

# THE EFFECT OF FLUORIDE ON CORROSION BEHAVIOUR OF AUSTENITIC STAINLESS STEEL

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**Abstract:** Austenitic stainless steels are widely used for various industrial, construction and biomedical application because of their high resistance to uniform corrosion and suitable mechanical properties. However, they are prone to local corrosion in aggressive halides environments. In contrast of corrosion resistance research in chloride containing environments, there have been few investigations into the effect of fluorides on passivity breakdown and pitting corrosion of stainless steels. This article focuses on the effect of fluoride added to chloride solution on corrosion resistance of AISI 316L stainless steel. Evaluation is based on results of exposition immersion tests performed in 0.9 % NaCl, 0.9 % NaCl + 0.05 % NaF and 0.9 % NaCl + 0.5 % NaF solutions (42 days) and on results of cyclic potentiodynamic polarization tests performed in the same solutions.

**Keywords:** AUSTENITIC STAINLESS STEEL, PITTING CORROSION, FLUORIDE, IMMERSION TEST, CYCLIC POTENTIODYNAMIC TEST

## 1. Introduction

Despite their high resistance to uniform corrosion, austenitic stainless steels are prone to local pitting corrosion in halides containing environments. This corrosion form is typical for passivating metals and alloys. Aggressive ions present in solution can penetrate through the weakened places of surface passive film and cause its local breakdown and initiation of the pitting corrosion [1-3].

Chlorides are the most common aggressive anions present in industrial environments. However, often they are not the only aggressive components but tend to be mixed with fluorides. In contrast of corrosion resistance research in chloride containing environments, there have been few investigations into the effect of fluorides on passivity breakdown and pitting corrosion of stainless steels. Moreover, the results obtained are inconsistent and do not lead to the same conclusions [4-8].

The authors [4] studied corrosion resistance of unspecified stainless steel wires in artificial saliva with 0.05 and 0.2 wt. % fluoride additions. Based on the potentiostatic and potentiodynamic tests the authors found that the addition of fluoride decreased the corrosion resistance of all archwires tested. Contrary to these conclusions the authors [7] studied resistance of austenitic stainless steel (alloy 22) to local corrosion and they described inhibitive effect of fluoride anions at the concentration ratio of fluoride to chloride anions higher than two. The authors [8] evaluated the pitting behavior of AISI 304 stainless steel in neutral chloride solutions. It has been confirmed by potentiodynamic measurements that fluoride anions inhibit the chloride induced pitting corrosion but promote the uniform dissolution of the steel [8].

AISI 316L is Cr-Ni-Mo austenitic stainless widely used in various industrial and biomedical applications. This paper deals with the effect of fluoride anions (0.05 % NaF and 0.5 % NaF) added to chloride solution (0.9 % NaCl) on the pitting corrosion resistance of the above mentioned steel. Evaluation of the corrosion resistance is based on the results of exposure immersion tests (microscopic observation of attacked surfaces, mass losses of specimens) and on the results of the cyclic potentiodynamic polarization tests. Results of immersion tests were evaluated on the bases of corrosion rates calculated from corrosion losses during immersion and by morphology of pitting. Results of potentiodynamic polarisation tests were evaluated by pitting potentials.

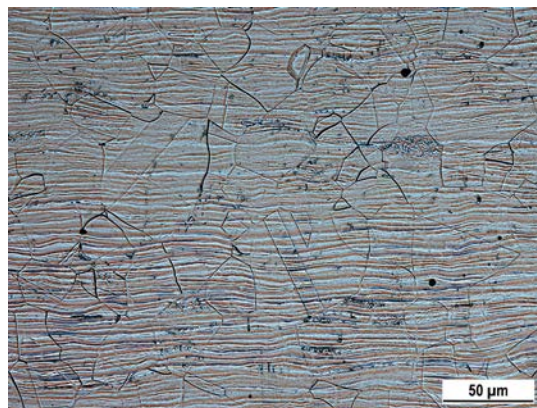
## 2. Experimental material

AISI 316L stainless, steel with chemical composition listed in Table 1, was used as an experimental material.

**Table 1:** Chemical composition of experimental material (wt. %)

Cr	Ni	Mo	Mn	N
16.79	10.14	2.03	0.82	0.05
C	Si	P	S	Fe
0.02	0.31	0.03	0.001	balance

Microstructure of experimental material (optical metallographic microscope Neophot 32) in longitudinal section is shown in Fig. 1. It is created by polyedric austenitic grains with observable twins, which could be created by annealing or by rolling. Parallel lines arose by the rolling during the technologic process. Observed microstructure contains numerous carbides. (Mo, Cr)<sub>23</sub>C<sub>6</sub> carbides [9] are localized along the above mentioned lines.



