Stainless Steel Corrosion Case Studies

Asst. Prof. Vinko Simunovic, Ph.D.

Prof. Vesna Alar, Ph.D

Asst. Prof. Mirko Jakopcic, Ph.D., rt. Colonel

University of Zagreb
Faculty of Mechanical Engineering and Naval Architecture
Department of Welded Structures
Chair of Materials Protection
10000 Zagreb
Ivana Lucica 5
CROATIA

vinko.simunovic@fsb.hr vesna.alar@fsb.hr mirko.jakopcic@morh.hr

ABSTRACT

High alloyed corrosion resistant Cr-Ni stainless steels are, as it is well known and confirmed by countless examples of their successful application over the last hundred years, a unique kind of materials with extraordinary corrosion resistance properties in many different media. Without these steels, many modern industrial fields would be unthinkable. However, these steels are not, contrary to their name in almost all world languages, absolutely immune to various corrosion processes, especially not to localized corrosion. In this paper, from a practical point of view, an overview of the various stainless steel corrosion failures caused by pitting corrosion, crevice corrosion, stress corrosion cracking and microbiologically influenced corrosion is presented, as well as possibilities of their avoidance based on the conducted failure analysis investigations.

1.0 INTRODUCTION

Stainless steels gain their corrosion resistance through natural process of passivation. When steel contains more than 12 % Cr, its surface is passivated, and extent of passivation depends on chromium content and type of corrosion agent. This property is of utmost importance for such steel grade, when industrial applications are considered. It should be mentioned that this protective layer is compact and thin. Thickness of the Cr_2O_3 passive layer for Cr-Ni steels is in range 1 to 10 nm. Being very thin, layer can be easily damaged. Any damage on the protective surface layer is seriously harmful to the corrosion resistance to bulk of material [1, 2].

In fabrication of equipment or components made of stainless steel, welding is basic method of joining. Stainless steels are weldable materials, and welded joint may provide adequate corrosion resistance and required mechanical properties, but during welding process of such materials, their specific features must be fully respected to achieve properties that are equal to those of base material. If this is not fulfilled, serious degradation of specified properties may occur, particularly of corrosion resistance in the area of welded joint. Beside the structural changes occurring in the weld metal caused by welding (figure 1-1), in heat affected zone and base material heat tint zones are created (figure 1-2). Considering the nature of corrosion resistance of such materials based on the spontaneously created passive layer of chromium oxides, heat tint zones have significantly adverse effect upon the corrosion resistance of welded joint (figure 1-3). It should be noted that certain treatment of surface after welding is essential factor for corrosion resistance of welded joint and structure as a whole. Treatment process may be mechanical, chemical or electrochemical [3, 4].

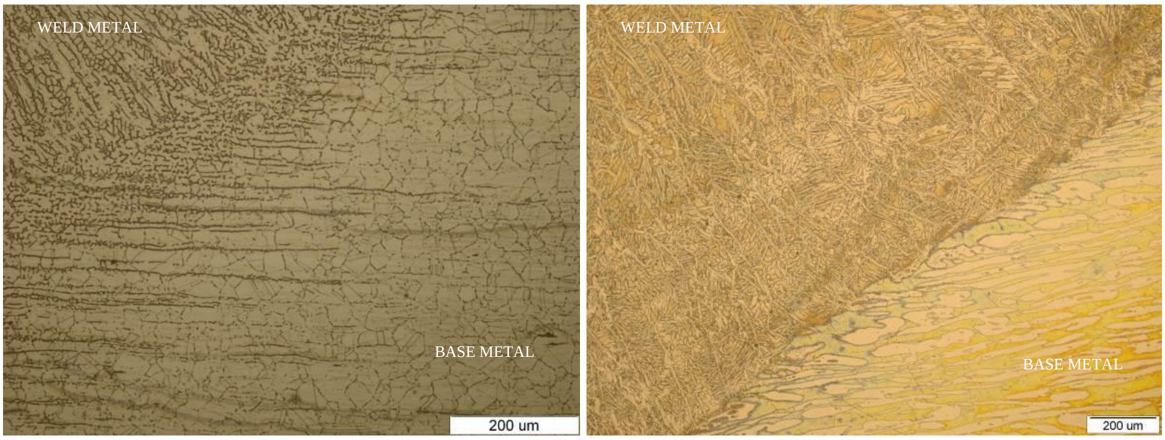


Figure 1-1: Structural changes in the weld area: austenitic stainless steel EN 1.4307 - AISI 304L (left), superduplex stainless steel EN 1.4410 – UNS S32750 (right)

