

Corrosion of Stainless Steel in Fire Protection Systems

Author Leena Carpén

Confidentiality Public

| | |
|--|--|
| Report's title Stainless steels used in fire protection systems | |
| Customer, contact person, address Outokumpu Stainless Oy | Order reference S622551 |
| Project name Palovesiputkiston tutkimus | Project number/Short name PALOMIC |
| Author(s) Leena Carpén | Pages 29/ |
| Keywords stainless steel, fire protection system, pitting corrosion, MIC | Report identification code VTT-R-01556-08 |
| <p>Summary</p> <p>Traditionally, many firewater mains are made of carbon steel or cast iron. At present, more and more stainless steel is used as material for firewater pipes due to usually better corrosion resistance in natural waters than iron or carbon steel. In some few cases, however, unexpected corrosion failures in systems using austenitic stainless steels have been observed only after a relatively short time of usage ranging from a few weeks to a few years. Most of these corrosion damages are associated on the weld nuggets or in the heat-affected zones of girth site welds. One of the most important factors affecting the corrosion resistance of stainless steel at welds and in heat-affected zones are the surface oxide films originating from the welding heat in the presence of oxygen. Therefore, proper root shielding is important especially when welding pipes for fire protection systems where the water is taken from natural sources (e.g. from rivers, lakes or tap water), as microbially induced corrosion (MIC) can increase the risk for corrosion damages significantly.</p> <p>Two failure cases in fire protection systems (FPS), one in stainless steel factory and one in power plant have been studied and are described in this study. A proposal for the corrosion/failure mechanism is suggested and general recommendations how to avoid or diminish the risk for unexpected localized corrosion failures in FPS are given.</p> | |
| Confidentiality | Public |
| Espoo 12.2.2008 | |
| Liisa Heikinheimo Technology Manager | Leena Carpén Senior Research Scientist |
| VTT's contact address PL 1000, 02044 VTT | |
| Distribution (customer and VTT) Outokumpu Stainless Oy, VTT | |
| <p><i>The use of the name of the Technical Research Centre of Finland (VTT) in advertising or publication in part of this report is only permissible with written authorization from the Technical Research Centre of Finland.</i></p> | |

Preface

Stainless steels have been used in various environments during the years. However, stainless steels are quite a new material used as pipes in fire protection systems (FPS). In spite of their usually good corrosion resistance there have been some unexpected failure cases in these fire protection systems. The fire protection system is a demanding environment in the aspects of corrosion. The water quality used in fire extinguishing systems depends on the source where it has been taken and the water stays stagnant most of the time thus increasing its corrosivity. There is always a risk for microbially induced corrosion (MIC) in natural or tap water. The aim of this study is to introduce two cases and the affecting factors which have to be taken into account while using stainless steel as a material in FPS. Also general recommendation how to avoid or diminish the risk for localized corrosion in these environments is given. This research was done at VTT during the year 2007 and was financed by Outokumpu Stainless Oy.

Espoo 12.2.2008

Leena Carpén

Contents

| | | |
|-----|---|----|
| 1 | Introduction | 4 |
| 2 | Goal | 5 |
| 3 | Description of cases | 5 |
| 3.1 | Case 1: Fire protection system in a stainless steel plant | 5 |
| 3.2 | Case 2: Fire protection system in a power plant | 7 |
| 4 | Experimental procedures of studied cases | 7 |
| 4.1 | Metallurgical analysis | 7 |
| 4.2 | Water analyses | 7 |
| 4.3 | Microbiological assays | 7 |
| 4.4 | Electrochemical measurements | 8 |
| 5 | Results | 9 |
| 5.1 | Case 1 – Stainless Steel Plant | 9 |
| 5.2 | Case 2 – Power Plant | 21 |
| 6 | Discussion | 25 |
| 7 | Conclusions and recommendations | 27 |
| | References | 27 |

1 Introduction

Carbon steel or cast iron are traditional materials for firewater mains. Relatively few corrosion case histories of sprinkler or firewater systems have been published [1-7]. However, clogged tubes due to corrosion of carbon steel or cast iron have caused problems over the years and alternative materials have been considered. Stainless steel is nowadays adopted in firewater piping. Stainless steels have been extensively used in many technical applications involving natural waters (sea water, brackish water, river water, tap water etc.). These materials usually have an excellent corrosion resistance in cold, flowing, low-chloride containing water. In stagnant water, like it is usually found in firewater systems, the corrosion resistance evidently diminishes. This is the case also when the temperature or the chloride content increases. Also thiosulfate is known to have a detrimental effect on the pitting corrosion resistance of stainless steel if it exists in a proper ratio to chloride and/or sulfate [8,9].

Corrosion of stainless steels in natural waters and in systems using such water is typically localized corrosion, e.g. pitting and crevice corrosion. In welded structures, corrosion is often concentrated in the weld nugget itself or in the heat-affected zone. The openings of the corrosion pits are typically very small but large subsurface cavities are often formed. Especially on-site welds, like welded butt joints of pipes, are vulnerable to such pitting failures. On-site welds are usually welded from the outside of the pipe using shielding gas inside. Normally it is difficult or even impossible to clean the root of the weld after welding properly. If the shielding gas contains even a relatively small amount of oxygen, heat tint layers (colored oxides) will be formed close to the weld. These heat tint layers promote the initiation and growth of corrosion pits even in seemingly harmless environments [10,11]. The pit initiation potential in these areas as well as on the weld itself is usually lower than on the base metal.

Natural waters contain always a diversity of microbes and thus these seemingly harmless environments might turn out to be aggressive. Microbes can change the environment's corrosiveness either chemically or physically. This phenomenon is called microbially induced corrosion (MIC). It is generally accepted that the ennoblement (increase of the open circuit potential) of stainless steel surfaces detected all over the world in ocean waters, brackish waters, rivers and even tap water is caused by microbial colonization [12-18]. This ennoblement can exceed the pit initiation potential. However, the mechanism of ennoblement is not clear and many different hypotheses and theories have been suggested during the years. One of these is the role of manganese oxidizing bacteria [18,19]. As a result of bacterial activity, Mn^{2+} that is dissolved in waters is oxidized to Mn^{4+} . Mn^{4+} is a strong oxidant causing the potential of the metal to rise. Mn^{4+} reacts further and forms manganese dioxide (MnO_2). The reduction of MnO_2 according to the reaction $MnO_2 + H_2O + e^- \rightarrow MnOOH + OH^-$ offers the needed cathodic reaction. Sulfate reducing bacteria (SRB) have often been detected together with iron and manganese oxidizing bacteria from the failure areas of stainless steels. SRBs can, by producing sulfides (S^{2-}), lower the redox potential within the deposits on the surface. This diminished redox potential together with elevated corrosion potential

caused by MnO_2 rich deposits raise the interfacial potential difference within the deposits above the critical pitting potential and pits can nucleate.

Besides manganese oxidizing bacteria and SRBs, recently it has been shown that also a combination of iron oxidizing bacteria (IOB) and sulfate reducing bacteria yielded the highest localized corrosion rate of austenitic stainless steel type EN 1.4432 compared to IOB or SRBs alone [20].

Another way for SRBs to enhance the corrosion of stainless steel is to form thiosulfate ($\text{S}_2\text{O}_3^{2-}$). SRBs consume sulfate (SO_4^{2-}) by reducing it to sulfide, which can be oxidized to thiosulfate in the presence of air. In simulated paper machine water, it has been demonstrated that thiosulfate produced by the metabolic activity of SRBs caused severe pitting corrosion to stainless steel [9].

In this report, failure analyses of two case histories of fire protection systems suspected to be caused by MIC are presented.

2 Goal

The goal of this work was to look at the usage and possible problems of stainless steels used in fire water systems using natural fresh waters (including tap water) and to prepare guidelines to the safe use of stainless steels especially in pipes of fire protection systems.

3 Description of cases

This paper describes two different cases. The first one is taken from a fire extinguishing system of a stainless steel factory and the other case is from a fire extinguishing piping of a power plant in Finland.

3.1 Case 1: Fire protection system in a stainless steel plant

The fire extinguishing system in a stainless steel plant has been originally made of carbon steel. Gradually it has been partly changed to stainless steel type EN 1.4301. If new firewater tubes have to be installed, only stainless steel is used both in old and new building. The system under study still has both carbon steel and stainless steel parts. Removed carbon steel pipes were heavily corroded and had a huge amount of reddish brown deposit and tubercles inside the pipes after 20 years of usage, Figure 1. So they had become unusable and unsafe. The examined stainless steel parts have been installed to the fire protection piping in cold rolling mill at 2002 and some failures had occurred after less than three years of usage. The raw water comes from the river, it is not specially treated and stays stagnant most of the time in the fire protection piping of cold rolling mill. The temperature varies from about 5-10°C in some staircases during winter times to up to 50°C over furnaces of the annealing lines.

Stainless steel is also partly used in hot rolling mill fire protection system (FPS). The water comes from the same source but the water in the system is used for

washing once a week instead the stagnant situation at the cold roll mill. No failures have been detected in these stainless steel pipings after 15 years of usage.

The firewater of the whole factory comes from the same source, namely from the river. The firewater is stored in a concrete container nearby the cold rolling plant. The chloride content of the river is usually very low (~1 mg/l). Only very seldom higher chloride values have been measured, when brackish water (~1000 mg/l of Cl) from the sea nearby is mixed with river water during times of strong southern wind. Typical analysis of the water composition is given in Table 1. The pressure in the system is 13 bars due to the height of some buildings.

Four samples (samples no.1-4) taken from the piping system of cold roll mill as well as one sample (sample no. 5) taken from the FPS of hot rolling mill were examined. The girth welds in samples 1-4 were made by manual metal arc welding. Instead sample no. 5 had only longitudinal factory made weld.



Figure 1. A piece of carbon steel pipe taken from a fire extinguishing system of a stainless steel factory after 20 years of use.

Table 1. Typical water composition of firewater at the stainless steel factory. Given is the result of an analysis of firewater taken at the fire station in early November 2007. The water was slightly greenish, but clear.

| pH | Cl ⁻ | SO ₄ ²⁻ | Hardness | Fe | Mn | Alkalinity |
|-----|-----------------|-------------------------------|----------|------|-------|------------|
| | mg/l | mg/l | mmol/l | mg/l | mg/l | mmol/l |
| 7.0 | 1.1 | 3.1 | 0.17 | 0.51 | 0.006 | 0.35 |

3.2 Case 2: Fire protection system in a power plant

In Case 2 [21,22] the pipes in the system were also originally constructed from carbon steel and had been gradually replaced by austenitic stainless steel pipes (both EN 1.4301 and EN 1.4401). In the system there still were some parts made of carbon steel (main piping) or cast iron (larger valves) and the water contained high amounts of precipitated iron. The water used in this fire extinguishing system was tap water with a low chloride concentration (25 mg/l). The water was treated with chloramine (with hypochlorite and ammonium chloride reacting in water forming chloramine) when the system was filled with water. The water stayed stagnant most of the time and was usually changed once a year.

