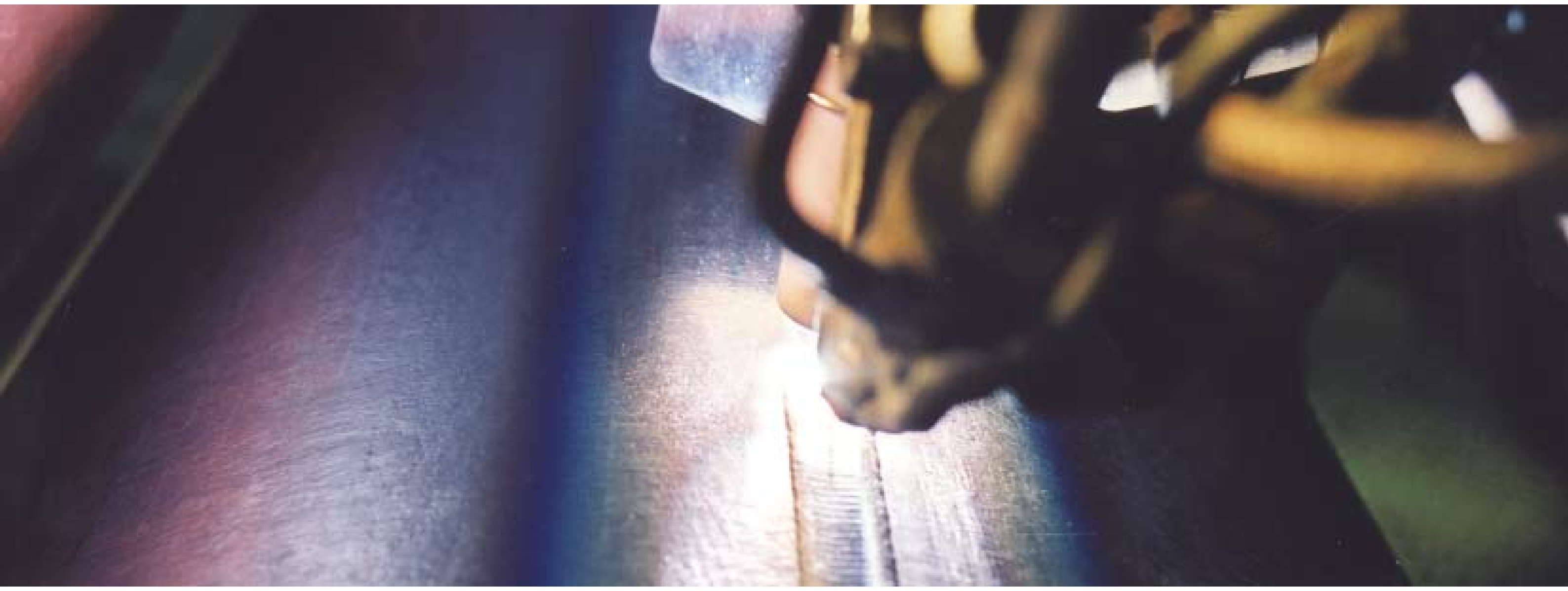


STAINLESS STEEL IN PRACTICE

BUTTING

Long standing Experience with Materials

Since corrosion resisting steels were first developed, BUTTING has been processing these materials and has since gathered extensive experience in forming, welding and heat treatment of these for all types of industry. As early as 1979, BUTTING produced the world's first longitudinally welded duplex pipes for an on-shore project. For over 20 years, we have been supplying pipes made of high-alloy nickel-base steels for the construction of chemical plants, off-shore installations and shipbuilding. Today, BUTTING processes more than 40,000 t of stainless steels a year, with a wide variety of material qualities.

Variety of Materials

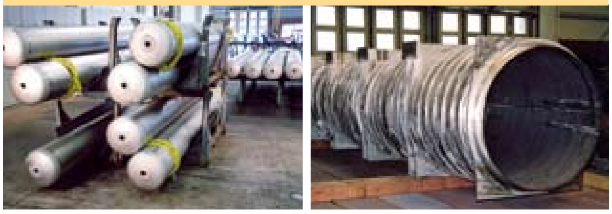
The BUTTING production programme offers a broad range of high-performance materials for specific corrosive applications in a variety of industries. In this area, the individual requirements of our customers demand ever more innovative solutions. Our metallurgists, welding engineers and production specialists daily face all kinds of challenges.

Heat-resisting Steels

Clad Materials

Aluminium & forgeable Aluminium Alloys

Non-magnetizable Steels



Optimised Material Properties

Where there are special requirements, e. g. in relation to corrosion resistance, workability, strength or micro-structure, BUTTING optimises the properties of the parent metal and the longitudinal weld by heat treatment and / or surface treatment, to adapt them to the requirements.

Prevention of Damage

The aim of processing and using pipes, vessels and components in corrosion resisting stainless steels and special alloys is to avoid corrosion damage. In pursuit of this goal, BUTTING deploys its broad experience and technical knowledge in material science, process technology and welding and forming technology. As prerequisites to avoid corrosion damages there are, apart from the selection of the appropriate materials, constructions suitable for the respective material, correct processing and operating conditions appropriate for the material.

Stainless Steels

Titanium & Titanium Alloys

Highly Corrosion resisting Alloys

Corrosion resisting Steels

Well before the beginning of the 20th century, it was discovered that the addition of nickel and chromium improves the corrosion resistance of steel. However, the individual steels enriched with these elements were not yet technically mature, or were unsuitable for practical use. The decisive breakthrough came in 1912 in Germany: the combination of nickel and chromium in conjunction with a precisely regulated heat treatment was the first to give optimum corrosion resistance along with good mechanical properties. In the same year, the first "stainless steel" was finally patented by Krupp in Essen. This patent was the start of the industrial use of stainless steel, which has established itself in many industries, especially since 1950.

High-grade Stainless Steel

The codes used at that time by Krupp, V2A (Cr18Ni8 steel) and V4A (Cr18Ni8Mo2 steel), where V stands for 'Versuch' (test) and A for 'austenite', are still used as synonyms for stainless steel. In the industry, the terms "high-grade stainless steel", or simply "stainless steel" or "Inox" are also used as neutral expressions.

A common international designation is 18/10 or 18/8, indicating the relative alloy content of chromium and nickel in the stainless steel. Since 1958, the German term

Ill. 2: Forming of a plate

"Edelstahl Rostfrei" ("high-grade stainless steel") has been a registered trademark. The importance of stainless steels today is reflected in constantly increasing production volumes: between 1990 and 2000, annual raw material production of stainless steels grew worldwide by over 40 %, from around 12.8 million to 18.4 million tonnes. From 2000 to 2004, a further growth of over 6.6 million tonnes (approx. 37 %) was recorded. Forecasts say that this growth will continue significantly.

The optimal Condition of Stainless Steels

The corrosion resistance of stainless steels is based on their ability to develop a passive layer in most of the media known to us, thus protecting the steel from further attack. This protective layer is only some atom layers thick and mainly consists of chromium oxide.

In case of specific conditions of attack – not only some extremely aggressive media but also a number of unwanted material and surface conditions – cracking or reduction (dissolution) of the above mentioned passive layer may occur. In this case even the stainless steel will "rust", although the appearance is often different to that we are used to with regard to common steels: stainless steels corrode as well, although without any visible rust and in most cases corrosion does not affect the full surface but is only localized at a few spots. However, the local corrosion may progress much quicker than in unalloyed steels.

The purpose of the following hints is to give some advice to the practician as to how to maintain the best condition of the stainless steel also during processing or what should be avoided to be done with stainless steels.

The best condition of stainless steels is subject to:

- the surface condition
- the forming condition
- the heat treatment condition

In order to obtain and to maintain these preconditions, the following should be observed.

