

# EFFECT OF SOLUTION ANNEALING ON CORROSION RESISTANCE OF AUSTENITIC STAINLESS STEELS IN CHLORIDE-CONTAINING ENVIRONMENT

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**Abstract:** Austenitic stainless steels are highly corrosion-resistant in common oxidation environments. However, aggressive chloride-containing solutions can evoke local corrosion, which performs an important risk in the safe use of these materials. This research deals with the effect of the solution annealing (1050 °C, 15 min) on the electrochemical parameters of AISI 304 and AISI 316L stainless steels. Corrosion resistance of the solution-annealed specimens is evaluated and compared to the as received specimens by the potentiodynamic polarization test performed in 1M pH neutral NaCl solution at the 20 ± 3 °C temperature. The obtained results did not clearly confirm the positive effect of solution annealing on corrosion resistance in the given aggressive solution. Although the pitting potentials indicating higher pitting corrosion resistance increased, the kinetics of the corrosion process intensified.

**Keywords:** austenitic stainless steels, corrosion resistance, solution annealing, potentiodynamic polarization

## 1. INTRODUCTION

In the field of material engineering, an ensuring the safety and longevity of structures and components is a critical concern, particularly in aggressive environments, where there is a serious risk of material degradation (Glass, 2010). Austenitic stainless steels, known for their superior corrosion resistance in common oxidation environments and appropriate mechanical properties, are frequently used in various applications including marine, chemical and food processing, construction and biomedicine (Chvalníková et al., 2023; Lai et al., 2012). However, these steels are susceptible to a disruption of the passive surface film and to the local pitting corrosion in chloride-rich solutions (Chen et al., 2021; Dastgerdi et al., 2019; Liu et al., 2022; Rustandi et al., 2017) Therefore, their performance must be rigorously assessed and optimized to meet safety standards.

Solution annealing is a heat treatment process widely applied to austenitic stainless steels to enhance their corrosion resistance by dissolving precipitated carbides (especially



$M_{23}C_6$ , the chromium-rich ones) and homogenizing the microstructure (Chen et al., 2018; He et al., 2016; Ramírez et al., 2023; Wu et al., 2024). The studies by some authors (Kumar and Gupta, 2020; Njoku et al., 2023) report, that this treatment can significantly improve the stainless steel resistance to localized corrosion phenomena in chloride-containing environments. According to the authors (Njoku et al., 2023), the annealed AISI 304 stainless steel specimens show up to 36 % corrosion resistance improvement in acid chloride solution compared to the untreated stainless steel specimens.

Since precipitation of  $M_{23}C_6$  occurs in the temperature range of 450 to 900 °C, the lower temperature limit for solution annealing should be above 900 °C. Maximum temperature of solution annealing is limited by the grain growth (Ofuyekpone et al., 2015; Pei et al., 2023). In particular, abnormal grain growth, also known as secondary recrystallization, must be avoided (Padilha et al., 2007). The authors Pei et al., 2023 studied the deformation mechanism of Cr-Ni stainless steel solution-annealed at various temperatures (850 °C, 950 °C, and 1050 °C). They found, that the grain size of the specimen increased with increasing annealing temperature while the yield strength decreased.

This research is focused on the effect of the solution annealing (1050 °C, 15 min) on the pitting corrosion resistance of AISI 304 and AISI 316L stainless steels used as the experimental material. The main goal of the article is to assess whether the performed solution annealing clearly improves the corrosion resistance of the given materials and also to what extent it is affected by differences in their chemical composition. The corrosion resistance of the solution-annealed specimens is evaluated and compared to the original non-treated (as received) specimens by the potentiodynamic polarization test performed in pH neutral 1M NaCl solution at the  $20 \pm 3$  °C temperature.

## 2. MATERIALS AND METHODS

AISI 304 and AISI 316L austenitic stainless steels purchased in sheets (1000 x 2000 mm) of 1.5 mm thickness (chemical compositions in Table 1) were used as the experimental material. Their manufacturing process was based on continuous casting in electric arc furnace. Then they were annealed (AISI 304 at 1040 – 1100 °C, AISI 316L at 1050 °C). The IIB surface finish (smooth and matte metallic glossy surface) was prepared by pickling after slightly smoothing rolling.

