Avesta Sheffield

CORROSION HANDBOOK

for Stainless Steels
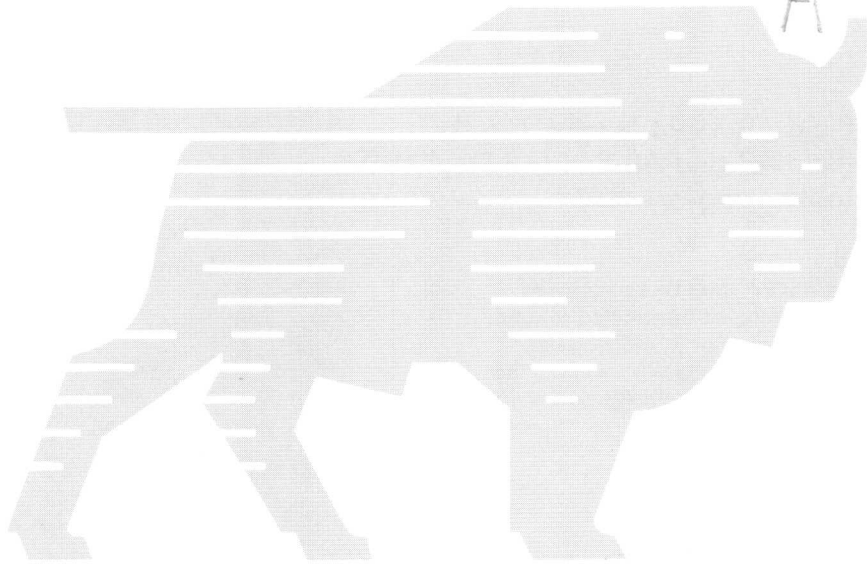
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Contents

Preface

This "Corrosion Handbook for Stainless Steels" is replacing an earlier edition published by Jernkontoret, Stockholm, which was jointly produced by the Scandinavian manufacturers of stainless steel in 1979. The previous edition, being a unique source of information for material specialists and designers, was highly appreciated but has now been out of print for some years.

Continued materials research has resulted in new grades and improved properties of the existing grades. New corrosion tests are continuously being carried out, often reflecting the more aggressive environments to which the materials are being exposed. The test methods used today are also more advanced and reliable than those previously used. A combination of these factors has motivated a complete revision of the corrosion tables, which on this occasion is the result of a co-operation between Avesta Sheffield AB and AB Sandvik Steel in Sweden.

As an introduction, a series of papers is presented on the corrosion theories in connection with stainless steels, their resistance to attack in atmospheric, wet and high temperature environments, as well as their use for various purposes, where these properties offer special advantages. These papers are then followed by corrosion tables and graphs describing the resistance of various materials to different environments (in alphabetical order) by concentrations and temperatures.

We are pleased that this work, which is based on more than 60 years' experience in solving corrosion problems with stainless steel, is now made available to industry. It is my belief that this Corrosion Handbook will be a valuable tool for all material specifiers when designing the process plant and equipment of today and tomorrow.

Stockholm, January 1994

Per Molin
President and Chief Executive Officer
Avesta Sheffield AB

Corrosion of Stainless Steels, General Introduction

Elisabet Alfonsson, Avesta Sheffield AB

INTRODUCTION

Stainless steels are not fundamentally noble materials in the same way as gold or platinum, which are more or less inert to most environments. Stainless steels derive their corrosion resistance from a thin, invisible surface layer, which is formed during a reaction between the metal and oxygen present in the ambient environment. This oxide layer drastically decreases the corrosion rate of the material, which is said to be passivated. Other materials that form passive layers are titanium and aluminium. Very slow consumption of the metal also takes place in the passive state as the passive layer is slowly dissolved but rebuilt again by oxidation of the underlying metal.

The passive layer on stainless steels consists mainly of chromium oxide and it forms spontaneously in environments containing enough oxidants. The metal surface exposed by mechanical damage, e.g. scratches, is also spontaneously repassivated. The oxygen content of air, and also of most aerated aqueous solutions, is enough for both the creation and maintenance of the passive layer of stainless steels.

There are, however, environments which cause permanent breakdown of the passive layer. Under circumstances where the passive layer cannot be rebuilt, corrosion occurs on the unprotected surface.

Different media cause corrosion attacks of dissimilar nature and appearance and there are several forms of corrosion that can occur on stainless steels. In this section only corrosion taking place in aqueous solutions is discussed.

UNIFORM CORROSION

Uniform corrosion occurs when the entire or at least large parts of the passive layer are destroyed. Corrosion reactions then cause a more or less uniform removal of metal from the unprotected surface. Attack by uniform corrosion on stainless steels occurs mainly in acids or in hot alkaline solutions.

Stainless steels generally show good resistance in oxidizing acids such as nitric acid, but are not always able to maintain their passive layer in non-oxidizing acids. The steel is then said to be activated. Hydrochloric and hydrofluoric acids are environments in which the use of most stainless steels is limited to relatively low concentrations and temperatures, as shown by the isocorrosion diagrams in the Corrosion Tables section.

Corrosion of stainless steels is possible also in strongly oxidizing environments such as concentrated nitric acid and chromic acid. Under such conditions the passive layer is not stable but is oxidized into more soluble species. This form of uniform corrosion is called transpassive corrosion.

