UDK 620.19:669.14.018.8:52-14
Professional article/Strokovni članek

ISSN 1580-2949
MTAEC9, 50(3)461(2016)

DEGRADATION OF AN AISI 304 STAINLESS-STEEL TANK

DEGRADACIJA REZERVOARJA IZ AISI 304 NERJAVNEGA JEKLA

Matjaž Torkar, Irena Paulin, Bojan Podgornik

Institute of Metals and Technology, Lepi pot 11, 1000 Ljubljana, Slovenia
matjaz.torkar@imt.si

Prejem rokopisa – received: 2016-01-28; sprejem za objavo – accepted for publication: 2016-02-10

doi:10.17222/mit.2016.027

Some austenitic stainless steels are sensitive to the stress corrosion cracking (SCC) that appears only localized and with the specific combination of a relatively high internal tensile stress and the presence of corrosion media with chloride ions. The presented results are from an investigation of the leakage from a tank containing medical disinfection liquids. Due to a crevice below the insulation and the presence of condensed moisture, the corrosion pits started to grow on the surface of the tank. These crevice corrosion pits led to the appearance of SCC, which was responsible for the leakage from the AISI 304 stainless-steel tank.

Keywords: tank, AISI 304, leakage, crevice corrosion, stress corrosion cracking, brittle fracture

Nekatera avstenitna nerjavna jekla so občutljiva na napetostno korozijsko pokanje (SCC), ki se pojavi samo lokalno pri specifični kombinaciji relativno velikih notranjih nateznih napetosti in prisotnosti korozijskega medija s kloridnimi ioni. Predstavljeni so rezultati raziskave puščanja rezervoarja z medicinskimi dezinfekcijskimi tekočinami. Zaradi špranje pod izolacijo in prisotnosti kondenzirane vlage, so pričele rasti korozijske jamice na površini rezervoarja. Jamice, nastale pri špranjski koroziji, so omogočile pojav SCC, ki je odgovoren za puščanje rezervoarja iz AISI 304 nerjavnega jekla.

Ključne besede: rezervoar, AISI 304, puščanje, špranjska korozija, napetostno korozijsko pokanje, krhek prelom

1 INTRODUCTION

Stress corrosion cracking (SCC) is a localized form of corrosion that occurs under the simultaneous action of a tensile stress and a corrosive environment such as a chloride. SCC is characterized by fine cracks that can propagate extremely rapidly, leading to failure of the component and, potentially, of the associated structure.[1,2]

Typical for SCC is the conjoint action of stress and a corrosive environment, which leads to the formation of a crack that would not have developed from the action of the stress or environment alone.[3]

Extensive research studies indicate that SCC appears only localized and under a specific combination of three conditions:

- the use of susceptible grades of material,
- a relatively high tensile stress relative to the yield strength (0.2 % proof strength), either from structural loading or present as residual stresses from forming or welding operations during manufacture and installation,
- the presence of a specific aggressive environment with chlorine-containing compounds (for instance by-products of disinfection) that can produce a highly corrosive film, which can lead to SCC.

Some grades of stainless steel, including 1.4301(AISI 304) and 1.4401 (AISI 316), have long been recognised as susceptible to SCC, but generally only above 55 °C. However, failures in swimming pools in recent years occurred at around 30 °C, in highly stressed components that had not been washed by pool water or frequently cleaned.[3] Suitable steels for safety-critical and load-bearing components in a pool hall atmosphere[3] are the grades 1.4547, 1.4529 and 1.4565. All three types of austenitic stainless steels have a high content of molybdenum and nickel, which provide good resistance to chloride SCC.

Several studies were made on the influence of the surface condition of austenitic stainless steel on SCC.[4–6] It was also revealed how highly cold-worked material showed a higher crack propagation rate.[4,5]

A model was proposed for the crack propagation based on brittle fracture, localized oxidation and shearing near the crack tip.[6] In all cases the cracks were initiated at the pitting sites.[7]

The mechanical fracture model of SCC assumes that the crack essentially propagates by dissolution, and then the remaining ligaments fail as a result of mechanical fracture (ductile or brittle). There are several proposed models described by the mechanical fracture model: the film-induced cleavage model, the tarnish rupture model, the tunnel model, the adsorption model and the hydrogen models.