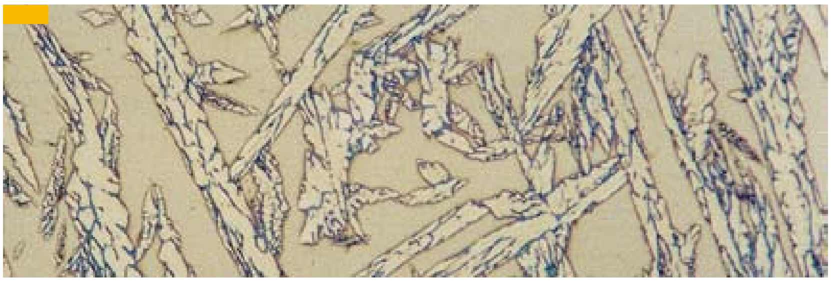
Ill. 1: Orbital welding of stainless steels

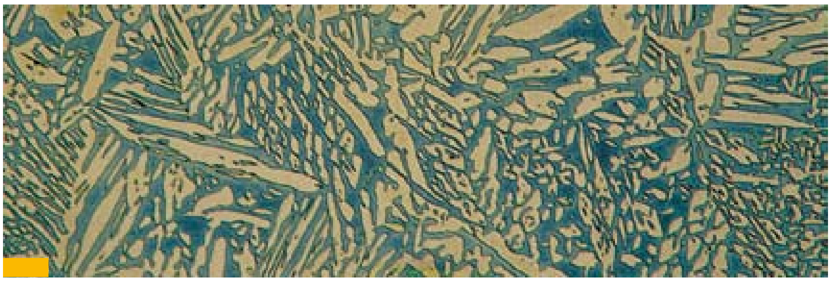
Selection of the right Material is crucial

The correct selection of the appropriate material is crucial for its specific usability. In order to fight against possible forms of corrosion in various sectors of industry, a large number of steels and alloys has been developed. Individual requirements should be tested, and materials specific to the project should be chosen after consultation with experts, taking account of the availability of raw materials. However, appropriate processing and operating conditions in accordance with the materials remain basic necessities.

The basic qualities of certain selected materials will be briefly outlined below.

Ill. 3: Structure of a weld in duplex, not heat treated, approx. 60 % ferrite





Ill. 4: Structure of a weld in duplex with PWHT, approx. 40 % ferrite

Strain caused by chlorine-containing attacking Agents

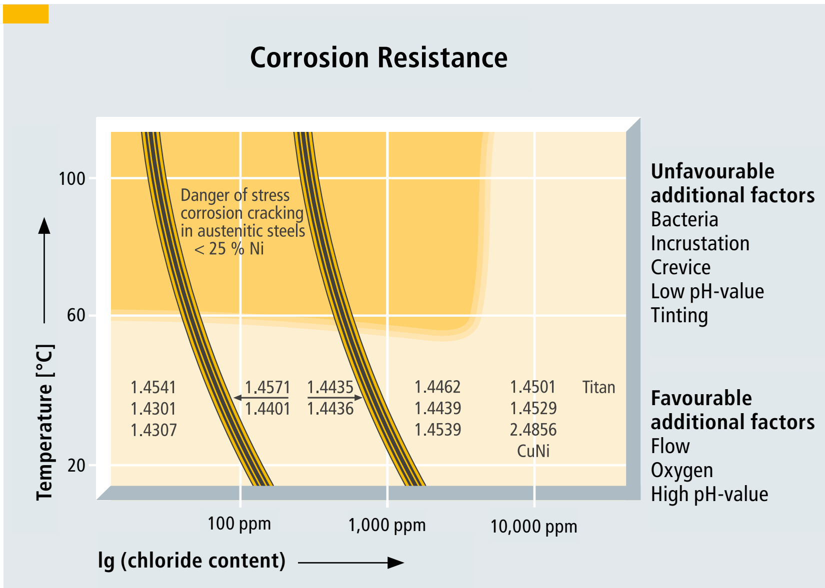
For strains in connection with halogene ions (chlorides, fluorides, iodides, bromides) the use of steels with increasing contents of chromium and molybdenum is recommended. Besides the estimation of the halogene-ion content there are also aggravating high temperatures and low pH-values.

Technically available steels are (in the order of their increasing alloy grade):

- 1.4571 (1.4404)
- 1.4435
- 1.4439 / 1.4462
- 1.4539
- 1.4529
- 1.4501

In case of especially high strains copper nickel alloys, high molybdenum-nickel alloys, e. g. 2.4610 and titanium will be considered.

Chart 1: Resistance of stainless steels to pitting corrosion and stress corrosion cracking in waters



Strain caused by sulphuric attacking Agents

Besides increased molybdenum contents above all copper nickel steels offer higher resistance.
Technically available steels are (in the order of their increasing resistance in sulphuric dilutions):

- 1.4571
- 1.4439
- 1.4505
- 1.4539
- Sandvik SX
- 1.4591 (Alloy 33)

In case of especially high strains (above all at high temperatures) lead lining and nickel alloys are suitable.

Strain caused by phosphoric attacking Agents

Mainly in pure phosphoric acids up to high temperatures the austenitic molybdenum alloyed steels have proved their worth. As to contaminated phosphoric acids high-alloyed special steels are to be used.

Technically available steels are (in the order of their increasing resistance):

- 1.4571
- 1.4435
- 1.4439
- 1.4462
- 1.4539
- 1.4562

Strain caused by nitric attacking Agents

Generally the resistance of stainless steels to nitric acids up to temperatures of about 50 °C is good. In case of higher temperatures special steels are to be used and attention must be paid to a high freedom from ferrite and only slightest contamination at the grain boundaries.

Technically available steels (in the order of their increasing resistance):

- 1.4306
- 1.4306 Electroslag Remelting Process
- 1.4335
- 1.4465
- 1.4361 (highly-concentrated nitric acid)

Ill. 6: Installation of piping systems, elbows, flanges and railings in stainless steel at a chemical plant

Strain caused by organic attacking Agents

Stainless steels are resistant in most of the organic solutions and chemicals, e. g. greases, oils, benzene, phenol and other carbon-hydrogen compounds and compared with unalloyed steels there is the advantage that these materials will not be contaminated by traces of rust.

Chlorinated hydrocarbons may represent a certain danger if they contain residual moisture and if chlorine ions are split off by the influence of oxygen and light (shares of ultraviolet radiation) and build up in the aqueous phase. In this case similar considerations as under section "Strain caused by chlorine-containing attacking agents" would apply.

Generally it is recommended to consult an expert prior to the material selection for a specific project. Producers of stainless steels and special alloys, like ThyssenKrupp Nirosta, ThyssenKrupp VDM or Outokumpu can be contacted. Furthermore, there are independent associations, like DECHEMA, with the aim to support the end user and to be in an open dialogue with him.

The expert staff of BUTTING is also at your disposal for any advice you may need regarding material selection, corrosion and heat treatment.

For information about materials, their processing or other questions relating to the selection and processing of stainless steel, our contacts are at your disposal.

Dr Iris Rommerskirchen
Managing Director BUTTING Knesebeck
Phone: +49 5834 50-7100, Email: iris.rommerskirchen@butting.de

Reinhold Hoffmann, BSc
Dept. Quality Assurance
Phone: +49 5834 50-216, Email: reinhold.hoffmann@butting.de

Ill. 5: Prefabricated piping components made from duplex steel for the shipbuilding industry

Ill. 7: Forming from a coil

Stainless Steels offer very good cold Forming Properties

Strength Values

Owing to their many ductility (elongation) reserves, austenitic stainless steels dispose of a very good cold workability. With growing forming below the so-called recrystallization temperature, i. e. below approx. 600 °C, the strength values of austenitic steels like tensile strength, yield strength (0.2 and 1 % yield strength) and hardness increase more than it is the case with unalloyed or low alloyed "black steels": they strengthen. This strengthening leads to a reduction of further elongation ability and toughness. The expenditure of energy for further forming increases as well as the danger of a fracture and stronger spring-back. Therefore, as a general rule the German standardization (AD-Regelwerk – Pressure vessel code) assumes that the degree of cold forming should not exceed 15 % in order to maintain a remaining elongation of 15 % unless the forming is followed by a heat treatment (see page 11).
This ratio of 15 : 15 is based on the rough estimate of a minimum breaking elongation of 30 %, which generally may be taken for granted with these steels.

Corrosion Resistance

Besides the toughness properties, also the corrosion resistance may be affected negatively by cold strengthening. It is mainly stress corrosion cracking which only occurs in case of temperatures above 50 °C, chloride ions and tensile stresses. Also the pitting corrosion resistance may be impaired in case of very high cold forming.

Ill. 8: Production of a long radius elbow

Ill. 9: Production of integrated bends according to isometric drawings

However, it should not be left unmentioned that also advantage may be taken of the great strengthening tendency of austenitic stainless steels: above all an increased hardness is desired in wear conditions, also one may count with a higher yield strength of cold formed parts. However, this only

Ill. 10: Production of a pipe by forming a plate

applies when there is no welding or only controlled welding after cold forming or if cold strengthening only takes place after welding. BUTTING benefits from such effects also during the production of pressure vessels.

If a condition of cold strengthening is to be eliminated an annealing treatment, generally a solution annealing, is necessary. The annealing time in this case is only some minutes (refer to page 11).

Peculiarities of the Welding of austenitic Steels

In this brochure some peculiarities of the welding of stainless steels as against the normal "black steels" shall be treated and primarily the austenitic steels, often called "V2A" and "V4A" steels of grades 1.43... 1.44... and 1.45... .

It would go beyond the limit of this brochure to deal with all the problems relating to the welding of stainless steels.