Unexpected pitting corrosion in stainless steel pipes of this FPS was observed after just a few years of service. The pits detected were situated in the welds or in the heat-affected zones. The first perforations were detected in EN 1.4401 stainless steel pipes after two years of operation. Later on, several pits causing leaks were also detected in the EN 1.4301 material. The pressure in the piping system is 10 bars and the temperature is same as ambient temperature, 20...25 °C.

4 Experimental procedures of studied cases

4.1 Metallurgical analysis

Metal samples were removed from the systems and were examined visually and under a stereomicroscope. The chemical composition of pipe material and the weld metal were analyzed with an optical emission spectrometer. Metallurgical examinations consisted of optical light microscopy of cross sections prepared from the samples, scanning electron microscopy (SEM) studies from failure areas and energy dispersive spectroscopy (EDS) of corrosion products or of the deposits on the inner surfaces of the pipes.

4.2 Water analyses

The water used in fire extinguishing system of stainless steel factory (Case 1) is taken from the river near by the factory.

In Case 2 water analysis were taken from the pipes a few months after the first leaks were detected as well as two years later simultaneously with leaking pipe samples to be studied. Also a typical analysis of the feed water was available. The amounts of iron, manganese, calcium, magnesium, chloride, sulfate, bicarbonate, nitrate and nitrite as well as pH of the water samples were analyzed.

4.3 Microbiological assays

In Case 1, the metal samples were totally dried when arriving to the laboratory for further studies. Thus the traditional methods, like cultivation could not be applied for detection of possible bacteria. However, preliminary trial with new PCR-method (Polymerase Chain Reaction method) was done with one metal sample

with corrosion failure (sample no. 3). The total DNA was isolated from the metal piece sample (deposit covering the pit) and purified. The DNA content was measured by spectral photometer. Bacterial DNA was multiplied by using PCR-primers P2 and P3 targeted for eu -bacteria [23] and SRB- specific primers for SRB Group 6, including e.g. *Desulfovibrio* species. PCR products were analyzed in DGGE (denaturing gradient gel electrophoresis).

In Case 2 microbiological assays were also performed. Total count of aerobic and anaerobic bacteria and the amount of sulfate reducing bacteria were analyzed by cultivation from the samples taken at site from the water inside the pipes as well as from the deposits on the surfaces of the pipes. Samples were scraped from several places on the surface of the opened pipe. The system had been opened half an hour before the sampling.

Microbiological analyses were performed also from the pipe samples delivered to the laboratory. Some of these samples were taken from dried deposits and some from deposits still wet or from pipe samples, which were transferred under the water taken from the system. In the last mentioned case the cultivation for the growth of iron bacteria in ferrous sulfide agar medium [24] was performed and the biofilm formation was studied with stainless steel coupons immersed to one dilution of the cultivation tubes. The incubation of these coupons was 6 d at the temperature of 25 °C. After the incubation the coupons were stained with acridine orange and examined by epifluorescence microscopy.

Plate count agar medium at 25 °C or 30 °C was used for the determination of viable count of heterotrophic aerobic bacteria and Shahidi-Ferguson medium (DIFCO) without antibiotic additions at 30 °C for the determination of total count of anaerobic bacteria. The presence of sulfate reducing bacteria (SRB) was verified on Postage's medium with incubation of 10 days at 25 °C in anaerobic jar and the amount of SRB was estimated using the most probable number (MPN) method.

4.4 Electrochemical measurements

In Case 2 also some polarization curve measurements were performed in order to study the influence of iron rich deposits as well as that of the chloramine treatment on the pitting potential of EN 1.4301.

Six pieces of the size 20 x 20 mm containing base material and 2 pieces of similar size containing the weld were cut from a pipe section removed from the fire extinguishing system. These samples were first cleaned with acetone and ethanol. To remove the dense deposits from the surfaces the samples were cleaned with diluted nitric acid (900 ml water, 100 ml 65 % nitric acid) for 2 min at room temperature.

The pitting behavior was investigated in water samples taken from the feed water of the fire extinguishing system, one after the chloramine addition (named water D, pH 7.7 and γ 185 μ S/cm) and one after activated carbon filtration but before chloramine addition (named water E, pH 6.0 and γ 165 μ S/cm). Because the conductivity (γ) and the chloride content (less than 30 mg/l) of the waters were so

low, 200 mg/l of Cl^- was added to accelerate and to highlight the phenomenon. To simulate the conditions in fire extinguishing system a modified tape test [25] was used in the laboratory. In this test electrolyte is brought into contact with the specimen surface with the aid of multi-layer textile tape. Advantages to use this method is that surfaces in as-received state as well as non planar surfaces (like welds) can be tested. A saturated calomel electrode (SCE) was used as a reference electrode and more alloyed stainless steel (EN 1.4401) was used as counter electrode. In the case where pitting potential was to be determined the specimens were polarized to the level where the current reached 1 mA/cm^2 , where the scan direction was reversed. The pitting initiation potential was chosen to be the potential where the anodic current clearly started to increase and had exceeded $10 \mu\text{A}$. The scan rate was 30 mV/min . Before the polarization measurements the open circuit potential was recorded for 10 min or until the potential had become steady. Some of the measurements were performed with the specimens covered with iron precipitate. This iron precipitate originated from a valve of the fire extinguishing system and was representing the iron precipitate detected in the water inside the pipes. All electrochemical measurements were performed using a Gamry CMS100 Corrosion Measurement System with PC3 Potentiostat. After the polarization measurements the specimens were inspected under a low magnification stereomicroscope to reveal possible pitting corrosion [21,22]

5 Results

5.1 Case 1 – Stainless Steel Plant

Samples no. 1 -4 were removed from the FPS of the cold roll mill after less than tree years of usage due to the occurred corrosion damages. Sample no. 1 had a dark brown deposit evenly distributed on the inner surface of the pipe, Fig. 2. The field welded joint on the inner surface was very uneven. A small section of the pipe was cut for further examinations. This piece contained a small shiny area with starting pitting, Fig. 3.



Figure 2. Inner surface of sample 1.



Figure 3. Starting pitting (an arrow) on the heat affected zone of a weld of sample 1.

The brown deposit area of sample 1 was found to contain iron (Fe), oxygen (O), carbon (C) and chromium (Cr) as main components as well as manganese (Mn), nickel (Ni), silicon (Si), aluminum (Al), calcium (Ca), sulfur (S) and phosphorus (P), Table 2, page 21. The corroded area contained besides the elements mentioned already also titanium (Ti) and molybdenum (Mo). The amount of chromium and nickel were higher at the corrosion area than on the uncorroded surface, Table 2. Iron, chromium and nickel are the main components of stainless steel, so main parts of these originate from the stainless steel. Also part of the manganese, molybdenum and silicon originates from the material and the rest of these as well as aluminum, calcium, sulfur and phosphorus originate from the environment (water).

Sample no. 2 did not have a continuous brown deposit layer as sample 1. Instead reddish brown deposit could be seen surrounding the corrosion areas on the heat tint areas as well as some deposits on the inner surface close to the weld, Fig. 4 and 5. Very strong heat tint colors (dark brown and blue) could be seen surrounding the field welds of this sample.



Figure 4. The inner surface of sample no. 2.

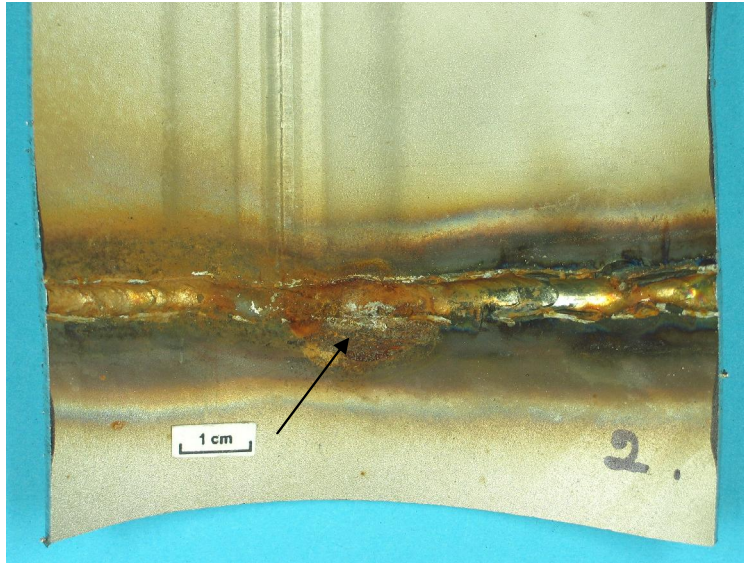


Figure 5. A closer look to the weld area with pitting corrosion (an arrow).

A piece of this sample (Fig. 5) was further divided for studies with SEM/EDS and to prepare a metallographic cross section of the failure area. SEM-examination revealed corrosion products (Fig.6) close to the several small openings of pits (Fig.7).

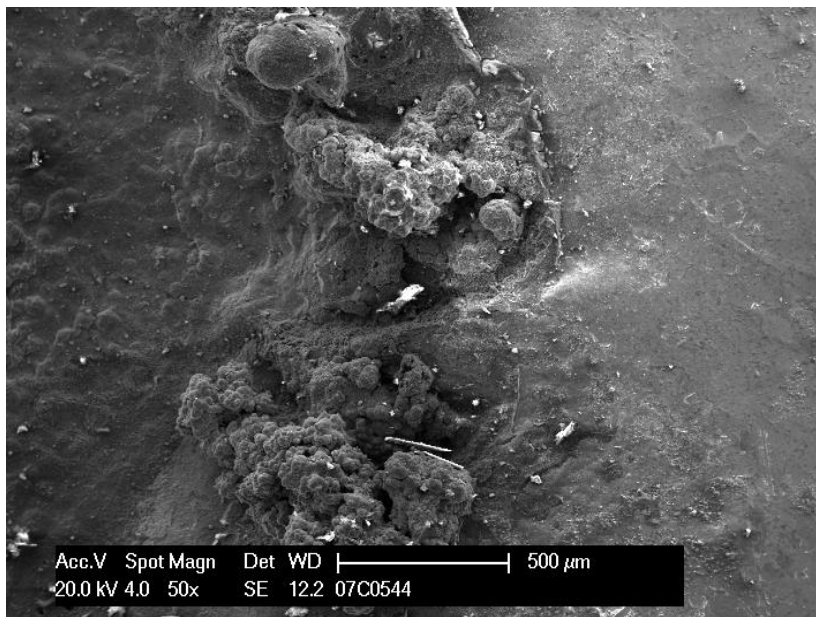


Figure 6. Corrosion products on the heat affected zone of a weld of sample no. 2. SEM-figure.