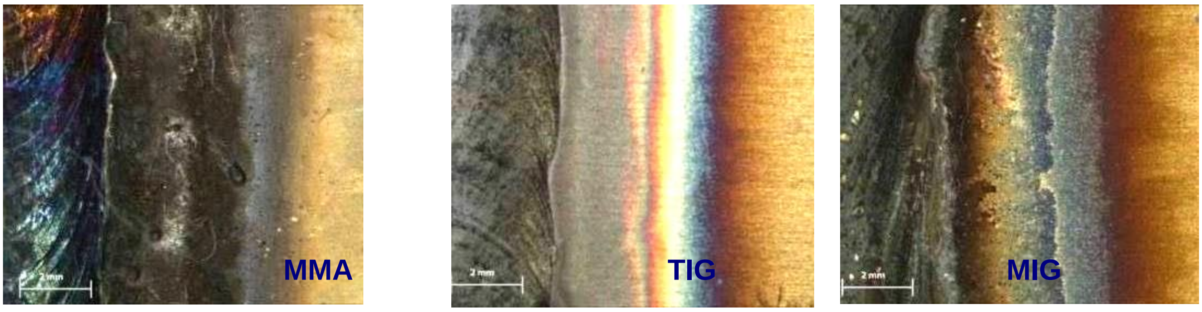


Figure 1-2: Formation of heat tints in the area of stainless steel welded joints by different welding processes

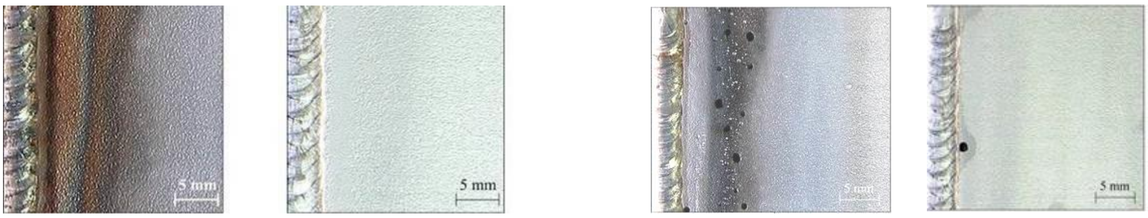


Figure 1-3: Comparison between untreated and chemically cleaned weld joint surface before (left) and after pitting corrosion testing according ASTM G48 (right). Austenitic stainless steel EN 1.4307 (AISI 304L), TIG welding.

Thereby, reliability of stainless steel structures in aggressive media where stainless steel structures are often used depends mainly on few paramount factors: selected material (base and filler), applied joining technology and applied surface treatment of welded joint or whole structure.

However, under certain circumstances, even in media which are less corrosive, local depassivation takes place resulting in localized corrosion of stainless steels and causing serious accidents, especially on structures with thin walls, e. g. pipes and tanks.

Pitting corrosion is the most frequent form of the electrochemical deterioration caused by local depassivation of metals that are usually in passive state like stainless steels. Chloride ions in water solutions are specific aggressive agents that often cause pitting corrosion on such materials. Similar adverse effects have also other halide ions (Br^-, F^-), causing destruction of passive film. Chlorides, considered by many authors as most important factor inducing local processes of destruction, are anions of a strong acids. Many metal cations have large solubility in chloride solutions. Additionally, chlorides are rather small anions with considerable power of diffusion, largely handicapping passivation. Pitting corrosion is considered as an autocatalytic process; once a pit is formed and corrosion process is initiated, significant changes in media occur in the area of the pit. Solution is depleted in cathodic reactants (such as dissolved oxygen) and enriched in metallic cations and chlorides. Also, pH value within pit is lowered. Thus created chloride media is highly aggressive, blocks repassivation and stimulates further propagation of pit. Initial processes when depasivation occur, such as deterioration of passive oxide film and formation of initial flaws are topics of numerous research and are not fully understood till now [5,6,7].

It should be noted that welded joints on stainless steels may be a serious problem due to possible corrosion damages caused most frequently by pitting, but also other mechanisms such as crevice corrosion, stress corrosion cracking, microbiologically influenced corrosion, intergranular corrosion may be encountered. Some of mentioned phenomena, despite the different mechanism of damaging, can have appearance that resembles pitting corrosion. The presence of chloride have severe negative influence to all localized corrosion phenomena.

2.0 REVIEW OF STAINLESS STEEL CORROSION CASES

Corrosion damages of stainless steel structures are generally localized and limited to area of welded joint and are mostly caused by:

- microstructural or surface changes within the weld joint area (caused by heating during welding)
- incorrect selection of base and/or filler material for given corrosion environment
- inappropriate welding conditions
- inappropriate design of welded joint
- residual stresses in the area of the welded joint
- inappropriate subsequent surface treatment of the welded joint area.