In this connection please refer to the publications of the "Informationsstelle Edelstahl Rostfrei", Düsseldorf.

Compared to unalloyed steels, some of the characteristics of austenitic CrNi-steels highly influence its welding behaviour. This different welding behaviour is characterised by the following points:

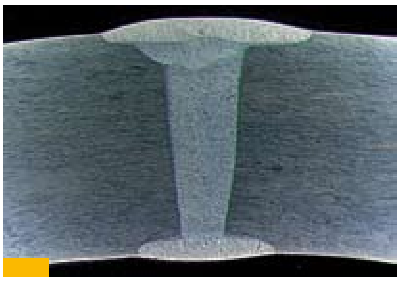
1. The high tendency to oxidation due to the high chromium content,
2. The twice as high heat expansion and only about half the thermal conductivity of austenitic steels as against unalloyed ferritic steels,
3. The hot-cracking sensitivity of fully austenitic steels.

Tendency to Oxidation

From the tendency to oxidation it can be deduced that during welding of stainless steels the weld pool and the heat affected zones close to the weld have to be protected against oxygen admission.
For the processing of austenitic steels the following arc welding and beam welding procedures can be applied:

Ill. 11: Competence in welding is gained through long years of experience

- **Manual metal-arc welding** using coated stick electrodes, where the developing slag protects against air.



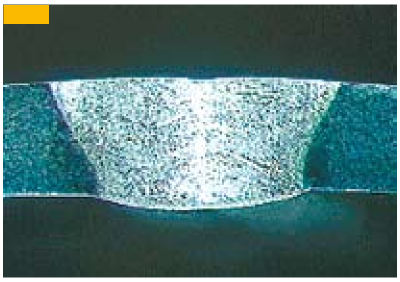
Ill. 12: EB-weld

- **Gas-shielded metal-arc welding (GMAW)**, where the arc and the weld pool are covered by gas. This process is mainly used with Argon + O_2 (1–3 %) or Argon + CO_2 (up to 3 % max). In order to achieve certain metallurgical effects, also gases with additions of helium, nitrogen and hydrogen are used.
- **Flux cored wire metal-arc welding with active gas shield** with higher CO_2-contents (approx. 18 %).

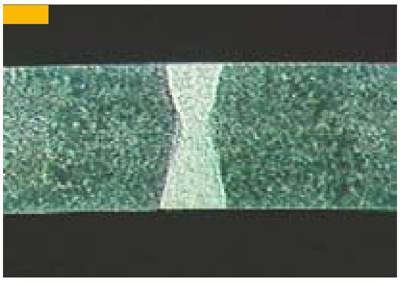
- **TIG welding and Plasma arc welding** using argon and argon/hydrogen mixtures. For special alloys also argon/nitrogen mixtures are used.
- **Submerged arc welding**, where again the slag produced by the powder protects the weld pool.
- **Laser welding** (protection: inert and reducing gases).
- **Electron beam welding** (protection: vacuum).

During the welding of austenitic CrNi-steels special attention has to be paid to the bottom side of the weld, the root pass, especially if this area may get in contact with corrosive media. In the case of unprotected or only poorly protected root passes with tinting (colouring) damages are inevitable. Besides argon, generally used backing gases are mixtures of argon and hydrogen or nitrogen and hydrogen. The hydrogen has a reducing effect, i. e. it removes residual oxygen which therefore cannot react on the surface. Pure argon or nitrogen and mixtures of these gases can also be used depending on the material grade to be welded.

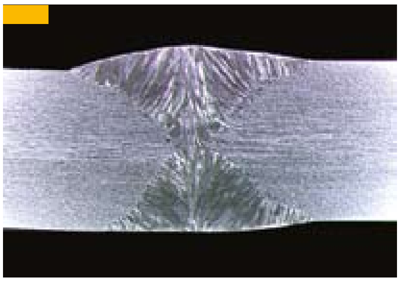
Ill. 13: TIG weld



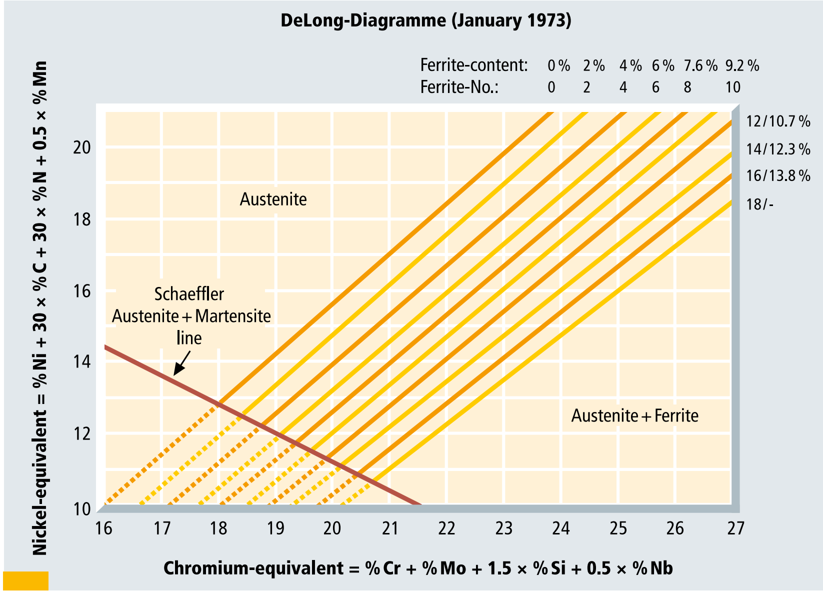
Ill. 14: Laser weld



Ill. 15: SAW weld



To keep the forming gas well directed in the area of the weld root, corresponding equipment, such as chambers and backing bars, is available for the various welding connections. In piping constructions with difficult access to the welds it may be necessary to fill the entire piping system with backing/forming gas.
The filler metals used must be adapted to the material grade to be welded and the operation conditions of the component. Generally identical or slightly over-alloyed filler metals are used. As regards coated stick electrodes and welding powders dry storage is a must. Prior to their use further drying may be necessary. The manufacturer's instructions for use should be observed.
The choice of the welding procedure to be used is essentially determined by the plate thickness, degree of mechanisation and material grade.



No guarantee for correctness

Chart 2: DeLong-Diagramme (January 1973)

Ill. 16: Manual welding of a piping component

Heat Expansion and thermal Conductivity

Compared with unalloyed steels the higher coefficient of thermal expansion entails a higher distortion and higher residual stress. Due to the reduced thermal conductivity the heat remains in the weld zone. If necessary, additional cooling has to be applied for a faster heat eduction.

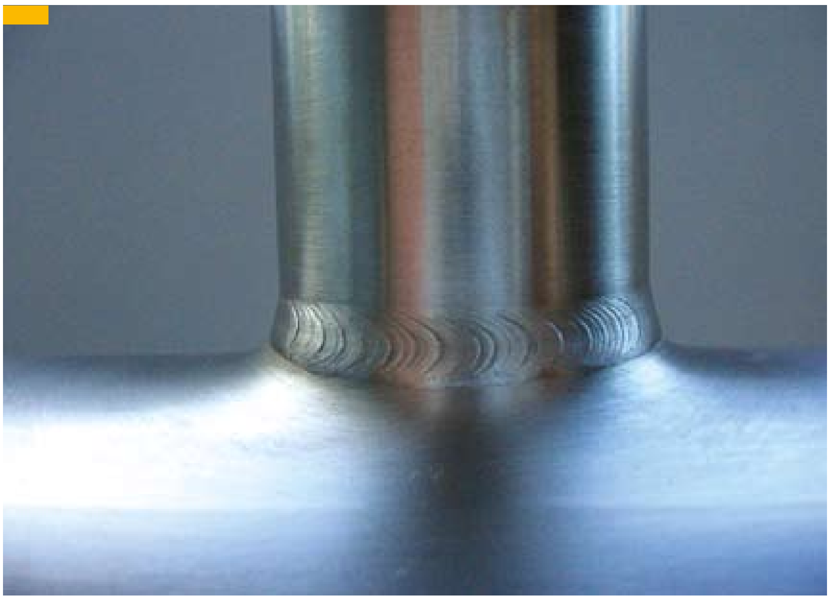
Susceptibility to Hot Cracking

The chemical composition of austenitic steels is controlled in such a way that – with the exception of some special alloys – the weld metal shows a small percentage (approx. 4 – 10 %) of delta ferrite. The advantage of this part ferritic solidification is the dissolving power for contaminations like phosphorus and sulphur leading to a decrease of the susceptibility to hot cracking. Normally, the alloy composition of plates and welding consumables ensures the maintenance of these values.