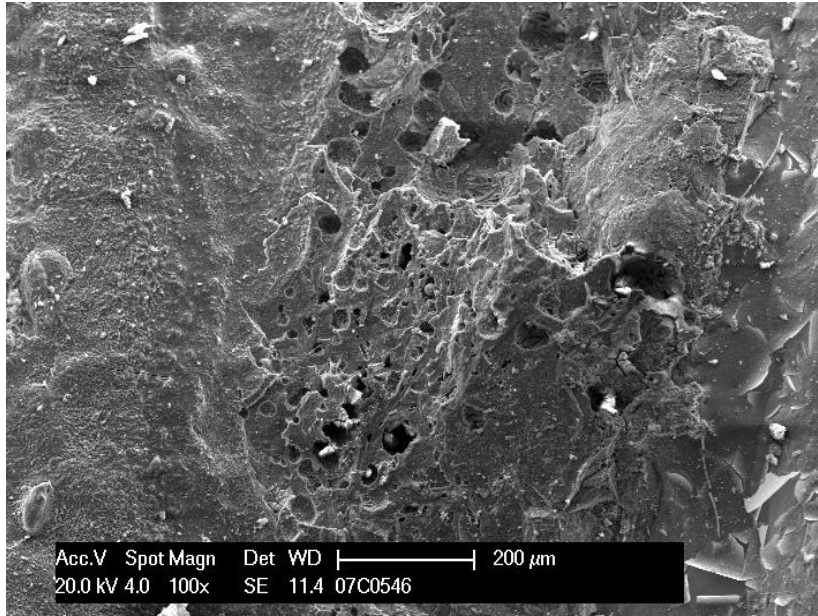


Figure 7. The corroded area of heat affected zone of sample no. 2. SEM-figure.

According to the EDS-analysis the corroded area was found to contain besides the main components iron, carbon and oxygen, also nickel, chromium, manganese, zinc (Zn), titanium (Ti), sulfur (S), chlorine (Cl) as well as sodium, calcium, potassium, silicon and aluminum, Table 2, page 21. Zinc, carbon, part of manganese, titanium, chlorine indicating the chlorides, sodium, sulfur and potassium originate from the water.

The cross section prepared from the failure area first revealed only a small opening of a pit adjacent to the weld at heat affected zone (Fig. 8). When the grinding was continued, it could be seen that corrosion had proceeded deeper inside the pipe, Fig. 9.

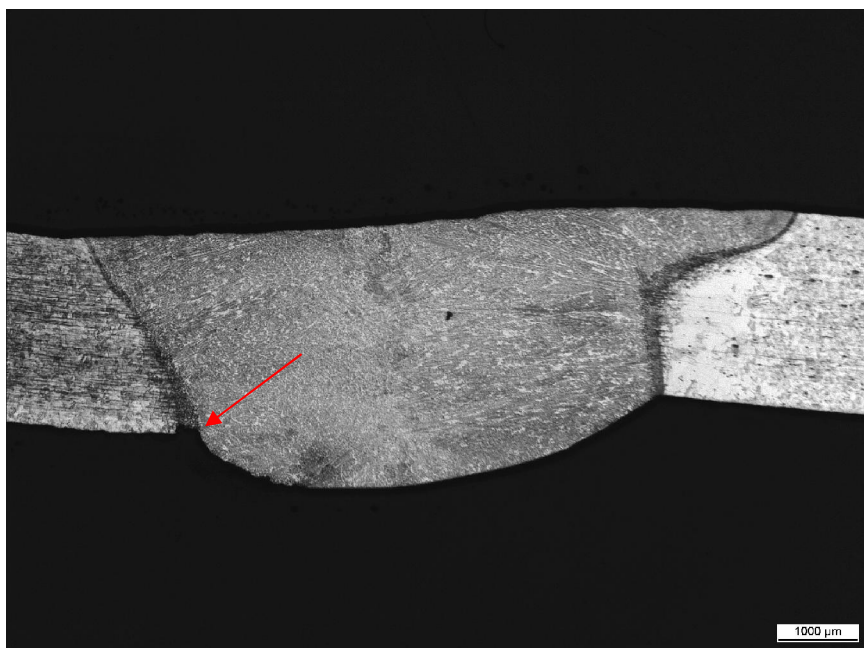


Figure 8. A small opening of a pit on the inner surface of the sample no. 2.

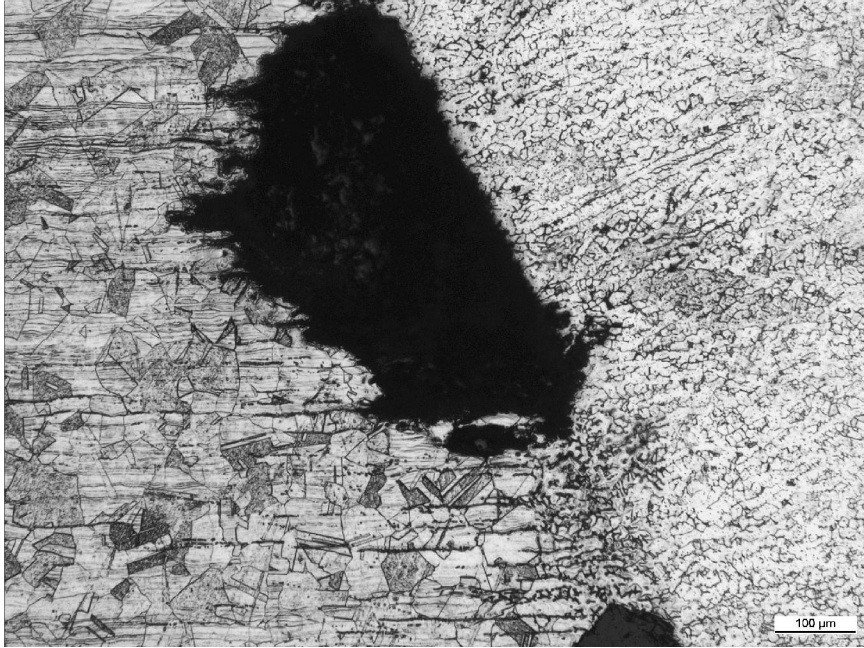


Figure 9. A corrosion pit growing along the heat affected zone (fusion line) of a weld of sample no. 2.

The microstructure of the pipe sample no 2 was normal austenitic structure. The chemical composition of pipe material as well as that of the weld metal analyzed by optical emission spectrometer is in Table 3, page 21. Both pipe material as well as weld are according to the requirements for EN 1.4307.

Sample no. 3 had a perforated pit, which could be seen on the outer surface of sample 3, Fig. 10. The outer surface was other wise clean and only a little brown deposit was seen under the stereomicroscopic study. On the contrary on the inner surface of sample 3 there was a lot of reddish brown deposit on and close to area with perforated pit, Fig. 11 and 12. Also in this sample dark colors (brown and dark blue) of heat tint were seen.



Figure 10. A perforated pit marked with an circle and an arrow on the outer surface of sample no 3.



Figure 11. The inner surface of sample no. 3.

The red brown deposit on the inner surface contained partly also some small metallic particles, which might be originating from the cutting the samples. After carefully removing some of the deposit, a shiny corroded area was revealed, Fig. 13. The red brown deposit was found to contain besides the main components; iron and oxygen, also carbon, manganese, sulfur and titanium among others, Table 2, page 21. Sulfur and manganese as well as copper was detected on the corroded shiny area. Phosphorus and sulfur were detected in the pit. Manganese and sulfur were detected also on the non-corroded area of the inner surface of sample no 3.

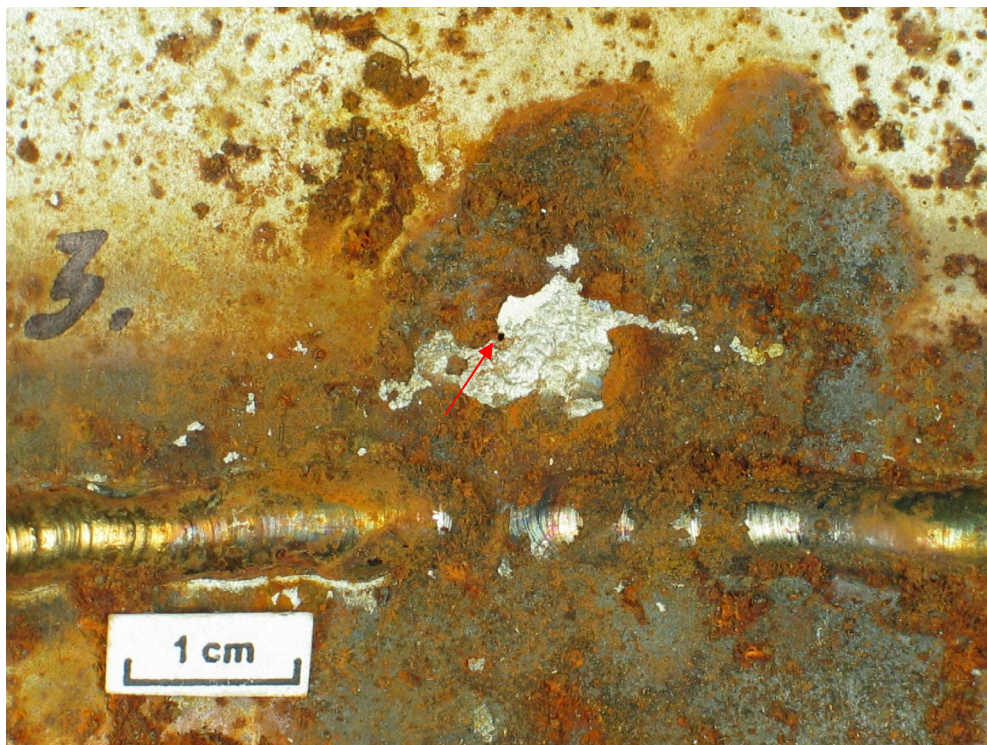


Figure 12. An opening of a perforated pit surrounded by corroded shiny area on the inner surface of sample no. 3.