Many cases of corrosion damages that occurred on welded structure made of stainless steels in actual service environment additionally indicate extreme importance of mentioned factors upon total corrosion resistance, and particularly for resistance to local corrosion phenomena. Several examples that are given in this paper, demonstrate in some cases questionable corrosion resistance of stainless steels. Furthermore they illustrate how sometimes various forms of corrosion mechanisms interact in damaging processes.

2.1. Pitting & stress corrosion of stainless steel water heaters

Water heaters for home boilers were made from longitudinally welded austenitic stainless steel pipes EN 1.4301 (AISI 304). The corrosion damages at first appeared after several days of service in form of pitting, especially in the area of longitudinal weld joint (figure 2-1). In most cases, such extremely destructive processes occur due to simultaneous action of several factors stimulating local corrosion. Beside the chemical composition of steel, various inhomogeneities have effects upon corrosion resistance. These differences may be in metallurgical structure, discontinuities in passive layer, occurrence of crevices and deposits on surfaces such as carbonates, differences in aerating and concentration of reacting agents, differences in temperature of certain areas of metal surfaces, etc. Combined action of listed factors lead to fast and severe corrosion damages. Afterwards, more corrosion resistant steel was selected for this purpose –

type EN. 1.4571 (AISI 316Ti) and after few months of exploitation heaters were again damaged, this time by stress corrosion cracking (SCC) which completely destroyed material (figure 2-2). Austenitic stainless steels are, at elevated temperatures very susceptible to this form of corrosion. In both cases incorrect selection of the base metal was the cause of corrosion.

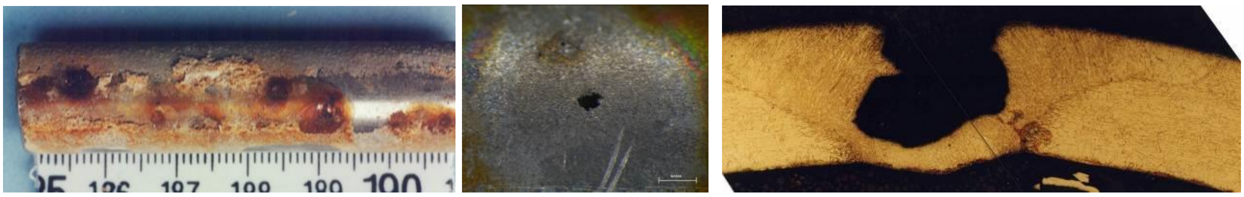


Figure 2-1: Pitting corrosion on sheathing tubes of heater, AISI 304, water, after several days.

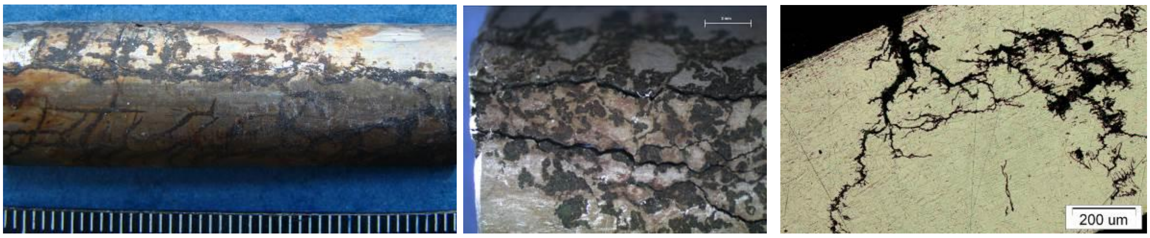


Figure 2-2: Stress corrosion cracking on sheathing tubes of heater, AISI 316Ti, water, after several months.

2.2. Pitting corrosion of stainless steel welded joints in desalinization plant

After only few months of exploitation, on the parts of the desalinization plant for brackish water (salinity up to 3500 mg/L) made from stainless steel intensive corrosion occurred in the area of welded joints causing leakage. Testing of chemical composition of used materials by use of XRF method have shown that pipeline was made of two types of austenitic stainless steels – segment with sealing ring was made from type EN 1.4372 (AISI 201) and the rest of the pipeline from steel EN 1.4404 (AISI 316L). Corrosion damages appeared on welded joints on both materials, but X-ray testing (figure 2-3) as well as macrostructural examination (figure 2-4) showed that parts made from type EN 1.4372 (AISI 201) have suffered more corrosion damage which is, of course, consequence of lower levels of alloying elements and the absence of Mo in comparison with the steel EN 1.4404 (AISI 316L). Both used steels have insufficient resistance to waters with this levels of chlorides, and corrosion was also accelerated in the weld joints area because heat tints caused by heat input during welding were not completely removed. By specifying more corrosion resistant stainless steels (for example superaustenitic or duplex stainless steels), correctly welded and cleaned, or by use of other materials, like polymer pipes (which was implemented during reconstruction) this damage would be prevented and associated costs avoided.