For the welding of different material grades the so-called Schaeffler diagram allows determination of the approximate delta ferrite and the alloy composition of the weld material. The so-called DeLong diagram (as per chart 2) also takes into consideration the nitrogen content. However, the ferrite as desired for welding may also have detrimental effects, e.g. on the resistance in nitric acids, on the toughness at low temperatures or on the hot forming of welds. This can be remedied for example by a subsequent solution annealing.

If for specific reasons high alloyed steels with full austenite solidification (e.g. nitrogen alloyed stainless steels, high temperature or non-magnetizable steels) are required, the increased susceptibility to hot cracking has to be observed.

Ill. 17: Orbital weld of excellent quality

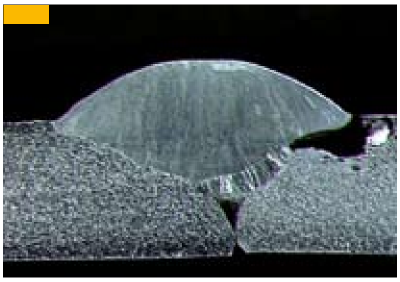


Ill. 18: MAG welding with flexible automatic welding machine

In order to weld high alloyed steels without cracks certain measures are required:
- reduced heat input, low volume of weld pool
- shrinkage stresses have to be kept low, creation of high residual stress has to be avoided constructively
- no high-performance processes
- appropriate welding consumables and backing gases should be used
- special training of welders

As a rule, ferritic steels, e.g. 1.4510/1.4511/1.4512, are disposed to poorer weldability, mainly with regard to big wall thicknesses. Among others, this deficiency is determined by:
- a basically poorer toughness of ferrite, leading to susceptibility to brittle fracture
- a tendency to formation of coarse grained structure
- the share of martensite in the heat-affected zone
- the strong tendency to precipitations (e.g. chromium carbides in the heat-affected zone), reducing the toughness

Ill. 19: Inadequate welding of a weld-seam exposes the area concerned to the threat of corrosion



General Recommendations

Weld edge preparation is done by cutting (e.g. by means of plasma or laser) or milling. The bevel shape depends on the welding process. Prior to welding it is crucial to clean the weld edge over an area of at least 20–30 mm, including the plate's rear side. Depending on the kind of soiling cleaning can be done mechanically or chemically. When cleaning mechanically, stainless steel brushes as well as abrasives free of ferrite and sulphur should be used. Even during tack-welding forming gas must be used. This is especially important for welds where the roots are not accessible. Prior to filling the tack welds, annealing colours and impurities have to be removed with brushes.

Wires and electrodes usual in the trade are used as filler metals, normally of the same kind or slightly over-alloyed. In order to select the appropriate filler metal the operating conditions such as strength, corrosion requirements, thermal load and, where needed, required approvals have to be observed.

Summary:

The welding of stainless steels requires:
- the selection of suitable welding procedures, adapted to the application
- well directed, moderate heat supply
- avoidance of tintings; attention to be paid to optimal root protection especially in the construction of pipelines
- consideration of increased shrinking and heat tensions
- greatest care in preparation of edges regarding removal of grease and dirt
- removal of scaling traces to regain the bright metallic condition (refer to section 'surface condition')

Point of contact:
Robert Sölch, BSc, EWE
Dept. Welding technology
Phone: +49 5834 50-424
Email: robert.soelch@butting.de

Heat Treatment of Stainless Steels

As a rule raw material (plates, coiled strips and bars) made of stainless austenitic steels is supplied in the solution annealed condition, however, it should be indicated in your order.

If after further processing of this material into e. g. pipes, vessels or profiles due to cold or hot strengthening or welding etc. a heat treatment prior to the use of these materials must be carried out depends on a great number of facts, e. g.

- degree of forming,
- degree of temperature,
- material grade,
- intended use

The AD2000-Regelwerk (pressure equipment directive) would be a guide concerning the proceeding after cold forming. The AD2000-Merkblatt HP 7/3 advises that a post weld heat treatment of austenitic steels is not necessary if the raw material shows a minimum breaking elongation of $A5 \geq 30\,\%$ and the cold forming degree does not exceed 15 %. As a rule heat treatment should be carried out if during processing there was uncontrolled heat input (e. g. bending with a flame) or if excessive cold forming had been carried out so that hardness values of more than 250 HV would be present. However, it should not be disregarded that there are applications where high strengths or hardnesses are deliberately being forced on account of the toughness in order to increase the resistance to wear and abrasion or similar.

Ill. 21: Heat treatment on line

Ill. 22: Heat treatment in a furnace

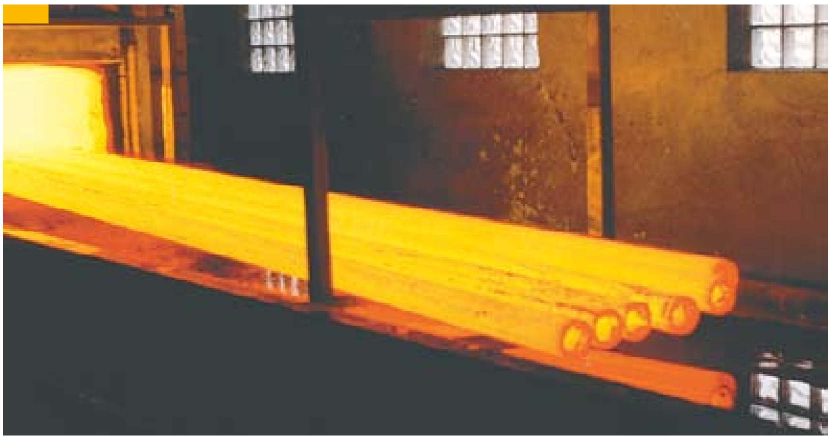
Take Care

One of the most important prerequisites of a proper annealing success is a clean surface of the material to be annealed. Lubricants and surface impurities of all kind have to be removed completely. Otherwise organic components of the impurities could bake into the surface during the annealing process followed by a detrimental carburization of the steel. Furthermore scale would be built irregularly requiring increased grinding and pickling processes during descaling and surface treatment.

Versatile Heat Treatment Processes

For stainless steels, there are various heat treatment processes available to achieve the "heat-treated state", e. g. solution annealing, stabilizing annealing, stress relieve annealing, re-crystallisation annealing and soft annealing. These can be performed during production by induction annealing or by annealing in a furnace.