Table 1

Chemical compositions of experimental stainless steels (wt. %)

	Cr	Ni	Mo	Ti	Mn	N	C	Si	P	S	Fe
304	18	8.01	-	-	1.40	0.075	0.027	0.38	0.031	0.0037	balance
316L	16.79	10.14	2.03	-	0.82	0.05	0.02	0.31	0.03	0.001	balance

Microstructures of the tested steels in the as received state (Figure 1) are polyhedral, created by austenitic grains with numerous twins, which could arise by annealing and/or rolling.

The rectangular specimens (15 mm x 40 mm x 1.5 mm) were used for the testing. The heat treatment for solution annealing was performed in furnace at 1050 °C for 15 minutes with cooling in the air. Microstructures of solution-annealed specimens were observed by optical microscope.

A part of the specimens was left in the as received state for comparison of the corrosion tests results.

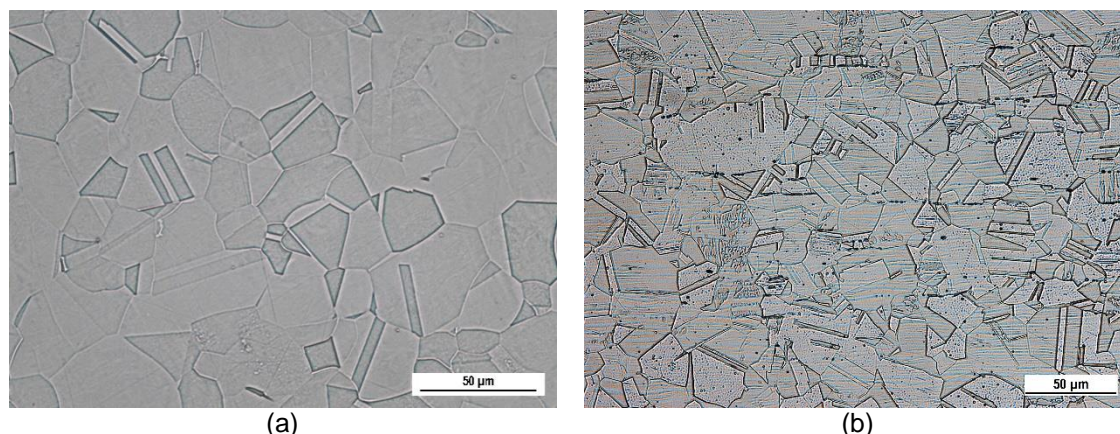


Fig. 1. Microstructures in the as received state, longitudinal sections: (a) AISI 316L (Kallings 2 etch.); (b) AISI 304 (glycerine + HNO<sub>3</sub> + HCl etch.)

Before the corrosion test, the solution-annealed specimens were pickled to remove high-temperature oxide scales (Cleaning and Descaling Stainless Steels A Designers' Handbook Series N° 9001, 2024; Donik, 2011; Elshawesh and Elhoud, 2004). The pickling conditions are listed in Table 2.

Table 2  
Conditions of pickling

Component	Volume (mL)	Temperature (°C)	Time (min)
HF	2	50	10
HNO <sub>3</sub>	15		
H <sub>2</sub> O	to 100 ml		

Potentiodynamic polarization (PP) was performed in pH neutral 1M sodium chloride solution (analytical grade) at the temperature  $20 \pm 3$  °C, in the conventional three-electrode cell system with the reference saturated calomel electrode (SCE, +0.248 V vs. SHE at 20 °C) and the platinum (Pt) auxiliary electrode, using BioLogic corrosion measuring system with PGZ 100 measuring unit. The time for potential stabilization between the specimen and the electrolyte was 10 minutes, the exposed specimen area was 1 cm<sup>2</sup>. The potentiodynamic polarization curves were recorded at the sweep rate of 1 mV/s in the potential scan range between -0.3 and 0.8 V vs. open circuit potential (OCP). At least three experiment repeats were carried out for each type of specimen and the representative curve was selected.