The resistance to uniform corrosion generally increases with increasing contents of chromium, since that element is of the utmost importance for passivity. Nickel has a positive effect mainly because it reduces the corrosion rate of a depassivated steel. Molybdenum enhances passivity, and a high molybdenum content is favourable in most environments. However, in strongly oxidizing environments, such as warm concentrated nitric acid, steels containing molybdenum are less resistant than steels without molybdenum. Copper has a positive effect in the presence of reducing acids such as dilute sulphuric acid.

In an environment of constant temperature and chemical composition, uniform corrosion occurs at a constant rate. This rate is often expressed as the loss of thickness per unit time e.g. mm/y. Stainless steels are normally considered to be resistant to uniform corrosion in environments in which the corrosion rate does not exceed 0.1 mm/y.

Impurities may drastically affect the corrosivity of acid solutions. The presence of reducing agents, such as hydrogen sulphide or sulphur dioxide, often makes the environment more aggressive with respect to uniform corrosion. Oxidizing compounds, such as ferric and cupric ions, nitric acid and dissolved oxygen may decrease the corrosivity.

Substances which are neither reducing nor oxidizing may also affect the corrosivity of acid solutions. Most important are halides, such as chlorides and fluorides, the presence of which increases the corrosivity of both organic and inorganic acids. Even small amounts of halides can have very large effects on corrosion of stainless steels.

Some guidance on materials selection in several environments capable of causing uniform corrosion is given in the tables and isocorrosion diagrams in the Corrosion Tables section and in the section "Uniform Corrosion Testing of Special Stainless Steels According to the MTI-1 Procedure". For more complex environments, such as most process solutions, materials selection can be based upon coupon immersion tests performed in the real or a simulated process environment. Uniform corrosion tests are in most cases evaluated by weight loss measurements in combination with microscopic examination of the specimen surface to assure the absence of various forms of localized attack.

In selecting material it is important to consider all the variations in temperature and chemical composition of the process environment which could occur. Conditions during start-up, shut-down periods and process upsets might differ considerably from those during normal operations. The effect of any chemicals used for cleaning the equipment should also be taken into consideration.

From a technical point of view, uniform corrosion could be considered as preferable to the much less predictable localized forms of corrosion which should be avoided completely if possible. Where uniform corrosion occurs, some metal loss by corrosion may be tolerable for process equipment which can be designed with corrosion allowance. Exceptions are applications where corrosion is unacceptable for hygienic reasons, e.g. equipment for food production. However, for most applications of stainless steels, grades considered to be fully corrosion resistant are chosen.
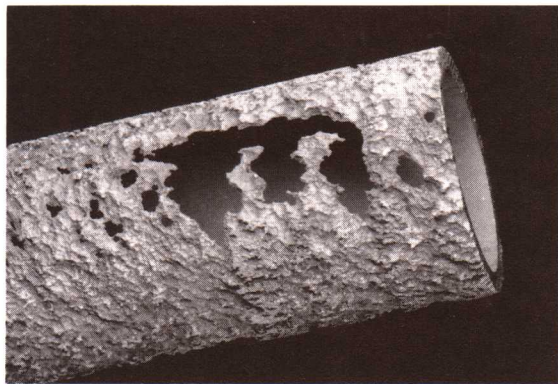

Figure 1. Uniform corrosion on the outside of a steam-tube exposed to sulphuric acid.

GALVANIC CORROSION AND ELECTROCHEMICAL PROTECTION

Galvanic corrosion

When two dissimilar materials are connected electrically and immersed in a conductive liquid, an electrolyte, their corrosion performance might be significantly different from that of the uncoupled metals. As a rule the less noble material, the anode, is more severely attacked, while the more noble metal, the cathode, is essentially protected from corrosion. The corrosion attack is normally most evident close to the junction of the two metals. This phenomenon is called galvanic corrosion.
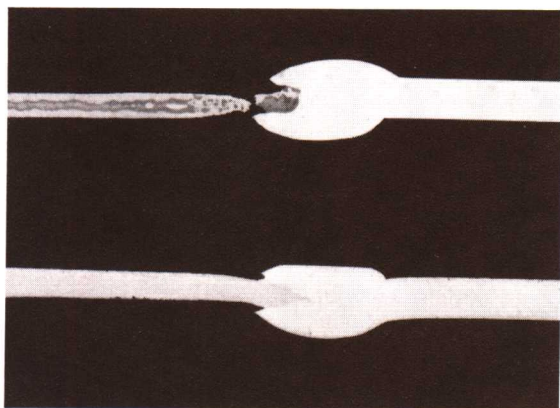

Figure 2. Galvanic couple including carbon steel (left) welded to stainless steel and exposed to seawater. Photograph taken from cut edge.