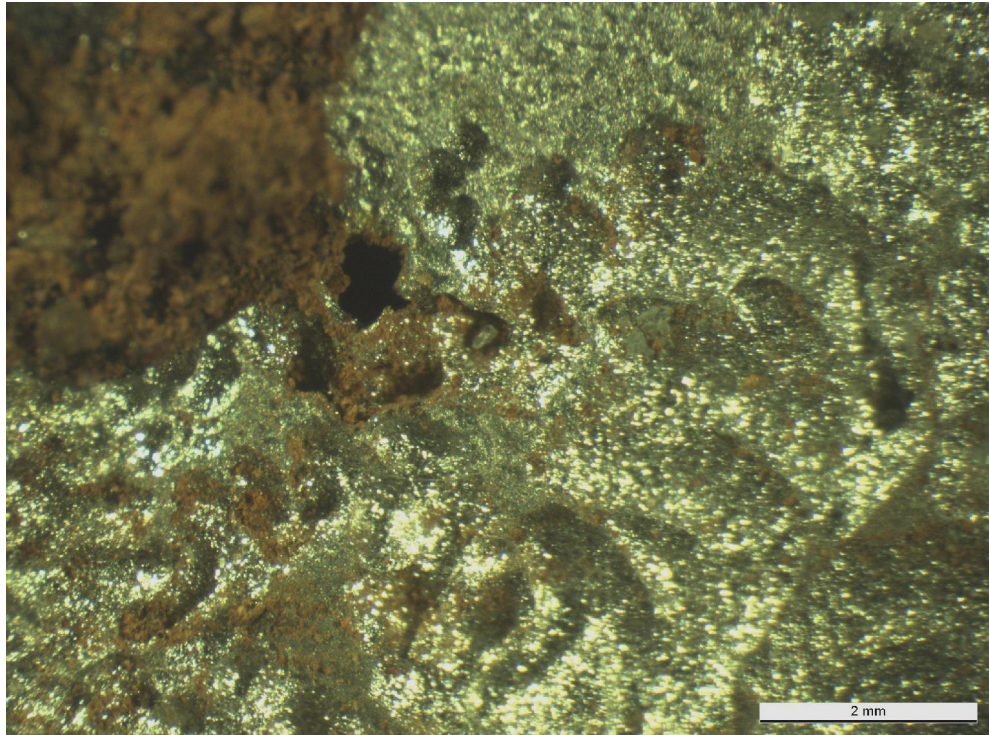


Figure 13. A closer look to the corroded area on the heat affected zone of a weld on the inner surface of sample no. 3.

A cross section was prepared from the area close to the perforation. From this cross section it could be detected that in this sample the weld had one gas pore, Fig. 14. A small pit could be seen on the base material (under the heat tint area) close to the perforated area, Fig. 15 as well as one on the fusion line (not seen in this figure).

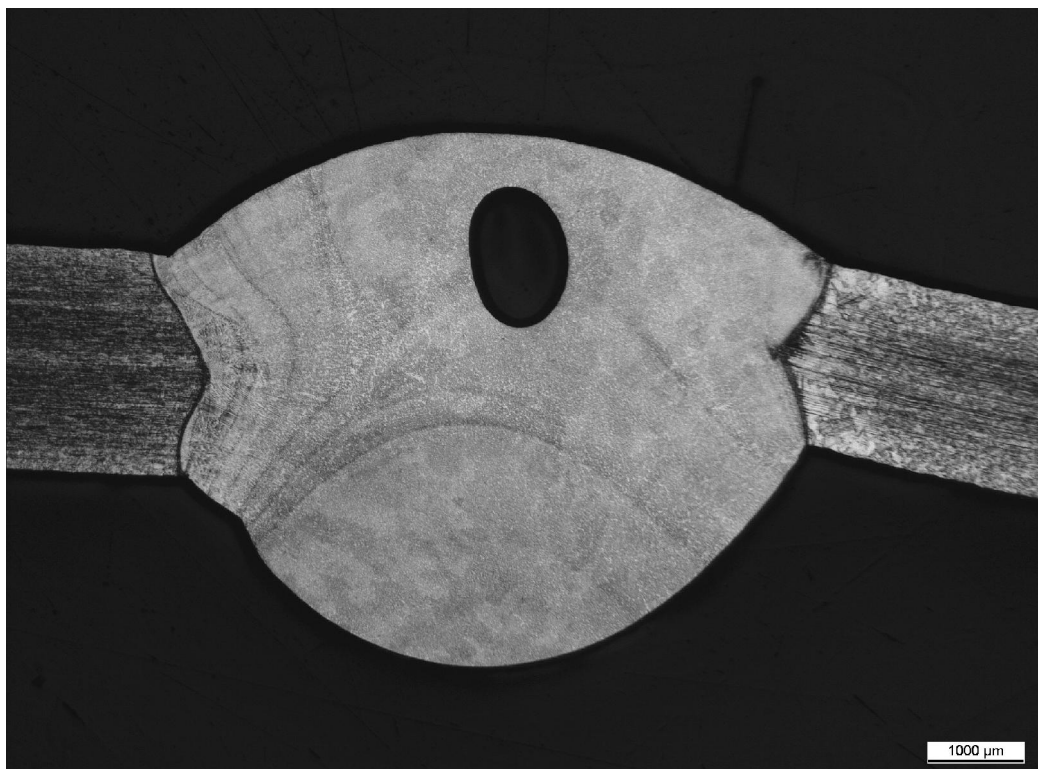


Figure 14. A pore in the weld of sample no. 3.

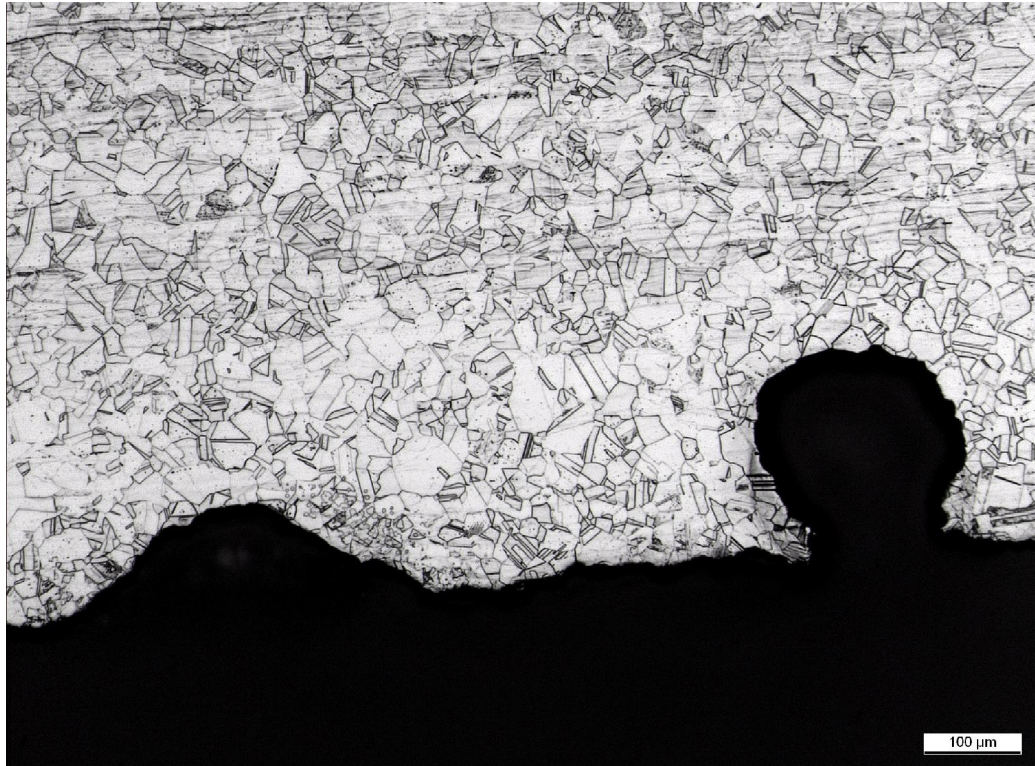


Figure 15. Corrosion on the inner surface of stainless steel pipe sample no. 3.

The metallographic examination did not reveal any abnormalities in the microstructure of this sample and the microstructure was considered to be normal austenitic structure (Fig. 15).

Microbiological results taken from the failure area of sample 3 revealed signs of bacteria. From this sample bacterial DNA could be isolated and multiplied with PCR using eu-bacteria primers. PCR products were run through DGGE gel. In DGGE gel, one clear band and six weaker bands were revealed representing different bacterial species. In DGGE, the bands represent the bacteria which are most abundant in the sample. However, without sequencing it was not possible to identify the different species. No SRB could be detected with this method. However, this does not mean that there could not have been also SRBs present.

Sample no. 4 was clean on the outer surface without any signs of perforation. The examination of the inner surface, Fig. 16 revealed again very dark heat tint colors and several small pits on the heat affected zone, Fig. 17 and 18.

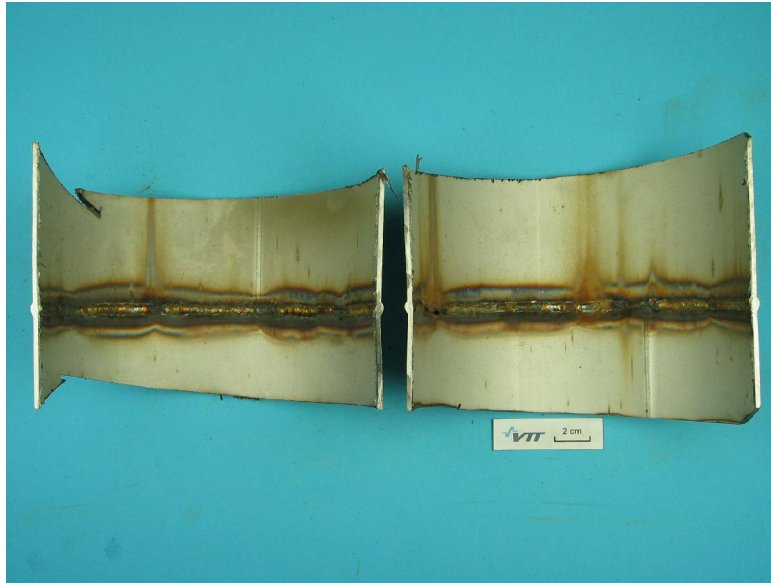


Figure 16. The inner surface of sample no. 4.

