very low additions. Electrolytes based on copper sulfate are used, from which, for example, copper foil for printed circuit boards are made. Also pure copper is deposited on ICs. In this case, next to the good conductivity, the very good throwing power of copper electrolyte is used, in order to produce the fine conductor by filling the structured silicon surface. On plastics (preferably ABS) copper is used to produce high gloss surfaces and good corrosion resistance. In combination with nickel and chromium copper layers have long been a part of the high-quality corrosion protection layers, for example, on valves parts of the plumbing industry. For cost concerns, copper is rarely used nowadays.

In addition to pure copper, important copper alloys are brass and bronze alloys, both of which can be produced by electroplating processes. Brass coatings are used in different compositions from white to gold, for example, in the furniture industry but also to improve the adhesion of rubber to steel wires in tire manufacturing. Copper-tin alloys (bronzes) can be deposited in different colours from white to red depending on the composition. The copper or copper alloy layers are characterised by a wide range of hardness and ductility. In general, the electrical resistance of the layers increases with the level of impurities from additives or alloy partner, so preferably high-purity copper is used for electrical purposes. Impurities and alloying metals increase the hardness and reduce the ductility of the copper layers. The latter is noticeable in the behavior of very thick layers on the coated parts, especially if the layer thicknesses will be in the region of a few millimeters. Depending on the application, the standard copper layer



Chemically nickel plated mold insert, high-gloss polished (Photo: NovoPlan)

thicknesses are in the range of a few micrometers to several millimeters (for electrical applications) when the mechanical properties are required. For decorative purposes, from about 5 microns up to 40 microns thick layers are used.

Nickel – Nickel and nickel alloys are the most important metals for plating, both electroplating and electroless plating. They are especially characterized by their good corrosion resistance and the wide range of coating hardness. From electrolytes based on nickel sulfamate very ductile nickel is deposited with the lowest level of impurities. The deposition operating parameters can be chosen so that the layer has compressive or tensile stresses. This property is particularly suitable for producing parts by the so-called electroforming. Here nickel up to thicknesses of several millimeters will be deposited on to a mandrel and then the mandrel removed, whereby a component can be produced, which may consist of a complex form and a complex surface structure.

Table: Properties of chemically deposited nickel-phosphorus compared to bright nickel

| Parameter | NiP (< 5 % P) | NiP (5–9 % P) | NiP (> 9 % P) | Bright nickel |
|-------------------------------|-------------------------------|---------------------------|---------------------------|----------------------------|
| Tensile strength | approx. 200 N/mm ² | 800–900 N/mm ² | 750–900 N/mm ² | 350–1500 N/mm ² |
| Ductility | 0,5 % | 0,7 % | 1,5 % | 4–10 % |
| Hardness | 650–700 HV | 550–600 HV | 500–550 HV | 200–500 HV |
| Hardness after heat treatment | | | 1000–1200 HV (400 °C) | |