

Semi-finished products

Steel products such as ingots, billets, blooms and slabs fall under the category semi-finished products. These products can be made by direct continuous casting of liquid steel or by pouring the liquid steel into ingots, which are then hot rolled into semi-finished products.

Ingots

Ingot is a semi-finished steel product obtained by casting the melt into fixed size moulds. This product must be processed by a break-down rolling mill or forged into desired wrought semi-finished products or in some cases rolled/forged into thicker finished sections.

Slab

Slab is a semi-finished steel product obtained by rolling or forging ingots or by casting a melt in a continuous caster and cut the strand into suitable lengths. The slab has a rectangular cross section and is used as a starting material in the production process of flat products, i.e. hot rolled coils or plates.

Blooms

Bloom, Figure 5:5, is a cast semi-finished steel product with a smaller cross section than slabs, often rectangular, typically larger than 200 mm × 200 mm. Blooms can also be cast to different shapes like I or H-beam profiles or rounds.

Billet

Billet, Figure 5:6, is a semi-finished steel product with a square cross section up to 200 mm × 200 mm. This product is either rolled or continuously cast and then further processed by rolling to produce finished products like wire rods, merchant bars and other sections. Billets, especially rolled billets, are used as a starting workpiece in many forging operations, e.g. flange production.

Rolled products

Hot rolling

Hot rolling is a metalworking process that occurs above the recrystallization temperature of the stainless steel, Figure 5:7. The starting material is usually semi-finished casting products, such as slabs, blooms, and billets. The semi-finished products are sometimes directly fed into the rolling mill but more often reheated from room temperature to the proper hot working temperature. This is done in a gas- or oil-fired furnace for slabs and blooms. For billets, a billet induction heating can be used.

The final flat products are either sheet or plate. According to the standard ASTM A480, the former are less than 4.76 mm thick and the latter thicker than this. According to the European standard EN 10079 a sheet has as a square or rectangular shape with a thickness less than 3 mm. The product can be rolled into coils or individual plates. In the latter case the plate are sometimes referred to as quarto plate, acknowledging the type of rolling mill used to produce the plate. The hot rolled coil product can be sheared into plates and supplied as a hot rolled product, CPP (Continuous Produced Plate) or as a hot band for the next processing step, often cold rolling. A special case of this is SHRP (Steckel Hot Rolled Plate), where a 10–25 mm thick strip is cut into plates directly in the hot

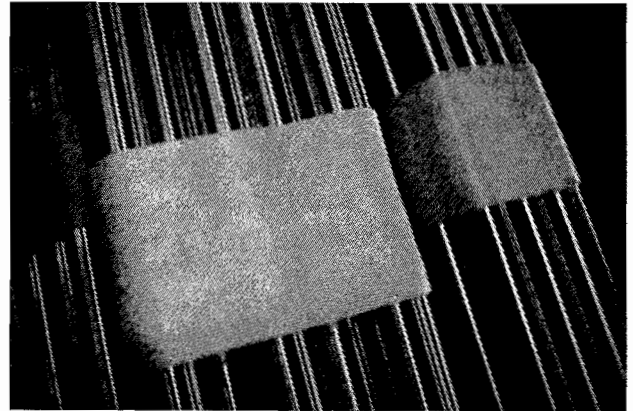


Figure 5:3. Long products, bar bundles.

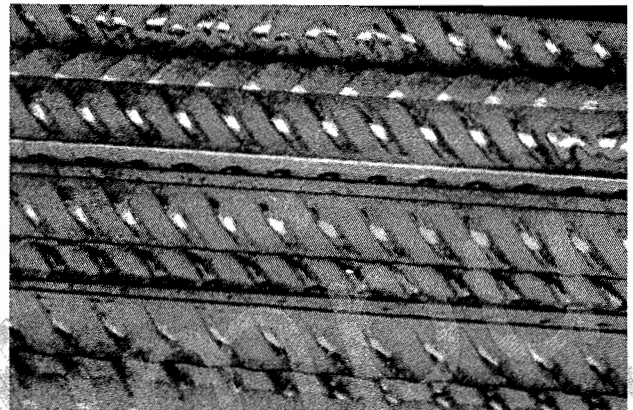


Figure 5:4. Long products, stainless steel reinforcing bars.



Figure 5:5. Long products, blooms.

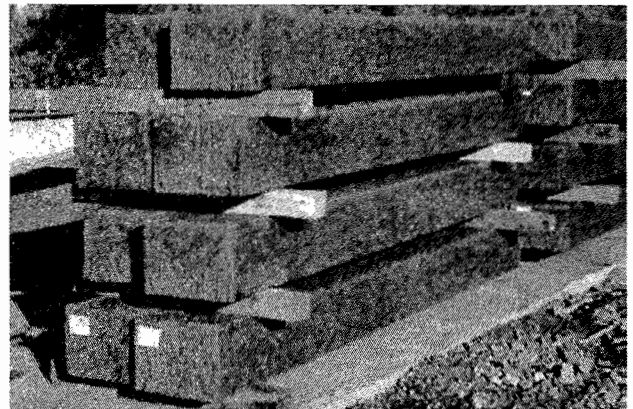


Figure 5:6. Long products, billets.

rolling mill without coiling. Products produced in narrow coil widths are referred to as strip. This means less than 600 mm for hot rolled products and less than 500 mm for cold rolled products. For long products the main hot rolled products are rods which are wound into coils, or bars that are produced as straight lengths, Figure 5.8.

The resulting surface on hot rolled products depends on the finishing operation and several types of finishes can be found in the standard EN 10088-2 (European designations) and in ASTM A480 (American designations). The most common is 1D/No. 1 finish according to EN 10088-2/ASTM A480 respectively, defined as hot rolled, heat treated, pickled and free of scale, Figure 5.10. This standard is used for most steel types to ensure good corrosion resistance and is also a common finish for further processing.