The degree of galvanic effects, as described above, is much dependent on the nature and kinetics of the electrochemical reactions taking place on the surfaces of the two materials forming a galvanic couple. Other factors which influence galvanic corrosion are:

• The difference in nobility of the two metals

• The surface area ratio between the two metals

• The conductivity of the solution

The relative nobility of different conducting materials in a certain environment is indicated by the so-called "galvanic series". A schematic galvanic series, valid for seawater at 10°C, is presented in Fig. 3. Such series are valid for one specific environment and are based on measurements of the corrosion potential of each material, uncoupled, in that environment. The higher the corrosion potential, the more noble the material. The smaller the difference in corrosion potential between the two metals forming a galvanic couple, the lower the driving force for galvanic attack. However, such differences should not be used to quantitatively predict the magnitude of galvanic attack. It should be noted that changes in electrolyte composition and temperature can cause significant changes in the positioning of different materials in a galvanic series.
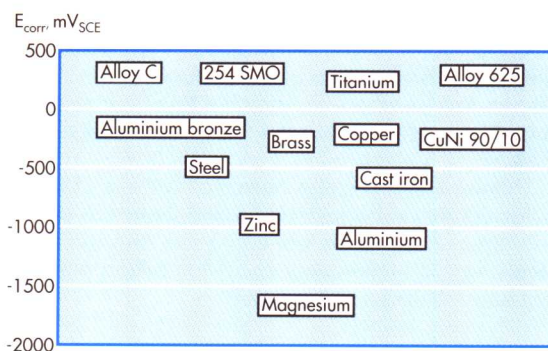
Figure 3. Galvanic series in flowing seawater, 10°C, from data presented in ref. (1). Note: Alloy C and Alloy 625 are both nickel-base alloys.

As long as stainless steels stay passive they are in most environments more noble than other metallic construction materials and thus form the cathode in most galvanic couples. Galvanic coupling to stainless steels might, on the other hand, increase the corrosion rates of less noble metals such as mild steel, galvanized steel, copper and brass. Galvanic corrosion between different grades of stainless steel is generally not a problem, provided that each grade of stainless steel is passive in the uncoupled state in the particular environment. If one of the grades should be active in the uncoupled state, galvanic coupling to a more noble grade may increase the corrosion rate.

Galvanic corrosion can be prevented by the use of insulated flanges and isolation spools, but these insulators may cause crevice corrosion in chloride solutions.

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A small anode-to-cathode surface area ratio causes an increased corrosion rate of the anode and should thus be avoided. Coating or painting of a less noble material galvanically coupled to an uncoated stainless steel should also be avoided, because very high corrosion rates could be obtained on small anodic areas formed at coating defects. Coating of the more noble metal in a galvanic couple is, on the other hand, an effective way of reducing the risk of galvanic attack.

The conductivity of the electrolyte affects the intensity as well as the location of the attack. A low conductivity tends to decrease the corrosion rate, but the attack can become very concentrated at the area adjacent to the contact site between the two metals.

Electrochemical protection

Cathodic protection

Galvanic effects between dissimilar metals can be used for protection against corrosion. So-called cathodic protection can be performed by connecting the object to be protected to a less noble metal, a "sacrificial anode", which is consumed by corrosion, while the more noble object is protected. Cathodic protection can also be performed by connecting the object to be protected to the negative pole of an external source of electric direct current.

Cathodic protection is only applied to stainless steels to a limited extent. In certain acid environments cathodic protection could cause breakdown of the passive layer, followed by active corrosion of the steel surface. In some cases, however, cathodic protection has been used to protect stainless steels against localized corrosion in oxidizing, chloride containing environments.

Anodic protection

In environments where stainless steels are, or could easily become, active, passivation could be obtained by the use of a form of electrochemical protection called anodic protection. The stainless construction is then connected to the positive pole of an external source of electric current and its potential is controlled by a potentiostat. Anodic protection of stainless steels has been used for instance in plants for the manufacture of phosphoric acid and sulphuric acid. In environments containing chloride the use of anodic protection may increase the danger of localized attack on stainless steels.

LOCALIZED CORROSION

It was stated earlier that uniform corrosion is a consequence of a widespread breakdown of the passive layer. The passive layer might, however, also break down locally, while the rest of the layer remains intact. The steel is then said to be attacked by localized corrosion. There are several forms of localized corrosion which can occur on stainless steels. In practice, corrosion failures of stainless steels are caused much more frequently by localized attack than by uniform corrosion.

Pitting and crevice corrosion

Pitting is characterized by attacks at small discrete areas. The pits often look rather small at the surface, but may have larger cross section areas deeper inside the metal. Attacks of this kind occur mainly in neutral or acidic solutions containing chloride.

Chloride ions facilitate a local breakdown of the passive layer, especially at imperfections in the metal surface. Initiation sites may be non-metallic inclusions, e.g. sulphides, microcrevices caused by coarse grinding, or deposits formed by slag, suspended solids etc. A break in the passive film may be considered as a galvanic cell, in which the bare metal becomes the anode while the surrounding area with an undamaged passive layer becomes the cathode. This unfavourable anode-to-cathode surface area ratio causes rapid corrosion of the anode. When the metal corrodes, dissolved metal ions generate an environment with a low pH and chloride ions migrate into the pit to balance the positive charge of the metal ions. Thus the environment inside a growing pit gradually becomes more aggressive and repassivation less likely. As a result pitting attacks often penetrate at a high rate, thereby causing corrosion failure in a short time. Since the attack is small at the surface and may be covered by corrosion products, pitting is often undiscovered until it causes perforation and leakage.