### 3. RESULTS AND DISCUSSION

As can be seen in Figure 2, the microstructure of solution-annealed specimens is similar to that in the as received state but the austenitic grains are markedly coarser and number of observable inclusions is reduced, especially in AISI 304 microstructure.

PP curves corresponding to the as received and the solution-annealed states of the AISI 304 and AISI 316L are shown in Figure 3 and Figure 4 respectively. The values of PP parameters are listed in Table 3.

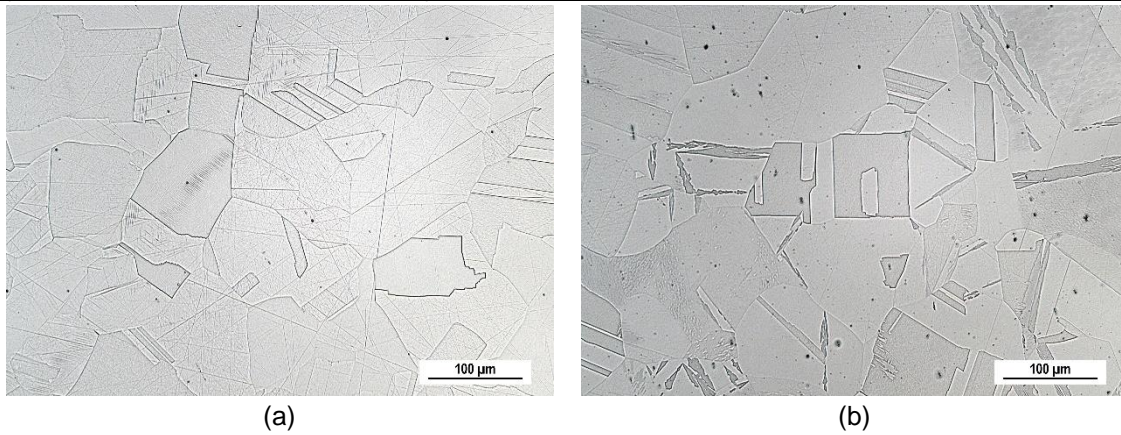


Fig. 2. Microstructures after solution annealing, longitudinal sections: (a) AISI 316L (Kallings 2 etch.); (b) AISI 304 (glycerine + HNO<sub>3</sub> + HCl etch.)

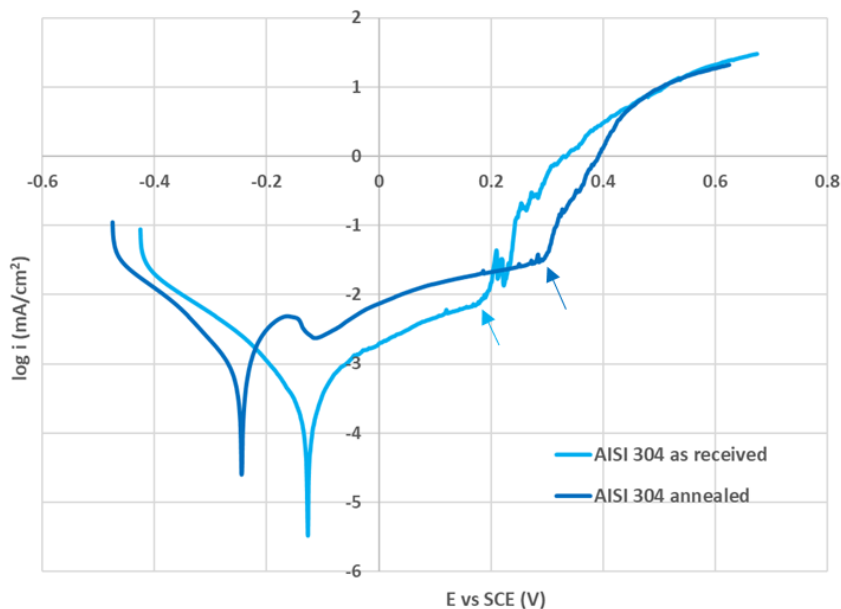


Fig. 3. PP curves for AISI 304 stainless steel: comparison of the as received and the solution-annealed states ( $E_p$  locations are marked by the arrows)