Cold rolling

Cold rolling occurs with the metal below its recrystallization temperature (usually at room temperature), which increases the material strength via strain hardening (work hardening). It also improves the surface finish and gives tighter tolerances compared to hot rolling. Cold-rolled products such as sheets, strips and bars are usually thinner than the same products that are hot rolled. Because of the smaller size of the workpieces and their greater strength compared to hot rolled stock, four-high or cluster mills are often used. Cold rolling cannot reduce the thickness of a workpiece as much as hot rolling in a single pass.

After cold rolling, the normal procedure is to recrystallize the material by annealing and remove the newly formed scale by pickling, Figure 5.9.

The most common cold rolled finish is 2B/2B defined as; cold rolled, heat treated, pickled and skin passed, Figure 5.11. This procedure ensures good corrosion resistance, tolerances, smoothness and flatness. It is also a common finish for further processing. Skin passing may also be done by tension levelling.

A second common cold rolling finish is 2E/2D defined as; cold rolled, heat treated, mechanically descaled, which is usually applied to steels with a scale which is very resistant to pickling solutions, Figure 5.12. The most modern processing lines include one or more cold rolling mills. The cold rolling can be carried out on a pickled surface similar to off-line cold rolling or on a black unpickled coil as in the Outokumpu RAP processing line. This line also include a skin pass mill and can produce both 2E/2D or 2B/2B products directly without any additional process steps.

The 2E surface is optimal for further fabrication and manufacturing of high quality stainless steel products like tubes and hollow sections. The surface has typically a rough and dull appearance, but can depending on the type of mechanical descaling in some cases compare with 2B surface roughness values. A third common practice is to use a bright annealing furnace where the material is heated in a protective atmosphere and no additional scale forms and thereby no further pickling is needed. This type of processes is often referred to as 2R/BA (Bright Annealed) and produces a surface that is smoother and brighter than 2B and with high reflectivity, Figure 5.13.

The ferritic grade 4016 is also produced with a 2BB surface (Figure 5.14) defined as; cold rolled, heat treated, bright pickled and skin passed. This surface is comparable to the bright annealed finish 2R/BA. The 2BB finish is an Outokumpu designation, but the product conforms to the standard 2B surface definition.

Skin pass rolling utilise a low amount of reduction: typical 0.5–1%. It is used to produce a smooth surface, a uniform thickness and for ferritic grades reduces the yield point phenomenon (by

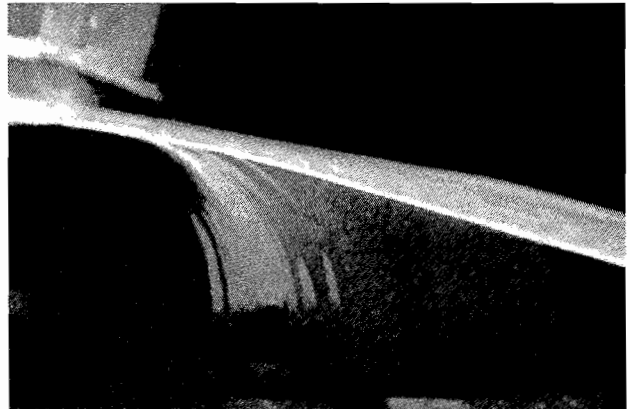


Figure 5.7 Hot rolling.

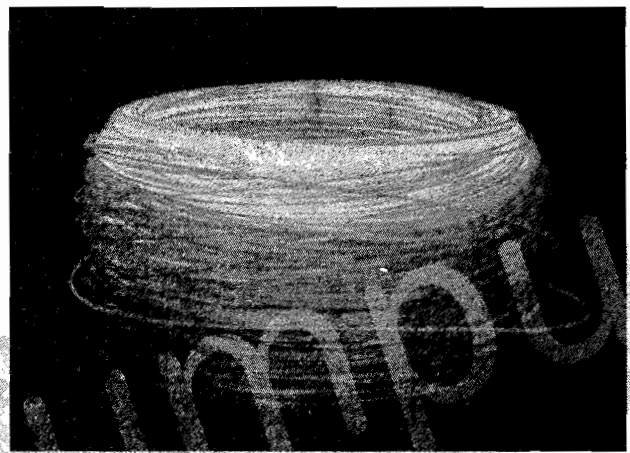


Figure 5.8 Long products, hot rolled rod coil.

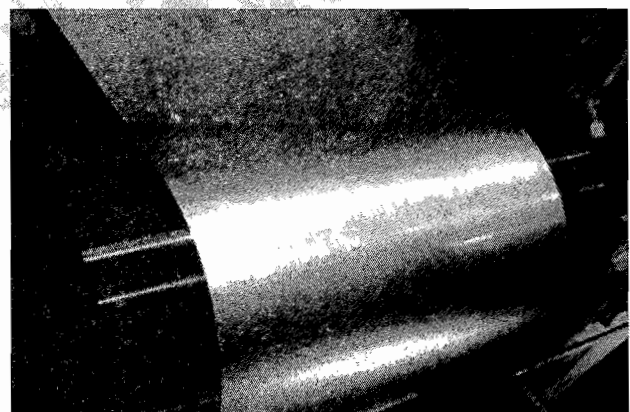


Figure 5.9 Cold rolled coil after annealing and pickling.

preventing Lüders bands from forming in later processing).