The dissolution mechanism of SCC assumes that the crack propagation is due to active dissolution at the crack tip. The different models under this mechanism are the slip-dissolution model or the film-rupture model and intergranular SCC.[8]

SCC causes a rapid, brittle failure of the steel without any prior indication, and for this reason it is considered to be catastrophic. Several major disasters have been attributed to the SCC of steel equipment, including the rupture of high-pressure gas-transmission pipes, boiler explosions and severe damage to power stations and oil refineries.[8–10]

The SCC propagation mechanisms can be divided into two groups: those which involve embrittlement of the metal due to corrosive reactions (mechanical fracture models) and those in which the cracks grow due to a localized dissolution process.[8]

The disinfection liquid storage tank was part of an industrial washer-disinfector assembly used for cleaning medical equipment and was made of 1.8-mm-thick cold-rolled AISI 304 stainless steel. The whole assembly was in operation for 2 years. Two kinds of liquids were stored in the tank: 1 % of volume fractions of solution of cleaning liquid in demineralized water with pH = 11.3, and 1 % of volume fractions of solution of neutralizing liquid in demineralized water with pH = 2.6.

The aim of this paper is to present a corrosion degradation investigation and the reasons for the leakage from the storage tank.

2 EXPERIMENTAL PART

The samples for the investigation were cut from the wall of the tank, in the corrosion-damaged area where the wall leaks. Metallographic samples of the cross-section of the wall were prepared by a standard metallographic procedure. The samples were observed with a Nikon Microphot FXA light microscope with a video camera and analySIS software. The surface and the cracks were observed using a JSM-6500F FE SEM scanning electron microscope and analysed by EDS (Energy-Dispersive Spectroscopy). The EDS analyses were performed on the corroded internal surface and on the fractures. The base material was analysed using the X-ray Fluorescence (XRF) method.

Figure 1: Corroded outer surface below the insulation
Slika 1: Korodirana zunanja površina rezervoarja pod izolacijo

Figure 2: Local corrosion damage inside the tank
Slika 2: Lokalne korozijske poškodbe znotraj rezervoarja

3 RESULTS AND DISCUSION

3.1 Visual examination

The corroded areas inside and outside the tank under the insulation are shown in **Figure 1** and **Figure 2**. Inside the tank the corrosion damage is limited to the area shown in **Figure 2**, while the corroded area on the outside surface below the insulation is spread much wider (**Figure 1**) and looks more uniform. In addition, the place where the sample material was cut from the tank wall is presented in **Figure 1**.

Inner surface of the tank, shown in **Figure 3,** looks like a general pitting-corrosion attack with some pits joining together to form interconnected pits.

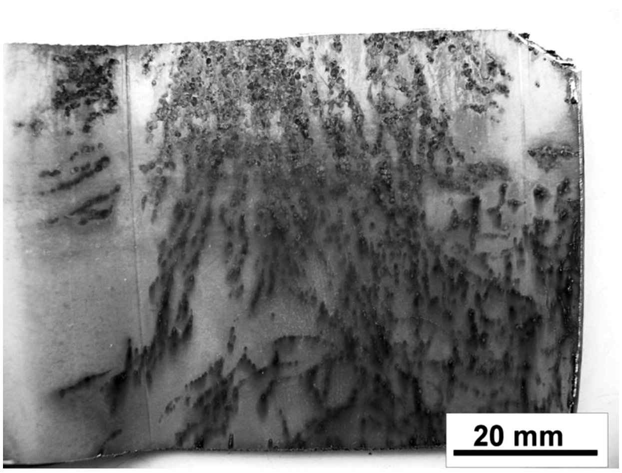

Figure 3: Corrosion damage on the inner surface of the tank
Slika 3: Korozijske poškodbe na notranji površini rezervoarja

