Corrosion of AISI 304L Austenitic Stainless Steel in Non-Stationary Aqueous HCl + NaCl Solution

Z.A. Opiekun [a]*, A.W. Orłowicz [a], B. Kupiec [a]

[a] Casting and Welding Department, Rzeszow Technical University, Al. Powstańców Warszawy 12, 35-950 Rzeszów, Poland
* Corresponding author's e-mail: zopiekun@gmail.com

Abstract

The paper describes the process of stress corrosion in a Ø50 mm rod made of AISI 304L austenitic chromium-nickel steel. Discs cut off from the steel rod were moved at a speed of 1.25 m/s for a test period of 408 h in a corrosive environment of aqueous solution containing 3% HCl and 8.6 g NaCl at room temperature. It was found that deepest cracks and irregular pitting occurred locally in areas of microstructure containing grains of hard lamellar α' martensite and along boundaries between filamentary delta ferrite (Feδ) precipitates and α' phase. The corrosion developed in a trans-crystalline manner with branches propagating along boundaries of lamellar α' phase grains.

Keywords: Austenitic stainless steel; α', Feδ-phase; Structures, Hardness and microhardness; Stress corrosion

1. Introduction

Austenitic chromium-nickel steels belong to the group of materials considered exceptionally resistant to corrosion in many aggressive environments. However, in solutions containing chloride ions, the steels are subject to pitting corrosion, and in presence of stress, also to stress corrosion [1–7]. Resistance of chromium-nickel steels to various forms of corrosion of the depends on many factors related to their microstructure, chemical composition, surface geometrical structure, level and direction of internal stresses and nature of the environment [8–12]. Chemical compositions of industrial austenitic steels are very diverse. According to EN 10088-1 standard, they contain 0.015–0.15% carbon, 16.0–28.0% chromium, 6.0–35.0% nickel, as well as manganese (0.0–4.0%), molybdenum (0.0–8.0%), nitrogen (0.0–0.6%), copper (0.0–4.0%), silicon (0.5–4.5%), tungsten (0.0–2.5%), titanium (0.0–0.7%), niobium (0.0–1.0%) and boron (0.0–0.005%).

In any case, in addition to main components, i.e. Fe, Cr, and Ni, steels contain several other alloying elements. These elements are added to the austenitic chromium-nickel steels in order to improve their service properties, and in particular to increase resistance to hot cracking, inter-granular, pitting, and stress corrosion, and improve mechanical properties at both room and elevated temperatures [13–16].

The objective of this article is to examine the course of corrosion of specimens in the form of discs cut off from a Ø50 mm rod made of AISI 304L (X2CrNi18-9 according to EN-10088-1) stainless steel and subject to transient interaction with aqueous solution containing HCl and NaCl.

2. Materials and methods

The specimens used in the study were 10-mm thick discs cut mechanically off from a Ø50 mm AISI 304L stainless steel rod. After cutting, surfaces of the discs were roughly polished with abrasive papers and finished with felt polishing discs moistened with aqueous suspension containing about 20% Al2O3 with 3 μm grain size. The chemical composition of AISI 304L steel discs, was determined by means of Q4 TASMAN (Bruker)[1] optical emission spectrometer: 0,017%C, 0,45%Si, 1,53%Mn, 8,4%Ni, 18,6%Cr, 0,34%Cu.

The discs prepared this way were then subject to interaction with aqueous solution containing about 3% of HCl and 8.6 g of NaCl at room temperature for a period of 408 h. Samples were mounted on the plastic (PVC) and set in rotational motion by