Finished cold-rolled sheets and strips may come in various conditions; fully annealed or work hardened (temper rolled) to certain tensile strength levels such as C700, C850 etc., indicating a tensile strength of 700 or 850 MPa. The temper rolled finish is designated as 2H/TR finish and exhibits a bright surface that is cold worked to obtain higher strength level.

For long products, cold working is most often achieved by cold-drawing, in which the cross section area reduction is achieved by drawing the rod coil or bar on a draw-bench or more commonly through a die. This process results in a hardness profile of the bar or wire, with a harder surface and softer middle.

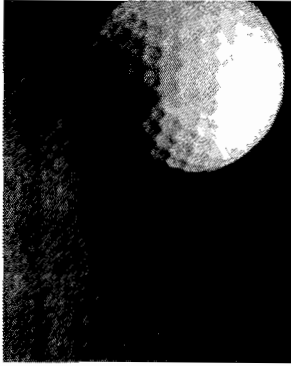


Figure 5:10. Hot rolled 1D/No. 1 finish surface.

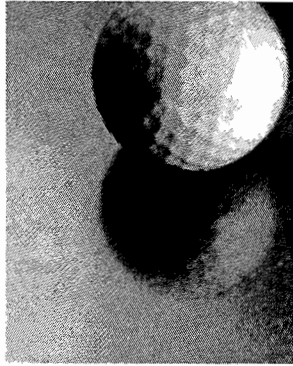


Figure 5:11. Cold rolled 2B/2B surface.

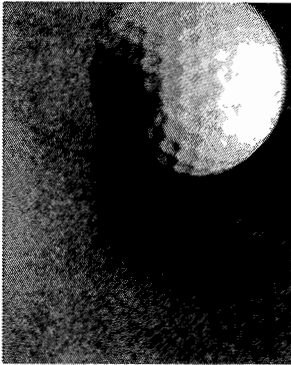


Figure 5:12. Cold rolled 2E/2D surface.

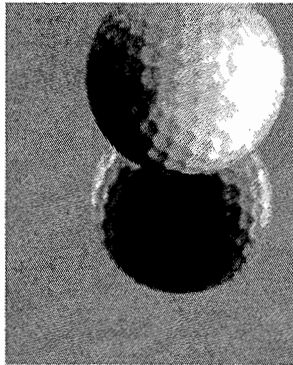


Figure 5:13. Cold rolled 2R/BA surface.

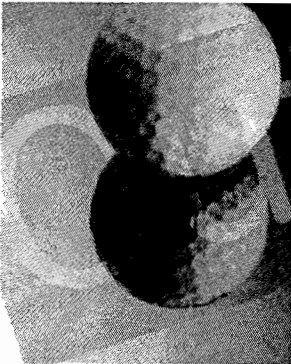


Figure 5:14. Cold rolled 2BB surface.

References

ISO 6927, "Buildings and civil engineering works – Sealants – Vocabulary".

EN 10079, "Definition of steel products".

ASTM A480, "Standard Specification for General Requirements for Flat-Rolled Stainless and Heat-Resisting Steel Plate, Sheet, and Strip".

EN 10088-2, "Stainless steels – Part 2: Technical delivery conditions for sheet/plate and strip of corrosion resisting steels for general purposes".

Corrosion and corrosion properties

Corrosion is the gradual degradation of a metal by chemical, often electrochemical, reaction with the surrounding environment. A result of corrosion can be loss of material properties such as mechanical strength, appearance and impermeability to liquids and gases. Stainless steels are often chosen because of their resistance to corrosion, but they are not immune to corrosion. Whether a stainless steel is corrosion resistant in a specific environment depends on the combination of the chemical composition of the stainless steel and the aggressiveness of the environment.

Corrosion can be divided into wet corrosion and high temperature corrosion:

- Wet (or aqueous) corrosion refers to corrosion in liquids or moist environments, and includes atmospheric corrosion.
- High temperature corrosion denotes corrosion in hot gases at temperatures from around 500 °C to 1200 °C.

The corrosion resistance of stainless steel is attributed to the thin passive film that forms spontaneously on the stainless steel surface in oxidising environments if the chromium content in the steel is minimum ~10.5%. A special passivating treatment is not required as the film forms instantly in oxidising media such as air or aerated water. This passive film is very thin (1–3 nm) and consists mainly of iron and chromium oxides and hydroxides as shown in Figure 6:1. As the passive film adheres strongly to the metal substrate and protects it from contact with the surrounding environment, the electrochemical reactions causing corrosion are effectively brought to a halt. Moreover, if locally destroyed, e.g. by scratching, the passive film has the ability to 'heal' by spontaneously repassivating in an oxidising environment.

All corrosion types affecting stainless steel are related to permanent damage of the passive film, either complete or local breakdown. Factors such as chemical environment, pH, temperature, surface finish, product design, fabrication method, contamination and maintenance procedures will all affect the corrosion behaviour of stainless steel and the type of corrosion that may occur.

This chapter gives a brief introduction to corrosion that can occur on stainless steel. More information on corrosion types, corrosion testing, and corrosion in specific environments and applications can be found in the Outokumpu Corrosion Handbook. It also contains a large collection of corrosion data for stainless steels.

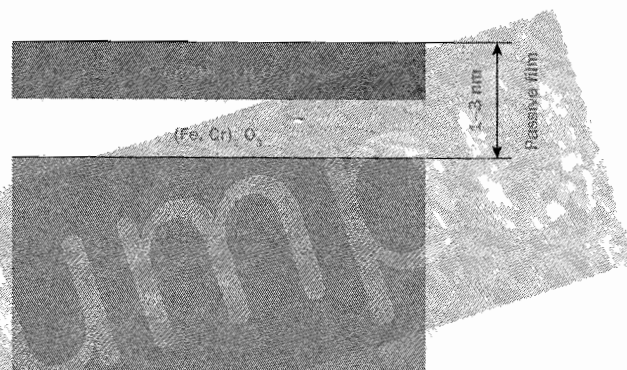


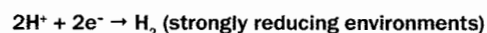
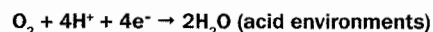
Figure 6:1. Two layer model of passive film on stainless steel.