The PP parameters  $E_{\text{corr}}$  (corrosion potential),  $i_{\text{corr}}$  (corrosion current density) and  $v_{\text{corr}}$  (corrosion rate) were obtained as the result of the Tafel extrapolation using EC-LAB software. Corrosion potential  $E_{\text{corr}}$  is the potential of the transition from the cathodic to the anodic branch of the polarization curve and expresses the level of the thermodynamic stability of the material in the applied solution. The higher  $E_{\text{corr}}$  value means the higher thermodynamic stability of the corrosion system.

Corrosion current density  $i_{\text{corr}}$  reflects the kinetic aspect of the corrosion process. It controls the dissolution rate of an actively corroding metal (Kuchariková et al., 2018). Corrosion rate  $v_{\text{corr}}$  was determined by the software, based on the corrosion current density, using Faraday's law. According to Figure 3 and Figure 4, the shapes of all presented curves are typical for passivating metals (they all have passive anodic branches). Therefore, the pitting potential ( $E_p$ ) as the potential of a breakdown of the passive surface film denoting the start of stable pit-growth, is the main PP parameter of the pitting corrosion resistance. The  $E_p$  values shown in Table 3 were determined directly

from the curves as the potentials of sudden strong increase of current density after the passivity state ( $E_p$  locations are marked by arrows in Figure 3 and Figure 4). The higher  $E_p$  values point to higher resistance of the material to the pitting corrosion (Szkłarska-Smiałowska, 2005; Li et al., 2018).

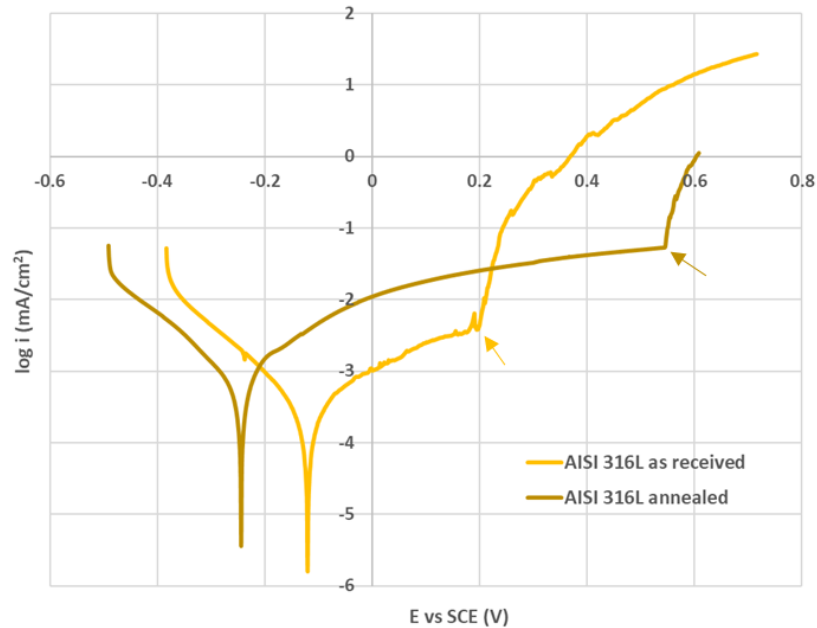


Fig. 4. PP curves for AISI 316L stainless steel: comparison of the as received and the solution-annealed state ( $E_p$  locations are marked by the arrows)

Table 3

Values of PP parameters

State of specimen	Pitting potential $E_p$ (V)	Corrosion potential $E_{corr}$ (V)	Corrosion current density $i_{corr}$ ( $\mu\text{A}/\text{cm}^2$ )	Corrosion rate $v_{corr}$ (mm/y)
AISI 304 as received	0.179	-0.128	0.347	0.004
AISI 304 annealed	0.286	-0.245	0.938	0.010
AISI 316L as received	0.196	-0.122	0.299	0.003
AISI 316L annealed	0.545	-0.245	0.729	0.008

According to the obtained  $E_p$  values, the performed solution annealing caused an expansion of passivity regions of both stainless steels, which points to an increase of their resistance to the pitting. It should be remembered, that the pickling solution used to remove high-temperature oxides could also have contributed to an improvement of the passive film's resistance to a breakdown due to nitric acid, which is also used as an oxidizing agent to strengthen the passive film (Donik, 2011; Zhang et al., 2020).