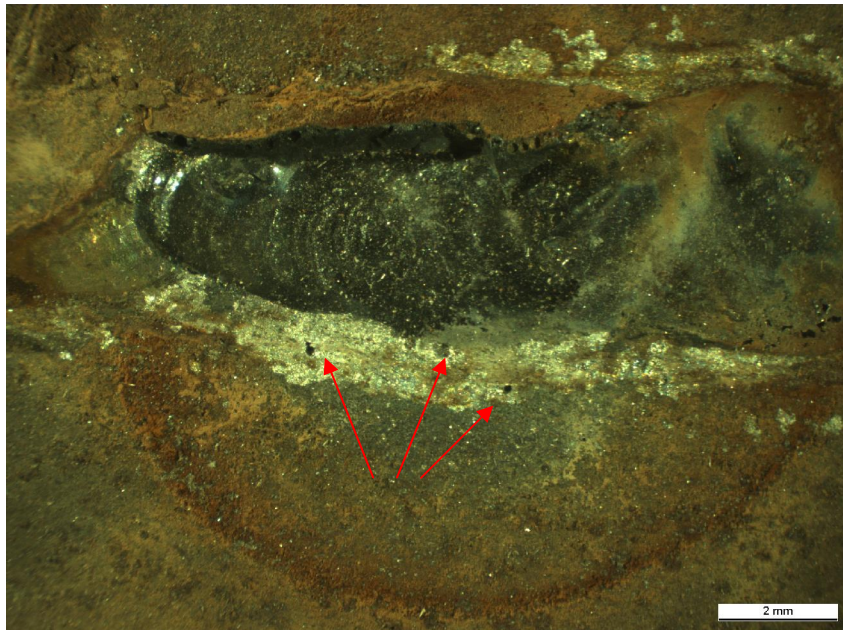


Figure 17. Pits (marked with arrows) on the heat affected zone of a weld on the inner surface of sample 4.

In sample 4 the fusion line of the weld was partly shiny and small pit holes could be seen on those areas. The weld was uneven and partly incomplete. In Fig. 17 a ring with remains of corrosion products can be seen, which is a typically seen on pitting corrosion cases of stainless steels in natural waters. The amount of deposit was low and probably most of the corrosion products were removed during the removal and transporting of sample.

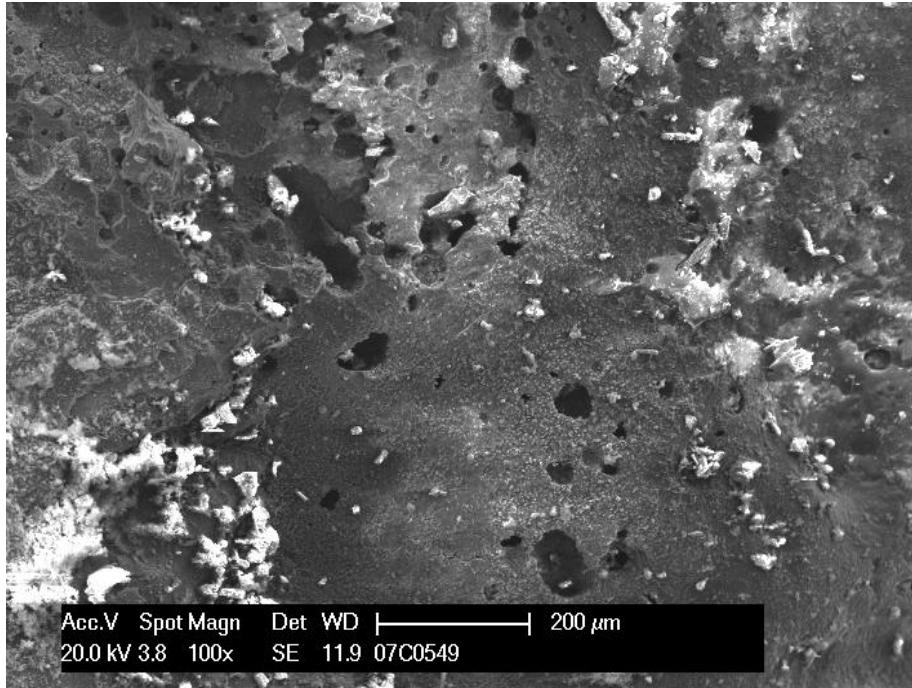


Figure 18. Corrosion pits on the heat affected zone of the weld of sample 4. SEM-figure.

A cross section from the failure area shows an example of a large pit in the heat affected zone, Fig. 19.

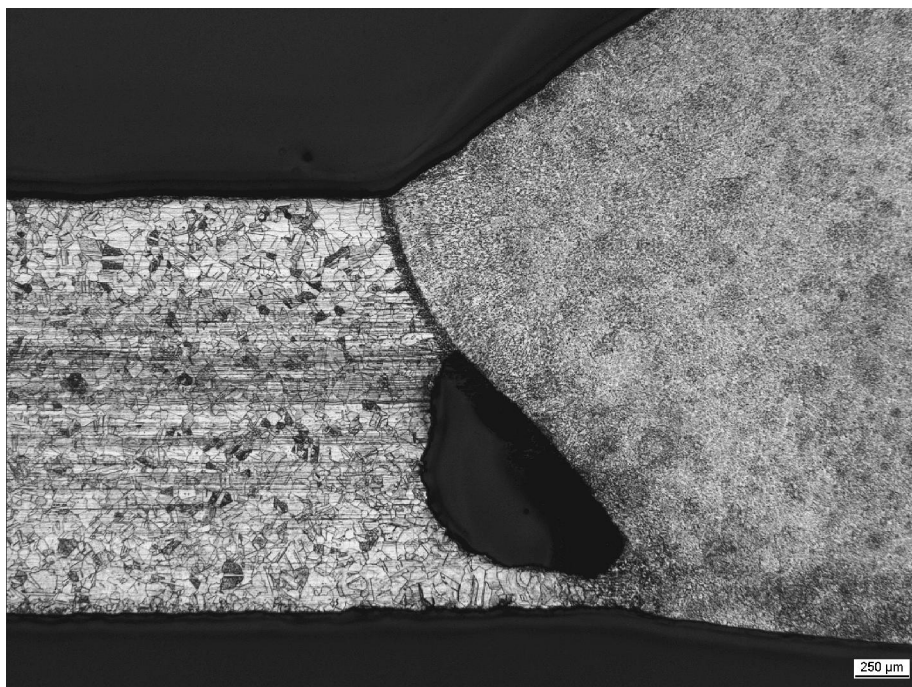


Figure 19. A large pit in the heat affected zone of sample 4.

The corrosion area of sample no. 4 contained high amounts of titanium (Ti), manganese and sulfur besides main components iron, chromium, carbon, oxygen and smaller amounts of sodium, aluminum, silicon, potassium, calcium and nickel, Table 2. Titanium was not found from the non-corrosion area and the amounts of manganese and sulfur were smaller than in the pit area, Table 2, page 21.

Sample no. 5 containing factory made weld, was taken from the hot rolling mill fire protection system (FPS). In this sample no corrosion could visually be seen, Figure 20. No heat tint areas were seen on this sample. No failures have been detected in this fire protection system, although field welds have been made also with manual metal arc welding, like in the FPS of the cold roll mill.



Figure 20. The inner surface of sample 5 taken from the hot rolling mill FPS.

The inner surface with thin brownish deposit was analyzed by EDS. Iron, chromium, carbon and oxygen were the main components. Besides also nickel, manganese, sulfur, phosphorus, aluminum, silicon, zinc and potassium were analyzed from the inner surface, Table 2, page 21.

A cross section performed from the weld area revealed a normal microstructure of the pipe material and a good quality weld seam, Figure 21. With a higher magnification some starting, negligible corrosion could be seen in the weld on the inner surface of the pipe, Figure 22.

Chemical composition of sample 5 base material and weld is presented in Table 3, page 21.

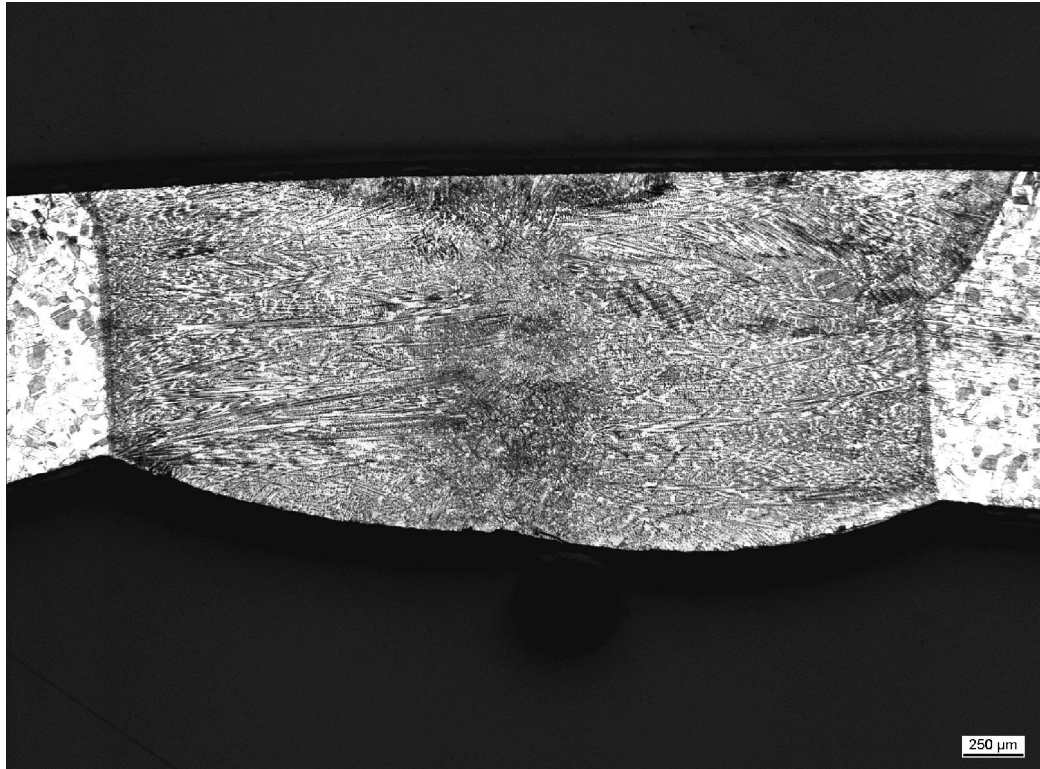


Figure 21. A cross section of the weld of sample no. 5.