Crevice corrosion occurs under the same conditions as pitting, i.e. in neutral and acid chloride solutions. However, attack starts more easily in a narrow crevice than on an unshielded surface. In environments containing chloride, crevices, such as those found at flange joints, are thus often the most critical sites for corrosion.

In narrow crevices the influence of capillary forces is significant and it is thus almost impossible to avoid the penetration of liquid into a crevice. Oxygen and other oxidants are consumed for the maintenance of the passive layer in the crevice just as on the unshielded surface. However, in the stagnant solution inside the crevice the supply of new oxidant is restricted. The composition of the solution within the crevice might thus gradually become different from that of the ambient solution. This difference in composition increases the risk for corrosion as a so-called "concentration cell" is created. Small amounts of dissolved metal ions cause a decrease of the solution pH inside the crevice and in the presence of chlorides an activation of the metal surface is facilitated. The bare metal surface behaves anodically to the passive areas and the attack propagates according to the same mechanisms as in the case of pitting. In some cases attacks by crevice corrosion look similar to pitting, but are usually wider and often similar in shape to the crevice former.

High chloride concentrations and low pH increase the probability of pitting and crevice corrosion as do high temperatures and stagnant solutions. These forms of corrosion occur on materials with a fully developed passive layer and thus only in solutions which are sufficiently oxidizing. Under certain circumstances, the oxidizing effect of dissolved oxygen might be enough to induce pitting and crevice corrosion in chloride solutions,

and stronger oxidants, such as chlorine, ferric ions or hydrogen peroxide drastically increase the risk of corrosion.

Other halides such as bromide and iodide might also cause pitting and crevice corrosion. Thiosulphates, also in very low concentrations, have been reported to increase the risk of pitting in chloride solutions on steels of type 316 and lower alloyed grades. Steels of type 304 can also pit in chloride-free solutions in the presence of thiosulphate and sulphate (2), see also the section "Stainless steels within the Pulp and Paper Industry".

The resistance of stainless steels to pitting and crevice corrosion increases with increasing contents of chromium and molybdenum. For austenitic and duplex grades, a high nitrogen content is also very beneficial.

Since it is practically impossible to avoid penetration of liquid into a crevice, equipment to be exposed to an environment containing chloride should be designed to have as few crevices as possible. Under such circumstances sealing welds are to be preferred to spot welds or bolted joints. Since creviced areas are the most vulnerable to corrosion, it is often advantageous to use more highly alloyed materials in flanges than in the pipes of a piping system. The resistance of a construction to crevice corrosion may also be enhanced by overlay welding with a more corrosion resistant material at potential sites of crevice corrosion.

Crevices are not always caused by the original design and construction, but can, for instance, form under marine organisms or under deposits of solid material. To reduce the formation of deposits, suspended solids could be removed by filtering.

To avoid areas in contact with stagnant solutions, equipment should be designed in a way that permits complete drainage, see also the section "Corrosion aspects on structural design of stainless steels".
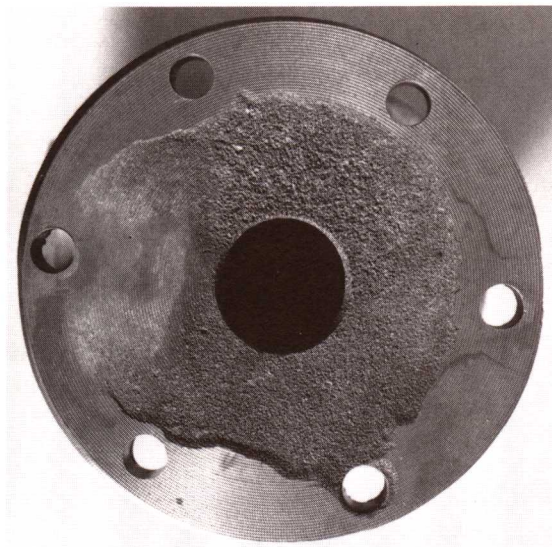
Figure 5. Crevice corrosion under a valve flange in a pipe which carried heated seawater.

Laboratory test results – pitting and crevice corrosion

General

Laboratory pitting and crevice corrosion tests can be performed either by immersion in oxidizing halide solutions or by electrochemical methods by which oxidizing conditions are simulated by using an electronic device, a potentiostat.

To derive the pitting test results presented here, Figs 8 and 9, one immersion test and one electrochemical (potentiodynamic) test were used. Crevice corrosion resistance was studied by an immersion test, the results of which are presented in Fig. 10.

Recently it has become common to use test methods by which the so-called "critical pitting or critical crevice corrosion temperatures", CPT or CCT, are established. These temperatures are usually defined as the lowest test temperature at which pitting or crevice corrosion occurs in a specific environment. Such critical temperatures can be used for ranking alloys with respect to resistance to pitting and crevice corrosion, but they do not serve as "safety limits" in practical service environments, in which corrosion might take place at lower as well as at considerably higher temperatures, depending on the environmental parameters.

Corrosion test results assessed in the same environment but at different laboratories might differ considerably, depending on the test procedure used. CPT or CCT values determined by subsequent immersion tests at different temperatures depend not only on the test solution and specimen surface treatment, but also on factors such as:

– whether the same specimen is exposed at subsequently higher temperatures or new specimens are used at each exposure

– whether the specimen is put into the solution at ambient temperature and heated/cooled together with the solution or immersed in the solution at the required test temperature.