Wet corrosion

Wet (or aqueous) corrosion of metals is an electrochemical process that involves an anode and a cathode, as well as an electrolyte connecting the two. At the anode the metal oxidises (corrodes) and forms rust or some other corrosion product:



At the cathode, a reduction reaction takes place. This is typically the reduction of oxygen or hydrogen evolution:



In order to prevent corrosion these reactions must be prevented.

Stainless steel typically does not corrode in the same manner as carbon steel or low alloy steel that rusts through constantly changing anodes and cathodes on the whole surface. In order for this to occur on stainless steel, the passive film needs to be completely broken down in environments such as non-oxidising

acids, e.g. hydrochloric acid.

More commonly the passive film is attacked at certain points, causing various types of localised corrosion. If localised corrosion occurs it is difficult to estimate the propagation rate to calculate for a corrosion allowance.

Pitting and crevice corrosion

Pitting and crevice corrosion are very similar with regards to the factors that affect their occurrence. Stainless steels are particularly susceptible to pitting and crevice corrosion in media containing halide ions such as chlorides. Therefore, environments that represent a risk for pitting and crevice corrosion include seawater and process solutions containing high concentrations of chlorides, but also low concentration of chlorides (< 100 ppm) can under unfortunate circumstances cause pitting or crevice corrosion. The presence of sulphides can increase the aggressiveness of the media, while sulphates can decrease the risk for corrosion. Other factors that increase the probability for pitting and crevice corrosion are increasing temperature, low pH and addition of oxidative chemicals (e.g. by chlorination).

For both types of corrosion an incubation period is observed before corrosion is initiated. The duration of the incubation period can vary from a few hours to many months, but once initiated propagation can be very fast. Therefore pitting and crevice corrosion must be avoided; otherwise the consequences can be serious damage and leakage.

Pitting corrosion

Pitting corrosion is highly localised corrosion with discrete pits on the free surface of stainless steels as shown in Figure 6:2.

If the passive layer is damaged or locally weak, pitting corrosion can initiate and the small area which is unprotected by the passive film becomes the anode. As this anodic area is very small compared to the large cathode area of the undamaged passive film, the corrosion rate is high and a pit is formed. Once initiated the pH in the pit will become lower than that of the surrounding environment due to hydrolysis of dissolved metal ions such as Fe^{2+} and Cr^{3+} . Moreover, the chloride concentration in the pit increases due to chloride ions migrating into the pit to balance the positive charge of the metal ions. Thus, the conditions in the pit gradually become more aggressive and propagation can continue at a high rate.

The size, shape and morphology of the pits can vary; some pits can be quite shallow while some penetrate deep into the material. They can also undermine the surface with attack that appears small but spreads out beneath the surface. Therefore, the full extent of pitting corrosion can be difficult to judge by just visual inspection as it may be concealed.

Crevice corrosion

As its name implies, this type of corrosion occurs in crevices and confined spaces. Crevices can be caused by component design or joints such as flanges and threaded connections, but also under deposits formed on the surface during service. As the oxygen content is limited inside a tight crevice the passive layer is weakened and just as for pitting dissolved metal ions in the crevice will lower the pH and allow chloride ions to migrate into the crevice. Eventually the passive layer breaks down and the aggressive environment facilitates the corrosion attack.

Figure 6:3 shows an example of crevice corrosion on a stainless steel valve flange. Compared to pitting, crevice corrosion results

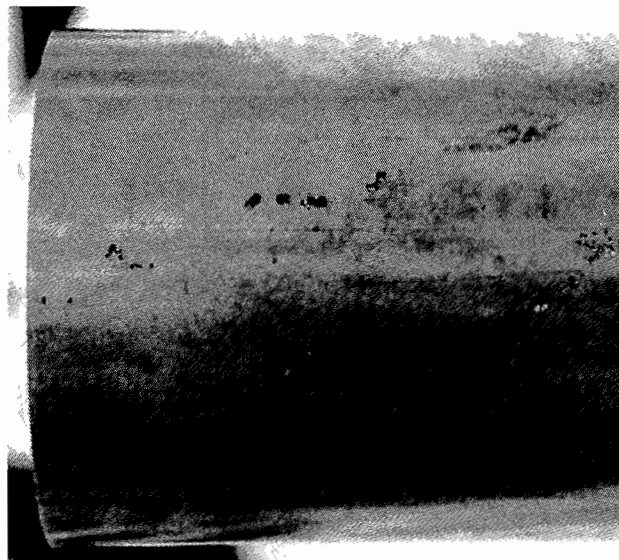


Figure 6:2. Pitting corrosion on the outside of a tube.