Unlike that, comparison of  $E_{corr}$  values of the as received and the solution-annealed specimens shows lower thermodynamic stability after solution annealing of the both stainless steels. Moreover, higher  $i_{corr}$  values of the solution-annealed specimens reflect their higher corrosion rate compared to the as received state. A similar trend of  $E_{corr}$  and  $i_{corr}$  values (in potentiodynamic micropolarization) after solution annealing of AISI 444 stainless steel in chloride-containing tap water was observed by the authors (Bitondo et al., 2014).

Detail of PP curves (in linear axes) in passivity region up to reaching of the  $E_p$  values is performed in Figure 5. It is clear, that passive current densities corresponding to the curves after solution annealing are substantially higher compared to the as received ones, which shows on higher ion transport through the passive film, resulting to less stable passive state from the kinetic point of view.

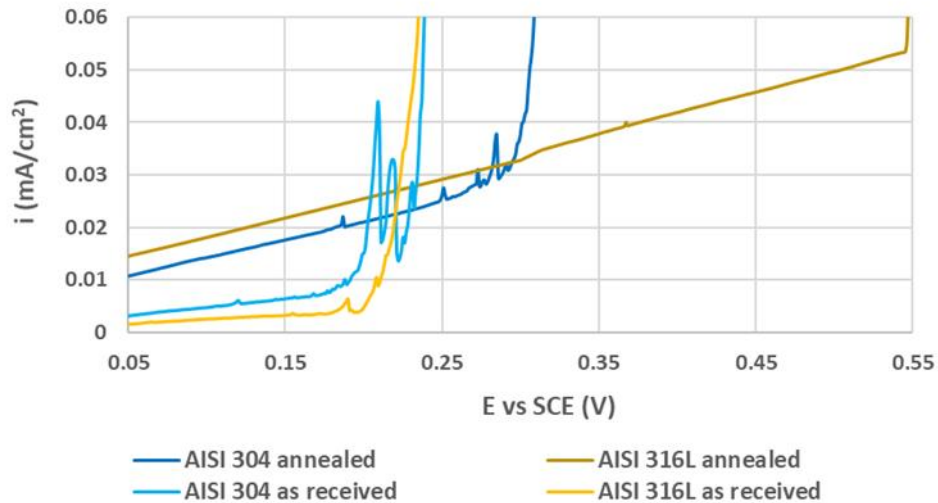


Fig. 5. Detail of PP curves in the linear axes

Comparison of AISI 304 and AISI 316L stainless steels PP curves for the as received and the solution-annealed state is shown in Figure 6 and Figure 7 respectively.

