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Failure of austenitic stainless steel tubes during steam generator operation

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ABSTRACT

Purpose: of this study is to analyze the causes of premature failure of steam generator coil made of austenitic stainless steel. Special attention is paid to corrosion damage processes within the welded joints.
Design/methodology/approach: Examinations were conducted several segments of the coil made of seamless cold-formed pipes Ø 23x2.3 mm, of austenitic stainless steel grade X6CrNiTi18-10 according to EN 10088-1:2007. The working time of the device was 6 months. The reason for the withdrawal of the generator from the operation was leaks in the coil tube caused by corrosion damage. The metallographic investigations were performed with the use of light microscope and scanning electron microscope equipped with the EDX analysis attachment.
Findings: Examinations of coil tubes indicated severe corrosion damages as pitting corrosion, stress corrosion cracking, and intergranular corrosion within base material and welded joints. Causes of corrosion was defined as wrong choice of austenitic steel grade, improper welding technology, lack of quality control of water supply and lack of surface treatment of stainless steel pipes.
Research limitations/implications: It was not known the quality of water supply of steam generator and this was the reason for some problems in the identification of corrosion processes.
Practical implications: Based on the obtained research results and literature studies some recommendations were formulated in order to avoid failures in the application of austenitic steels in the steam generators. These recommendations relate to the selection of materials, processing technology and working environment.
Originality/value: Article clearly shows that attempts to increase the life time of evaporator tubes and steam coils by replacing non-alloy or low alloy structural steel by austenitic steel, without regard to restrictions on its use, in practice often fail.
Keywords: Corrosion; Destruction of austenitic steel; Welded joints; Heat affected zone (HAZ)

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1. Introduction

Attempts to increase the life time of steam boiler equipment such as evaporator tubes and steam coils by replacing non-alloy or low alloy structural steel by austenitic steel, without regard to restrictions on its use, in practice often fail. Austenitic stainless steels have much higher resistance to general corrosion than low alloy steel, but the root cause of risks of austenitic steel use is local corrosion (stress corrosion, pitting, intergranular corrosion) [1-9], which may be accelerated especially in the areas of welded joints [1-3].

Traditionally steam boiler evaporator tubes and steam generators coils are made of unalloyed or low alloy steel grade 16Mo3, 13CrMo4-5 (16 M, 15 HM). Temperatures of these elements are not high hence the structure degradation and creep failure is not a threat. Limitation of working time is affected by corrosion processes. Corrosion of pipes may proceed from the outside, where the main factor is the atmosphere of combustion gases and from the inside of pipe, where electrochemical corrosion take place. Corrosion processes of pipes from the outside are less common and usually associated with overheating or adverse burning conditions (such as substoichiometric combustion in low-emission coal-fired boilers). More likely damage processes act from the inside of the tubes, where the environment is water or steam-water mixture. Corrosion resistance in these conditions depends on the ability to create a sealed, protective layers of magnetite. Formation of such layers is favored by high purity water supply, with the limited amount of limescale forming ions and minimum concentration of chloride ions. In unfavorable conditions, such as local inhomogeneities of the pipe surface, sulfide inclusions in the steel, increased chloride content in water, a porous layer of magnetite may arise. Porous layers do not protect pipe surface against corrosion and under such conditions a rapid thinning of the pipe (uniform corrosion) and more rapid deterioration caused by pitting corrosion is observed [6,8,9].

Replacement of non alloy or low alloy steels by stainless austenitic steels, may seem to be the best option if the increased cost of the investment result in the extended operation time of the steam generator. But there is no certainty that this is such a simple relationship.

Initiation of corrosion at non alloy steels are related primarily to water quality, while corrosion resistance of austenitic stainless steels, beyond the water quality, depends on the durability of the passive film and microstructure stability. The destruction of the passive film on austenitic steel surface and the lack possibilities of its reconstruction cause a very rapid progress of localized corrosion. In such conditions the life time of the austenitic steel installation is often shorter than if it was made of low alloy steel [1].