**Fig. 1** Microstructure of AISI 316L stainless steel in longitudinal section (Kalling's etch)

## 3. Experimental conditions and methods

0.9 % (0.15 M) NaCl solution was used as the basic corrosion environment for both immersion and potentiodynamic polarisation tests. The basic solution was applied without fluoride and with two additions of sodium fluoride: 0.05 % NaF and 0.5 % NaF. All solutions were pH neutral, their specific conductivities are listed in Table 2.

**Table 2:** Composition and specific conductivities of solutions

Composition [wt. %]	Specific conductivity $\chi$ [mS.cm <sup>-1</sup> ]
0,9 % NaCl	15.44
0,9 % NaCl + 0,05 % NaF	16.32
0,9 % NaCl + 0,5 % NaF	24.4

### Immersion tests

The specimen's shape for immersion tests was rectangular (30 mm x 80 mm x 1.5 mm). The specimen surface was not treated

(mechanically or chemically) only the edges were grinded by abrasive paper grain 600. The grease was removed by diethyl ether. The specimens were weighted out with accuracy  $\pm 0.00001$  g (Mettler Toledo XS 205). Immersion tests were 42 days and they were carried out at elevated ambient temperature  $37 \pm 0.5$  °C. The group of three parallel specimens was tested for each solution. After exposure the specimens were carefully brushed, washed by demineralized water, freely dried up and weighted out again [10, 11].

Pitted surfaces of specimens after immersion tests were observed by the optical microscope NIKON AZ 100. Average corrosion rates ( $\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ ) were calculated from corrosion losses ( $\text{g}\cdot\text{m}^{-2}$ ) during the immersion tests.

#### Cyclic potentiodynamic polarization tests

Cyclic potentiodynamic polarization tests were carried out in a three electrode cell of corrosion measuring system (VoltaLab 10 with VSP unit). Potentiodynamic polarization curves were obtained by the EC-LAB SOFT software. Potential between the sample and the electrolyte has been settled for 10 minutes before the polarization. Scan range was  $-0.3\text{V} - 1.2\text{V}$  vs the open circuit potential and the scan rate was  $1\text{mV/s}$ . The surface of working electrode AISI 316Ti of  $1\text{cm}^2$  area was not mechanically treated, only rinsed with diethyl ether before measurement. The saturated calomel electrode (SCE) was applied as the reference electrode and platinum foil as a counter electrode. All experiments were carried out at ambient temperature of  $37 \pm 0.5$  °C. At least five experiment repeats were carried out for all specimens.

#### 4. Experimental results and discussion

Tested specimens were locally damaged by pitting during immersion test. The corrosion failure was not visible to the naked eye it was visualized at a microscopic observation. As can be seen (Fig. 2), the pit's shape is generally irregular, pit's size varies. Edges of corrosion pits seem to copy austenitic grains and it points to possibility of combination of two forms of corrosion attack, pitting and intergranular corrosion [1-3, 9]. There is no marked difference between pits appearance according of fluoride content (Fig. 2), but the damaged area of specimens with the highest content of fluoride seems to be slightly smaller than in the other two cases.

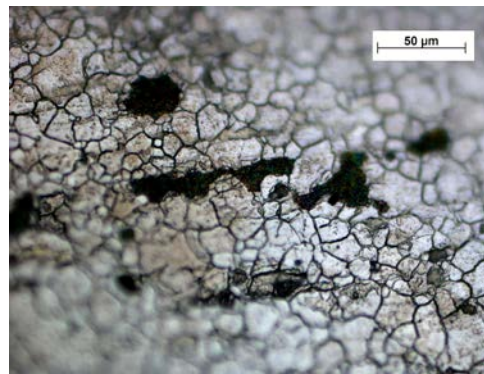
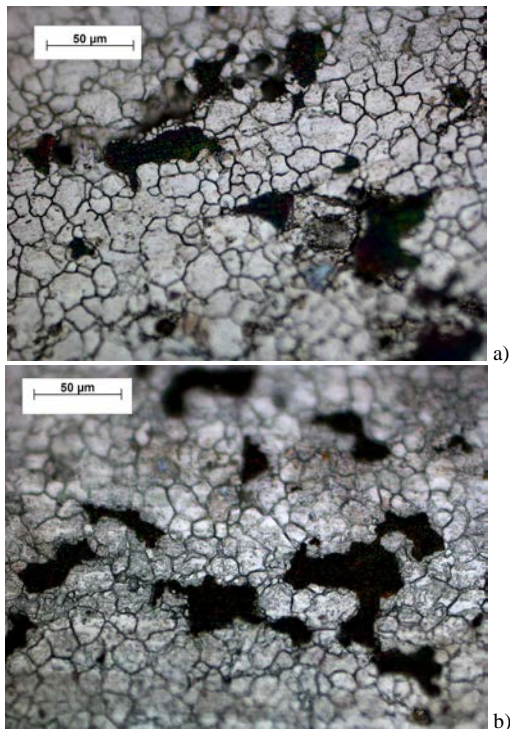