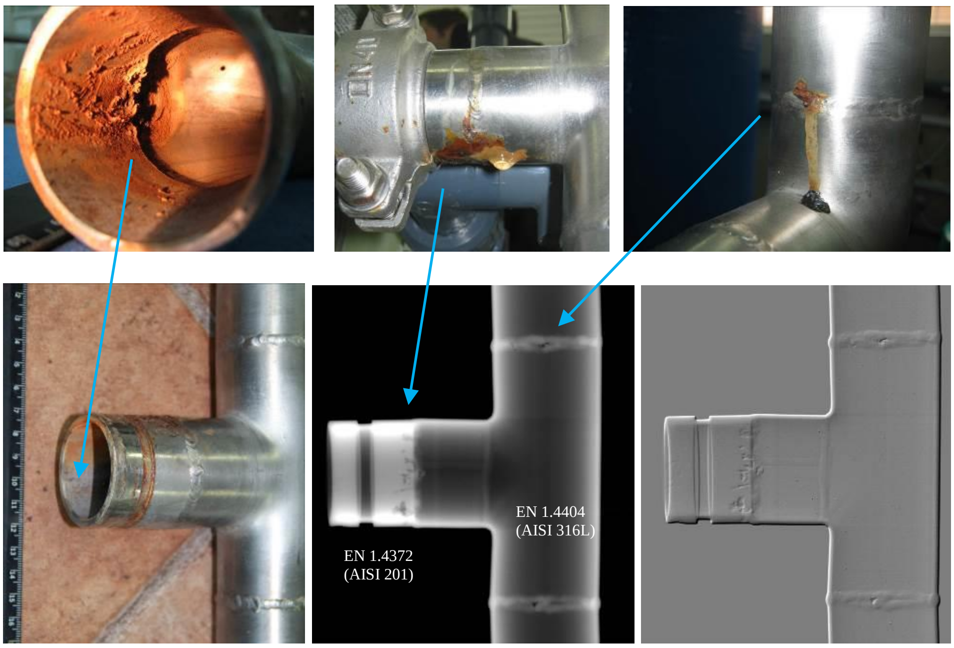


Figure 2-3: Visual examination, results of X-ray testing and X-ray 3D view. Corrosion damages are clearly visible in the weld joint areas and are more intensive on the part made from steel EN 1.4372 (AISI 201).

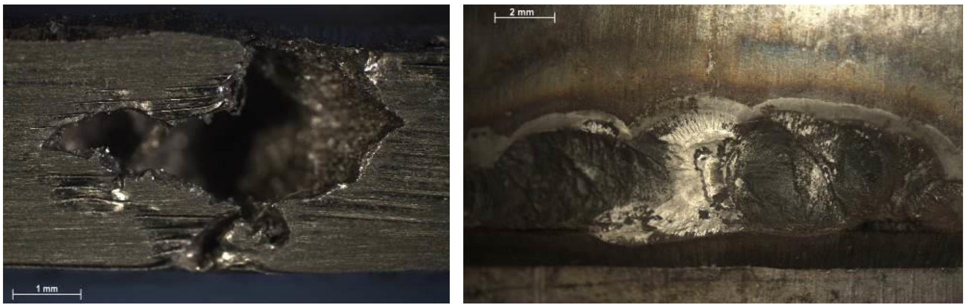


Figure 2-4: Undercutting pitting (left) and surface of the weld joint with heat tints not removed (right).

2.3. Crevice corrosion of heat exchangers installed on ships

Heat exchangers ware made of austenitic stainless steel EN 1.4404 (AISI 316L) and after few weeks during which they were exposed to sea water severe corrosion occurred on the heat exchanger pipes. Damages were located in the area of contact between tube and tube wall and the longitudinal weld seam was dominantly attacked by corrosion (figure 2-5). Character of damages indicate influence of the design solution of tube-to-tube wall joint. In such designed joint, which is by its form crevice, easy accumulation of foreign matters and aggressive components (chlorides) and their retention is enhanced. In the same time, this crevice area is depleted in oxygen reducing the ability of passive layer to recover (repassivate) and resist corrosion.

Figure 2-5: Crevice corrosion damages of heat exchanger pipes in the area of contact with tube wall. Longitudinal weld seam is completely destroyed.

2.4. Crevice corrosion of plate heat exchangers

After few months of exploitation severe corrosion with complete perforation occurred on plate heat exchangers made from austenitic stainless steel EN 1.4404 (AISI 316L) installed in hydroelectric plant located on the river close to sea coast causing rise in generators lubricating oil temperature and plant shutdown. Although raw water with low chloride levels (~60 ppm Cl^-) was used during plant operation, when plant was out of the operation, because of the design of water inlets, sea water with high chloride levels (up to 30000 ppm) was able to periodically enter the system. This caused localised corrosion damages on most sensitive areas of exchanger plates – in localities which are in contact, i.e. in crevices between two plates (figure 2-6). Used grade of stainless steel is not resistant in waters with such a high chloride content, and use of titanium heat exchanger plates instead of stainless steel plates would be a better solution.