means electric motor (Figure 1). To ensure that the flow the corrosive solution around the moving samples remains laminar, the motor speed has been experimentally determined and adjusted so that the linear velocity of specimens with respect to the solution was constant and equaling V = 1.25 m/s.
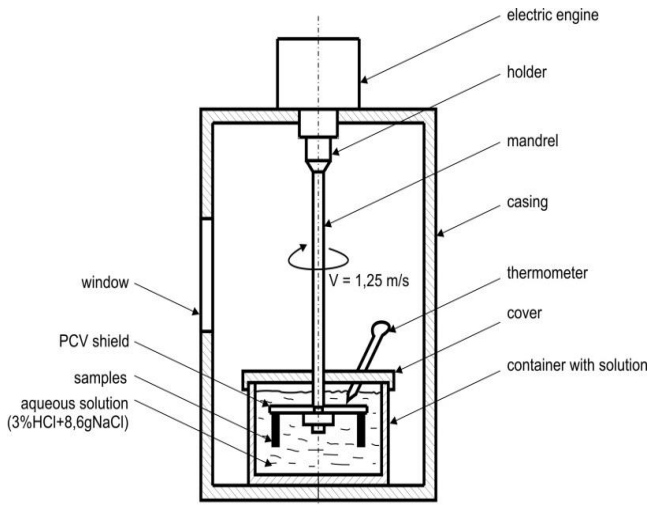

Fig. 1. Schematic diagram of the set-up for corrosion tests in non-stationary solutions

Structural tests of AISI 304L stainless steel specimens were carried out using Neophot2 (Zeiss) optical light metallographic microscope equipped with Videotronic CC20P camera, image from which was acquired and analysed by means of SEM Multi-scan V.08 VEGA 3 (TESCAN)[2] system coupled with INCA X-ACT (Oxford) attachment for the X-ray microanalysis.

Content of delta ferrite (Feδ) and ferromagnetic martensitic phase (α′) in the structure of AISI 304L steel discs was determined with the use of Feritscope FMP 30 (Fischer). Before measurements, the instrument was calibrated with the use of standards (%Fe standards - WCR 0.3-10, serial No.: N1-0322). FMP 30 allowed to determine the content of ferromagnetic phases in the examined AISI 304L steel specimens with accuracy of ± 0.1%.

HV5 hardness measurements were performed with the use of ZHV10 hardness tester (Zwick Roell), while microhardness of Feδ, γ, and α′ phases present in microstructure of AISI 304L steel were measured by means of Berkovich penetrator (HV0.05) using Nanoindentation Tester (NHT, CSM Instruments).

3. Results and discussion

Figure 2 shows a disc made of AISI 304L steel subject to interaction with non-stationary corrosive solution for the period of 408 h and images representing the resulting stress corrosion over its cross-section. In the panel showing macrostructure of the disc cross-section (Figure 2b), HV5 hardness values and (Feδ + α′) content percentages are marked.
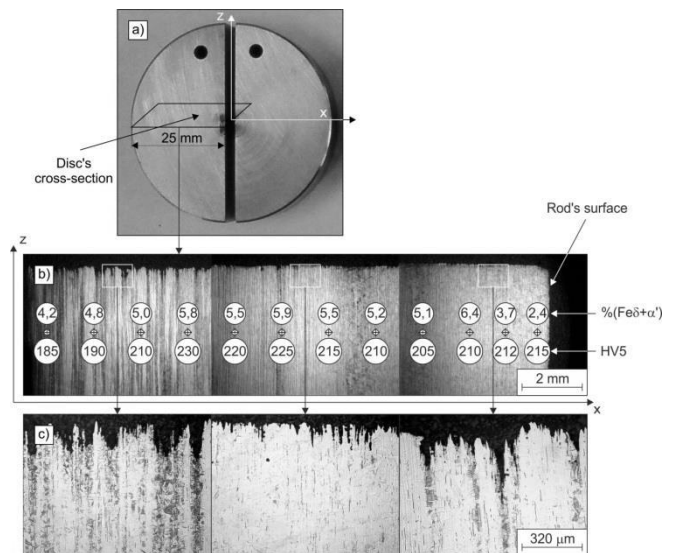

Fig. 2 Ø50mm disc made of AISI 304L steel subjected to the influence of non-stationary corrosive aqueous solution (3% HCl + 8.6 g NaCl) during 408h at room temperature (a). The macrostructure of the cross section of the disc and applied HV5 values (Feδ + α ') (b), the stress corrosion morphology from different areas in the cross-section (c). Metallographic specimen was electrolytically treated in the reagent: 10g C2H2O4 + H2O 90ml at 5V.

Cross-section of the Ø50 mm AISI 304L steel rod is characterised by diverse macrostructure and microstructure. The macrostructure reveals presence of a texture manifesting in orientation of the material fibres along the direction of plastic working applied to the rod (Figure 2b). Intensive plastic deformation during the manufacturing process resulted in local a thermal martensitic transformation α′ [17,18]. In the areas where the martensitic phase occurs, deep corrosion pitting/cracking can be seen (Figure 3).