Fig. 2 Typical shapes of pits after 42-days immersion test: a) 0.9 % NaCl, b) 0.9 % NaCl + 0.05 % NaF, c) 0.9 % NaCl + 0.5 % NaF

Average corrosion rates calculated from corrosion losses during the immersion tests in dependence on the fluoride content in solution are shown in Fig. 3. As we can see, average corrosion rates decrease with the increase of fluoride content. However the corrosion rate based on the corrosion loss cannot be generally considered as the essential factor of evaluation of pitting corrosion resistance because of non-uniform, local character of pitting. However, it helps make an idea about probable changes in the pitting corrosion kinetics [2, 10].

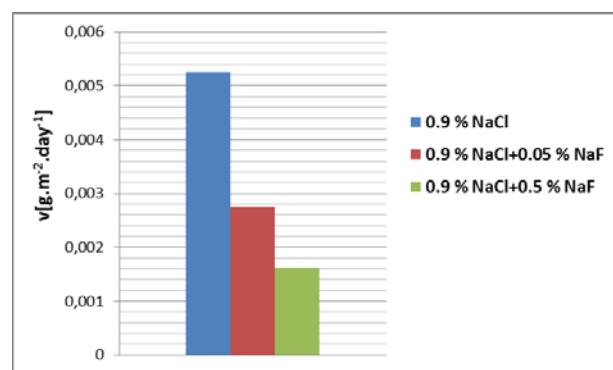


Fig. 3 Average corrosion rates in dependence on fluoride content

Cyclic potentiodynamic polarization curves enable determination of the pitting potential ( $E_p$ ), which is an important electrochemical characteristic of the passive film quality and of the resistance to pitting. When the potential reaches this critical value, current density suddenly increases, denoting the breakdown of the passive film and the beginning of stable pit growth. The shift of  $E_p$  to more positive values on the polarization curve means the rise of stability to pitting [1, 2, 10, 11].

Cyclic potentiodynamic curves of the tested steel in three experimental solutions are shown in Fig. 4.

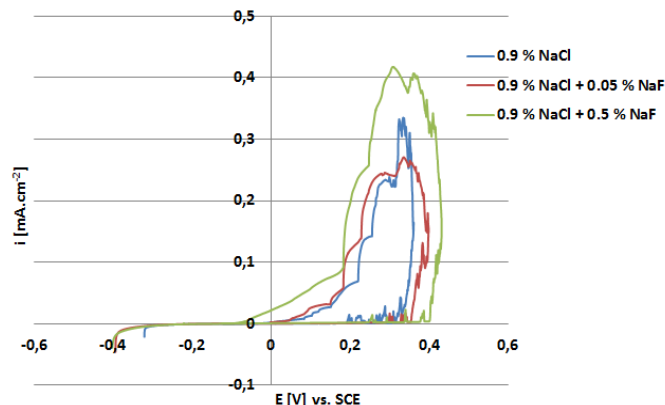


Fig. 4 Cyclic potentiodynamic curves of AISI 316L working electrode in dependence on fluoride content in solution

Curves are of typical lode shape with clearly observable pitting potential (located in the point of strong increase of current density). The pitting potentials  $E_p$  in dependence on fluoride content, are compared Fig. 5.  $E_p$  values (it means the resistance of passive film) increase with growing fluoride content in solution. The obtained results are consistent with authors [8], who consider fluorides the inhibitors of pitting corrosion in neutral chloride solutions.