Protection against corrosion of evaporator tubes begins with selecting the type of steel at the design stage. The primary factors to be taken into account are the type and concentration of aggressive ions in the work environment and the temperature of the corrosion medium. Secondly, the strength characteristics, type of processing and welding technology should be taken into account [10].

Corrosion resistance of austenitic stainless steels is not the same for all grades and depends on the participation of chromium and nickel in steel's chemical composition [11-14]. Chromium content of 15 to 25% and nickel from 8 to 20% provide a stable microstructure and corrosion resistance of the steel. In addition to chromium and nickel other alloying elements such as Mo, Ti, Nb, Si, Cu can effectively improve the corrosion resistance of austenitic stainless steel under certain conditions. Increasing steel's resistance to intergranular corrosion is achieved by lowering the carbon content to less than 0.03% (with 18% Cr [15]), or carbon bound into carbides by the addition of titanium or niobium. Additions of molybdenum and nickel increase steel's resistance to pitting and crevice corrosion by increasing the stability of the passive layer and in this way increase resistance to stress corrosion cracking in environments containing chlorides.

Austenitic stainless steel welds are areas with differential microstructure and sometimes differential chemical composition. These areas may have different electrochemical potentials and create a local galvanic cells. It is known that the weld can not have a lower electrochemical potential than the parent material, because the smaller surface area exposed to the aggressive environment will rapidly rust. However weld area may become an anode due to the occurrence of oxide scale after welding. It is therefore necessary to clean the joints after welding in order to remove oxide layers, discolorations, and allow repassivation of the surface. Irregularities in the weld geometry (craters, lack of fusion) form depressions where crevice corrosion can occur, hence they should be carefully avoided [3,14,16].

Despite a very good weldability of austenitic steels, the resistance to intergranular corrosion at weld area can be drastically reduced due to the so-called sensitization. Hot cracking can also occur along grain boundaries in the welds and in the heat affected zone (HAZ) near the fusion line during cooling. Brittleness of the joints is possible for high Cr steels due to the evolution of intermetallic phases of high hardness, such as σ phase, when steel is heated to elevated temperatures [3].

Sensitization is a consequence of the precipitation of chromium-rich carbides $M_{23}C_6$ from supersaturated austenitic phase in the vicinity of the weld. This phenomenon may occur after heating of austenitic steel at 500 to 800°C. Carbides nucleate and grow at grain boundaries forming a nearly continuous net. Due to the fact that these carbides contain at least 60% Cr reduces the Cr concentration in the adjacent austenite to a level below 12%, which results in loss of ability to form passive layers and increase susceptibility to corrosion. Electrochemical dissolution of the layer reduced in chromium can proceed at high velocity in environments to which steel is generally resistant. Therefore, the steels susceptible to sensitization should not be welded [1,14,15].

From the point of view of working environment, the main threats for austenitic steels are: chloride ions of alkali metals (Na, K, Mg), lack of sufficient oxygen to enable the re-passivation of steel, low pH and elevated temperature [1,17,18].

A typical effect of the environmental influence in the steam generators is idle corrosion that occurs in components that are allowed to stand for long periods, such as several days and are not maintained. The remaining water condensate saturated with oxygen or sucked air is the cause of corrosion. Installation can be protected against corrosion by drying with the use of blowing hot air, or filling installation with water containing addition of corrosion inhibitors [2,17].

2. Experimental - characteristics and description of coil damages

The steam generator studied worked with a nominal pressure of 12-16 bar, under outlet steam temperature 160°C. The working time of the device was 6 months, with numerous intermissions in service. The reason for the withdrawal of the generator from the operation was leaks in the coil tube caused by corrosion damage.

The coil is made of seamless cold-formed pipes ∅ 23.0x2.3 mm, of austenitic stainless steel grade X6CrNiTi18-10 according to EN 10088-1:2007 (0H18N10T), which corresponds to AISI 321. Chemical composition determined from the control analysis is presented in Table 1.