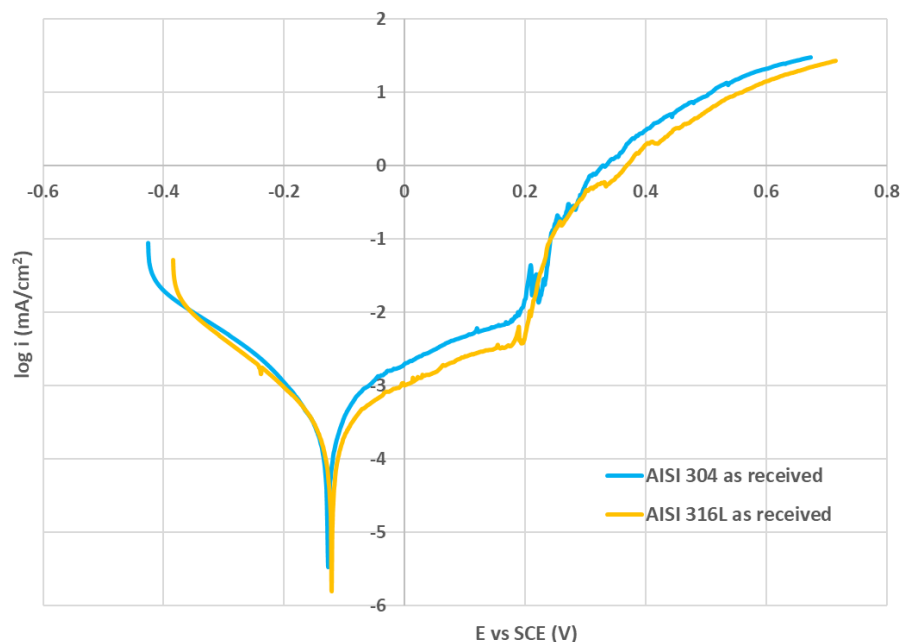


Fig. 6. The as received state: comparison of PP curves of the both tested stainless steels

It is clear (Figure 6), that behavior of both stainless steels in the as received state is similar. Slight differences in  $E_p$  values and passive current densities point to somewhat more stable and resistant passive film of AISI 316L stainless steel. After solution annealing, the

$E_p$  value of AISI 316L is significantly higher compared to AISI 304 stainless steel (Figure 7). A higher resistance of AISI 316L to the pitting corrosion could be related to the molybdenum, which tends to concentrate in the passive film and to strengthen its stability (Chen et al., 2021; Ha et al., 2018; Szewczyk-Nykiel, 2015). Molybdenum oxides resist dissolution even under low pH conditions within the pit and therefore they stabilize the local chemistry around the pit initiation site (Ibrahim et al., 2009; Upadhyay, et al., 2020). An even distribution of molybdenum in AISI 316L microstructure after solution annealing could also contribute to higher pitting corrosion resistance compared to AISI 304.

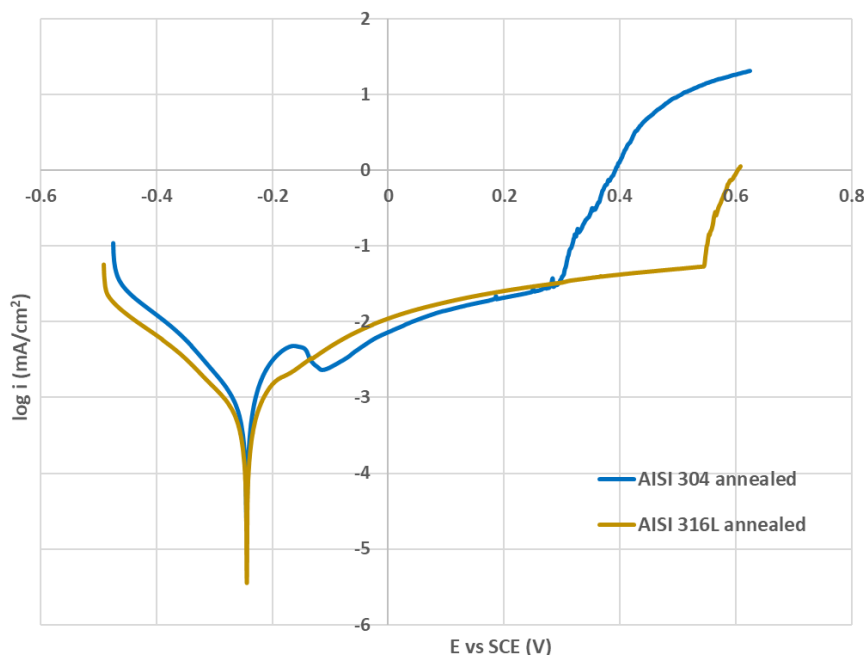


Fig. 7. The state after solution annealing: comparison of PP curves of the both tested stainless steels

#### 4. CONCLUSION

Based on the performed experiments can be concluded:

- Microstructure after solution annealing consists of the markedly courser austenitic grains and number of observable inclusions is reduced compared to the as received state.
- Solution annealing caused a shift of pitting potentials to the higher positive values, which points to a better resistance of passive films of the both steels to the pitting corrosion. The pitting potential of the solution-annealed AISI 316L is significantly higher compared to the solution-annealed AISI 304.
- Lower  $E_{corr}$  values of solution-annealed specimens revealed their lower thermodynamic stability compared to the as received state.
- Higher  $i_{corr}$  values and passive current densities reflect an intensification of the corrosion kinetics after solution annealing.