Ill. 20: Water quench of 6 m pipes after heat treatment

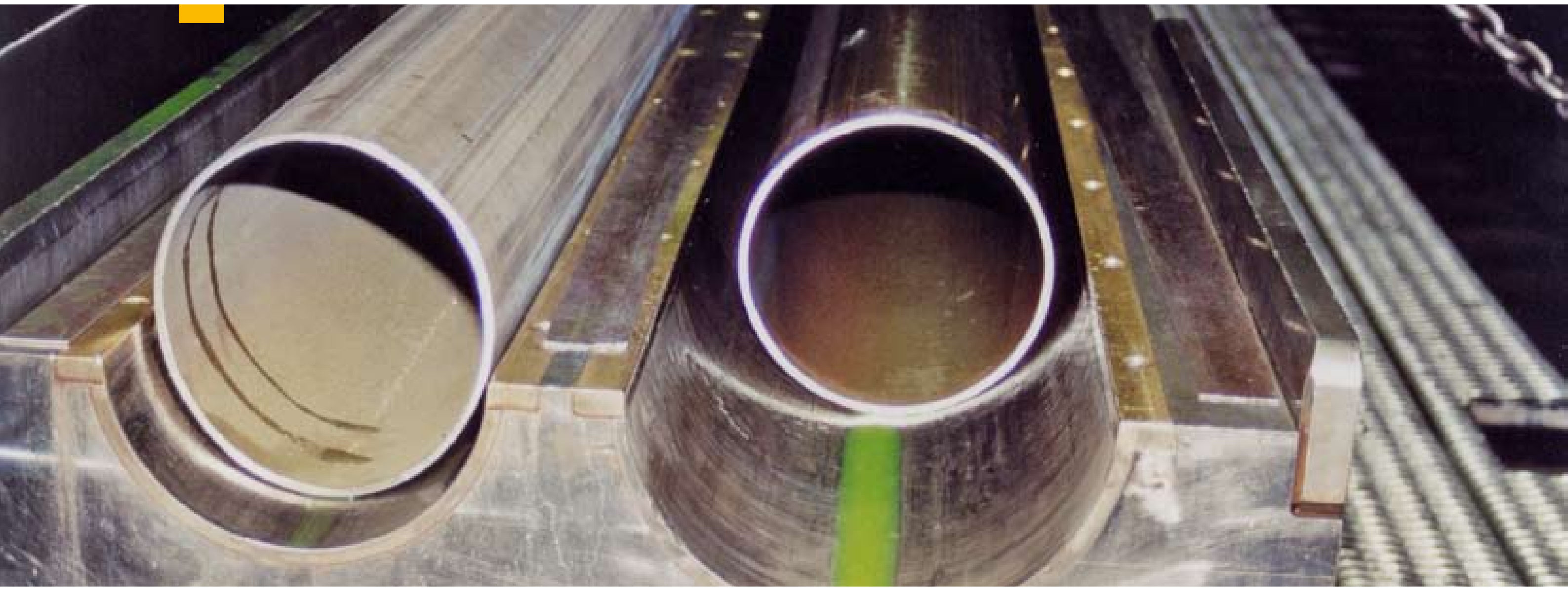


Solution Annealing

Generally the solution annealed condition is the most favourable condition of austenitic stainless steels desired for further processing and intended use. It is achieved by an annealing (usually in a slightly oxidizing atmosphere) at approx. 1,050 °C for the non molybdenum alloyed steels and at approx. 1,070 °C for the molybdenum alloyed steels with subsequent cooling as rapid as possible. For nickel alloys rich of chromium, solution annealing temperatures would go up to 1,180 °C. As a rule the annealing time is estimated at 2 min/mm wall thickness but 20 min at minimum. In case of plate thicknesses up to about 6 mm the cooling may take place in still air, or even better in stirred cold air. In case of higher wall thicknesses quenching in water is preferable. The reason for this is the necessity to suppress the creation of chromium carbides which preferably takes place in a temperature range of 600 – 800 °C and which may lead to an impairment of the resistance to intergranular corrosion. Therefore, as a thumb rule, the cooling range between 800 and 600 °C should be passed through in less than 5 min.

On the one hand annealing removes the strengthening caused by the processing and on the other hand it provides the most favourable structural condition against corrosion. If annealing takes place in an oxidizing atmosphere, subsequent removal of annealing scale by pickling has to be carried out.

Ill. 23: Calibration of pipes distorted by prior heat treatment



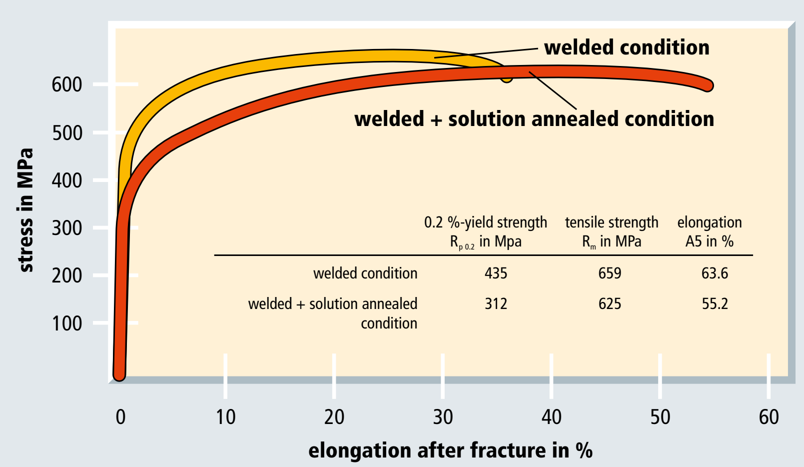
Stabilization Annealing

Stabilization annealing should only be used for stabilized steels, i. e. titanium or niobium alloyed steels (1.4541). It consists of a heat treatment at approx. 870 – 950 °C for 30 min. at minimum and by developing stable carbide precipitations it prevents the danger of inter-granular corrosion. Like the solution annealing it neutralizes existing conditions of cold strengthening by re-crystallisation. However, stabilization annealing should only be used if the material had already previously been solution annealed, as is the case with the processing of usual in trade plates and welded pipes.

Stress-Relief Annealing

Stress-relief annealing takes place in a temperature range of 500 – 650 °C. It is used in case of high residual stresses or strengthening and where solution annealing is not possible because of the danger of distortion. It has to be taken into account that in this case only stresses up to the hot yield strength at max. are being diminished, i. e. they are not being removed completely. Heat treatment times of 6 – 16 hours have to be applied and an impairment of the corrosion resistance has to be anticipated above all in the presence of ferrite parts which, for instance always exist in the welded, not pickled condition.

Chart 3: Stress-elongation-diagram of tensile test specimens taken across the pipe's longitudinal weld; pipe material 1.4541, wall thickness 2 mm



	0.2 %-yield strength $R_{p0.2}$ in Mpa	tensile strength R_m in MPa	elongation A5 in %
welded condition	435	659	63.6
welded + solution annealed condition	312	625	55.2

Soft Annealing

Soft annealing is used to neutralize cold strengthening. The ferritic stainless steels are heated up to 750 to 800 °C and cooled slowly. With austenitic stainless steels, complete "softness" is achieved by heating up to relatively high temperatures (generally 950 to 1,100 °C) then cooling quickly (the "quenched" state).

Experience has shown that an exposure time of 1 minute per 2.5 mm wall thickness is sufficient. Thin-walled work pieces can cool in the air. Thick-walled pieces must be cooled with a fan or quenched in water.

Re-crystallisation Annealing

In re-crystallisation annealing, the microstructure is reconstituted after cold-forming. The annealing restores the mechanical properties that existed before forming. Re-crystallisation annealing of stainless steels takes place between 800 °C and 1,000 °C. The re-crystallisation temperature depends on the chemical composition of the steel, the degree of forming and the exposure time during annealing. The greater the forming degree, the lower the temperature required for re-crystallisation.

In the heat treatment of unstabilised austenitic chromium-nickel and chromium-nickel-molybdenum steels, it is important to ensure that, depending on the carbon content, the temperatures and times fall outside the grain disintegration ranges.

Higher Quality by Surface Treatment

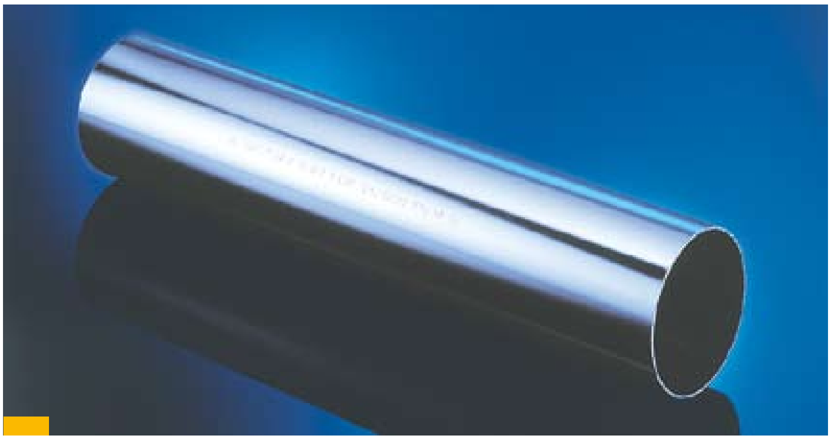
The surface of stainless steels shall be metallic bright – even after fabrication. The maintenance of the – bright – delivery condition may be achieved by a very careful treatment (handling) during fabrication. For example, the following measures should be taken:

Handling with Stainless Steel Tools only

Practically at every touch with other material, in particular with steel tools abrasion will be created by these tools on the stainless steel. This abrasion behaves the same way as any steel: it corrodes.

Unfortunately the corrosion is not limited to the abrasions, as under the rust the passive layer of the stainless steel will be damaged. Also the stainless steel will be affected under such spots: it will be activated.

The above mentioned abrasion by tools may also be caused unintentionally, e. g. by rust film, contact with nailed shoes, by chains during loading and unloading etc. Also any contact with zinc and / or copper materials should be avoided as such contamination may penetrate into the surface during subsequent welding or heat treatment at temperatures exceeding 500 °C causing cracking. Besides workmanlike handling with stainless steel tools, it is recommended to use abrasion protecting coverings, adhesive films or similar. If necessary, the originated abrasion must be removed, preferably by pickling.



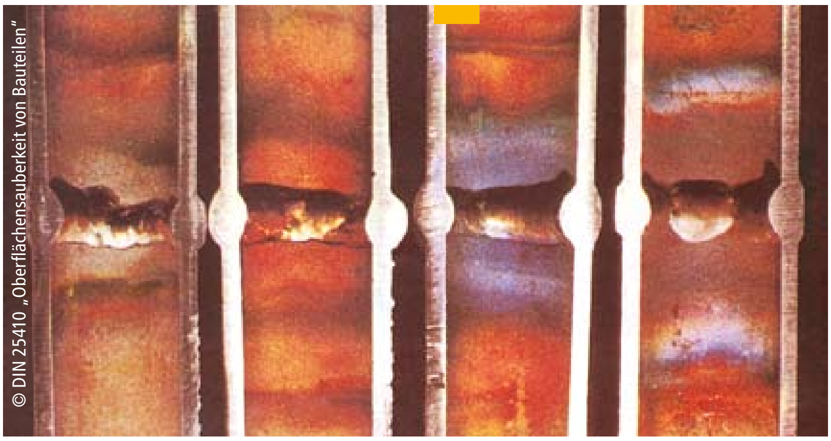
Ill. 25: Metallic bright surface finish

Shielding Gas cover of Surfaces heated up to more than approx. 500 °C

Primarily during welding, but also during hot forming annealing colours are being developed and – in case of longer heat reaction – layers of scale. Severe annealing colours or scale also destroy the passive layer and represent areas of increasing corrosion threat.