Additionally, delta ferrite (Feδ) present in the martensitic phase in the form of elongated filamentous precipitations favours propagation of corrosion pitting (Figure 4).

Diversified structure of the rode over its cross-section is reflected in corresponding variability of HV5 values (Figure 2b). Hardness in the central part of the rod is about 185 HV5 and varies depending on the measurement point, with a local maximum of about 230 HV5.

Similarly, the fraction of ferromagnetic phases (Feδ + α′) in the microstructure of the Ø50 mm AISI 304L steel rod varies depending on the measurement area. The volume percentage of these phases on the rod axis is about 4.2% compared to about 2.4% near the surface. The maximum observed fraction of (Feδ + α′) phases in the rod cross-section was (5.9 ± 0.2)%.

Using a computerised image analysis system, Feδ volume fraction in microstructure of the Ø50mm AISI 304L steel rod was determined as (1.4 ± 0.1)%. Delta ferrite in the form of elongated strands or "threads" (Figure 3) favours propagation of stress corrosion cracks.
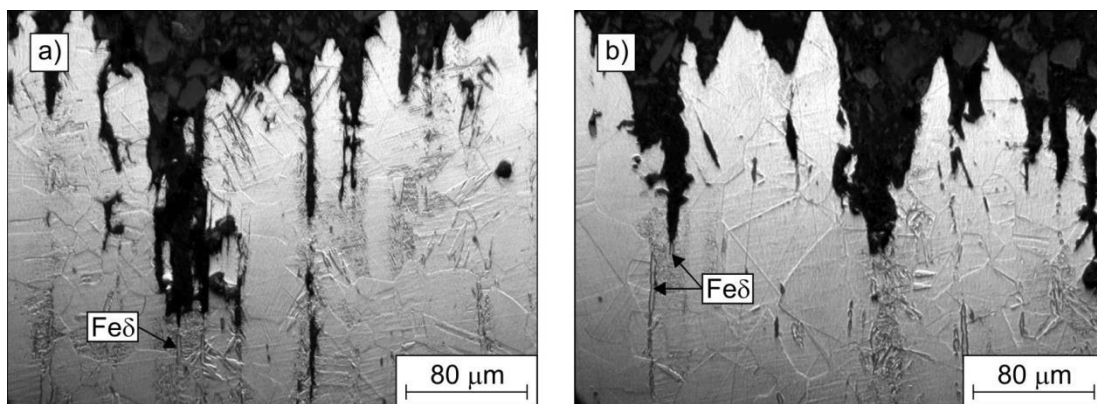
Fig. 3. Examples of deep corrosion pitting in steel AISI 304L Ø50mm discs subjected to the influence of an non-stationary aqueous solution containing 3% HCl + 8.6 g NaCl during 408h. Optical microscope. Metallographic specimen electrotically treated in the reagent of 10g C2H2O4 + H2O 90ml, voltage 5V
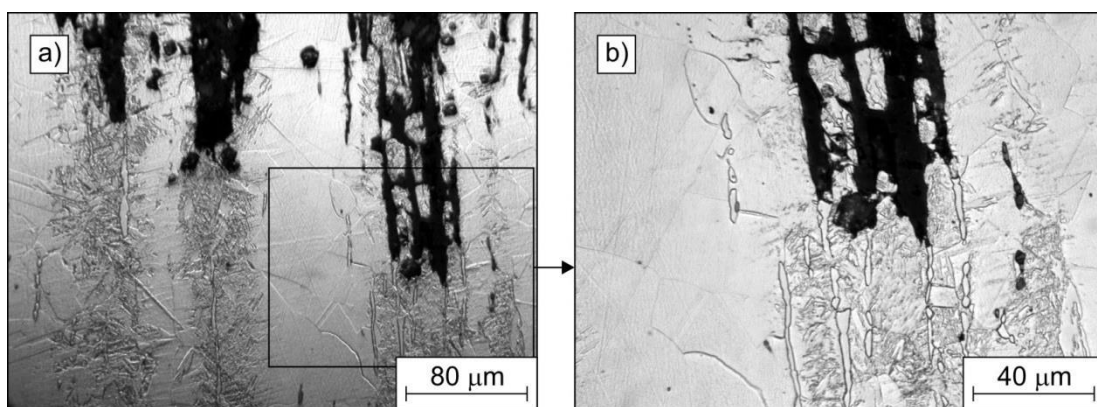