Table 1.
The chemical composition of the tested coil tube, wt. %

	C	Si	Mn	Cr	Ni	Ti
X6CrNiTi18-10 acc. to PN-EN 10088-1	max 0.08	max 1.0	max 2.0	17.0 19.0	9.0 12.0	5xC <0.7
Tube ∅ 23x2.3 mm	0.04	0.48	0.88	17.4	8.8	0.31

Inspection and macroscopic observations of the internal and external surfaces of the coil pipe segments revealed circumferential cracks, clusters of small pits, a single topical water spills and significant corrosion damage in the areas of welded joints. Discolored outer surface of the pipe was detected in the form of rusty and very dark coatings. The inner surfaces of tubes were covered with a fairly thick layer of deposits with different color and morphology. The color of deposits was significantly different, from light rust to a very dark, almost black. Figure 1 shows schematically the defect types at observed steam coil pipe.

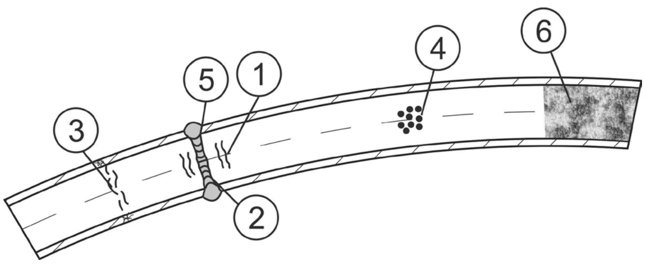


Fig. 1. The observed damages of the steam coil pipe: 1 - circumferential cracks in the HAZ, 2 - depressions, cracks and voids in the root of the weld, 3 - cracks in the areas of stress concentration, 4 - clusters of pits, 5 - corrosion on welding joints defects, 6 - a thick layer of deposits

For investigations sections of pipe were taken from places with visible leaks, clusters of pits and cracks, paying particular attention to welds. In the absence of detailed data about the parameters of the boiler water used in the steam generator operation, the chemical compositions of sediments were taken as an important evidence of corrosion processes.

2.1. Pitting corrosion (deposit corrosion)

It was found that in certain sections of the coil deposits on the inner surfaces of pipes consist of two layers, the outer thick and brittle and inner layer strongly adherent to the wall of the pipe. The thickness of deposits reached 500 microns. So thick layers of deposits were characteristic for sections of the coil where an intense evaporation of water took place.

When deposit thickness inside the pipes reaches 50 microns it is a sign for more accurate supervision over the quality of boiler water. In practice deposits with a thickness of 200 to 300 microns are permitted, but there is a significant risk of disruption of layer, then transport of loose sediments through the medium to the places where they may block the flow [2,16]. The composition of deposits studied by X-ray microanalysis of both layers, showed the presence of aggressive ions (Fig. 2): O, Na, Ca, Mg, Si, K, S.

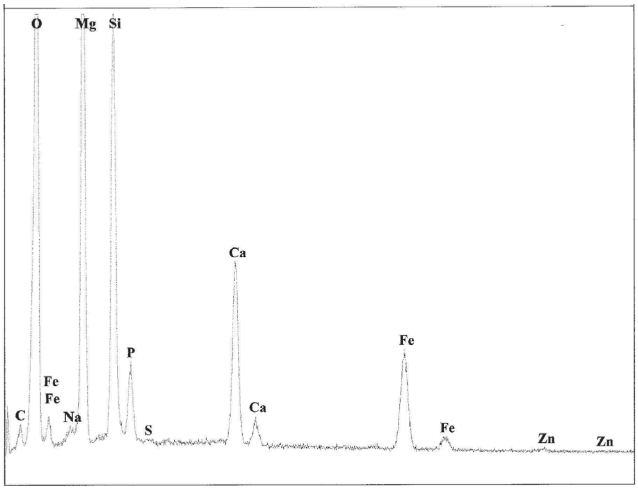


Fig. 2. The results of microanalysis of deposit

The high concentration of Mg and Ca ions in the deposits indicates that water quality monitoring and its treatment was insufficient. Sparingly soluble carbonates and sulphates of calcium and magnesium formed a hard and porous layer called boiler scale. Excessive deposition of minerals, due to disorders of the boiler water composition has a significant influence on the temperature of the pipe wall, which can be overheated (up to 500-600°C) and can deform, which accelerates the initiation of cracks and corrosion processes [2,19]. Corrosion processes are accelerated by water penetrating into the sediment and producing superheated steam. In such conditions all salts can evolve out of the water, even these very soluble, then react with the metal ground and form corrosion products [11,12]. Examples of deposit corrosion as deep pits in the tube wall are shown in Fig. 3.