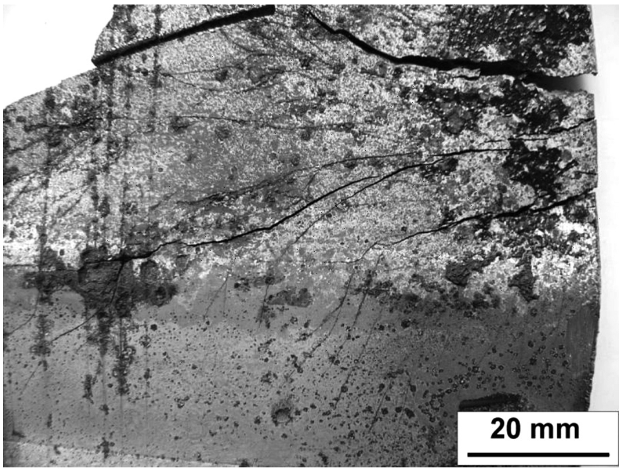

Figure 4: Corroded external surface of the tank with corrosion pits and cracks
Slika 4: Zunanja površina rezervoarja s korozijskimi jamicami in razpokami

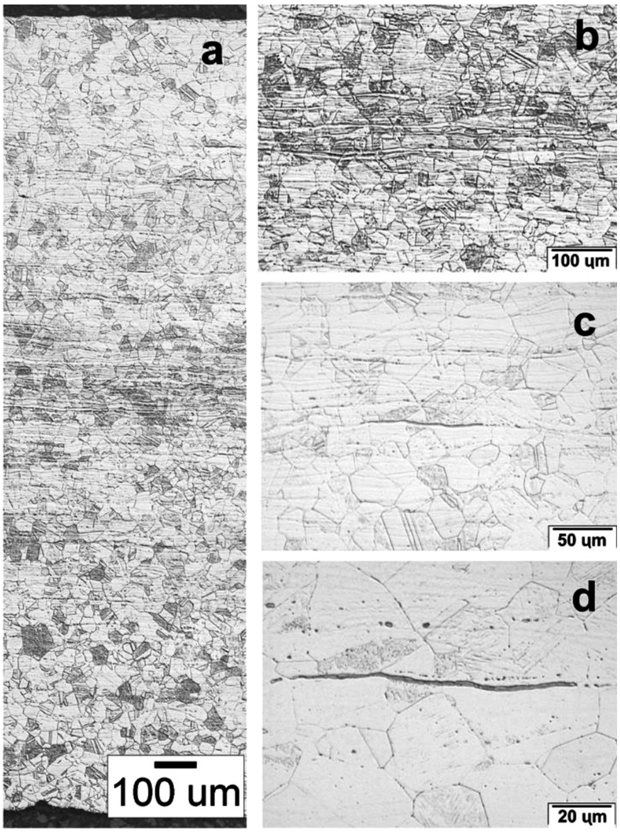

Figure 5: Microstructure of the cross-section of the wall
Slika 5: Mikrostruktura preseka stene

Table 1: Chemical composition of the tank sample in mass fractions (*w*/%)
Tabela 1: Kemijske sestave vzorca rezervoarja v masnih deležih (*w*/%)

	C	Si	Mn	Cr	Ni	Mo	Fe
tank sample	0.07	0.68	1.2	19.2	9.1	–	69.75
AISI 304	Max 0.08	Max. 1.00	Max. 2.0	18–20	8–10.5	–	