Figure 4. Pitting from the outside of a detail in stainless steel grade 17-12-2.5, which was exposed to a hot, concentrated sodium chloride solution.

Such differences in test procedures are, however, more likely to influence the absolute values of CPT/CCT than the ranking order of different grades of stainless steel.

Obtaining a high degree of reproducibility in crevice corrosion tests requires considerable effort because the crevice geometry drastically affects the severity of the test. The crevice width is especially important, tighter crevices being more prone to generate corrosion attack. Crevice geometry can be influenced by the dimensions and the material of the crevice former, as well as the clamping force by which the crevice former is mounted to the specimen and the surface conditions of the specimen and the crevice former.

Experimental

Pitting test in 6% FeCl$_3$

Critical pitting temperatures were determined according to a modified ASTM G48 procedure. Specimens of the size 50x25xt mm were exposed in a 6% FeCl$_3$ (10% FeCl$_3$· 6H$_2$O) solution for periods of 24 h. Specimens were cut from cold rolled or hot rolled material in the delivery condition (solution annealed and pickled). Rolled surfaces were left in the delivery condition, while cut edges were ground to a 320-grit finish. The test specimen was immersed in the solution at the test temperature and new specimens were used at each exposure. The critical pitting temperature (CPT) was defined as the lowest test temperature at which the specimen was attacked by pitting corrosion. Pitting attacks on cut edges or at mechanical damage were excluded. The test temperature was changed by increments of 2.5°C. Normally duplicate specimens were tested at each temperature, but only with one specimen per test vessel.

Pitting test in 1M NaCl

Critical pitting temperatures in 1M NaCl were determined according to a potentiodynamic method, by which breakdown potentials are recorded from anodic polarization curves obtained at a series of temperatures. With a special electrochemical cell, crevice corrosion in the specimen holder can be completely eliminated during the test, and thereby a very sharp transition from high to low breakdown potentials occurs at the critical pitting temperature. Specimens were cut from cold rolled and hot rolled sheet. A circular section, 1 cm^2, of the rolling face was exposed to the test solution. The exposed surface was wet ground to a 360 grit finish. Anodic polarization curves were obtained at a series of temperatures in 1M NaCl solution. The potential was raised at a rate of 20 mV/min, starting from −300 mV$_{SCE}$. The breakdown potential was defined as the potential where the current density continuously exceeded 100 μA/cm^2. The CPT was determined from plots of breakdown potential versus test temperature, as shown in Fig. 6. The electrochemical cell and the test procedure are described more thoroughly in ref. (3,4).
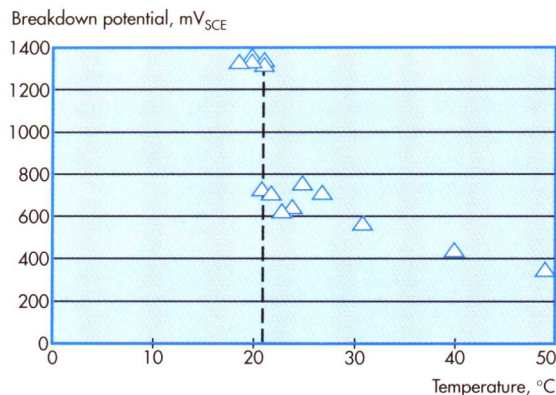

Figure 6. Typical plot of breakdown potential versus test temperature, when using the Avesta Sheffield cell. The critical pitting temperature is indicated by the dashed line.

Crevice corrosion test in 6% FeCl$_3$

Critical crevice corrosion temperatures, CCT, were determined according to MTI, manual No. 3, procedure MTI–2, which is a modified ASTM G48 procedure. The specimens were mounted between crevice formers made of PTFE. All specimen surfaces were ground with a 120-grit paper. The crevice formers were of serrated nut type, each with 12 possible crevice areas on one side, and the bolt was torqued to 0.28 Nm (40 oz-in). Crevices were considered corroded if the local attack was 1.0 mil (0.025 mm) or deeper. Specimens were exposed in a 6% FeCl$_3$ (10% FeCl$_3$· 6H$_2$O) solution for periods of 24 h. The specimen was immersed in the solution at the test temperature and new specimens were used at each exposure. CCT was defined as the lowest test temperature at which crevice corrosion attacks according to the above definition occurred. The test temperature was changed by increments of 2.5°C. For the most highly alloyed materials a slightly modified procedure was used. Specimens were tested with rolling faces in the as-delivered (pickled) condition and crevice formers were mounted using a torque of 1.58 Nm (14 lbf·in).
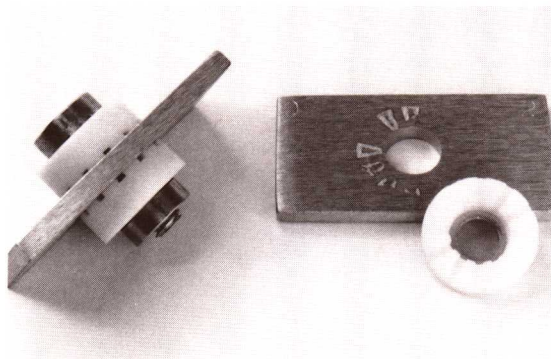

Figure 7. Crevice former according to MTI Manual No. 3, Method MTI–2.