The cause of corrosion attack in the crevices (in place of welding defects), or under adjacent to the pipe surface sediment is reduced oxygen access, and thus insufficient surface passivity.

A very dangerous phenomenon occurring in porous deposits of boiler scale is development of condensate containing dissolved oxygen and chloride ions and sulfate. There may be a strong reduction of the pH solution under sediments up to a value of 1.0 and in the presence of chloride ions formation of hydrochloric acid, which rapidly accelerates the progress of pitting corrosion. Studies with the use of scanning electron microscope revealed the existence of local spherical particles of different morphology that is more compact than the surrounding sediments, Fig. 4. Microanalysis of the chemical composition of sediments revealed the presence of aggressive ions O, Na, Ca, Mg K, while the spherical particles also contain Cl ions, Fig. 5, which shows selective adsorption of this element and the local increase in concentration.

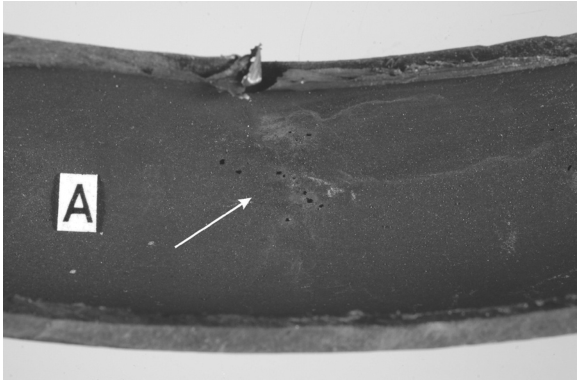


Fig. 3. Pitting corrosion on the inner surface of the tube

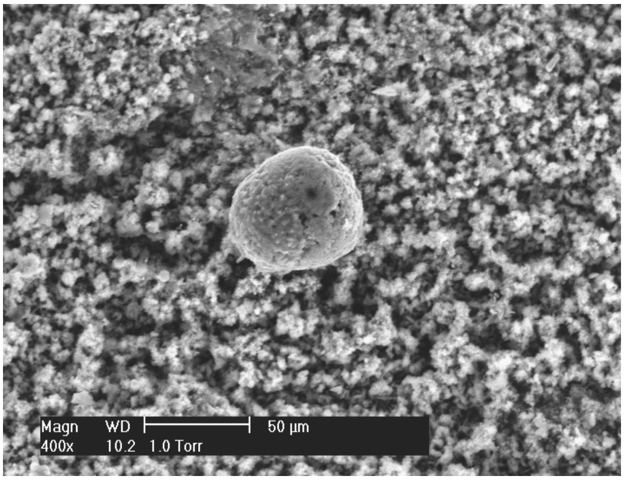


Fig. 4. View of the inner surface of the pipe. The spherical particle of different morphology than the rest of the surface sediment

Aggressive effect of sediments against austenitic stainless steel surface increases particularly strongly with increasing alkali metals chlorides content, which presence in high concentrations were detected. Under such conditions, the rapid progress of local corrosion leads to perforation of the pipe walls and destruction of structural elements what was proven by attempts to repair of perforated pipe walls by welding which ended in failure Fig. 6 a. Application of padding welds on the outer tube side (without whole penetration), caused warm-up to the inner tube's surface and its oxidation. These oxide layers are rich in chromium, which is taken from the steel matrix adjacent to the oxide layer. This process depletes the chromium in metal surface and consequently reduces the corrosion resistance [16].

