Corrosion behaviour of superferritic and austenitic stainless steel for food application

M. Franchi, R. Valle

The food industry makes extensive use of conventional stainless steels, AISI 304 and AISI 316, for their high corrosion resistance in several aggressive environments, especially in the stage of cleaning and sanitizing. In this paper, among the possible alternatives available in the market, superferritic stainless steels are studied comparing them with the more common austenitic grades. The characterization work aimed at defining, through corrosion tests carried out in the specific operating conditions, if some ferritic / superferritic stainless steels may represent, from the perspective of resistance to corrosion, possible substitutes to the austenitic grade. For any selected materials, two different surface finishes were characterized. Potentiodynamic tests were carried out at room temperature in 0.5M NaCl and in alkaline foaming cleanser; at a temperature of 55°C in alkaline detergent; at a temperature of 70° C in an environment of 35% hydrogen peroxide. In addition, crevice tests have been performed. The tests allowed to define the corrosion limits and applications of ferritic/superferritic steels and to define operating conditions for which they can be considered substitutes equivalent of austenitic steels.

Keywords: Corrosion - Stainless Steel - Food industry applications

INTRODUCTION

In recent years, the increasing demand from the industrial world of materials independent by the nickel price fluctuation with good corrosion resistance, led markets to invest more and more on research in order to find alternative to the classical austenitic stainless steels. At present the food industry extensively uses conventional stainless steels, AISI 304 and AISI 316, for their high corrosion resistance showed against some specific environments, for example during cleaning and sanitizing, in which the materials must undergo to aggressive chemicals and relatively high temperatures. Among the possible alternatives that offer various steel mills, in the present work, some ferritic / superferritic stainless steels were selected, comparing them with the traditional austenitic grades. The choice of the most suitable material for the specific function, should consider the real operating conditions. Therefore, the characterization work aimed at defining, through corrosion tests carried out in the specific operating conditions, if superferritic steels can be considered, from a corrosion resistance perspective, equivalent to the austenitic one and be their possible substitutes.
Potentiodynamic tests were carried out at room temperature in 0.5M NaCl, in the alkaline foam cleaner at a temperature of 55°C, in the alkaline detergent at room temperature and in the environment of 35% hydrogen peroxide at a temperature of 70°C. In addition, crevice test have been performed. The test allowed to define the corrosion limits and applications of ferritic / superferritic steels and to define appropriate operating conditions for which they can be considered substitutes equivalent of austenitic steels.

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MATERIALS AND METHODS

On the Table 1 and Table 2 the material characterized in the present work are reported. The Steel 1 and Steel 2 are commercial products and the authors do not have the permission to give details.
Concerning the satin polished samples, only one side was satin polished, while the other was 2B.

Stainless Steel	Type	Surface finishing
AISI 304L (EN 1.4307)	Austenitic	2B, satin polished
460LI (prEN 1.4611)	Superferritic	2B, satin polished
Steel 1	Ferritic	2B
441 (1.4509)	Ferritic	2B, satin polished

Table 1 - Stainless Steels alternative to AISI304

Tabella 1 - Acciai alternativi all'AISI 304

Stainless Steel	Type	Surface finishing
AISI 316L (EN 1.4404)	Austenitic	2B, satin polished
470LI (prEN 1.4613)	Superferritic	2B, satin polished
Steel 2	Ferritic	2B, satin polished

Table 2 - Stainless Steels alternative to AISI316

Tabella 2 - Acciai alternativi all'AISI 316

Chemical Analysis

The chemical analysis was performed to compare the steel composition with the nominal ones in accordance to EN 10088-2 standard. The majority of the elements were determined by means of XRF (X-Ray Fluorescence) technique with the instrument PHILIPS Magic Pro or by means ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy) analysis utilizing the instrument Perkin Elmer Optima 3300 DV. Carbon and Sulphur content was determined by means of LECO CS600, Oxygen and Nitrogen by mean of Leco TCH600.

Metallographic Investigation

The samples microstructures were observed by means of OM (Optical Microscopy) techniques utilizing Nikon Metaphot instrument. The sample preparation was done according to ASTM E3 standard in cross section along the milling direction. After mechanical polishing specimens were electrochemically etched in a solution of nitric acid and hydrochloric acid. The intergranular susceptibility was evaluated by means of chemical attack with ossalic acid according to ASTM A262-A, ASTM A763-W standards.

Roughness Measurement

The surface investigation was done by means of roughness measurement on the as received samples. The measurements were done in the transversal direction with the instrument Hommelwerke T1000 referring to ISO 4287/1. R_a and R_t were evaluated setting a stroke of 4.8mm and a cut-off of 0.8mm.

Electrochemical tests in different environments

Cyclic potentiodynamic curves have been carried out on as received samples by means of a three-electrode cell; a calomel electrode was used as a reference, and platinum as counter electrode; Potentiostat Solartron 1287 (or 1286) model, interfaced to a computer, permitted to control the test cell by the dedicated Corware Software. Working electrode was left to stabilize at its OCP for 1h, then polarization curves started from -0.1V vs. OCP in the anodic direction at 1mVs-1 scan rate. Current was automatically recorded as a function of potential and the polarization scan was reversed at 100mA.
Four environments, simulating as much as possible the "in field" conditions, were selected to evaluate the seven stainless steels: 0,5M NaCl, 2 different alkaline cleaning fluids and a 35% hydrogen peroxide solution; all solutions were aerated and materials have been tested with the as received surface finishes.
The working electrode surface for tests in H_2O_2 was 0.7 cm^2, while in the other cases 1 cm^2 was characterised.
At least two tests were carried out on each sample.
Evaluated parameters were the free corrosion potential (Ecor), the pitting potential (Ep) and the protection potential (Epp). [1, 4].
After the test samples were characterised by O.M. to verify the surface condition.