Results

Pitting

The test results are presented in Figs 8 and 9. For most steel grades samples from 3 to 10 heats were tested. In general, lower CPT values were obtained in the ferric chloride test than in the potentio-

dynamic test in 1M NaCl. The ranking order, however, is much the same. The test results clearly show the beneficial effect of chromium, molybdenum and nitrogen on the pitting resistance of both austenitic and duplex steels. The highest resistance was shown by grade 654 SMO, which did not pit in either of the two tests.
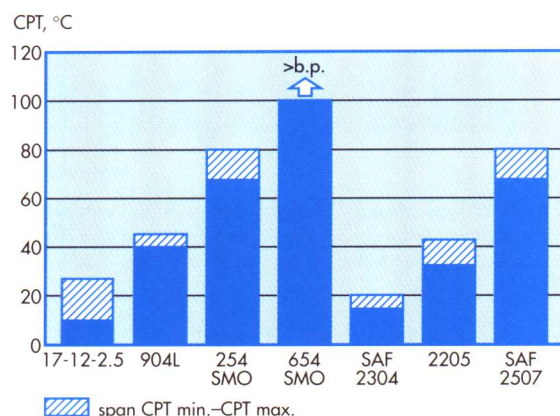
CPT, °C

Figure 8. CPT in 6% FeCl$_3$. Normally 3–10 heats per steel grade tested.
Note: b.p. = boiling point of the solution.
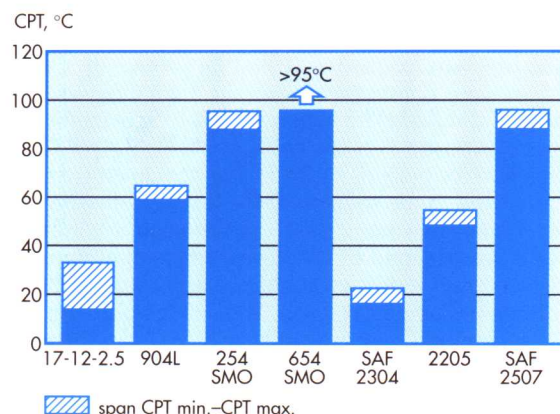
CPT, °C

Figure 9. CPT in 1M NaCl. Normally 3–10 heats per steel grade tested.

Crevice corrosion

The test results are presented in Fig. 10. The CCT is in general considerably lower than the CPT in 6% FeCl$_3$ for the same steel grade. High contents of chromium, molybdenum, and nitrogen are also beneficial for resistance to crevice corrosion. 654 SMO is superior to the other steel grades tested, although it was tested with crevice formers mounted under a higher torque.

Stress corrosion cracking

Stress corrosion cracking (SCC) is a brittle failure mode caused by the combined effect of tensile stress and a corrosive environment. Like pitting and crevice corrosion, stress corrosion of stainless steels is most frequently caused by solutions containing chloride. However, most cases of stress corrosion cracking on stainless steels occur at high temperature. In such conditions also solutions which, because of their low concentrations of chlo-
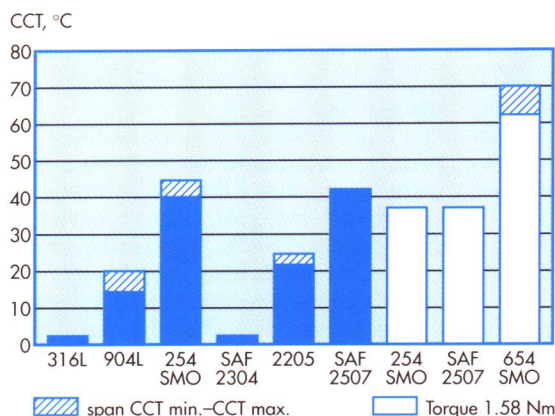
CCT, °C

Figure 10. CCT in 6% FeCl$_3$, according to MTI Manual No. 3, Method MTI-2 and to a slightly modified procedure including a higher torque (1.58 Nm).

rides and oxidizing species, are unlikely to cause pitting and crevice corrosion may give rise to stress corrosion. The presence of hydrogen sulphide (H$_2$S), existing for instance in oil and gas wells, increases the risk of attack in chloride solutions. Other environments which might give rise to stress corrosion include very alkaline solutions at high temperatures (pH >14, temp. >120°C).

Depending on the environment, relatively low engineering loads may provoke stress corrosion. Residual stresses from different manufacturing operations, such as forming, coarse grinding, and welding, can be high enough to cause failures. In some practical situations these can be reduced by annealing at an appropriate temperature, but this approach is difficult for large constructions.

Most cases of stress corrosion occur at temperatures above 50°C but failures at ambient temperature on conventional austenitic steels, such as 304 and 316, are possible if a certain combination of extremely low pH and high chloride concentration is attained, a combination that rarely appears in practical service.

The corrosion attack typically takes the form of thin, branched cracks.

Failures caused by stress corrosion cracking often happen abruptly and without warning, because of the high propagation rates of the cracks. In the most severe cases, failure of a component may happen within a few days or even hours.