The rapid progress of corrosion on the inner tube surface under padding welds was detected, Fig. 6 b. Probably padding welds were performed without the simultaneous protection of internal surfaces of tubes with an inert gas.

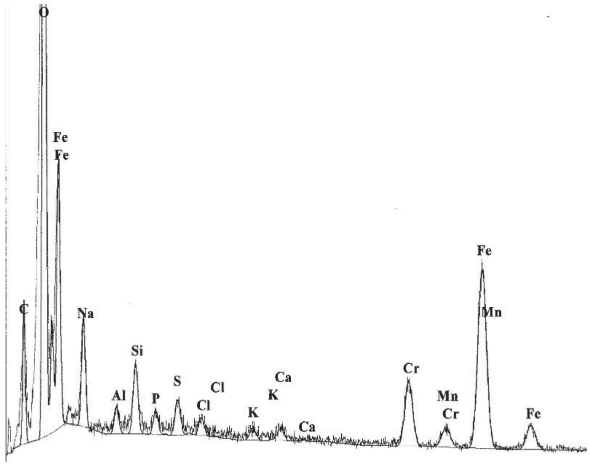


Fig. 5. The results of microanalysis of sediments in the form of spherical particles with a higher concentration of chlorine, as shown in Fig. 4

Intense pitting corrosion was also found on the inner surface of pipes under welds connecting coil stiffeners. Figure 7 b clearly shows two pitted areas under the welded joints where the inner surface of the pipe is heated to high temperatures.

a)

b)

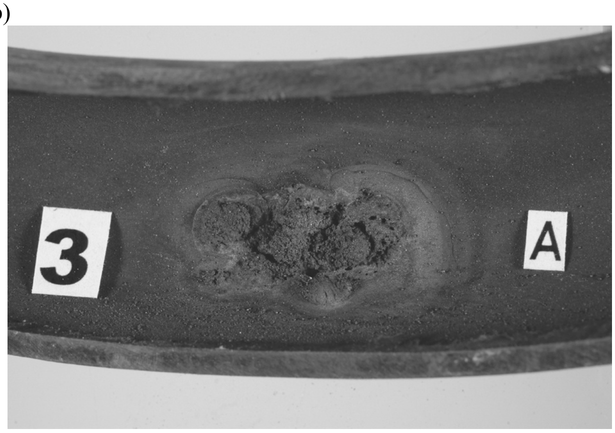
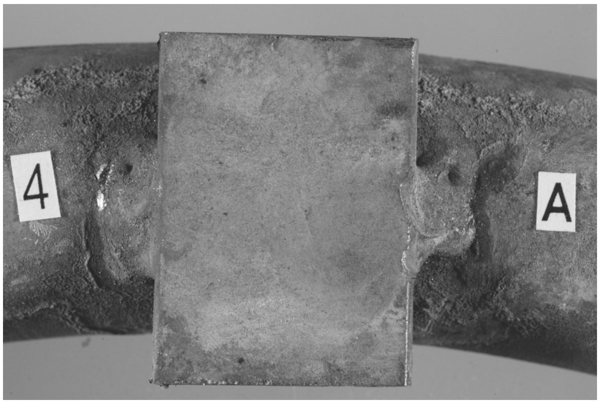


Fig. 6. a) The padding weld on the outer tube surface; b) the view from the inside - the progress of corrosion processes

a)



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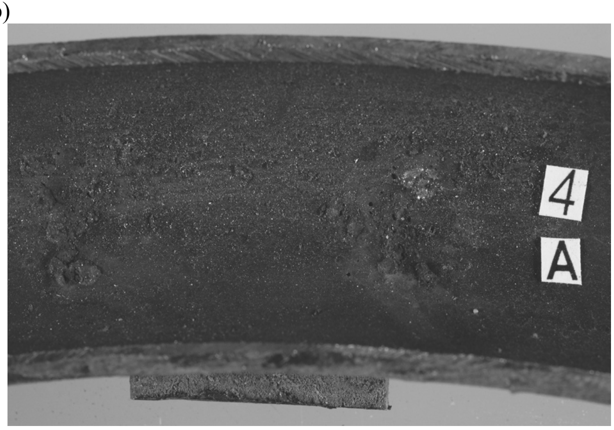


Fig. 7. Stiffener welded to the pipe coil, a) outer surface, b) the inner surface attacked by pitting corrosion

2.2. Intergranular corrosion

Many cracks were observed in the welded joints area. These cracks propagated parallel to the joints at heat affected zone Fig. 8.