To avoid this, heated spots have to be covered with shielding gas during welding (refer to chapter "Welding"). As it is only rarely possible to cover completely the total area heated up to over 500 °C, the annealing colours should be removed by a subsequent mechanical or, even better, a chemical treatment. Therefore, prefabrication of components as large as possible at the manufacturer's workshop with full-body pickling and the reduction of welding on job sites are recommended. A generally valid statement on leaving thin oxide layers (annealing colours) cannot be made as the total system of media of attack, materials and surface condition has to be taken into consideration.

Ill. 24: Tintings on austenitic CrNi steels, chromium steels



The February 1993 edition of the standards DIN 50930, section 4, paragraph 6.2 states as follows:

"The probability of corrosion will not be influenced by thin straw coloured oxide films in waters being composed like drinking waters with a temperature not exceeding 100 °C. In pressure bearing systems at increased temperatures and generally in systems designated by influencing properties increasing the probability of corrosion, even straw coloured annealing colours may increase the probability of corrosion."

To avoid Mixture of Materials

In pipe assemblies it has been noticed repeatedly that for the fixing, suspension or connections of stainless steel components accessories like clamps, screws, even socket ends and similar parts made of steel or galvanized steel are used. This mixture of materials is problematic for several reasons: Owing to the "noble" condition of the stainless steels there is a danger of contact corrosion, primarily leading to an accelerated corrosion attack in the less precious material.

Ill. 26: Axial internal grinding

Ill. 27: Radial external grinding

As this also applies to galvanized parts, consequently also the stainless steel will be damaged by the developed rust layers and the line between only optical impairment and danger of corrosion is swimming.

So, if – although desirable but owing to economic reasons not always feasible – the exclusive use of stainless steel accessories is not possible, at least care should be taken to furnish these parts with a long-life surface protection on synthetic base. In order to avoid wetting with ferriferous condensation water, stainless steel line pipes should not be placed underneath structural steel piping.

Subsequent Work to restore the Original Condition

If during the processing of the bright, passive surface condition e. g. during welding, heat treatment or forming with steel tools, ferrite or scale deposits have been created, subsequent work has to be provided to restore the original condition of stainless steels in order to maintain their corrosion resistance. Subject to the prevailing possibilities and mobility of the component, subsequent surface treatment may be carried out by:

- brushing, grinding,
- blasting or
- pickling.

Brushing, Grinding

Surfaces covered with scale or annealing colours due to not very aggressive attack may be cleaned with stainless steel brushes or surface grinding tools, provided these tools will only be used for the treatment of stainless steels and provided they have not been used for lower alloyed steels before.

During grinding care has to be taken to only work with moderate pressure which will not result in a strong heating up and thus leading to a new development of annealing colours or / and high surface tensions.

The final grinding operation should not be too coarse and should correspond to a 120 grit or finer. After grinding or brushing it is recommended to rinse with clear water, or – even better – with diluted nitric acid (approx. 10 – 15 %) to accelerate the formation of the passive layer.

During brushing and grinding the area containing little chromium underneath the surface covered by annealing colours is not removed completely. The corrosion resistance is thus impaired.

Chart 4 shows the influence of different grit sizes on pitting corrosion resistance. Surface treatment by brushing and grinding is also used for optical reasons.

Ill. 28: External grinding machine at BUTTING for surface treatment of pipes

Surface Blasting

Blasting is used for cracking the scale prior to pickling:

- especially for highly corrosion resistant steels in order to reduce the pickling periods and the acid consumption
- to create a defined surface, e. g. optically uniform surfaces in the sector of apparatus engineering, surfaces with Raumatic finish for the transport of plastic granulates etc.
- for roughening of surfaces in order to achieve better adhesive conditions for decorative surface coatings (varnish, enamel or similar)
- to create a compression stress in order to reduce the danger of stress corrosion cracking

Ill. 29: Spray pickling for large components

By blasting, non-directional surface structures with matt finish can be created. Predominantly, reusable blasting agents are used. For stainless steels only non-metallic blasting agents (e. g. glass beads, ceramic balls, garnet sand) as well as metallic blasting agents made of stainless steel must be used.

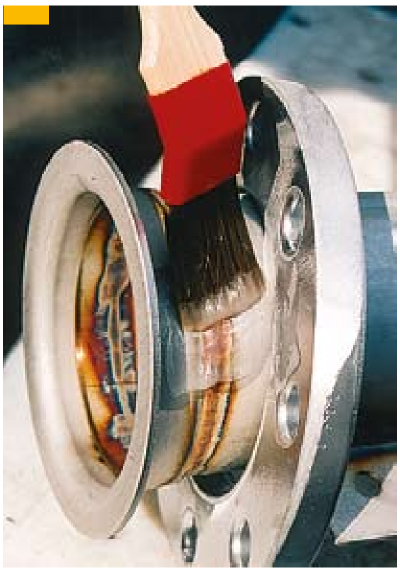
Prior to blasting residues of other blasting agents have to be removed from the blasting devices in order to avoid extraneous rust.
After blasting, subsequent pickling is necessary for good corrosion resistance.

Pickling
Pickling is still the most common and best procedure for the surface treatment of stainless steels after processing, i. e. the removal of not identic contaminations or oxides by chemical means. Primarily one has to distinguish between two procedures:

Full-body Pickling
This is a convenient method of surface treatment, although limited by the components' size. The mixture of acids and the temperature (20 – 65 °C) are selected in relation to the material grade and the scale. With rising temperature the aggressiveness of the acid strongly increases, i. e. the pickling speed can be accelerated extensively by an increased temperature. The increase of the pickling bath temperature by 10 °C may halve the pickling time, but temperature limits have to be considered.

When temperatures are too high overpickling leads to a coarse surface in low-alloy stainless steels. Beside the acid concentration and the temperature the pickling results also depend on the content of free metals (mostly iron) in the bath.

Ill. 30: Pickling pastes



Ill. 31: Full-body pickling – an economically and environmentally sound surface treatment

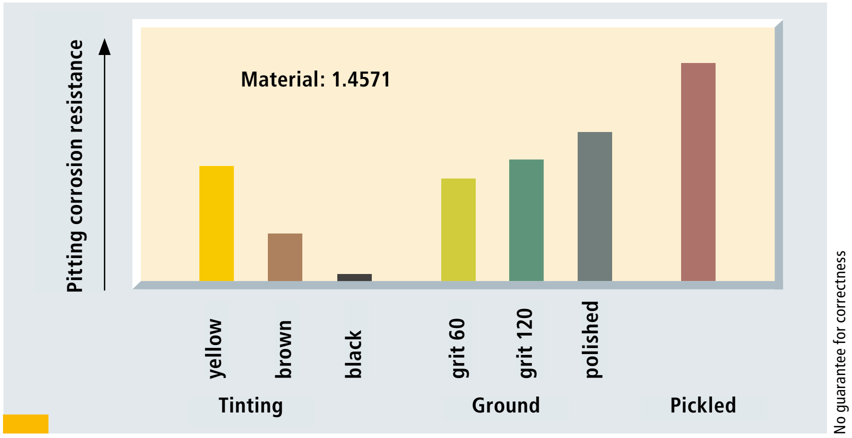


Chart 4: Influence of surface condition on the pitting corrosion resistance of an austenitic CrNiMoTi steel

A constant analysis of the pickling bath and regular cleaning of the basin are urgently required for a good pickling result and a uniform appearance. After a sufficient residence time the loosened scale remnants can be removed with a brush or by pressurized water. Recently sulphur / mixtures of hydrofluoric acids are increasingly being used due to sanitary and environmental reasons.

Pickling Pastes
For local pickling of welds produced on site but also in workshops, the use of pickling pastes as offered in special shops may by all means be recommended. These are either applied with a brush or by spraying and will dry automatically after reaction and by this the pickling time is generally limited by itself. When using such means attention must be paid to the fact that they are chloride free which is ensured with most of the products on the market. According to the instructions of use pickling remainders are to be removed by brushing and subsequent rinsing.

Hint: Owing to corresponding experience with stainless steel, BUTTING carry out pickling on a hire work basis.