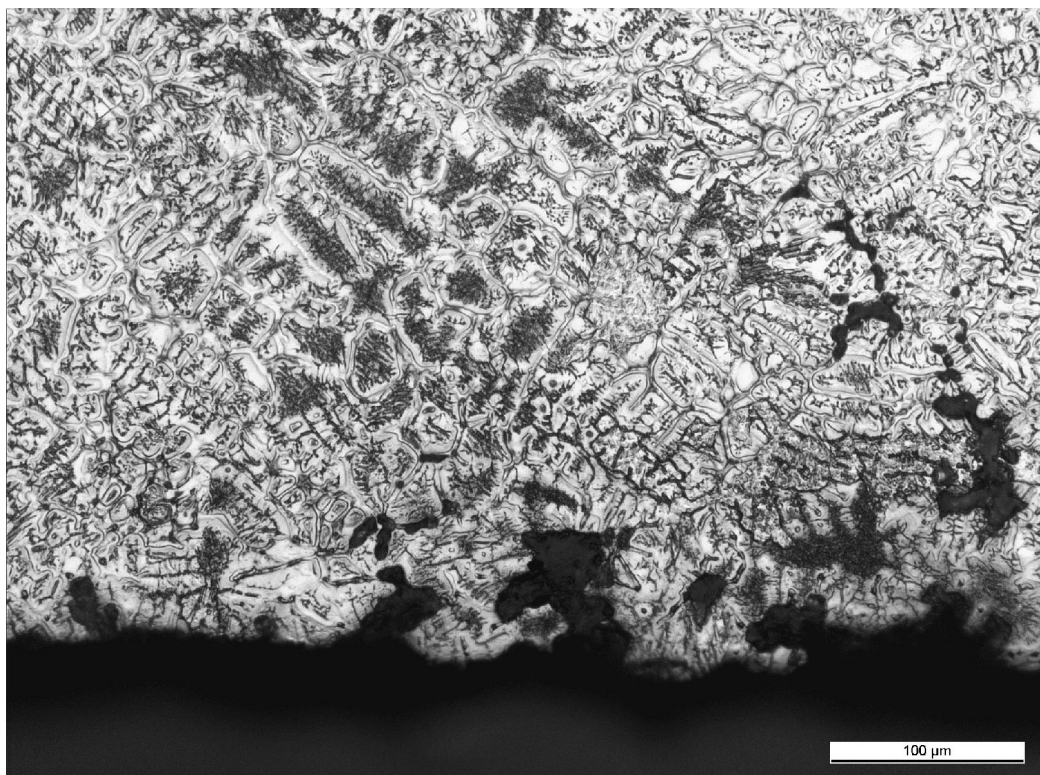


Figure 22. A closer look to the weld area with incipient corrosion.

Table 2. Semi-quantitative results of the EDS-analyses performed from the inner surfaces of chosen specimens.

| Sample | C | O | Fe | Cr | Mn | Ni | P | S | Ti | Al | Si | others |
|------------------------------|------|------|------|------|-----|-----|-----|-----|-----|-----|-----|----------------------------|
| 1a: brown undamaged | 30.9 | 30.3 | 30.7 | 3.4 | 1.4 | 0.9 | 0.2 | 0.3 | - | 0.7 | 0.7 | 0.5Ca |
| 1a: pit | 25.9 | 17.3 | 38.1 | 11.6 | 1.2 | 4.3 | 0.1 | 0.4 | 0.4 | 0.2 | 0.4 | 0.1Ca, Mo, Mg |
| 2, undamaged | 18.3 | 24.0 | 40.6 | 10.0 | 1.4 | 4.0 | - | 0.2 | - | 0.3 | 0.6 | 0.4K, 0.1Cl, 0.1Mg |
| 2, pit | 24.8 | 32.0 | 35.7 | 1.6 | 0.8 | 1.9 | - | 0.2 | 0.2 | 0.4 | 0.8 | 0.5Zn, 0.4Na, 0.3Ca, 0.1Cl |
| 3, noncorroded | 14.9 | 24.1 | 42.6 | 10.2 | 1.4 | 3.4 | - | 0.2 | - | 0.6 | 1.5 | 0.6K, 0.3Na, 0.2Mg |
| 3, brown deposit (corrosion) | 11.7 | 31.8 | 48.1 | 2.5 | 0.5 | 0.7 | - | 0.3 | 0.4 | 0.4 | 1.2 | 1.9Zn, 0.2Ca, 0.1K |
| 3, pit (deposit) | 17.3 | 39.9 | 32.8 | 6.9 | - | 0.6 | 0.1 | 0.7 | - | 0.3 | 1.3 | 0.1 K 0.1 Na |
| 3, pit (clean) | 16.8 | - | 56.5 | 16.9 | 1.8 | 6.5 | - | 0.4 | - | 0.1 | 0.6 | 0.5Cu |
| 4, noncorroded | 16.0 | 11.3 | 50.4 | 13.8 | 1.5 | 5.6 | - | 0.2 | - | 0.4 | 0.4 | 0.3K |
| 4, pit | 21.5 | 35.6 | 15.2 | 6.4 | 3.4 | 0.6 | - | 0.5 | 7.3 | 1.3 | 2.7 | 3.5Ca, 1.7K, 0.4Na, 0.1Mg |
| 5, noncorroded | 37.5 | 17.4 | 31.1 | 7.7 | 1.9 | 2.8 | 0.1 | 0.2 | - | 0.7 | 0.3 | 0.1Zn, 0.1K |

Table 3. Chemical composition (w-%) of studied stainless steels in Case 1.

| sample | C | Si | Mn | S | P | Cr | Ni | Mo | Cu | Al | V | Ti | Co |
|---------|-------|------|------|-------|-------|------|-----|------|------|-------|------|-------|------|
| 2, base | 0.023 | 0.47 | 1.49 | 0.001 | 0.027 | 18.1 | 9.0 | 0.13 | 0.17 | 0.011 | 0.05 | 0.005 | 0.11 |
| 2, weld | 0.026 | 0.39 | 1.45 | 0.004 | 0.026 | 18.3 | 9.1 | 0.21 | 0.15 | 0.011 | 0.05 | 0.006 | 0.16 |
| 5, base | 0.044 | 0.40 | 1.47 | 0.011 | 0.035 | 18.1 | 8.5 | 0.10 | 0.17 | 0.008 | 0.06 | 0.004 | 0.14 |
| 5, weld | 0.048 | 0.43 | 1.50 | 0.015 | 0.039 | 18.0 | 9.0 | 0.10 | 0.18 | 0.008 | 0.06 | 0.005 | 0.17 |

5.2 Case 2 – Power Plant

The first through wall pits in this fire extinguishing system were observed in type EN 1.4401 stainless steel pipe with a diameter of 140 mm and the wall thickness of 3 mm. The leaks situated in the heat affected zone of site weld. Chemical composition is shown in Table 4.

Table 4. Chemical composition (w-%) of stainless steel of Case 2.

| sample | C | Si | Mn | S | P | Cr | Ni | Mo | Cu | Al | V | Ti | Co |
|----------|-------|------|------|-------|-------|-------|-------|------|------|-------|------|-------|------|
| EN1.4401 | 0.032 | 0.67 | 1.45 | 0.007 | 0.034 | 16.89 | 10.70 | 2.47 | 0.21 | 0.005 | 0.08 | 0.017 | 0.23 |

Visual inspection of the pipe sample revealed two perforations on the outer surface of the sample. These perforations situated at the heat affected zone close to the fusion line of the weld. A plenty of reddish brown deposit was seen on the opposite inner side (Fig. 23a). Similar reddish brown deposits and deposit rings were observed on the inner surfaces of type EN 1.4301 stainless steel removed from the fire extinguishing system later on (Fig. 23b). Typically the openings of the pits were very small but having large subsurface cavities (Fig. 24). The chemical compositions of these type EN 1.4301 stainless steel samples were according to the specifications in ASTM standards except for some of the samples having less than 18 % Cr (17 and 17.7 %). The microstructure of both materials was normal austenitic structure. Pits were typically situated close to or in girth site welds. There were clear signs of oxidation of heat affected zone (heat tints) but no other clear signs of welding defects on the failure areas.

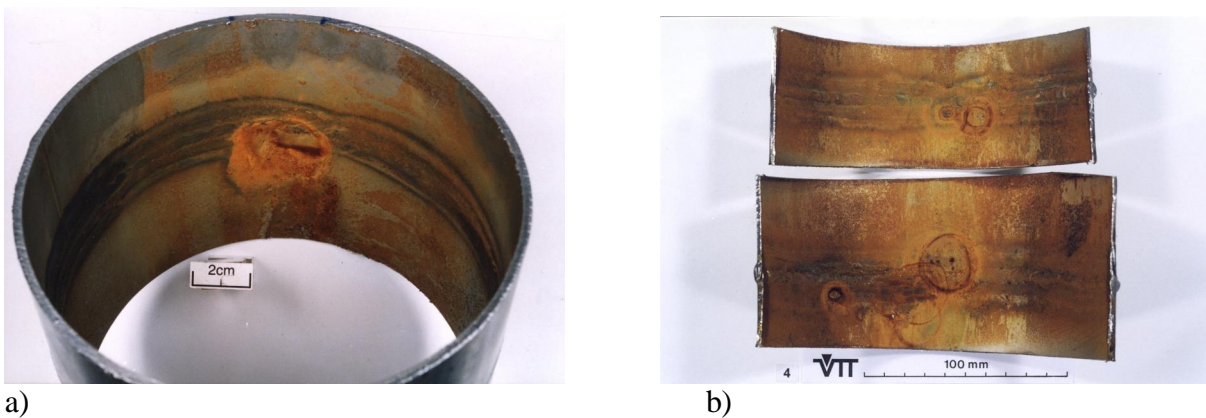


Figure 23. a) Reddish brown deposit seen on the inner surface of stainless steel type EN 1.4401 pipe section removed from the fire extinguishing system b) deposit rings surrounding pits on the welded areas of stainless steel type EN 1.4301 pipe samples removed later from the same fire extinguishing system.

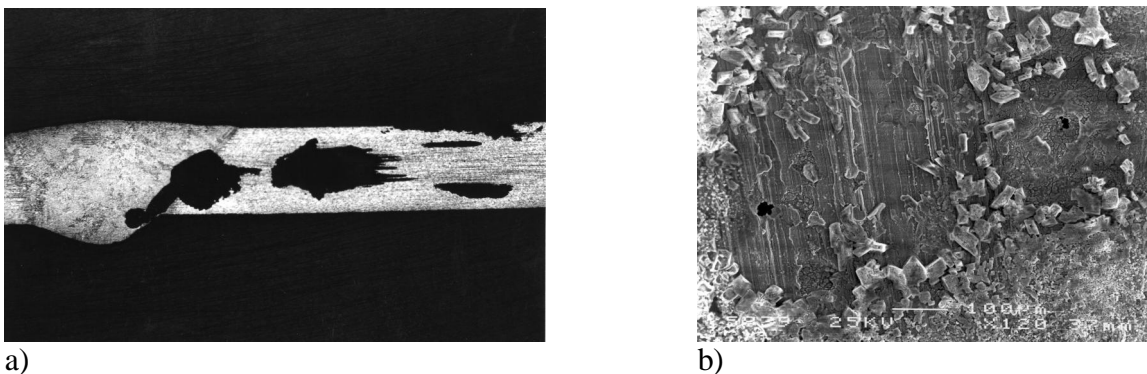


Figure 24. a) An optical micrograph of a through wall, mainly subsurface pitting corrosion in EN 1.4401 type of stainless steel after two years service in fire extinguishing water b) Two small openings of pits revealed on the inner surface of stainless steel EN 1.4301 after corrosion products were removed by pickling.