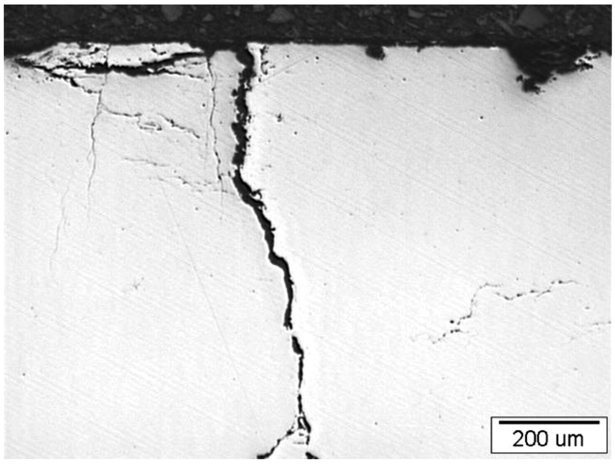

Figure 6: Cross-section of the tank wall
Slika 6: Presek stene rezervoarja

Figure 4 depicts the sample material cut from the tank wall. Corrosion pits due to crevice corrosion and cracks due to stress corrosion are present on the outer surface of the tank.

3.2 Chemical analysis

An XRF analysis was performed on the sample material from the tank. The results of the analysis are shown in **Table 1**.

The sample chemical composition analysis results are in accordance with the AISI 304 grade stainless steel's specification requirements.

3.3 Metallographic examination

During the cutting of the samples for metallography it was evident that the material is brittle in the region of the corrosion and did not resist even a small bending force. In contrast, out of the region of corrosion the

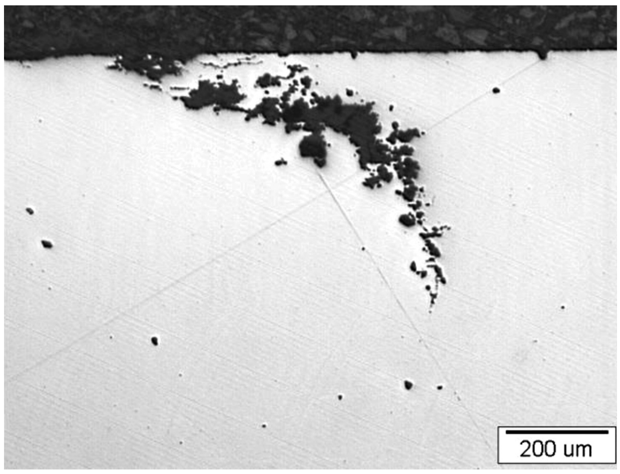

Figure 7: Crevice-corrosion pit
Slika 7: Špranjska korozija

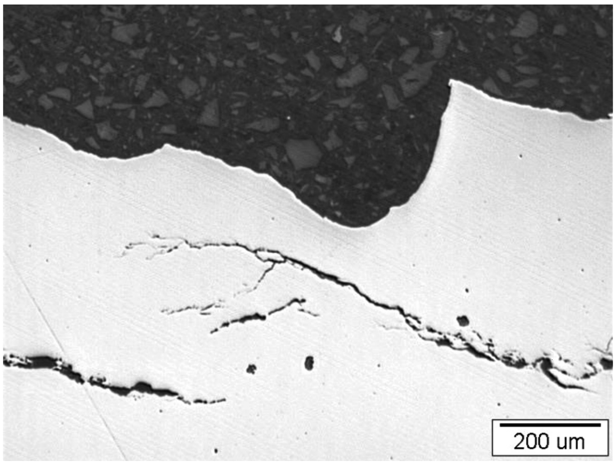

Figure 8: Internal surface pitting corrosion stress corrosion cracks
Slika 8: Jamičasta korozija na notranji površini rezervoarja in napetostne korozijske razpoke

material behaved normally and was bent at an angle of 180° without any damage.

The microstructure of the cross-section in the sound part of the material is presented in **Figure 5a**. In the central part (**Figure 5b**) are the elongated grains. The elongated inclusions of MnS are shown in **Figures 5c** and **5d**, both oriented in the cold-rolling direction.

The cross-section of the degradation area, below the tank insulation, is presented in **Figure 6**. The crack originates from the crevice corrosion on the external surface of the tank.

The presence of condensed moisture in the gap between the insulation and the tank's external surface caused the development of a crevice-corrosion pit shown in **Figure 7**.