According to the above listed partial conclusions, a higher corrosion resistance of the tested solution-annealed stainless steels in the given aggressive environment, was not clearly verified. Therefore, carefulness especially at a long-term exposure in chloride-containing environment, is recommended.

## ACKNOWLEDGEMENTS

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## REFERENCES

- Bitondo, C., Bossio, A., Monetta, T., Curioni, M., Bellucci, F., 2014. *The effect of annealing on the corrosion behaviour of 444 stainless steel for drinking water applications*. Corrosion science, 87, 6-10.
- Chen, X., Li, J., Cheng, X., Wang, H., Huang, Z., 2018. *Effect of heat treatment on microstructure, mechanical and corrosion properties of austenitic stainless steel 316L using arc additive manufacturing*. Materials Science and Engineering: A, 715, 307-314.
- Chen, X., Liu, H., Sun, X., Zan, B., Liang, M., 2021. *Chloride corrosion behavior on heating pipeline made by AISI 304 and AISI 316 in reclaimed water*. RSC Advances, 11, 61, 38765-38773.
- Cleaning and Descaling Stainless Steels. A Designers' Handbook Series N° 9001, Available online: <https://nickelinstitute.org/media/4399/cleaning-and-descaling-stainless-steel-9001-updated.pdf> (accessed on 18 June 2024).
- Chvalníková, V., Uhrčík, M., Palček, P., Slezák, M., Šikyňa, L., Drímalová, P., 2023. *Austenitic steel AISI 304 under static and cyclic loading*. Manufacturing Technology, 23, 5, 623-629.
- Dastgerdi, A.A., Brenna, A., Ormellese, M., Pedferri, M.P., Bolzoni, F., 2019. *Experimental design to study the influence of temperature, pH, and chloride concentration on the pitting and crevice corrosion of UNS S30403 stainless steel*, Corrosion Science 159, 108160.
- Doník, Č., 2011. *Surface characterization and pickling characteristics of the oxide scale on duplex stainless steel*. Materials and technology, 45, 4, 329-333.
- Elshawesh, F., Elhoud, A., 2004. *Role of heat tint on pitting corrosion of 304 austenitic stainless steel in chloride environment*. Proceedings of EUROCORR - Prevision a Long Terme et Modelisation de la Corrosion, Nice, France, 12–16 September 2004.
- Glass, J., 2010. *Sustainability of construction materials*. International Journal of Sustainable Engineering, 3, 1, 65.
- Ha, H.Y., Lee, T.H., Bae, J.H., Chun, D.W., 2018. *Molybdenum Effects on Pitting Corrosion Resistance of FeCrMnMoNC Austenitic Stainless Steels*. Metals, 8, 8, 653.
- He, V., Guo, Y.J., Wu, X.Y., Jiang, Y.M., Li, J., 2016. *Effect of Solution Annealing Temperature on Pitting Behavior of Duplex Stainless Steel 2204 in Chloride Solutions*. Journal of Iron and Steel Research International, 23, 4, 357-363.
- Ibrahim, M.A.M., Abd El Rehim, S.S., Hamza, M.M., 2009. *Corrosion behavior of some austenitic stainless steels in chloride environments*. Materials Chemistry and Physics, 115, 1, 80-85.
- Kuchariková, L., Liptáková, T., Tillová, E., Kajánek, D., Schmidová, E., 2018. *Role of Chemical Composition in Corrosion of Aluminum Alloys*. Metals, 8, 581.
- Kumar, V., Gupta, R.K., Das, G., 2020. *Influence of Deformation and Annealing on Microstructure and Corrosion Behavior of Austenitic Stainless Steel*. Materials Today-Proceedings, 22, 4, 3347-3352.
- Lai, J.K.L., Lo, K.H., Shek, C.H., 2012. *Austenitic stainless steel*. In: *Stainless steels: An introduction and recent developments*. Bentham Science Publexecutive STE Y-2, Sharjah, U Arab Emirates.
- Li, Y., Qiu, J., Zhao, J., Ye, Q., Zhu, Y., Mao, J., 2018. *Enhancement of Pitting Corrosion Resistance of Austenitic Stainless Steel Through Deposition of Amorphous/Nanocrystalline Oxy-nitrided Phases by Active Screen Plasma Treatment*. Materials Research, 21, 6.
- Liu, W., Yang, H., Li, X., Zhang, Z., Lin, Y., Deng, K., 2022. *Effect of Chloride and Iodide on the Corrosion Behavior of 13Cr Stainless Steel*. Metals, 12, 11, 1833.
- Njoku, R.E., Obikwelu, D.N., Ugwuoke, B., Ocheri, C., 2023. *Investigation of Solution Annealing Treatment Effect on Corrosion Resistance of AISI 304 Austenitic Stainless Steel for Oil Industry*