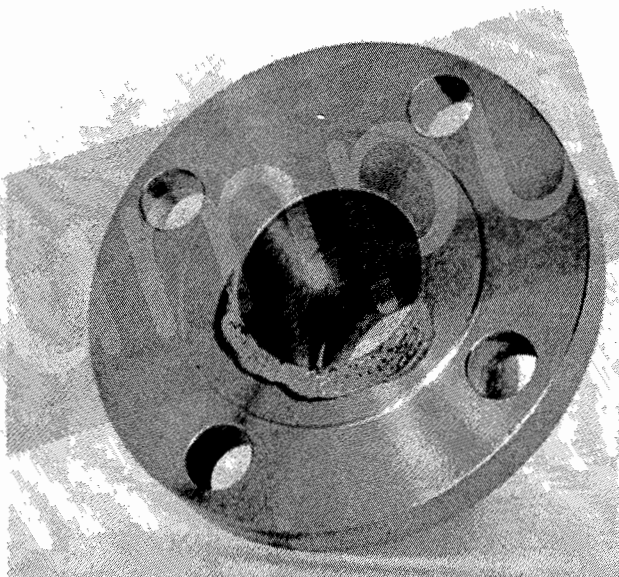


Figure 6:3. Crevice corrosion under the sealing on a flange exposed to chlorinated seawater.

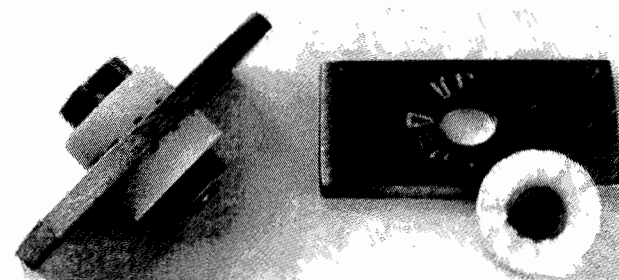


Figure 6:4. Crevice formers used in the ASTM G48 Method F test.

in larger but shallower attack and can occur in environments that normally do not cause pitting on free surfaces.

Resistance to pitting and crevice corrosion

It is well known that increasing the chromium content and adding molybdenum and nitrogen as alloying elements increase the resistance to pitting and crevice corrosion of stainless steels. The



Figure 6:5. ASTM G150 test performed in the flush port Avesta Cell.

Pitting Resistance Equivalent (PRE), often also given as PREN to indicate the influence of nitrogen in the steel, can be used in order to rank and compare stainless steels in terms of their resistance to pitting corrosion. It takes into account the effect of the most important alloying elements. One frequently used equation for stainless steels is:

$$\text{PRE} = \% \text{Cr} + 3.3 \times \% \text{Mo} + 16 \times \% \text{N}$$

Other formulas exist that includes addition of alloying elements such as manganese, tungsten, sulphur and carbon. In Table 6:1 the PRE values, calculated with the formula above, are listed for some stainless steels. It is important to remember that the calculated PRE only gives an indication of the resistance of stainless steels and gives no information on their behaviour in real service environments. Therefore, it should only be used for roughly comparing the pitting corrosion resistance of different grades of stainless steels. Experimental ranking of individual grades can be performed by using accelerated laboratory tests which are described in ISO, ASTM and national standards.

ASTM G48 methods E and F use the highly oxidising environment of acidified ferric chloride solution (6 % FeCl_3 + 1 % HCl) where specimens are exposed for a period of 24 hours. Method E determines the critical pitting temperature (CPT) while method F uses PTFE crevice formers (see Figure 6:4) to determine the critical crevice temperature (CCT). The tests are performed at increasing temperature in 5 °C steps until pitting or crevice corrosion is detected. In Table 6:1 typical CPT and CCT values are presented. The results show that CCT values are considerably lower than CPT values for the same steel grade although the test solution and the

Pitting resistance equivalent (PRE) and typical CPT and CCT values for some stainless steel grades

Table 6:1

Outokumpu grade	PRE	ASTM G48		ASTM G150
		Method E CPT [°C]	Method F CCT [°C]	CPT [°C]
DUPLEX				
FDX 25™	25	10	n.t.	14 ³
LDX 2101®	26	15	<0	17±3
2304	26	25	<0	25±3
EDX 2304™	28	30	5	36±3
FDX 27™	27	30	n.t.	27 ³
LDX 2404®	33	35	15	43±2
2205	35	40	20	52±3
2507	43	65	35	84±2
AUSTENITIC				
4301/4307	18	10	<0	<10 ⁴
4401/4404	24	20	<0	20±2
4436/4432	26	25	<0	27±3
4438	28	n.t.	<0	33±3
904L	34	40	10	62±3
254 SMO®	43	65	35	87±3
4529	45	60	35	>90
4565	46	90	40	>90
654 SMO®	56	>b.p.	60	>90

¹The standard specifies that values below 10 °C are not valid for ranking

²test surface ground to 320 mesh

³limited amount of test results

n.t. = not tested

b.p. = boiling point

No ferritic grade is included in the table. These grades have PRE values varying from 11 to 25, but the local corrosion resistance is too low for determination according to the methods mentioned.

Different products and different surface finishes may show CPT and CCT values that differ from the above.

test duration is the same. This illustrates the fact that crevice corrosion occurs more readily than pitting corrosion, i.e. even under conditions that do not cause pitting.

ASTM G150, as well as ISO 17864, evaluates the CPT using a solution of 1M NaCl and an applied potential of +700 mV_{SCE}. By using the flush port Avesta Cell shown in Figure 6:5, crevice corrosion is avoided at the contact between the specimen and the specimen holder. The temperature is increased from initial 0 °C at a rate of 1 °C/min and the CPT is defined as the temperature where the current density exceeds 100 µA/cm². Typical ASTM G150 CPT values for some stainless steels are presented in Table 6:1.

It is important to remember that it is not possible to compare CPT values measured using the two different test methods. Also, CPT and CCT values from these standard test methods cannot be used for predicting whether or not pitting or crevice corrosion will occur under specific service conditions, only for ranking.