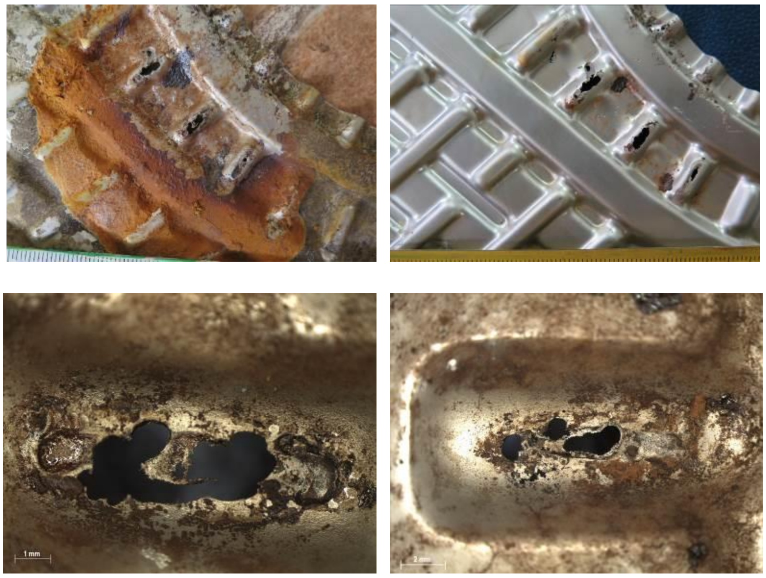
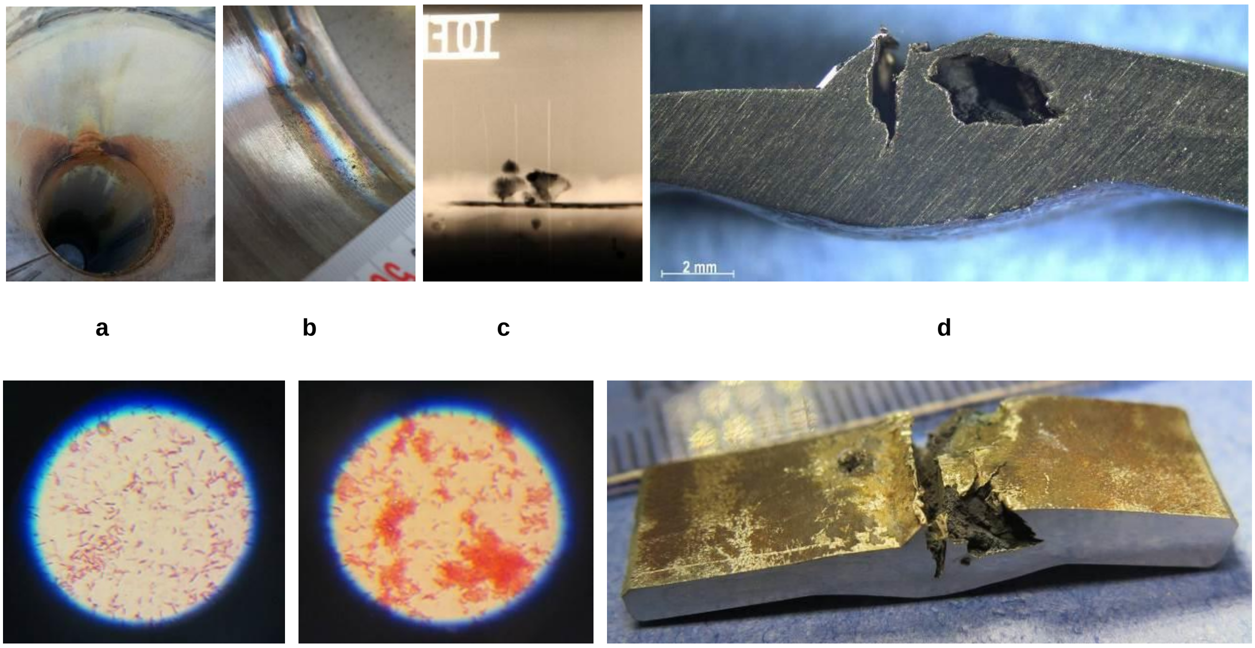


Figure 2-6: Crevice corrosion damages of heat exchanger plates.