- Application. Nanotechnology & Applications*, Available online: <https://www.scivisionpub.com/pdfs/investigation-of-solution-annealing-treatment-effect-on-corrosion-resistance-of-aisi-304-austenitic-stainless-steel-for-oil-indust-2749.pdf> (accessed on 25 October 2024).
- Ofuyekpone, O., Amaechi, C. and Utu, O.G., 2015. *Effect of Solution Annealing Temperature on the Microstructure and Mechanical Properties of AISI 304L*. *International Journal of Applied Research and Technology*, 4, 4, 65–75.
- Padilha, A., Lesley, R., Rios, P.R., 2007. *Stainless steels heat treatment (Chapter 12)*. In: *Steel Heat Treatment Handbook (Second Edition)*. Boca Raton: CRC Press, 695-739.
- Pei, W., Yang, S., Cao, K., Zhao, A., 2023. *Effect of Annealing Temperature on Mechanical Properties and Work Hardening of Nickel-Saving Stainless Steel*. *Materials*, 16, 3988.
- Ramírez, J., Berrio, E., Alvarado-Avila, M.I., Field, D., Onate, A., Sanhueza, J.P., Montoya, L.F., Meléndrez, M.F., Rojas, D., 2023. *Effect of solution annealing temperature on the localised corrosion behaviour of a modified super austenitic steel produced in an open-air atmosphere*. *Materials Chemistry and Physics*, 299, 127498.
- Rustandi, A., Setiawan, S., Fathurrahman, I., 2017. *The Effect of Sodium Chloride Concentration on Corrosion Resistance of Austenitic Stainless Steel 316L and SMA Weldment*. *Solid State Phenomena*, 263, 120-124.
- Szewczyk-Nykiel, A., 2015. *The influence of molybdenum on corrosion resistance of sintered austenitic stainless steels*. *Technical Transactions*, 4, 131-142.
- Szklarska-Smialowska, Z., 2005. *Pitting and Crevice Corrosion*. Houston: NACE International: Houston.
- Upadhyay, N., Shankar, A.R., Balakrishnan, A., George, R.P., Pujar, M.G., Philip, J., Amarendra, G., 2020. *Effect of Molybdenum on Pit Initiation Rate and Pit Growth Using Electrochemical Noise and Its Correlation with Confocal Laser Scanning Microscopic Studies*. *Journal of Materials Engineering and Performance*, 29, 5337-5345.
- Wu, B., Li, N., Zhang, Y., Ming, H., Shu, M., Sun, Y., Hou, D., Li, Y., Wang, J., Han, E.H., 2024. *Effect of solution annealing and Al addition on the corrosion behavior of austenitic stainless steel in supercritical carbon dioxide at high temperature*. *Corrosion Science*, 234, 112131.
- Zhang, C., Wei, Y., Yang, J., Emori, W., Li, J., 2020. *Effects of nitric acid passivation on the corrosion behavior of ZG06Cr13Ni4Mo stainless steel in simulated marine atmosphere*. *Materials and Corrosion*, 71, 9, 1576-1590.