Instead, engineering diagrams based on laboratory tests and field tests, as well as practical experience are important tools for material selection. Figure 6:6 shows an example of an engineering diagram for pitting and crevice corrosion of some high alloyed stainless steels. It indicates the temperature limits of use in slightly chlorinated (< 1 mg/l) and naturally aerated water with varying chloride content. It is crucial to remember that other environmental factors

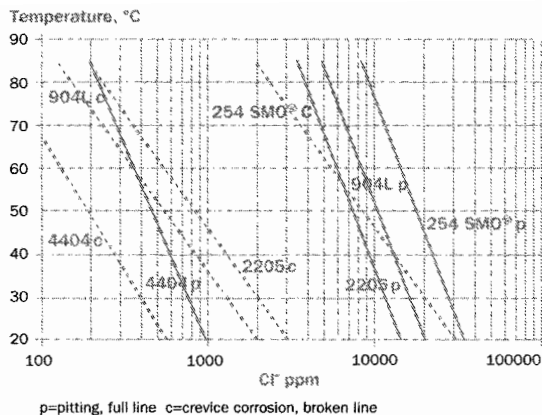


Figure 6:6. Engineering diagram indicating the maximum temperatures and chloride concentrations allowed for some stainless steels in slightly chlorinated (< 1 ppm) water.

such as pH, oxygen content, microbial activity, degree of chlorination and whether or not the water is flowing or stagnant can influence the resistance of the material. Also material factors such as surface finish and the presence of weld oxides and weld defects can have an effect. In the case of crevice corrosion the position of the lines in Figure 6:6 is dependent on the severity of the crevice geometry.

avoiding pitting and crevice corrosion

There are a number of measures that can be taken in order to avoid pitting and crevice corrosion on stainless steel. These include:

- Select a highly alloyed stainless steel grade. As shown with the PRE formula, the resistance to pitting and crevice corrosion increases with increasing content of chromium and by adding molybdenum and nitrogen.
- Lower the chloride content of the corrosive environment.
- Increase the pH, as a higher pH reduces the risk for pitting and crevice corrosion.
- Decrease the content of, or remove, oxygen and other oxidising species from the environment.
- Use a favourable design that avoids tight crevices, stagnant conditions and formation of deposits.
- Employ good fabrication practices that produce smooth and clean surfaces and ensure that weld oxides are removed.

Uniform corrosion

Uniform corrosion occurs when the passive layer is destroyed on the whole, or a large part, of the surface as shown in Figure 6:7. Thus the anodic and cathodic reactions occur on the same surface at constantly changing locations much like corrosion on carbon steel. The result is more or less uniform removal of metal from the unprotected surface. Uniform corrosion can occur on stainless steels in acids or hot alkaline solutions. Generally the aggressiveness of the environment increases with increasing temperature, while the effect of concentration is variable.

In an environment with constant temperature and chemical composition, uniform corrosion occurs at rather a constant rate. This means that in contrast to pitting and crevice corrosion, a corrosion rate can be measured. The corrosion rate is often expressed as loss of thickness over time, e.g. mm/year. Stainless steel is normally considered to be resistant to uniform corrosion in a specific environment if the corrosion rate does not exceed



Figure 6:7. Uniform corrosion on the outside of a steam tube exposed to sulphuric acid.

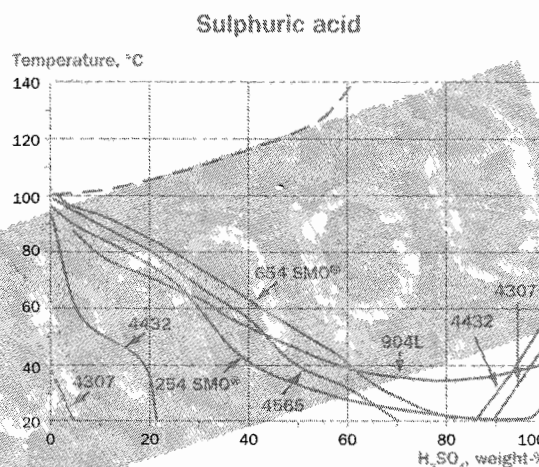


Figure 6:8. Iso-corrosion diagram, 0.1 mm/year, for austenitic stainless steels in pure sulphuric acid.

0.1 mm/year. The effect of temperature and concentration can be presented as iso-corrosion diagrams where the individual lines represent a corrosion rate of 0.1 mm/year for a specific grade. Figure 6:8 shows such an iso-corrosion diagram for sulphuric acid.

In oxidising acids such as nitric acid, stainless steels are generally able to maintain their passive layer and are thus not susceptible to uniform corrosion. However, in strongly oxidising environments such as hot concentrated nitric acid and chromic acid, the passive layer can become unstable and oxidised to more soluble species by so-called transpassive corrosion. The resistance to uniform corrosion generally increases with increasing levels of chromium, nickel and molybdenum, but in these strongly oxidising environments molybdenum has proved to be detrimental to the corrosion resistance.

Strongly reducing acids such as hydrochloric acid and hydrofluoric acid readily break down the passive layer of stainless steels with little chance of repassivating. This means that the use of most stainless steels is limited to dilute solutions of these acids.

Sulphuric acid is an example in which corrosion does not necessarily increase with increasing concentration. This acid is reducing at low and intermediate concentrations, but oxidising when concentrated. Furthermore, the degree of ionisation reaches a maximum at intermediate concentrations. As a result, sulphuric acid is most

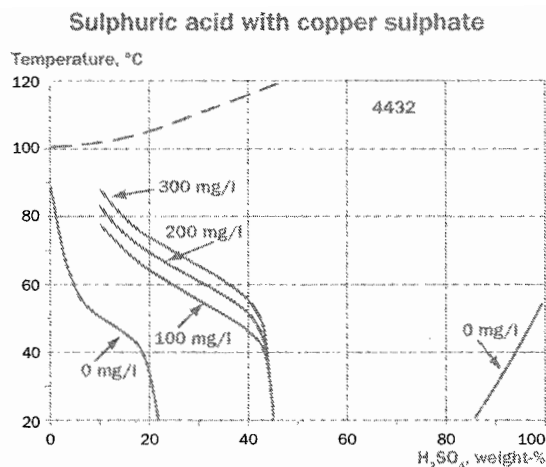


Figure 6:9. Iso-corrosion diagram, 0.1 mm/year, for steel 4432 in sulphuric acid with additions of copper sulphate.