The cracks (**Figures 6** and **8**) are typical for SCC and spread through the wall, mostly across the grains (trans-crystalline). Through the wall the cracks caused the leakage of the liquid stored in the tank. The cracks are connected with the pits and the pits act as initiation

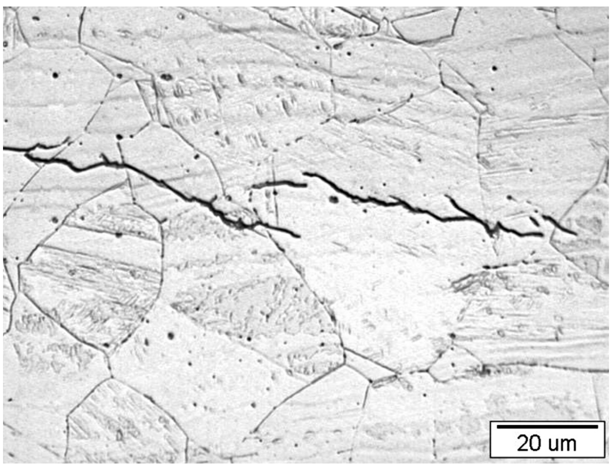

Figure 9: Trans-crystalline crack formed during SCC
Slika 9: Transkristalna razpoka, nastala pri napetostnem korozijskem pokanju

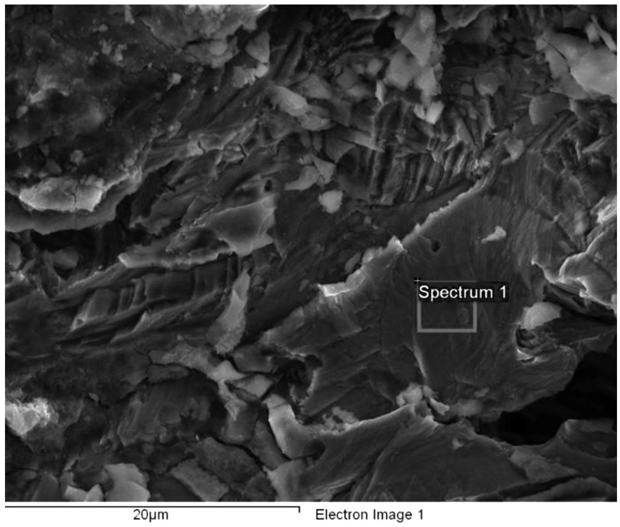

Figure 10: Brittle fracture of the wall
Slika 10: Krhek prelom stene

places for the cracks' formation. We can conclude that the corrosion processes started as crevice corrosion on the external surface below the insulation.

The internal surface of the tank is shown in **Figure 9**. Wide corrosion pits can be seen (**Figure 9**). These pits can be classified as pitting corrosion. Branched stress corrosion cracks are also present.

3.4 Scanning electron microscopy

The brittleness of the material was observed only in the areas damaged by corrosion. The fracture of the wall is brittle (**Figure 10**) and typical for the SCC of stainless steel. The region of the EDS analysis (SEM) is marked as Spectrum 1.

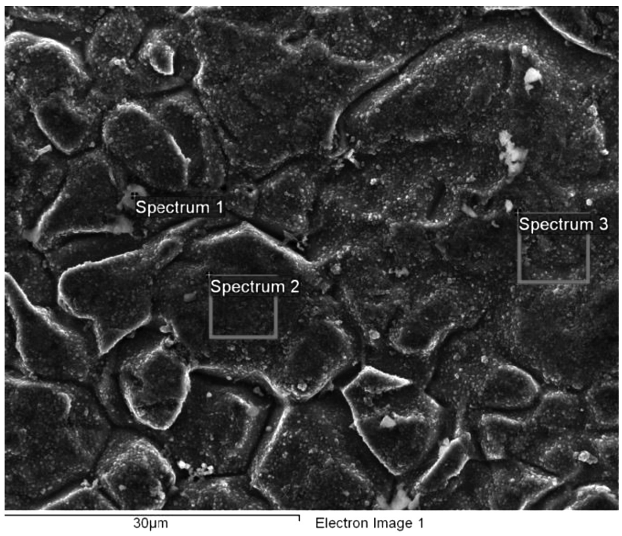

Figure 11: Surface with deep-etched grain boundaries and corrosion products with marked areas of EDS analysis (SEM)
Slika 11: Površina z globoko jedkanimi mejami med zrni in korozijski produkti z označenimi področji EDS-analize (SEM)