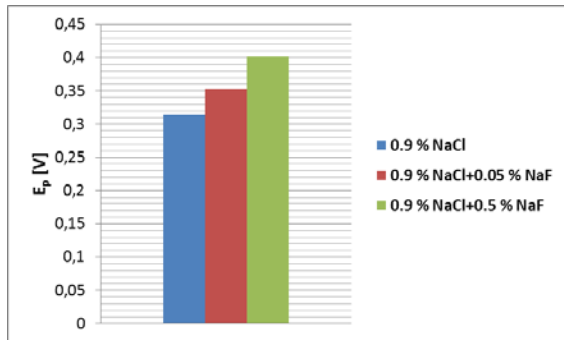


Fig. 5 Comparison of the pitting potentials ( $E_p$ ) in dependence on fluoride content in 0.9 % NaCl solution

A fluoride inhibitive effect on local corrosion of stainless steel could be based on formation of stable metal-fluoride complexes (with higher equilibrium constants than for metal-chloride complexes) [7, 12] which may strengthen the surface passive film and prevent its breakdown.

## 5. Conclusions

Based on the results of performed experiments can be concluded:

- A surface of AISI 316L stainless steel was attacked by local pitting corrosion during 42 days immersion test in all experimental solutions. A corrosion failure was not visible to the naked eye it was visualized at a microscopic observation.
- Observed corrosion attack was reflected in mass losses during immersion tests. Average corrosion rates calculated from mass losses decreased with increase of fluoride content in solution.
- According to the pitting potential values determined from cyclic potentiodynamic curves, resistance of tested stainless steel to pitting corrosion increases with the growing fluoride content in 0,9 % NaCl solution.

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## References

1. SZKLARSKA-SMIALOVSKA, Z. *Pitting and crevice corrosion*. Houston, Nace, 590 p., (2005).
2. LIPTÁKOVÁ, T. *Bodová korózia nehrdzavejúcich ocelí. (Pitting corrosion of stainless steels.)* Žilina, EDIS – Žilinská univerzita, 67 p., (2009).
3. HADZIMA, B., LIPTÁKOVÁ, T. *Základy elektrochemickej korózie kovov (Fundamentals of electrochemical corrosion of metals)*, Žilina: EDIS - Žilinská univerzita, 116 p., (2008).
4. HERAVI, F., MOAYED, M. H., MOKHBER M. *Effect of Fluoride on Nickel-Titanium and Stainless Steel Orthodontic Archwires: An In-Vitro Study*. Journal of Dentistry of Tehran, vol. 12, 1, pp. 49–59, (2015).
5. GHOSH, R., SINGH, R.J., SINGH, D. D. N. *Role of fluoride in accelerating corrosion and pitting of steel in concrete environments*. Transactions- Indian Institute of Metals, vol. 56, 4, pp. 391-397, (2003).
6. BASTIDAS, J. M., FOSCA, C., CHICO, B., OTERO, E. *Corrosion behaviour of highly alloyed stainless steels in mixed chloride and fluoride aqueous solutions*. Materials and Corrosion, vol. 48, pp. 216-220, (1997).
7. CARRANZA, R. M., RODRIGUEZ, M. A., BEBAK, R. B. *Inhibition of chloride induced crevice corrosion in Alloy 22 by fluoride ions*. Corrosion/2006 Conference and Exposition; 2006 March 12-16; San Diego, CA, USA, (2006).
8. YAMAZAKI, O. *Effect of fluoride ion on the pitting corrosion of type 304 stainless steel in neutral NaCl solution*. Zairyo-to-Kankyo, vol. 43, pp. 265-271, (1994).
9. PARDO, A., MERINO, M. C., COY, A. E., VIEJO, F., CARBONERAS, M., ARRABAL, R. *Influence of Ti, C and N concentration on the intergranular corrosion behavior of AISI 316Ti and 321 stainless steels*. Acta Materialia, vol. 55, pp. 2239-2251, (2007).
10. ZATKALÍKOVÁ, V. *Bodová korózia ocele AISI 316Ti pri rôznych prevádzkových podmienkach. (Pitting corrosion of AISI 316Ti at various operating conditions.)* PhD Thesis: ŽU v Žiline, Žilina, 77 p., (2008).
11. BABOIAN, R. *Corrosion Test and Standards: Application and Interpretation, ASTM Manual Series*. Philadelphia, USA, PA 19103, (1995).
12. GÁLVEZ, J. L., DUFOUR, J., NEGRO, C., LÓPEZ-MATEOS, F. *Hydrolysis of iron and chromium fluorides: mechanism and kinetics*. J. Hazard. Mater., vol. 154, 1-3, pp. 135-145, (2007).