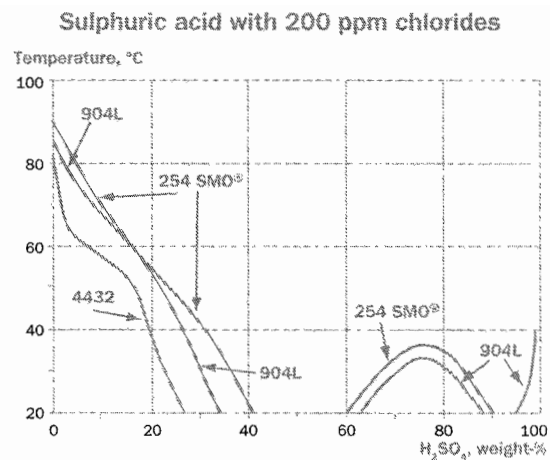


Figure 6:10. Iso-corrosion diagram, 0.1 mm/year, for austenitic stainless steels in sulphuric acid with an addition of 200 ppm chlorides.



Figure 6:11. Stress corrosion cracking in a stainless steel tube.

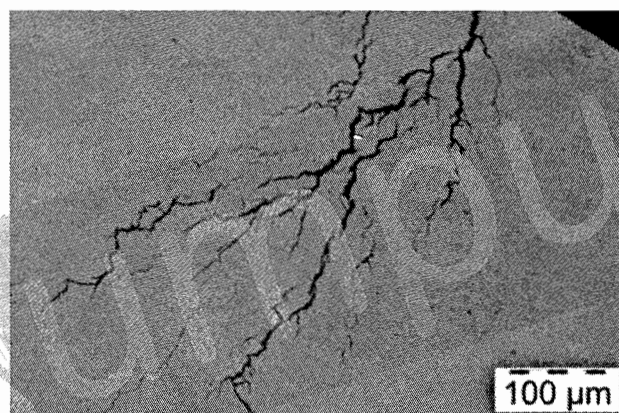


Figure 6:12. Micrograph of stress corrosion cracking.

corrosive to stainless steel in concentrations between 30 and 80 weight-% and less aggressive at low and high concentrations, Figure 6:8. Molybdenum and copper alloying improve the corrosion resistance, especially in the intermediate concentration range, as exemplified by grade 904L in Figure 6:8.

Impurities can have a dramatic effect on the corrosivity of acid solutions. Reducing agents, such as hydrogen sulphide or sulphur dioxide, may increase the uniform corrosion rate. On the contrary to the case of pitting and crevice corrosion, oxidising impurities such as ferric and cupric ions, nitric acid, and dissolved oxygen, can promote passivation and reduce the corrosivity as shown in Figure 6:9. The presence of halide ions, such as chlorides and fluorides, may also affect the corrosivity, Figure 6:10. Even small amounts of halides may increase the corrosion rate of stainless steels in both organic and inorganic acids, as exemplified by comparing Figures 6:8 and 6:10.

Uniform corrosion is considered easier to predict compared to localized corrosion. Moreover, while pitting and crevice corrosion should, if possible, be avoided completely, some degree of metal loss due to uniform contamination can often be tolerated. Exceptions are applications where contamination is unacceptable, e.g. for hygienic reasons in equipment for food handling.

Environmentally assisted cracking

Environmentally assisted cracking is a phenomenon that is caused

by the combined action of mechanical stress and corrosive environment. It is not unique for stainless steel; many other alloys are also susceptible in different media, e.g. brass alloys in ammonia environments and carbon and low alloy steels in alkaline solutions. Once initiated, crack propagation can be very rapid and result in critical failure. Environmentally assisted cracking can be caused by a number of environmental species including chlorides, hydrogen and hydroxides.

In order for cracking to occur the mechanical tensile stresses must exceed a critical level. The required stresses need not necessarily be applied stresses, but can be residual stresses from manufacturing operations, such as forming and welding.

Stress corrosion cracking

Like pitting and crevice corrosion, stress corrosion cracking (SCC) most frequently occurs in chloride-containing environments, but it can also occur in concentrated alkali solutions such as sodium hydroxide. Elevated temperatures ($> 60^{\circ}\text{C}$ for chloride environments and $> 100^{\circ}\text{C}$ for alkaline environments) are normally required for stress corrosion cracking to occur in stainless steel. Nevertheless, there are cases where cracking can occur at temperatures as low as 30°C , e.g. in swimming pool atmospheres. A common cause of stress corrosion cracking is evaporation on hot stainless steel surfaces. In this manner liquids with low chloride content that normally would be considered harmless, can cause

chloride concentrations high enough to cause stress corrosion cracking. One such example is under thermal insulation on piping. Figures 6:11 and 6:12 depict some typical stress corrosion cracks.

Stress corrosion cracking caused by chlorides, is typically transgranular, i.e. occurs across the grains. Standard austenitic grades, such as 4307 and 4404, are generally sensitive to chloride induced stress corrosion cracking. High contents of nickel and molybdenum increase the resistance of austenitic stainless steels. Thus, high alloyed austenitic grades 904L, 254 SMO® and 654 SMO® show excellent resistance to chloride induced stress corrosion cracking. Stainless steels with a duplex microstructure generally have high resistance to stress corrosion cracking, as have ferritic grades.