The pits were typically surrounded by dark brown circular deposit ring and the inner surfaces were most of the times covered with thin rather smooth layer of yellowish brown deposit. Sulfur and occasionally also high amounts of manganese as well as small amounts of phosphate were detected on the deposits in or surrounding the pits (Fig. 25). These elements are often found in the cases of MIC.

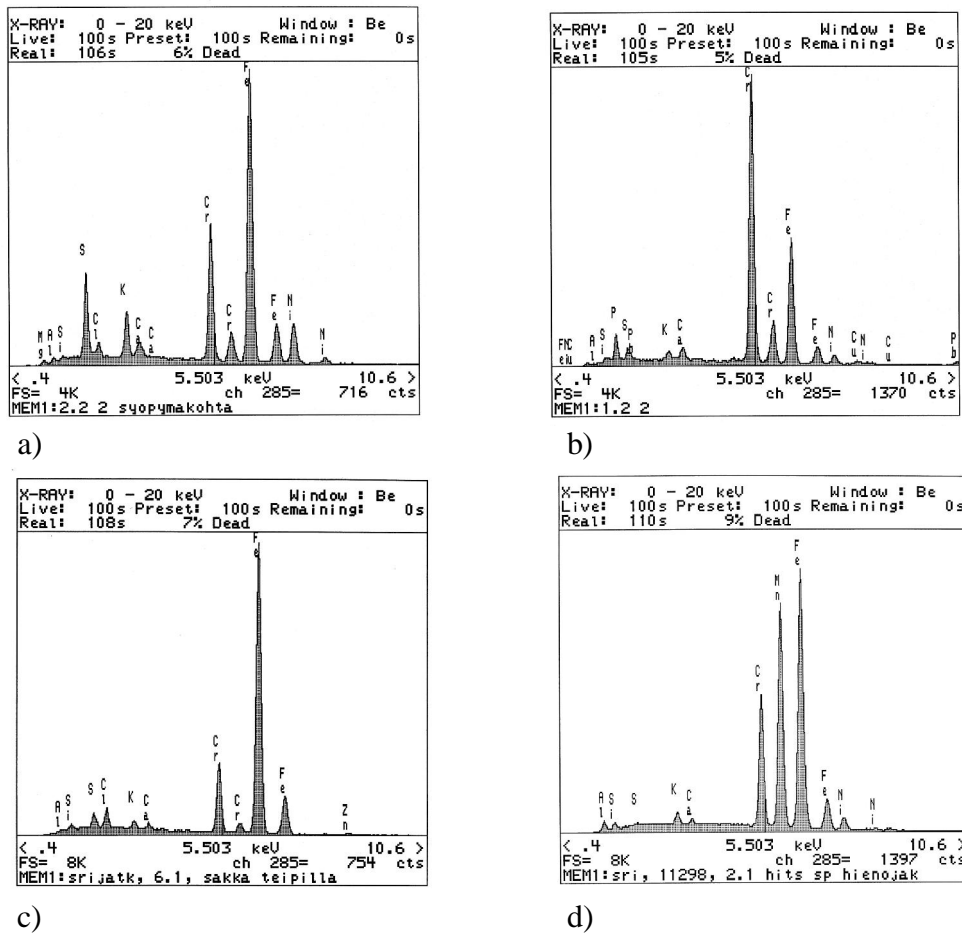


Fig. 25. EDS-analysis performed a) and b) from a pitted area on the inner surface of type 304 stainless fire extinguishing pipe, c) from a dark deposit removed from the surface of a weld, d) from the deposit covering the inner surface containing a transversal weld.

The results of the water analysis from a water sample taken a few months after the first leaks (water A) is in Table 5. In the same table is the analysis of the water sample taken from fire extinguishing system two years later simultaneously with leaking pipes (Water B).

Table 5. The chemical analysis of the water samples taken from the fire extinguishing system of power plant. Water C is the analysis of the tap water used as feed water for the system.

| Water | pH | Fe mg/l | Mn mg/l | Ca mg/l | Mg mg/l | Cl ⁻ mg/l | SO ₄ ²⁻ mg/l | HCO ₃ mg/l | NO ₂ mg/l | NO ₃ mg/l |
|-------|-----|------------|------------|------------|------------|-------------------------|---------------------------------------|--------------------------|-------------------------|-------------------------|
| A | 6 | 0.01 | 0.4 | 8.8 | 4 | 28 | n.a.* | n.a.* | n.a.* | n.a.* |
| B | 7.2 | 0.44 | 0.53 | 12 | 4.4 | 21 | 34 | 20 | <0.01 | 1 |
| C | 7.8 | 0.05 | 0.02 | 12 | 4.7 | 24 | 27 | 26 | <0.01 | <1 |

* not analyzed

The tap water (water C, one typical analysis) used as feed water for the fire extinguishing system is typical drinking water with conductivity typically between 15-19 mS/m. Normally this kind of water with low chloride content is not considered harmful to the stainless steel types EN 1.4301 or EN 1.4401.

The total count of aerobic bacteria in samples taken directly from the surfaces of opened system was clearly higher (from 1.1×10^3 to 7.3×10^3 cfu/ml) than in the water sample (32...50 cfu/ml). Low values of anaerobic bacteria were detected both from the pipe surfaces and from the water. The total count of anaerobic bacteria being 0.5...1 cfu/ml in water and 5.5...9.5 cfu/ml in the samples taken from the surfaces. Also the amounts of sulfate reducing bacteria (SRB) were low, 0.5 cfu/ml in water and 0.2...4.1 cfu/ml in the surface samples. However, the system had been opened half an hour prior sampling which might have had an influence to the low amounts of anaerobic bacteria detected.

Sulfate reducing bacteria could be detected from the pipe sample delivered to the laboratory with a moist deposit still on the surface. Also the amount of aerobic bacteria in this moist pipe sample were rather high, 4.3×10^6 cfu/cm² which was clearly higher than in the pipe sample with dried deposit, 20 cfu/cm². Both these samples contained through wall pits.

The presence of iron bacteria (bacteria growing on ferrous sulfide medium) was verified from the sample delivered to the laboratory under the water taken simultaneously from the fire extinguishing system under consideration. The amount of heterotrophic aerobic bacteria both in this sample as well as in the water taken simultaneously from the system was rather high (4.3×10^5 and 2.4×10^5 cfu/ml respectively). A plenty of individual rod-shaped bacteria as well as cell aggregates and starting biofilm formation on the stainless steel coupons incubated 6 d in iron bacteria culture medium could be seen under the epifluorescence microscopy, Fig.26.

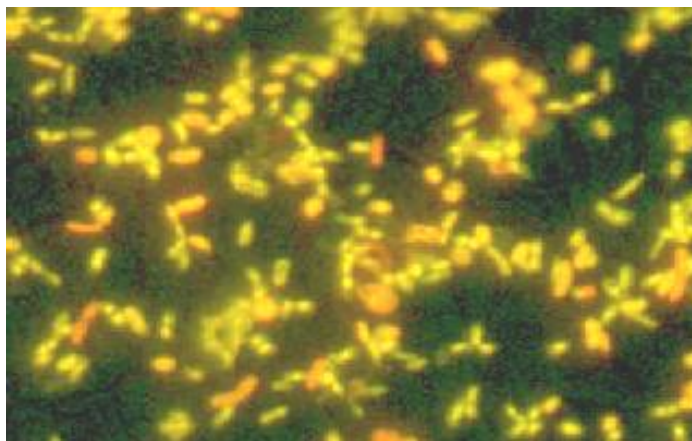


Figure 26. A plenty of bacterial cells and starting biofilm formation in the deposit analyzed from the failure area on the inner surface of fire extinguishing pipe [22].

The influence of iron-rich deposit and the chloramine treatment on the pitting corrosion initiation of EN 1.4301 type of stainless steel can be seen in Table 6 where the results of measured anodic polarization curves are gathered. The values for first three tests are mean values of two separate measurements. Chloramine is considered as an oxidizing biocide. However, the concentration in treated water is quite low and no oxidizing influence on the open circuit potential (E_{op}) could be seen (Table 6). The open circuit potential was measured after 10 min of immersion.

Table 6. The pitting initiation potential (E_{pn}) and the potential for repassivation (E_{pp}) determined for stainless steel samples (EN 1.4301) in water containing chloramine (water D) and in water without chloramine treatment (water E).

| Water/Test | E_{pn} (mV _{SCE}) | E_{pp} (mV _{SCE}) | E_{oc} (mV _{SCE}) |
|----------------------------|-------------------------------|-------------------------------|-------------------------------|
| D+200 Cl | 680* | 185* | -9* |
| E+200 Cl | 548* | 213* | 63* |
| D+200 Cl+deposit | 540* | 100* | -17* |
| D+ 200 Cl +weld+deposit | 316 | 50 | 54 |
| E+ 200 Cl +weld+deposit | 343 | -22 | 54 |

* Average of two measurements, without star: only one measurement

From the E_{pn} values it can be seen that iron-rich deposit on the surface of the sample lowered clearly the pitting initiation potential in chloramine containing water (540 mV versus 680 mV). The same effect could be seen on E_{pp} values, with iron deposit the E_{pp} was lower than without the deposit (100 mV versus 185 mV). In the presence of iron rich deposit the pitting initiates at lower potential and also continues to a lower potential than without deposit. Instead, no accelerating influence on chloramine treatment on the pitting initiation was observed. With welded specimens both E_{pn} and E_{pp} values were distinctly lowest in the presence of iron deposit in both waters. After the tests pits were detected in all of the polarized samples.

6 Discussion

Both failure cases occurred after a short time of usage in water with low chloride content. Under normal conditions, these types of water are not regarded as corrosive to the stainless steel types EN 1.4301 or EN 1.4401. However in these cases, the water was stagnant most of the time and only occasionally used. In stagnant waters with the possibility for deposit formation, the corrosion resistance of stainless steels is clearly diminished. During long stagnant periods, the stainless steel surface is not cleaned and bacterial activity may increase. The presence of bacteria was verified for Case 2 and indications of bacteria growth were found also in Case 1. It is generally accepted that the noble shift of the open circuit potential of stainless steels detected all over the world in natural waters is caused by microbial colonization. This ennoblement can exceed the pit initiation potential even in low chloride waters. Usually the pit initiation potential on the weld and on the heat-affected zone is lower than on the base metal. Therefore, pitting corrosion starts often in these areas. Heat tint layers are also rich in iron and manganese oxides, which might explain why harmful bacteria tend to attach to these areas as well.