The EDS analysis of the fracture surface (**Table 2**) detected the presence of chlorine, which is a regular companion in the corrosion of stainless steels and acts as the main accelerator of the pitting corrosion.

The deep-etched grain boundaries presented in **Figure 11** are due to the pickling of the sheet's surface. The surface is partially covered with corrosion products. The EDS analysis (**Table 3**) of the grain (Spectrum 1) revealed an increased content of oxygen, silicon, chlorine, manganese and nickel. On the other two areas analysed (Spectrum 2 and 3) traces of rust prevailed with contents of iron, chromium, nickel and oxygen. The origin of the chlorine is not known. This chlorine was detected on the corroded external surface as well as on the surfaces of the brittle cracks.

Table 2: EDS analysis of a brittle fracture surface, in mass fractions (*w*/%)

Tabela 2: EDS-analiza površine krhkega preloma, v masnih odstotkih (*w*/%)

Spectrum	Cr	Ni	Si	Mn	Fe	Cl
1	19.24	8.99	0.68	1.14	69.56	0.40

Table 3: EDS analysis of corroded surface (*w*/%)

Tabela 3: EDS analiza korodirane površine (*w*/%)

Spectrum	O	Si	Cl	Mn	Cr	Ni	Fe
1	35.62	0.61	5.78	4.37	5.76	23.14	24.71
2	14.51	0.49		1.08	13.83	6.41	63.69
3	12.92	0.54		1.14	14.46	6.78	64.15

The cracks were formed due to the internal or external stresses or a combination of both in the presence of the corrosion media. It is typical for the cracks to form at relatively low stresses. The crack spreads through the material, either in a trans-crystalline or inter-crystalline direction, depending on the material, the stress and the corrosion environment.

The real mechanism of SSC is not quite understood, despite there being several explanations for it. In general, the mechanism of SSC can be divided into two main parts: the mechanism of anodic dissolving and the cathode mechanism that causes hydrogen embrittlement of the material.[2]

For some types of austenitic stainless steels, like AISI 304 and AISI 316, it has been known for a long time that they are sensitive to SCC, but mostly at temperatures above 55 °C.

The performed investigations revealed that the local damage and leaks are a result of SCC phenomena. The SCC in austenitic stainless steel appears locally in the form of thin branched cracks that can grow very quickly and can cause failure of the structure.

One possible reason for SCC of the tank is the longitudinal orientation of the crystal grains due to cold rolling of the sheet (**Figure 5**). The directed microstructure is evidence that the material was not properly recrystallization annealed after the cold rolling, and thus the internal stresses remained in the material. This was also confirmed with cracks in the longitudinal direction following the longitudinally deformed crystal grains.

Additional possible sources of stresses are the cold forming and the welding of the tank.

The elimination of internal stresses and the stabilization of austenite is possible in austenitic stainless steel with annealing to a temperature of 1050 °C, followed by rapid cooling in water. Such measures also prevent the formation of brittle phases in the steel, typical for a slow cooling process.

In general, SCC can be prevented by the:

- selection of a more resistant material,
- elimination of internal stresses with material annealing,
- elimination of chloride ions in the storage liquid.

The corrosion pits were observed on the external surface of the tank due to crevice corrosion in the gap between the insulation and the tank surface. Crevice corrosion is typical for narrow crevices with a lack of oxygen. At such places the formation of a new protective layer of chromium oxide (re-passivation) on the steel surface is not possible and crevice corrosion proceeds. The corrosion process is also accelerated by the presence of chloride ions. Crevice corrosion led to the formation of pits where the initiated cracks and SCC started. The brittle cracks due to SCC that spread from the surface through the tank wall are probably a consequence of hydrogen embrittlement.