2.5. Crevice – favourite site for microbiologically influenced corrosion: water pipelines in underground parking garage

Stainless steel (EN 1.4571, AISI 316Ti) water pipelines in underground parking garage suffered extensive corrosion in the weld joints areas after only few months of use. The system was filled with drinking water, but during the hydrostatic testing raw untreated water was also used. In both cases chloride level in water was lower than 75 ppm to which this type of steel is corrosion resistant. The conducted failure analysis established that damaged welded joints were of insufficient quality because weld root was not completely melted thus creating crevice in which microbiologically influenced corrosion (MIC) started resulting in numerous pits which perforated the material. Additionally weld joints were not cleaned after welding (heat tints were not removed) which additionally lowered overall corrosion resistance (figure 2-7). If the welds were correct (completely melted) and afterwards cleaned (like other welds on the same piping system which were undamaged) colonization of microorganisms would be prevented, passive state maintained and corrosion would be avoided.



a b c d

e f g

Figure 2-7: Review of results: a - corrosion products and tubercles in the weld joint area
b - heat tints in the weld joint area
c - X-ray testing – incomplete penetration and pitting
d - macrostructure of the damaged joint
e and f – aerobic and anaerobic bacteria in corrosion products (1000×)
g – intensity of corrosion process is clearly visible.

2.6. Microbiologically influenced corrosion of stainless steel water tanks in firefighting vehicles

On several firefighting vehicles on the water tanks made from stainless steel EN 1.4301 (AISI 304) the corrosion damages which caused the leakage from the tank appear in couple of months during the guaranty period. Firefighting system in vehicles consists of water tank, foam tank and suitable equipment for mixing and distribution of agents for extinguishing fire. Damages are found only in water tanks. On other equipment there were no damages. Firefighting vehicles were located in various parts of the world, and on all of them water tanks were filled with raw, untreated water.

Corrosion damages have led to leakages on the side and floor walls of water tanks (figure 2-8), and the corrosion deposits were found primary in area of welded joints and bolt joints. Beside the corrosion deposits and tubercles, characteristic discolorations of stainless steel surfaces not caused by welding were visible (figure 2-9).

Figure 2-8: Water leaking on outside wall of the tank (left) and leaking in the area of welded joint on the bottom of the tank.

Figure 2-9: Corrosion damages in the area of welded joints, crevices and edges with discoloration of the surface and characteristic deposits in the form of tubercles.

Although welded joints have correct structure (figure 2-10) and were cleaned after welding (heat tints were chemically removed) severe localised corrosion occurred in weld joint area in the form of pitting. Corrosion processes have ‘depth propagating’ character – there is a little initial damage but the bulk of the corrosion damage is inside the material (undercutting form of pitting), going sideways and in the depth (figures 2-11). Corrosion processes were more intensive in the area of the melting line (figure 2-12), and there are no corrosion damages of the base material away from the welded joints.

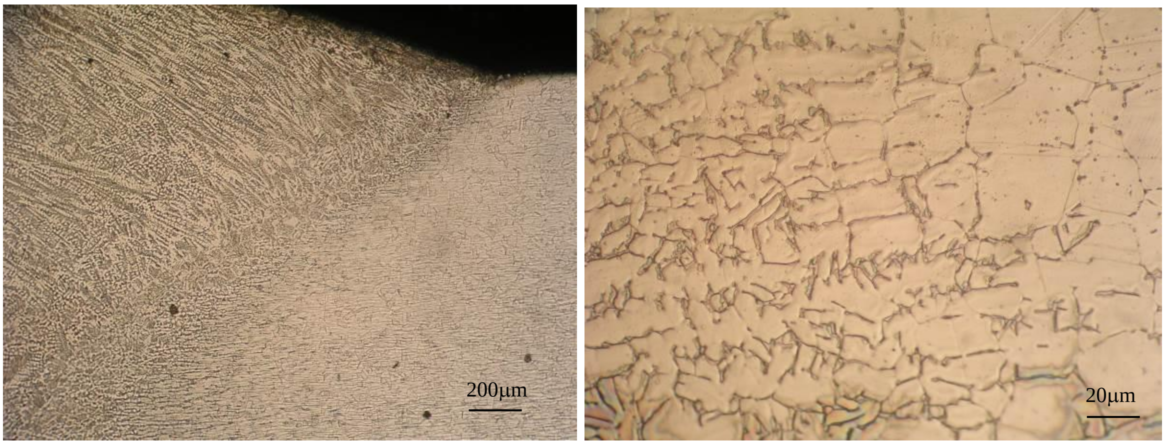


Figure 2-10: Correct structure of the welded joint.