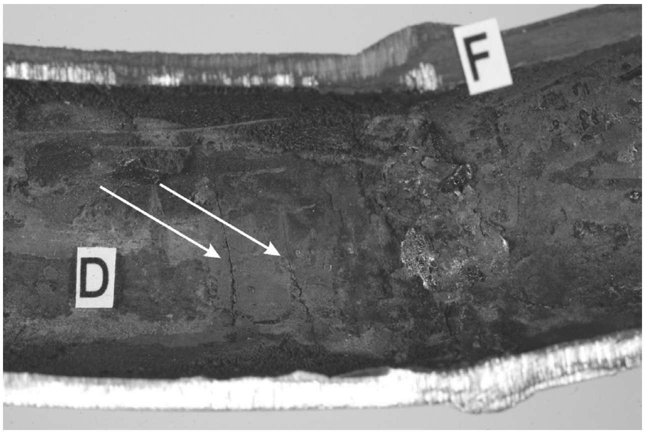


Fig. 8. Cracks in the HAZ of the circumferential weld

Initiation of cracks come from the inside of the pipe. Metallographic examination of pipe wall sections showed that crack initiated in the HAZ propagate in different directions and the development of cracks in some cases has been blocked and changed direction at the fusion line. Figure 9 shows crack of considerable thickness, it is associated with subsequent reactions inside the crevices and electrochemical dissolution of cracks walls.

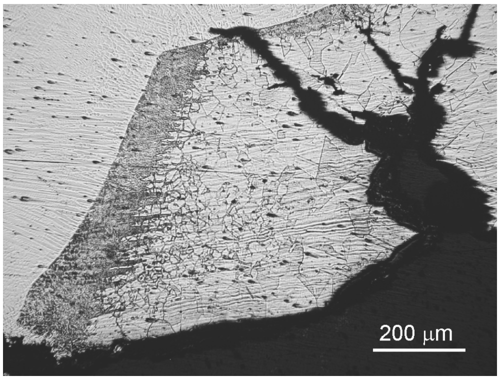
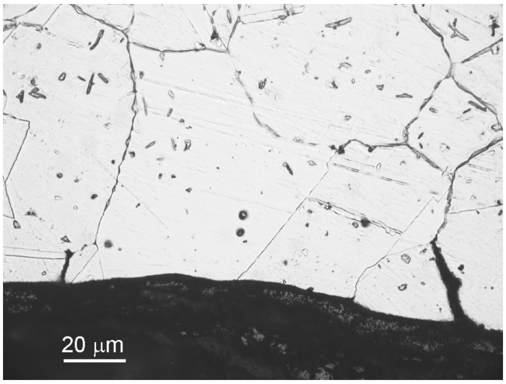


Fig. 9. The propagation of cracks initiated by intergranular corrosion

a)



b)

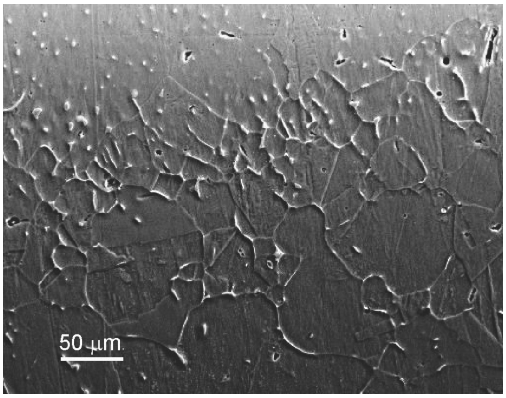


Fig. 10. The structure of sensitized zone of austenitic stainless steel, a) light microscope image, b) SEM image - visible carbides net at grain boundaries of austenite