Intergranular stress corrosion cracking, where cracking occurs along grain boundaries, can occur in high purity water at high temperatures (200–300 °C) with relatively high oxygen content (~ 0.2 ppm). This has been a concern in nuclear boiling water reactors (BWR), and mainly in sensitised steels where carbides have precipitated along the grain boundaries.

Sulphide stress cracking (SSC)

Sulphide stress cracking (SSC) is the cracking of a material under the combined action of mechanical tensile stress and corrosion in the presence of water and hydrogen sulphide (H₂S), and it is a form of hydrogen-induced cracking. Sulphide stress cracking is of particular importance in the oil and gas industry, as natural gas and crude oil can contain considerable amounts of hydrogen sulphide (often referred to as sour service).

To assess the corrosivity of process fluids containing hydrogen sulphide the partial pressure of hydrogen sulphide has to be considered, together with pH, temperature, chloride, carbon dioxide and oxygen contents. Susceptibility to hydrogen embrittlement is most severe at, or below, ambient temperature, whereas chloride induced stress corrosion cracking is most severe at high temperatures. Consequently, the combined risk of cracking due to hydrogen sulphide and chlorides tends to be most severe for austenitic and especially duplex stainless steel grades in the range 80–100 °C.

A standard, ISO 15156-3, for material requirements in hydrogen sulphide containing environments in oil and gas production has been developed. This standard provides guidance on the application limit and qualification procedure for cracking resistant alloys.

Hydrogen induced stress cracking (HISC)

Another hydrogen embrittlement failure mode that can be of concern in the oil and gas industry is hydrogen induced stress cracking (HISC), where hydrogen is introduced when the material is under cathodic protection in seawater. The hydrogen is a result of the increased cathodic reaction, hydrogen ion reduction, on the stainless steel surface. Even high alloyed stainless steels can be subjected to full cathodic protection in offshore applications as these steels typically are connected to carbon steel and other low alloyed steels already under protection.

The ferritic phase in stainless steels is generally more susceptible to hydrogen embrittlement than austenitic phase. This means that ferritic, martensitic and duplex stainless steels may suffer hydrogen induced stress cracking at ambient or low temperatures.

In the case of duplex stainless steels, failures have usually involved materials with an unfavourable microstructure (e.g. large grain size, intermetallic phases and high ferrite content) in combination with unusually high mechanical stresses. A guideline (DNV RP F-112) has been published with recommendations regarding the

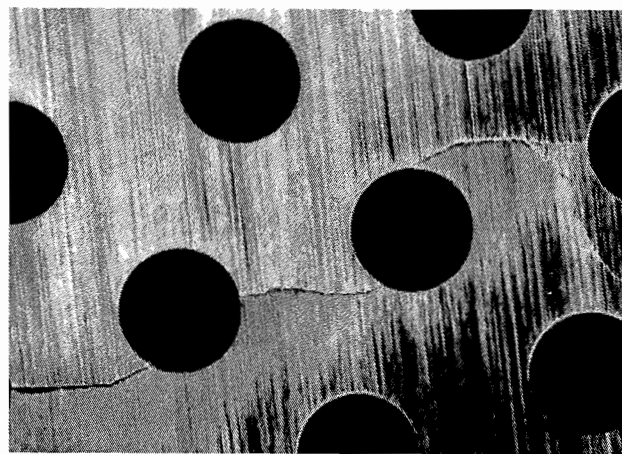


Figure 6:13. Corrosion fatigue cracks in a paper machine suction roll shell.

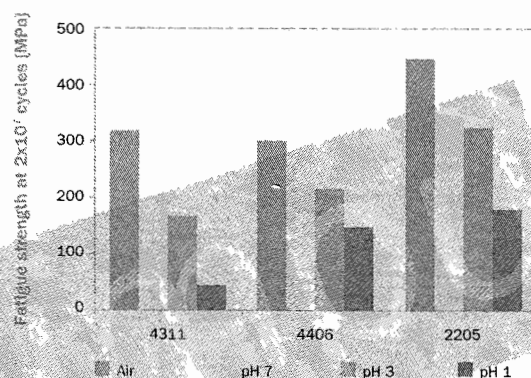


Figure 6:14. Effect of environment on fatigue strength for some stainless steels. Fatigue strength at 40 °C and rotating bending stress at 100Hz. Tested in air and 3% NaCl at various pH.

design of duplex stainless steel subsea equipment under cathodic protection, which specifies material requirements as well as best practice for design.

Corrosion fatigue

A material that is subjected to a cyclic load can fail owing to fatigue, at loads far below the ultimate tensile strength; see chapter on Mechanical properties. If the material is simultaneously exposed to a corrosive environment, failure may occur at even lower load levels and after shorter periods of time. This failure by a combination of cyclic load and corrosive environment is known as corrosion fatigue, Figure 6:13.

In many cases there is no pronounced fatigue limit, as observed in air, but a gradual lowering of the fatigue strength with increasing number of load cycles. The more aggressive the corrosive conditions and the lower the loading frequency the higher the effect of the environment. During very high frequency loads there is little time for the corrosion to act and the fatigue properties of the material will determine the service life. At lower frequencies, the corrosive action is more pronounced and an aggressive environment may also cause corrosion attack that can act as a stress concentrator and thus contribute to a shorter life.

Corrosion fatigue cracks are usually less branched than stress corrosion cracks (Figure 6:13), although both forms of corrosion cause brittle failures. Corrosion fatigue can occur at ambient temperature and in environments that could be considered harm-