Fig. 4. Microstructure (a, b) in the cross-section of steel Ø50mm disc AISI 304L subjected to the influence of an non-stationary aqueous solution containing 3% HCl + 8,6g NaCl during 408h. Metallographic specimen electrotically treated in the reagent of 10g C2H2O4 + H2O 90ml, voltage 5V

4. Conclusions

Microstructure of the examined Ø50 mm AISI 304L steel rod comprised three phases: twinned equiaxial γ austenite grains that constituted the matrix, locally occurring areas of strongly plastically deformed of austenite grains with lamellar martensitic α′ phase, and a small fraction (about 1.4%) of delta ferrite (Feδ). The latter phase, in the form of elongated threadlike grains, was located at boundaries of austenite grains and in martensitic phase prevalence areas.

Distribution of the α' phase in the microstructure of the rod was uneven, and its fraction ranged from 1.0% to 4.5%, depending on location. Discs cut off from a AISI 304L steel rod and polished were subject to action of non-stationary aqueous solution containing 3% HCl + 8.6 g of NaCl at room temperature for a period of 408 hours. At the constant speed of 1.25 m/s with respect to the solution, the specimens travelled the total distance of 1836 km in the reagent.

The largest pits caused by stress corrosion, up to 1.6 mm deep, are visible in these microstructure areas where hard lamellar α′ martensite and delta ferrite (Feδ) "threads" are present (Figures 3b).

Acknowledgments

References

[1] Fossati, F. Borgioli, E. Galvanetto, T. Bacci: Corrosion Science 48 (2006), 1513 – 1527

[2] X. M. Zhu, M. K. Lei: Surface Coating Technology, 131 (2000), 400

[3] D. L. Williamson, J. A. Davies, P. J. Wilbur, J. J. Vajo, R. Wei, J. N. Matossian: Nuclear Instrum. Meth. B127/128 (1997), 930

[4] E. Menthe, U. A. Bulak, J. Olfe, A. Zimmermann, K. T. Rie: Surface Coat. Technol. 133 – 134 (2000), 259

[5] X. Li, T. Bell: Corrosion Science 46 (2004), 1527

[6] Iskhisa Hamada, Kiyoshi Yamauchi: Metall. and Mater. Trans. A, vol. 33A, 2907 – 2919, 2002

[7] F. Otsubo, K. Kishitake, T. Akiyama, T. Terasaki: Journal of Thermal Spray Techn., vol. 12(4), 555 – 559, 2003

[8] G. Sui, E. A. Charles, J. Congleton: Corrosion Science, vol. 38, No. 5, p.p. 687 – 703, 1996

[9] K. Tosha and K. Lida: Int. J. Japan Soc. Prec. Eng, 29(1), 46-47, 1995

[10] E. Wilde: Corrosion 44, 699 (1988)

[11] K. N. Krishnam, K. P. Rao: Corrosion 46, 734 (1990)

[12] B. R. Taneva, L. B. Fachikov, R. G. Raicheff: Journal of App. Electrochem, 36, 247 – 353 (2006)

[13] H. Baba, T. Kodama, Y. Katada: Corrosion Science, 44, 2393 – 2408 (2002)

[14] R. F. A. Jargelius – Pettersson: Corrosion Science, 41, 1639 – 1648 (1999)

[15] M. Luppo, A. Hazarabedian, A. Ovejero – Garcia: Corrosion Science, 41, 87 – 103 (1999)

[16] Y. Cui, C. D. Lundin, V. Hariaharan: J. Mater. Process. Technol, 171, 150 – 155 (2006)

[17] H. F. Gomez de Abreu: Material Research, 10(4), 359 – 366 (2007)

[18] W. Ozgowicz, A. Kurc, M. Kciuk: Archives of Mat. Sci. and Eng., 43(1), 42 – 53 (2010)