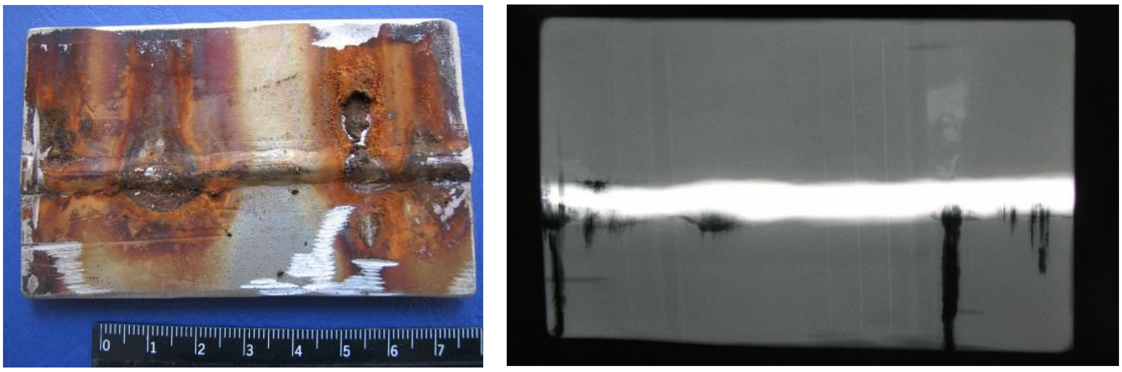


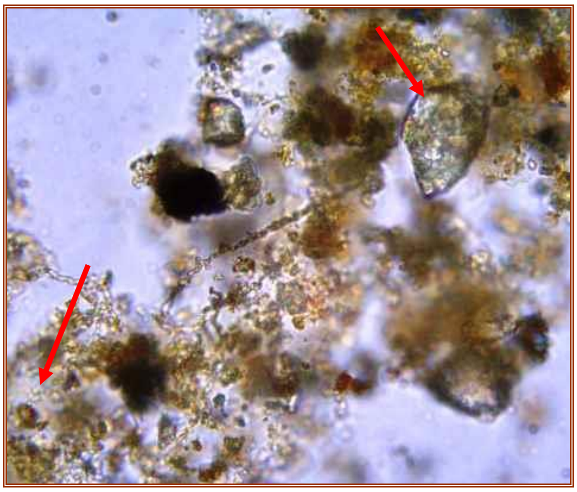
Figure 2-11: Sample of welded joint (with visible residues of tubercles) cut out from water tank of the firefighting vehicle (left) and results of X-ray testing (right).

Figure 2-12: Macro and microstructural pictures of damaged welded joints.

Testing of the water samples showed that the chemical parameters of the water are acceptable regarding the corrosion resistance of the used steel, but microbiological testing of the deposits (tubercles beneath which corrosion occurred) as well as water which was in tanks, showed presence of the aerobic heterotrophic bacteria, which produce organic acid during their metabolism. Furthermore, there were ferrous and manganese oxidation bacteria present, which in the presence of the dissolved oxygen in the water, dissolved ions of Mn and Fe used as source for their growth and expansion (figure 2-13). All mentioned microorganisms, by different mechanisms, are well known to influence corrosion processes on stainless steels. Prolonged stagnant water conditions acted adversely too on the corrosion resistance because this led to colonization of bacteria on the metal surface in the most susceptible areas – welded joints and various crevices. By use of treated water, or agents for disinfection which are appropriate for stainless steels, this kind of damage could be avoided.

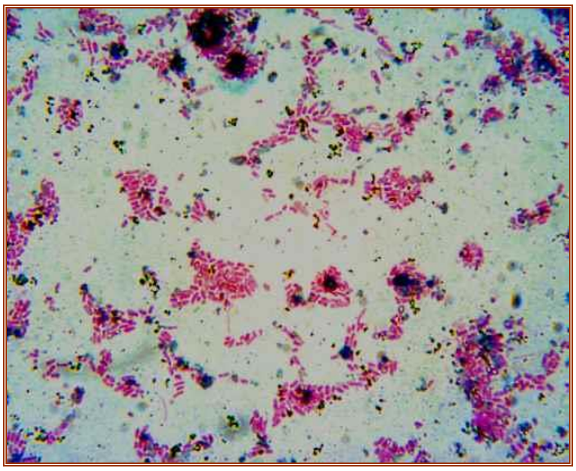
This case, as well as previous one, clearly describe one of the main characteristics of microbiologically influenced corrosion of stainless steels in water: unexpected intensive damage in media (water) which, by its chemical composition (primarily chloride content) is not corrosive to the used grade of stainless steel.

Filamentous bacteria from *Gallionella* family



Deposits of spherical bacteria from *Siderocapsa* family

Mixed cultures of bacteria which belong to *Leptotrix* and *Siderocapsa* family



Bacterial cell from *Leptotrix* and *Siderocapsa* family with beginning of deposition of metal oxides on bacterial cells

Figure 2-13: Results of the microbiological testing of the deposits, magnification 1000×.