A detailed analysis of cracks showed their intergranular propagation along the austenite grain boundaries which were decorated by chromium carbide precipitates. Figure 10 shows the microstructure of sensitized HAZ zone, with clearly visible coagulated carbides located mainly at the austenite grain boundaries, forming an almost continuous net. Such a distribution of carbides in the HAZ was also observed by scanning electron microscope, Fig. 10 b. This was confirmed by EDX field qualitative analysis of the chromium distribution and is direct evidence of steel sensitization in the HAZ area where the temperature reached 500 to 800°C.

2.3. Corrosion within the welded pipe joints

Numerous corrosion damages were observed in the root of welded circumferential joints of the coil. The predominant type of corrosion was pitting and crevice. There are several reasons for the progress of corrosion in the analyzed area. Slots, root reinforcements, and porosity were observed at incorrectly formed welds, Fig. 11. Welds were performed with the use of TIG method probably without backing gas protection. Root of the welds and heat affected zone areas were subject to intense oxidation, which after a short operation time resulted in a degradation of the passive layer and initiate corrosion.

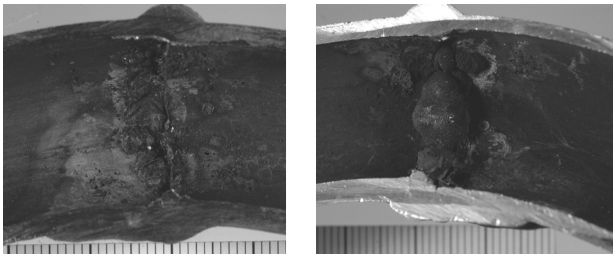


Fig. 11. Improper shape of the root of the pipe welds

2.4. Stress corrosion cracking

Many cracks were revealed in the parent material of the coil. The cracks were located perpendicular to the tube axis passing through the entire thickness of the pipe wall and causing leaks. The places of crack initiation were pits on the inner surface covered with a dense sludge of corrosion products. Cracks have characteristic branching shape and transgranular propagation typical for stress corrosion. Figure 12 shows the fissure of stress corrosion cracking filled with corrosion products. The results of microanalysis of corrosion products and deposits are shown in Table 2 and as EDS spectra at Fig. 13.

High concentrations of Cr and the presence of Ti were detected in the pit, which is the result of the destruction of the passive film. The composition of corrosion products in the pit, show a much lower content of Cr and Ti, (Table 2).

Stress corrosion cracking is preceded by a certain incubation period for crack initiation, during which the rupture of the passive film occurs and which is typically much longer than the subsequent propagation of cracks [1]. So, sufficiently high concentration of chloride ions in certain areas of the environment, high temperature, the presence of oxygen ions in the feedwater, high level of tensile stresses received from welding, cold bending and stresses generated during the operation, create conditions for the development of stress corrosion cracking.

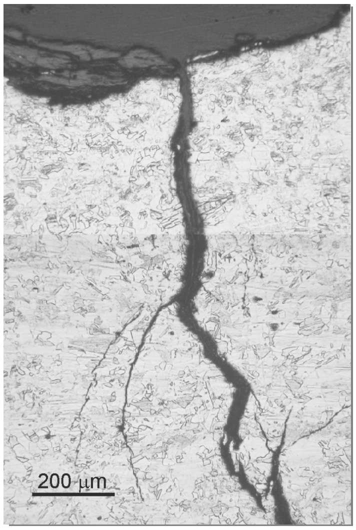


Fig. 12. Transgranular propagation of stress corrosion crack through the pipe wall with characteristic branching

Table 2.
The results of microanalysis of corrosion products and deposits related to stress corrosion

	Chemical composition of corrosion products and deposits, wt. %						
	O Cr	Na Ni	Si Fe	P	Cl	Ca	Ti
In the corrosion pit	22.34 27.16	3.28 1.51	5.80 bal.	1.02	0.42	1.49	0.53
In the main gap of crack	20.94 3.96	4.03 2.38	11.75 bal.	0.44	0.50	2.04	-