A common cause of stress corrosion is the concentration of chlorides from evaporation on hot steel surfaces. The evaporating liquid might be fresh water, or other very dilute solutions, which because of their low chloride concentrations are considered harmless. When water evaporates, the chloride concentrations of these liquids might, however, become high enough to cause stress corrosion. Severe evaporative conditions can be established when water penetrates under thermal insulation used to maintain temperature in piping and vessels containing hot media. Several cases of stress corrosion cracking have been observed under such circumstances.

Chlorides exist naturally in various concentrations in most waters, but might also originate from gaskets and insulation materials containing chloride.

Steels with a ferritic or duplex (ferritic-austenitic) structure in general show high resistance to stress corrosion attack. High contents of nickel and molybdenum increase the resistance of austenitic grades to stress corrosion and thus grades 904L, 254 SMO and 654 SMO show excellent resistance.
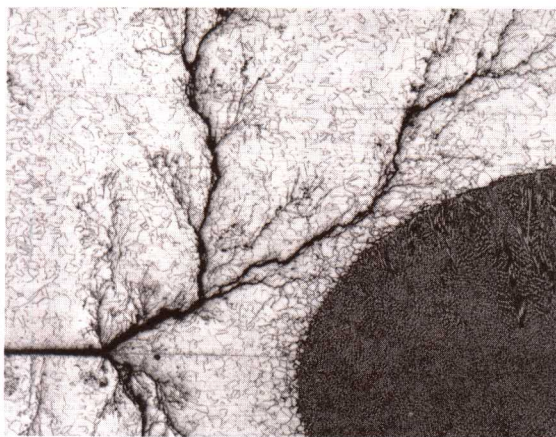

Figure 11. Micrograph showing stress corrosion cracking in a lamellar heat exchanger;
process side: hydrocarbons, 130°C,
cooling side: brackish water (400–1000 ppm Cl⁻).

Laboratory test results–stress corrosion cracking
General

Laboratory testing of resistance to stress corrosion cracking is often performed in concentrated chloride solutions but there are also tests in which evaporative conditions are simulated.

Tensile stresses can be applied by different methods; by bending to different shape (constant deflection), by constant load, or by so-called "slow strain rate testing" (SSRT) by which the specimen is strained at an extremely low rate until failure.

The test results presented here were obtained by two different methods, one a constant deflection test and the other a constant load test.

Experimental
U-bend test in $MgCl_2$

This test was performed according to MTI Manual No. 3, Method MTI-3 and included testing of U-bend specimens (127x13 mm) in 45% magnesium chloride solution boiling at 155°C. Triplicate specimens were exposed in each of three vessels. Specimens were removed from the first vessel after 24 hours, from the second after 96 hours and from the third after 500 hours. Specimens were considered as failed if they had cracks, visible under a 20x binocular microscope. The time to failure is the shortest test duration at which one or more failures were observed. The results are presented in Table 1.

The results show clearly that none of the tested materials are immune to stress corrosion cracking. The best resistance was shown by the high nickel steel 904L. A high nickel content is known to be favourable in this kind of test, the use of which has been debated because in some cases it has generated rank orders which are contrary to practical experience, for instance under evaporative conditions. Cracking of high alloy grades such as 254 SMO and 654 SMO in less than 24 hours clearly indicates the extremely severe conditions established in this test.

TABLE 1
Stress corrosion cracking test of U-bend specimens in boiling 45% $MgCl_2$ according to MTI Manual No. 3, Method MTI-3.

Steel grade	Number of cracked specimens after exposure for	
	24 h	96 h
904L	0 out of 3	3 out of 3
254 SMO®	3 out of 3	–
654 SMO®	3 out of 3	–
2205	3 out of 3	–
SAF 2507™	3 out of 3	–

Drop evaporation test

A dilute (3500 ppm Cl⁻) sodium chloride solution slowly drips onto an electrically heated horizontal tensile specimen and thus severe evaporative conditions are established. The test was originally described by Henriksson and Åsberg (6) and later adopted in MTI manual No. 3. The test procedure used here is based on MTI manual No. 3, method MTI-5, although slightly modified. Applied stresses were up to 100% of the yield strength at 200°C. The steps between stresses were 10%. The ranking parameter is the minimum relative stress for failure at a test duration of 500 h. Results are presented in Fig. 12.
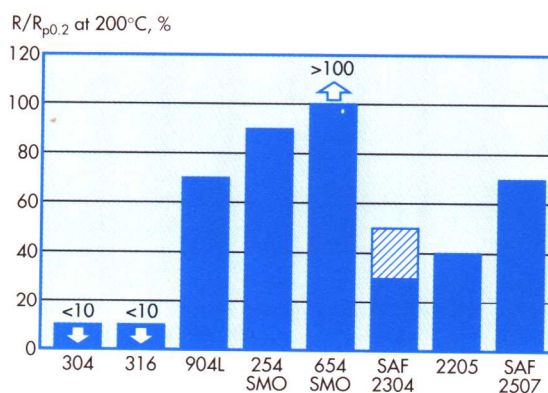

Figure 12. Threshold stresses, determined in the drop evaporation test, according to ref. (5). At loads represented by a hatched bar, no cracking occurred but the specimen failed because of uniform corrosion thinning.