Point of contact:
Henning Lütkemüller, BSc
Dept. Surface technology
Phone: +49 5834 50-458
Email:
henning.luetkemueller@butting.de

Selective or local Corrosion

Contrary to the unalloyed and low alloyed steels, the stainless steels and alloys are less threatened by a general abrasive corrosion over the full surface, but would under certain circumstances suffer from a so-called selective or local corrosion, i. e. most of the surface remains undamaged and only at a few isolated and preferred spots apartly very quick wear of material or material separation occurs. Please find hereafter the most important kinds of corrosion:

Intergranular Corrosion

The cause of this kind of corrosion lies in an inappropriate heat treatment condition of the steels. Due to long dwell times in the range of 600 °C and 800 °C the carbon in the steels tends to form with the chromium a high-chrome carbide of the $M_{23}C_6$ kind and to precipitate at the grain boundaries and thus low-chrome areas are being formed in the close vicinity of the grain boundaries, as contrary to carbon the chromium is unable to remelt fast enough so that locally the chromium content of approx. 12 %, which is necessary to maintain the passive condition, is not reached. This entails the so-called grain desintegration, i. e. preferred corrosion attack along the grain boundaries, even in conjunction with the evidence of rust towards the outside.

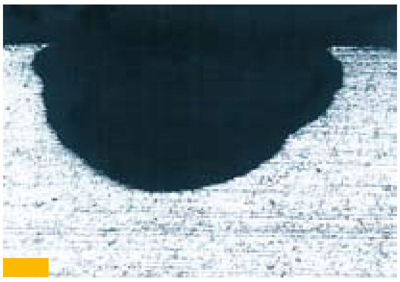
Such disadvantageous heat treatment conditions may occur for instance during inappropriate welding processes. In order to avoid this kind of corrosion, either the carbon content of the steels is kept below 0.03 % or the stabilizing elements Nb or Ti, which are compatible with chromium, are added.

Pitting Corrosion

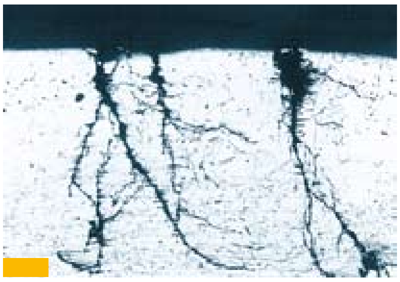
Mainly responsible for this kind of corrosion, where statistically isolated holes which are more or less deep are formed over the surface and which may penetrate the wall, are halogen-ions, usually chloride-ions, which settle down in the oxidic passive layer and would break through at this spot. Preferably this takes place in negatively affected surface areas, e. g. in areas of annealing colours. In this case we face a dimensionally very small active anode and a very large passive cathode, which may lead to very high speeds of desintegration and thus to the destruction of the component within a few months. From an alloying point of view the risk of pitting corrosion can be avoided by raising the so-called Pitting Resistance Equivalent (PRE) in the steels. The PRE value is calculated using the following formula:

$$PRE = \% CR + 3.3 \times \% Mo + 16 \times \% N.$$

Steels with a PRE of more than 33 provide increased pitting corrosion resistance.

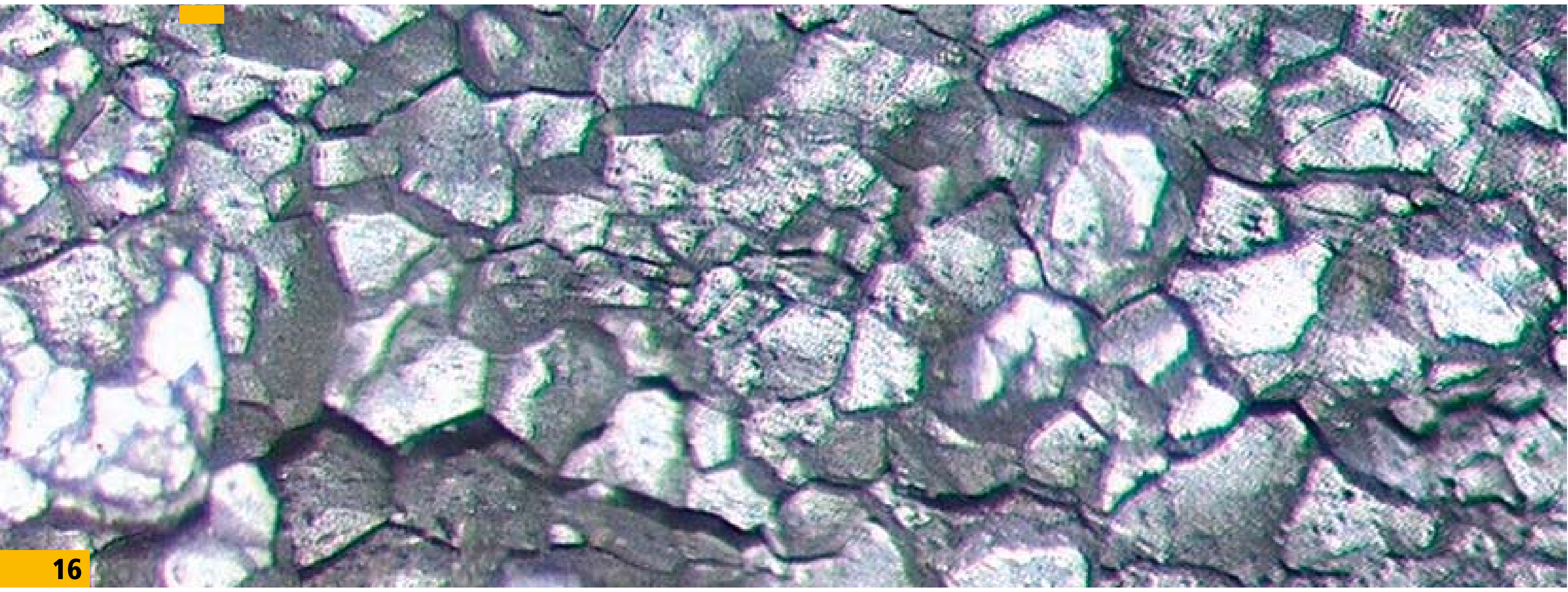


Ill. 33: Pitting corrosion of high alloy CrNi steel type 1.4541



Ill. 34: Stress corrosion cracking of high alloy CrNi steel type 1.4541

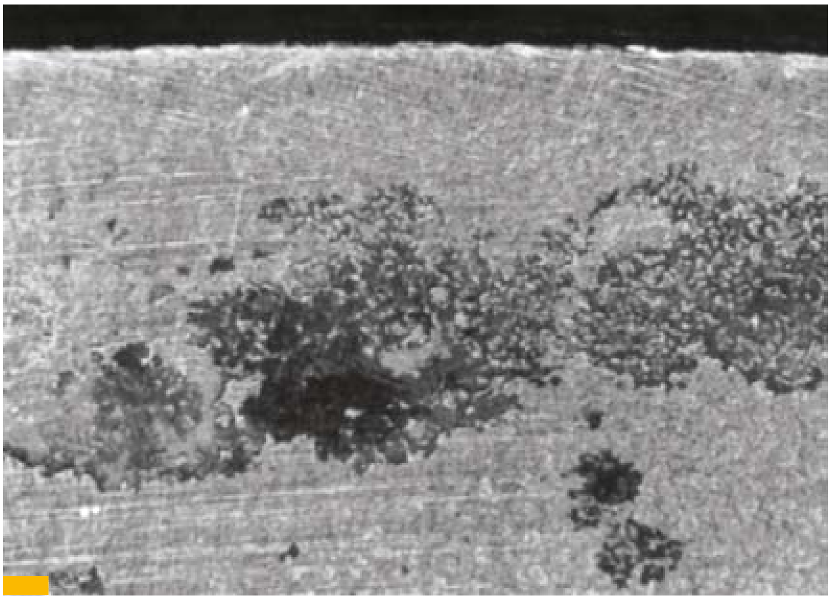
Ill. 32: Surface of the austenitic CrNi steel type 1.4301, damaged by intergranular corrosion



Stress Corrosion Cracking

Besides a specific attacking agent, which also in this case are practically only chlorine media, this form of corrosion also needs increased temperatures of over 50 °C as well as tensile stresses being present at the same time. These stresses may have been caused by either operating conditions or by inherent stresses, e. g. in the area of welds. Generally only austenitic steels and thus the normal V2A and V4A steels are affected by this corrosion. Typical of this kind of corrosion is an almost clean break of the components and at first glance one would not assume that corrosion had been the cause.