Both stored media in the tank have a pH from 2.6 to 11.3. The content of the tank was either acid or alkaline, both of which accelerate the corrosion processes on the internal surface of the tank.

For the investigated tank the corrosion process could be prevented by good contact between the insulation and the wall. This would prevent the formation of condensed water on the surface of the tank from the trapped moisture in the gap.

4 CONCLUSIONS

Our investigations confirmed that the leakage of the tank, made of AISI 304 austenitic stainless steel, is a consequence of the interaction of several localized corrosion processes and the presence of internal stresses in the material. The SCC originates in the crevice corrosion pits on the external surface of the tank. The moisture captured in the gap below the insulation condensed during the cooling of the tank and together with the presence of chloride ions enabled the start of crevice corrosion.

All the necessary factors were met for the appearance of SCC: sensitive material, internal stresses in the material and corrosion media. With the proper combination of all three, the crevice corrosion pits start to grow and later the SCC developed. Cracks, as a result of SCC, are responsible for the leakage of the tank.

5 REFERENCES

[1] C. L. Page, R. D. Anchor, Stress corrosion cracking of stainless steels in swimming pools, The Structural Engineer, 66 (**1988**) 24, 418

[2] S.P. Lynch, Mechanisitc and fractographic aspects of stress-corrosion cracking (SCC), Stress Corrosion Cracking, Theory and Practice , A volume in Woodhead Publishing Series in Metals and Surface Engineering, 2011, 3–89, doi:10.1533/9780857093769.1.3

[3] N. Baddoo, P. Cutler, Stainless steel in indoor swimming pool buildings, The Structural Engineer, 82 (**2004**) 9, 24–26

[4] M. Tsubota, Y. Katayama, Y. Saito, Stress Corrosion Crack Growth Behavior of Cold Worked Austenitic Stainless Steel in High Temperature Water, Environmental Degradation of Materials in Nuclear Systems XII, Proc. 12th International Conference on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors, ed. by T.R. Allen, P.J. King and L. Nelson, TMS, Warrendale, PA 2005, 109–115

[5] A. Turnbull, K. Mingard, J.D. Lord, B. Roebuck, D. Tice, K. Mottershead, N. Fairweather, A. Bradbury, Sensitivity of stress corrosion cracking of stainless steel to surface machining and grinding procedure, Corros. Sci., 53 (**2011**) 10, 3398–3415, DOI: 10.1016/j.corsci. 2011.06.020

[6] S. Lozano-Perez, T. Yamada, T. Terachi, M. Schroder, C.A. English, G.D.W. Smith, C.R.M. Grovenor, B.L. Eyre, Multi-scale characterization of stress corrosion cracking of cold-worked stainless steels and the influence of Cr content, Acta Mat., 57 (**2009**) 18, 5361–5381, doi:10.1016/j.actamat.2009.07.040

[7] G. Hinds , L. Wickström, K. Mingard, A. Turnbull, Impact of surface condition on sulphide stress corrosion cracking of 316L stainless steel, Corrosion Science, 71 (**2013**) 43–52, doi:10.1016/j.corsci. 2013.02.002

[8] A. Bhattacharya, Stress Corrosion Cracking of Duplex Stainless Steels in Caustic Solutions, Georgia Institute of Technology, Atlanta, GA 2008, 8

[9] J. Orlikowski, S. Krakowiak, Pitting corrosion and stress corrosion cracking of buffer tanks in a brewery, Engineering Failure Analysis, 29 (**2013**) 75–82, doi:10.1016/j.engfailanal.2012.10.013

[10] J. Woodtli, R. Kieselbach, Damage due to hydrogen embrittlement and stress corrosion cracking, Engineering Failure Analysis, 7 (**2000**) 6, 427–450