All duplex steels tested showed better resistance than standard austenitic steels such as 304 and 316. The highest resistance was, however, shown by the high alloy austenitic grades 254 SMO and 654 SMO.

This test also implies severe conditions. Grades 254 SMO and 904L crack in this test at the highest applied loads, but have for many years shown excellent resistance to stress corrosion cracking in practical service.

Corrosion fatigue

It is well known that a material which is subject to a cyclic load can fail at loads far below the ultimate tensile stress of the material. If the material is simultaneously exposed to a corrosive environment, then failure may take place at even lower loads and after shorter times. This is caused by a form of corrosion known as corrosion fatigue, which has similarities to stress corrosion cracking. Both corrosion forms cause brittle failures. Cracks evolved from corrosion fatigue are, however, seldom branched. Corrosion fatigue often takes place at ambient temperature and in moderately concentrated solutions that could be considered harmless with regard to other forms of corrosion.

Residual stresses from manufacturing can have a negative influence on the resistance to corrosion fatigue. These may be reduced by an appropriate heat treatment or by the introduction of compressive stresses in the surface, as is achieved by shot peening. High mechanical strength increases the resistance of a stainless steel to corrosion fatigue. Duplex (ferritic-austenitic) steels are thus often superior to conventional austenitic steels. One application where a change from austenitic to duplex steels has reduced the number of failures caused by corrosion fatigue is suction roll shells in paper machines, see also the section "Stainless steels within the pulp and paper industry".
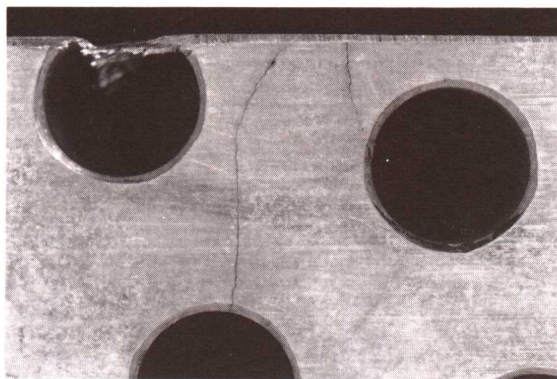

Figure 13. Corrosion fatigue cracks in a paper machine suction roll shell, made in austenitic grade 17-12-2.5.

Intergranular corrosion

Intergranular corrosion means preferential corrosion of the grain boundaries of a material. Intergranular corrosion of stainless steel might occur as a consequence of precipitation of chromium carbide or intermetallic phases.

If austenitic steels are exposed to temperatures in the range 550–850°C, chromium carbides $(Fe,Cr)_{23}C_6$ can precipitate in the grain boundaries. The chromium content of the carbide precipi-

tates is very high, and since the diffusion rate of chromium in the austenite is low, the alloy adjacent to the grain boundary becomes chromium depleted. Since chromium is essential to passivity, the chromium depleted region becomes less corrosion resistant than the matrix. In a corrosive environment the depleted area may be depassivated and corrosion will take place in very narrow areas along the grain boundaries. The unfavourable anode-to-cathode surface area ratio accelerates the attack which, in extreme cases, can penetrate the entire thickness of the material. Such attack might drastically change the mechanical properties of the steel.

A stainless steel which has been heat treated in a way that produces grain boundary precipitates and adjacent chromium depleted zones is said to be "sensitized". Sensitization might occur as a result of welding, or of hot forming at an inappropriate temperature.

Intergranular corrosion can take place in solutions in which the alloy matrix is passive while the chromium depleted grain boundaries are not. Thus intergranular corrosion occurs mainly in non-reducing acids. Strongly oxidizing conditions are often needed to generate intergranular attack. Sensitization might, however, also increase the sensitivity of a stainless steel to other forms of corrosion, e. g. pitting, crevice corrosion and stress corrosion cracking.

Measures to increase the resistance of stainless steels to intergranular corrosion caused by chromium carbide precipitation are:

- solution annealing
- lowering the carbon content
- alloying with titanium or niobium (stabilizing)

Stainless steels are usually delivered from the steel producer in the solution annealed condition. Solution annealing consists of heating to temperatures in the range 1000–1200°C, at which chromium carbides are dissolved, followed by rapid cooling in air or water. Such an operation leaves the carbon in solid solution in the steel. A steel having a sensitized structure may be recovered by a further solution annealing procedure.

A low carbon content extends the time required for significant sensitization. (See TTS-diagram in the section "Intergranular Corrosion and Acceptance Testing".) Until a few decades ago intergranular corrosion caused by sensitization during welding procedures was potentially a problem. Modern steelmaking methods enable much lower carbon contents to be achieved in steels than in the past. This has given a considerable reduction in such problems. Steels with a maximum allowed carbon content of 0.05% often contain even less carbon and are, in most environments, resistant to intergranular corrosion even after welding. In environments which cause rapid intergranular corrosion, such as hot, concentrated nitric acid, low carbon grades with a maximum carbon content of 0.03% should be used.

Stabilized steels, containing titanium or niobium, show good resistance to intergranular corrosion even though their carbon contents may be fairly high. This is due to the fact that titanium and

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