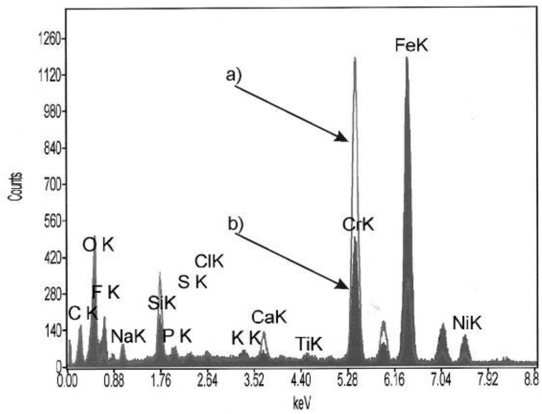


Fig. 13. The results of microanalysis of corrosion products and deposits, a) in the pit from which was initiated stress cracking (unfilled), b) in the main gap of crack

3. Summary

The coils of steam generators are working in difficult and changing conditions of thermo-mechanical loads exposed to corrosive environment. They may be subject to failure due to the high temperature exhaust gases corrosion from the outside as well as steam-water corrosion and idle corrosion on the inside. At longer operation times - the processes of creep and fatigue corrosion can take place [1-3, 6,9,17].

With regard to the tested coil consideration of corrosion fatigue and creep is not justified because of the relatively short lifetime, of 6 months, and a significant number of outages.

Replacing the coil material from low-alloy steel to austenitic stainless steel, which was intended to bring a profit in the form of extended operation time, proved to be ineffective. Short working time of the tested coil is an effect of a few factors that can be divided into those relating to the choice of material and technology and operating conditions.

Selection of austenitic stainless steel for steam coil should be regarded as proper, but also one should be aware of the limitations of this group of steels. Under certain processing procedures and service conditions this steels can demonstrate a long-term reliable operation. However, the majority of steam boilers or steam generators are produced from low-alloy steels. It is mainly connected with the operating conditions. In devices with closed and tightly controlled circulation of water the austenitic stainless steels can be successfully used, such as evaporator tubes in U.S. coal power plants. This use is profitable even assuming the higher cost of material, design and implementation, and worse physical properties, especially thermal conductivity of austenitic steels. In steam generators it is more difficult to control the quality of water supply and this is usually the reason for operating problems.

4. Conclusions

Based on the obtained research results and literature studies the following recommendations can be formulated in order to avoid failures in the application of austenitic steels in the steam generators. These recommendations relate to the selection of materials, processing technology and working environment.

- The most important issue is the choice of austenitic steel grade suitable for the working environment in certain chloride concentration and temperature. It should take into account the possibility of sudden, uncontrolled increases in the concentration of aggressive ions, which in the case of installation of significant value should be protected by the choice of steel grade with a higher resistance to corrosion. In the case of coil for steam generator, it could be a grade of steel with molybdenum and reduced carbon content, such as AISI 316L (X2CrNiMo17-12-2).
- In order to avoid intergranular corrosion austenitic steels with a carbon content below 0.02% should be selected instead of steel stabilized with Ti or Nb, which does not fully protect against such corrosion.
- Strictly use the backing inert gases for welding. The use of welding in the test case without forming gases resulted in oxidation of the inner surface of pipes and abnormal formation of the weld root, and in consequence, the porosity cracks and potential sites for corrosion development.
- Avoid excessive stiffening of the tubes. Welding of the coils stiffeners should be performed with minimal heat input.
- It is advised to apply stress relief annealing after cold bending of the tubes to remove internal stresses.
- Cleaning the inner surfaces of the coil tube surface passivation of the surface should be performed after welding.
- Water quality monitoring. Keep the feed water pollution at the appropriate level.
- Flooding of the evaporator tubes with water or completely remove water and drain installation at each stopping installation.
- Procedures for the periodic removal of scale in the coils should be supplemented by passivation of the pipe.

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