2.7. Stress corrosion cracking of a shell of a water heating tank

On water heating tanks which were made of austenitic stainless steel EN 1.4301 (AISI 304) intensive damages – numerous cracks (figure 2-14) which caused leakage of water occurred in few months of exploitation. The tanks were filled with drinking water (low chloride content) and the temperature of water was around 80°C. Tanks were made by welding.

The conducted failure analysis established that damages were caused by intensive transgranular stress corrosion cracking (SCC) (figure 2-15), the phenomena to which austenitic stainless steels are susceptive at elevated temperatures especially if residuals stresses made by manufacturing processes (welding, deforming) are present as in this case. If they were removed by proper heat treatment after manufacturing, or, better, if the ferritic or duplex stainless steels were used, which have greater resistance to SCC, this type of corrosion would be prevented.

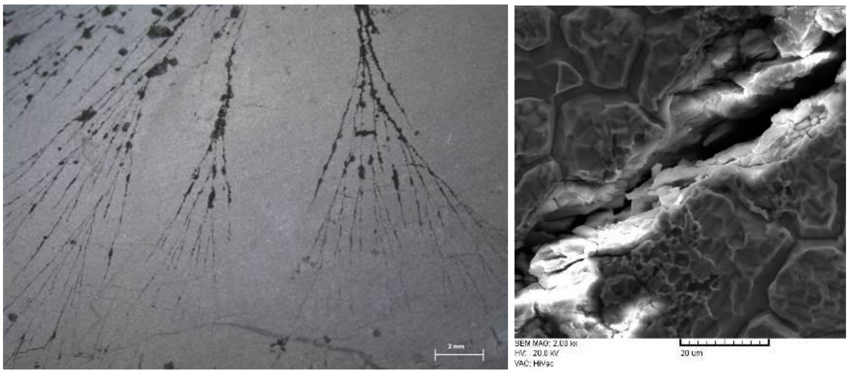


Figure 2-14: Cracks on the surface of the base material (left) and SEM image of the surface (right).

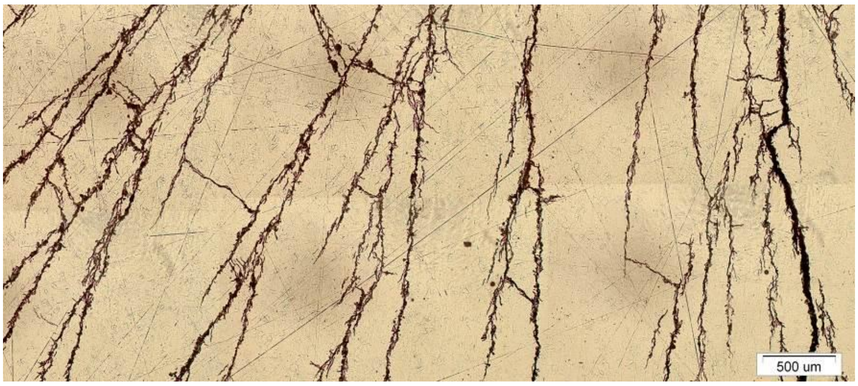


Figure 2-15: Microstructure of failed tank – numerous transgranular cracks.

3.0 CONCLUSION

Corrosion resistance of structures made from stainless Cr-Ni steels in most cases depends on understanding mechanisms at which their corrosion resistance properties are based, i.e. on importance to maintain the passivity, especially when manufacturing structures by welding.

Localised corrosion damages of stainless steel structures are very often intensive and abrupt leading to unexpected failures and shutdowns of plants and installation's, or their important parts. These corrosion processes are the main form of corrosion attack on stainless steels.

From presented stainless steel corrosion cases it may be concluded that by proper choice of suitable type of stainless steel for given purpose (environment), as well as by appropriate design solutions, correct welding procedures and subsequent surface treatment for removing heat tints caused by heat input during welding and restoring passive state, the risks and hazards from corrosion damages could be greatly minimalised or avoided. In this way, stainless steel structures can maintain their basic property – high corrosion resistance for long periods of use without failures.

REFERENCES

[1] Dilon, C.P.: Corrosion resistance of stainless steels, Marcel Dekker, Inc., New York, 1995.

[2] Sendriks, A.J.: Corrosion of stainless steels, John Wiley & Sons, Inc., New York, 1996.

[3] J.R. Davis: ASM Speciality Handbook Stainless Steels, ASM International, 1994.

[4] S. Lamb: CASTI Handbook of stainless steels & Nickel Alloys, CASTI Publishing Inc., 2000.

[5] Cramer, S.D., Covino, B.S: ASM Handbook, Vol 13A, ASM International, 2003.

[6] Jessen, C.Q.: Stainless steel and corrosion, Damstahl, 2011.

[7] Francis, R: Stainless steels, EFC Publication: The corrosion performance of metals for the marine environment, EFC, 2012.