There are certain resemblances or at least transitions to vibrational corrosion which is subject not to static but dynamic mechanical strain. Ferritic-austenitic steels, e. g. 1.4462 and steels with nickel contents of more than 25 % are by degrees not susceptible to stress corrosion cracking.



Ill. 36: Crevice corrosion at the face of a collar

Crevice Corrosion and other Processes of Depassivation

As described above the creation of a passive layer requires oxygen. This does not apply to the single process only. As also in the passive condition there are corrosion processes – although only insignificant – the passive condition has to be constantly restored in order to remain stable. If therefore every transport of oxygen is prevented (stopped) due to rather long ways of diffusion in tight crevices, under deposits, in dead spaces etc. and depending on other conditions of attack, where again the chloride-ion has a dominant position, decomposition of the passive layer occurs, the metal is activated at these spots and corrodes.

Contact Corrosion

With this kind of corrosion the electrochemical character of any corrosion becomes evident: as already mentioned above, for any metal or alloy resp. in any solution given potentials would set in (appear) which are typical of this system. So if one puts two different material grades in the same solution and if the grades are in direct metallic contact with each other, a so-called mixed potential is created where the nobler one is shifted to the less noble potential values and vice versa; how far they are moving away from their specific potential position depends not least also on the surface ratios of both the short-circuited metal surfaces: a small galvanized screw will corrode much quicker in combination with a stainless steel flange than without this contact. In this connection a trivial precondition should not be overlooked: contact corrosion can only take place if contact is made also through the electrolyte, i. e. through the attacking agent. Thus the closed circuit is as follows:
metal A – metal B – attacking agent – metal A.

Ill. 35: MIC attack – rust pustules on a circular weld

Microbiologically Influenced Corrosion (MIC)

Besides the evaluation of the aggressiveness of waters, above all at temperatures below 60 °C, the presence of bacteria and their possible cause has to be taken into account. Reduction-oxidation processes can take place especially in the presence of slime developing bacteria which may severely damage the passiveness of stainless steels causing pitting corrosion. Weak areas in the material or caused by further fabrication, e. g. small weld defects, annealing colours or increased roughness represent a potential risk. Steels containing molybdenum are less susceptible to MIC than molybdenum-free grades.

Protection of the Surface

Today stainless steel products have to ar rive throughout the world safely, quickly and undamaged at their place of destination. Good packing is not an end in itself but primarily serves to prevent goods from mechanical damage such as dents or scratches. In addition, within the framework of overall quality assurance, packaging of stainless steels has to protect the passive layer that is responsible for the corrosion resistance.
Taking this into account, packing and transport of stainless steel products gain special importance. During transport and transhipment contact with "standard steel", copper or zinc coatings must be avoided. Even the slightest pressure or attrition of e. g. St37 would lead to the emission of this material to the stainless steel's surface. In the case of e. g. outside storage this attrition corrodes and brown spots appear that may affect the passive layer. Therefore, transport methods and transhipment devices or tools such as crane chains and skids of forklifts must be chosen or modified correspondingly in order to protect the product surface. Furthermore, the packing has to cope with static (safety), economic, logistic (handling) and ecological (ability for recycling) requirements. Pipes made of stainless steel especially are considered as a bulky and long product with sensitive surfaces and therefore do not comply with the systemised logistics of reputable forwarders.

Ill. 38: To protect the surface, packaging is defined and tailor-made for each specific project

The BUTTING packing methods streamline logistic processes in different ways, e. g. by shorter loading and unloading times, less efforts for securing the cargo, easier transhipment of piece goods and storage without additional equipment, enabling the picking of single pipes. BUTTING stainless steel pipes are secured to packing units by means of wooden crates and non-metallic straps, thus certainly avoiding ferrite contaminations and damages.

Corrosion Protection

During transport of stainless steel products additional corrosion protection can generally be dispensed with unless extraordinary impairment is expected by atmospheres containing ferrite or chlorides.
In the case of airfreight and sea freight where the material is exposed to sea air or subject to multiple handling and intermediate storage, appropriate packing becomes more important. In this case, the packing units are protected against the atmosphere by additional PE-foil. This packing has to be designed in such a way that condensates can drain via the lower side of the packing units. For storage in unfavourable atmospheric conditions or for sea transport seaworthy cases with insulating liners and desiccant can be used. The insulating liners generally consist of aluminium composite film preventing the ingress of water vapour and air. Combined with an intact insulating liner the desiccant can guarantee a humidity level of less than 40 %.

The VCI-method (Volatile Corrosion Inhibitor) is an approved alternative, but the inhibitor has to be adapted to the respective metal and should be tested before use.

Conclusion: Primarily, the packing of stainless steel products has to be understood as an all out measure of quality assurance. The products must arrive safely at their destination showing the same condition as provided by the manufacturer. The most careful material selection and production would come to nothing if contamination or damage occurred due to inadequate packing.

Ill. 37: Pipes in TP 316L packed in type BK07 – wooden caps, shrink-wrapped

PRODUCTION & SERVICE PROFILE

Longitudinally welded pipes

- Produced continuously from coil in sizes of 15 mm – 762 mm OD and wall thicknesses up to 16 mm
- From plate: in sizes of 33.7 mm – 3,000 mm OD and wall thicknesses up to 60 mm
- Pipes in special shapes

In random length up to 24 m with circumferential welds

Clad pipes

- Mechanically bonded BuBi®-pipes in sizes of 114.3 mm – 660 mm OD
- Metallurgically clad pipes

In random length up to 24 m with circumferential welds

Vessel construction

- Up to 6,000 mm OD: complete prefabrication at the mill
- Above 6,000 mm OD: prefabrication at the mill and assembly on site

Prefabrication

- Piping components ready for assembly
- Pipe bends acc. to drawings, piping segments, isometric drawings

Fittings

- Tees, reducers, special fittings
- Pipe bends acc. to DIN 2605
- Collars acc. to DIN 2642
- Elbows with long radii

Piping technology

- Pipes with special tolerances, e.g. furnace rollers, jackets for pumps
- Pipes with special surface requirements, e.g. for the pharmaceutical industry, architecture
- Further processing of pipes using forming, grinding, laser cutting, e.g. jackets for pumps, valves and lamps
- Special products, e.g. BUTTING HeRo® (an uncooled furnace roller)

Assemblies

- Vessels
- Linepipes
- Special constructions, equipment

Surface treatment

- Pickling (also on subcontract basis)
- Blasting, peening (also on subcontract basis)
- Grinding (also on subcontract basis)

Services

- Expert technical and metallurgical guidance
- CAD-facilities, isometric drawings
- Metallurgical testing and non-destructive testing

Material selection

- **Steels containing 10.5 % Cr min,** e.g.
  - ➜ Stainless steels
  - ➜ Heat resisting steels
  - ➜ Creep resisting steels
- **Nickel alloys**
- **Titanium**
- **Aluminium and aluminium alloys**
- **Special alloys**
- **Clad materials**

Approvals

- By TÜV acc. to AD-WO/HPO and TRD 100/201 and DIN EN 729-2
- DGRL (pressure equipment directive)
- Acc. to the water supply rules (WHG) § 19 l
- Quality Management System acc. to DIN EN ISO 9001 : 2000
- Accreditation of the laboratory acc. to DIN EN ISO / IEC 17025 : 2000
- Statement of Assessment ASD-EASE acc. to EN 9100 (without design)
- Environmental Management System acc. to DIN EN ISO 14001
- Work Safety Management acc. to OHSAS 18001

Photographs
- Title: Rutzen & Scherer / HenryN.
- Aerial view: Thomas Keller
- Inside: Heike Butting, Rutzen & Scherer, S. Schneider, S. Wilke, Company archive

Edition 2008

Editor: **H. BUTTING GmbH & Co. KG,** Layout: **HenryN.** Braunschweig

Aerial view BUTTING Knesebeck

BUTTING

H. BUTTING GmbH & Co. KG
Gifhorner Straße 59
29379 Knesebeck
Germany
Phone: + 49 5834 50-0
Fax: + 49 5834 50-320
Email: info@butting.de

Internet: www.butting.de

BUTTING

BUTTING Anlagenbau
GmbH & Co. KG
Kuhheide 13
16303 Schwedt / Oder
Germany
Phone: + 49 3332 2097-0
Fax: + 49 3332 2097-18
Email: info@butting-schwedt.de

BUTTING CHINA

BUTTING (Shanghai) Co., Ltd.
Jingxue Rd. 199 / 2
Malu Jiading
201801 Shanghai
China
Phone: + 86 21 69157598
Fax: + 86 21 69157599
Email: info@butting.com.cn

BUTTING CANADA

BUTTING Canada Ltd.
239 Crawford Place
Cochrane, Alberta
T4C 2G8
Canada
Phone: + 1 403932 5844
Fax: + 1 403932 4237
Email: canada@butting.de