Ennoblement alone cannot cause pitting corrosion. There has to be also some anions able to produce strong acid solutions inside the pit. Chlorides are the most common anions causing pitting corrosion of stainless steels by forming concentrated metal chloride solutions inside the pits. In typical pure drinking waters hav-

ing low chloride concentrations (6...30 mg/l) the pitting potential for stainless steels at room temperature determined by anodic polarization is very high (>1000 mV_{SCE}). This high potential means that no pitting is actually occurring but the increase of current is due to oxygen evolution and possible transpassive dissolution of stainless steel. The potentials needed for pitting to initiate in these pure waters are quite high even with higher chloride content. In Case 2 the pitting initiation potential was determined as 680 mV when 200 mg/l chloride had been added to the original water. In the same environment the welded specimen (cleaned by pickling, 2 min in 6.5 % HNO₃) covered with iron deposits had a pitting initiation potential of 320 mV. In our earlier study [10], the effects of heat tints on pitting corrosion were examined in chloride solutions at room temperature. It was shown that pits could initiate at substantially lower potentials in heat tint areas than in areas without heat tints. However, the potentials required for continued growth of open pits in a dilute (106 mg/l Cl) plain chloride environment were considered still quite high for serious pitting in seemingly harmless environments to be explained by the presence of heat tints alone. In the presence of sulfates, the needed amount of chlorides to initiate corrosion is even higher and is depending on the molar ratio of chlorides and sulfates.

In many cases where pitting corrosion of stainless steels in fresh waters occurred, manganese and/or iron oxidizing bacteria (like *Leptothrix*, *Siderocapsa*, *Gallionella*) had been detected. Iron oxidizing bacteria can oxidize ferrous iron to ferric iron, which then reacts with the chloride ions producing ferric chloride [26]. Ferric chloride is extremely aggressive oxidizing agent causing pitting corrosion on stainless steel. The deposits from the bacteria are rich in ferric chloride and attack aggressively austenitic stainless steels. Manganese oxidizing bacteria oxidize Mn²⁺ to Mn⁴⁺, which is a strong oxidizer as well. In the studied cases, indications of iron oxidizing bacteria were detected from the deposits. The presence of manganese oxidizing bacteria was not tested. Anaerobic SRBs were also found in failure areas often together with manganese- and iron-oxidizing bacteria, as was shown also in our Case 2.

Another mechanism of how microbes can affect the initiation of pitting corrosion of stainless steels is the formation of thiosulfate. This type of pitting does not need the ennoblement of the steel but can occur at lower potentials than in pure chloride environments. SRBs consume sulfate by reducing it to sulfide and which in the presence of air can be oxidized to thiosulfate. During the stagnant periods in the system, anaerobic bacteria like SRBs produce sulfide. During occasional usage of the fire extinguishing system when oxygen or oxygen containing new water can enter the system, thiosulfate is formed. In simulated paper machine water, it has been demonstrated that thiosulfate produced by the metabolic activity of SRBs caused severe pitting corrosion of stainless steel type EN 1.4301 [9].

The waters in both cases contained also a high amount of precipitated iron. The high concentration of iron in the water can offer suitable conditions for iron oxidizing bacteria. Besides iron hydroxides can behave as anion selective membrane at neutral pH and had been shown [27] playing a certain role for the occurrence of localized attack of stainless steel.

7 Conclusions and recommendations

The influence of microbial activity has played a decisive role in these pitting corrosion cases of stainless steel piping in firewater mains. The presence of precipitated iron and remains of oxidized regions (heat tint areas) of welded structures have accelerated the danger for pitting failures.

The best way to prevent forming of deleterious oxide layers is to remove oxygen from the piping by shielding gas flushing before welding and using backing gas during the whole welding and as well as little time after welding. The oxidization of root can be reduced also by using root paste. This paste reacts with the welding heat and forms a slag layer on the root side of the weld. However, the results achieved with root paste are not anywhere near to the results achieved by using the backing gas. Alternatively the heat tints can be removed by pickling after welding. However, this is not always possible while considering the welding of piping.

To avoid this kind of failures one should use water as clean as possible with low amounts of solids, of chlorides, manganese and iron as well as a low amount of organic substances and avoid stagnant conditions or very low flow conditions. If the continuous flow is not possible the water should be changed frequently enough and the amounts of bacteria should be checked regularly and when necessary to treat the water to minimize the bacterial activity. In Case 1 no failures had been detected in the system using the same water with regular use (once a week). In Case 2 the problems have been solved by using very clean water (demineralized water) and circulation. Using demineralized water, however, is very expensive solution. More research is needed to be able to determinate what is frequently enough (using or changing the water) and is some oxidations allowable or should all the heat tint areas to be removed.

References

1. B. Christ. Corrosion Control Inside Water-filled Steel Fire Sprinkler Piping. *Journal of Fire Protection Engineering*, Vol.16, 105-130, 2006.
2. R.I.Garber & D.G. Chakrapani. Some recent failures of fire sprinkler system components: corrosion case histories, *CORROSION* 2004, paper 04511. Houston, Texas: NACE International; 2004.
3. D.H. Pope & R.M. Pope. Microbiologically influenced corrosion in fire protection sprinkler systems, *CORROSION* 2000, Paper 00401. Houston, Texas: NACE International; 2000.
4. D. Haagensen. Microbiologically Influenced Corrosion of Fire Sprinkler Systems. <http://www.periodisinfest.biz/corrosion.html>, 22.11.2005.
5. J. Roland & P.E. Huggins. Microbiological Influenced Corrosion. What It is and How It Works. <http://www.sprinklernet.org/technical/mic/articles/article4.html>.
6. Technical Bulletin C-13. The many corrosion factors affecting a fire sprinkler system. http://www.corrview.com/tech_c_13.htm, 22.11.2005.
7. Technical Bulletin M-15. The true threat of a high corrosion problem to a fire sprinkler line. http://www.corrview.com/tech_m_15.htm, 22.11.2005.

8. A.Garner. Thiosulphate Pitting of Austenitic Stainless Steels. Corrosion Australasia, Feb.1988, pp. 16-18.
9. L. Carpén, L. Raaska, K. Kujanpää, K. Mattila, P. Uutela, M. Salkinoja-Salonen & T. Hakkarainen. Simulation of MIC at splash zone areas of the paper industry. CORROSION 2001, paper no. 245. Houston, Texas: NACE International; 2001.
10. T. Hakkarainen and L. Carpén. Effects of Heat Tints on Pitting Susceptibility of Stainless Steel. Paper No. 061. 7th International Symposium on Electrochemical Methods in Corrosion Research, EMCR2000. Budapest, Hungary- May 28-1 June 2000; 2000.
11. L.Carpén, L.Raaska, K.Kujanpää and T.Hakkarainen. Effects of *Leptothrix discophora* on the potential behavior of stainless steel. Materials and Corrosion 54, 515-519; 2003.
12. V. Scotto, M. Beggiato, G. Marcenaro and R. Dellepiane, Microbial and Biochemical Factors Affecting the Corrosion Behavior of Stainless Steels in Seawater, European Federation of Corrosion Publications Number 10, (London, Great Britain: The Institute of Materials, 1993), pp.21-33.
13. S.C. Dexter & G.Y. Gao, Corrosion 44 (1988): p.717
14. S. Motoda, Y. Suzuki, T. Shinohara and S. Tsujikawa, *Corrosion Science*, 31 (1990): pp. 515-520.
15. Carpén, Leena; Raaska, Laura; Salkinoja-Salonen, Mirja; Hakkarainen, Tero. 1995. Microbially induced corrosion of stainless steels in the Baltic seawater. In: Proc. of Int. Conference on Microbially Influenced Corrosion. New Orleans, Louisiana, 8 - 10 May 1995. Eds. P. Angell et al. Houston, TX, NACE International. S. 11/1 - 11/13.
16. Carpén, Leena; Raaska, Laura; Mattila, Katri; Salkinoja-Salonen, Mirja; Hakkarainen, Tero. 1996. Laboratory Simulations with Natural Bacteria Populations. In. Proceedings of EUROCORR' 96, September 24-26, 1996. S. V-OR 12-1 - 12-4.
17. J. Korkhaus, J.T.Titz and G.H.Wagner. Microbial deterioration of materials – simulation, case histories and countermeasures for metallic materials: Pitting corrosion caused by microbiological activity at austenitic stainless steel pipes used for river water (in German). Werkstoffe un Korrosion 45 (1994), pp.87-95.
18. P. Linhardt. Pitting of Stainless Steel in Freshwater Influenced by Manganese Oxidizing Micro-organisms. Dechema Monographs Vol133- VCH Verlagsgesellschaft 1996, pp. 77-83.
19. W.H. Dickinson & Z. Lewandowski. Manganese Biofouling and the Corrosion Behavior of Stainless Steel. Biofouling, Vol. 10 (1-3), pp. 79-93; 1996.
20. C. Xu, Y.Zhang, G. Cheng and W. Zhu. Localized corrosion behaviour of 316L stainless steel in presence of sulfate-reducing and iron-oxidizing bacteria. Materials Science and Engineering A 443 (2007) 235-241.
21. L. Carpén, L. Raaska, K. Kujanpää and T. Hakkarainen. Mikrobiologinen korrosio käyttövesijärjestelmissä (in Finnish). VTT Tutkimusraportti BVAL74-011169, Espoo 2002. pp. 28 + 30.
22. L. Carpén, U. Ehrnstén, L. Raaska, K. Kujanpää and T. Hakkarainen. Microbially induced corrosion (MIC) in austenitic stainless steels used as fire extinguishing pipes. Paper presented at Eurocorr 2001, The European Corrosion Congress, Riva del Garda, Italy 30.9-4.10.2001.
23. G. Muyzer, E.C. de Waal & A.G. Uitterlinden. Profiling of complex microbial populations by denaturing gradient gel electrophoresis analysis of polymerase

- chain reaction-amplified genes coding for 16S rRNA. *Applied and Environmental Microbiology*, vol. 59, no. 3 (1993) pp. 695-700.
24. R. Atlas. *Handbook of Microbiological Media*, second edition (Ed. L. Parks). C.RC Press, Boca Raton, USA 1997.
 25. T. Hakkarainen, in: *Laboratory Corrosion Tests and Standards*, ASTM STP 866 (Eds. G.S. Haynes, R.Baboian), American Society for Testing and Materials, Philadelphia, 1985, pp. 91-107.
 26. S.W. Borenstein. *Microbiologically influenced corrosion handbook*, Woodhead Publishing Ltd, England, 1994. 288 pp.
 27. M.H.W. Renner. Corrosion engineering aspects regarding mic related failures on stainless steels. *CORROSION* 1998, paper no. 285. Houston, Texas: NACE International; 1998.