Crevice corrosion resistance test

Critical crevice temperature was evaluated referring to ASTM G48-F. According to the standard, it shall be considered crevice when the corrosion attack has a minimum depth of 0.025mm; in this case the test is repeated decreasing the temperature of 5° C.
Because of the high corrosivity of the solution prescribed by the standard, in this study the corrosion test has been carried out in a modified solution, containing NaCl 0.5M in distilled water. Specimen sizes were 30mm x 40mm, with edges rounded and in the centre of them a hole has been drilled, to accommodate the bolt and insulating sleeve used to attach the PTFE crevice formers. A torque of 1.6 Nm has been applied using a 6.35-mm drive torque limiting nut driver. Specimens have been tested in duplicate with the as-received surfaces.

RESULTS AND DISCUSSION

Chemical Analysis

On Table 3 the chemical composition of the characterized stainless steel is presented. The compositions are in line with the reference provided by the supplier and defined by the UNI EN 10088 -2.

Metallographic Investigation

The whole steels analyzed didn't show any criticality from a metallographic point of view: they showed always recrystallized grains and acceptable etching structures without any susceptibility to intergranular attack.

Steel	Element (%)											
	S	C	Cr	Nb	Ni	Ti	Si	Mn	P	N	Mo	Sn	Fe
304L	<0.001	0.026	17.8	-	7.92	<0.05	0.29	1.66	0.024	0.060	0.15	-	bal
316L	<0.001	0.020	16.5	-	10.10	<0.05	0.35	0.87	0.027	0.038	2	-	bal
Steel1	<0.001	0.003	14.3	0.13	-	0.080	0.085	0.096	0.024	0.017	-	0.13	bal
Steel2	<0.001	0.002	16.1	0.13	-	0.081	0.06	0.054	0.021	0.0096	-	0.31	bal
441	0.001	0.017	17.8	0.40	0.49	0.140	0.48	0.460	0.027	0.016	0.02	-	bal
460LI	<0.001	0.009	21.0	0.21		0.140	0.28	0.130	0.027	0.012	0.013		bal
470LI	0.001	0.012	23.4	0.21		0.110	0.31	0.310	0.015	0.015	0.015		bal

Table 3 - Chemical composition of characterized stainless steels

Tabella 3 - Composizione degli acciai caratterizzati nel presente lavoro

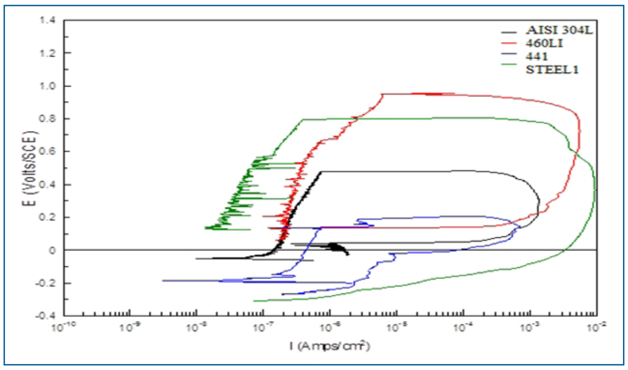

Fig. 1 - Potenziodynamic curve for AISI 304L(black line), 460LI (red line), 441 (blue line) and Steel 1 (green line), 2B surface finishing

Fig. 1 - Curve potenziodinamiche rappresentative di AISI 304L (linea nera) 460LI (linea rossa), 441 (linea blu) e Steel 1 (linea verde) finitura 2B.

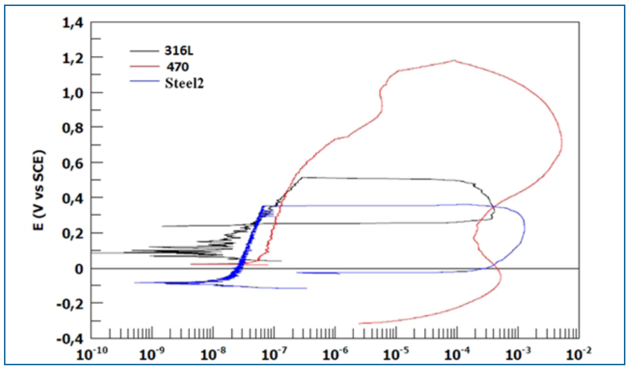

Fig. 2 - Potenziodynamic curve for AISI 316L (black line), 470LI (red line), and Steel 2, (blue line) 2B surface finishing

Fig. 2 - Curve potenziodinamiche rappresentative di AISI 316L (linea nera), 470LI (linea rossa), e Steel 2 (linea blu) finitura 2B.

Roughness Measurement

The samples showed similar surface roughness in terms of Ra; Ra and Rt measured are in line with the reference values for 2B finishing (Ra 0.10-0.20 μm) and for the requested satin polished finishing (Ra 0.20-1.5 μm).

Electrochemical test in different environments

In the following the results of the tests carried out in different environments are presented.

Evaluation of Pitting corrosion resistance in NaCl 0.5M at room Temperature

Results in NaCl 0.5M at room temperature are reported in Figure 1 and Figure 2 for surface finishing 2B. Same tests were performed for satin polished surfaces on samples showed in Table 1 and Table 2.

For the satin polished steels the lower critical pitting potential due to the surface finishing facilitated the closure of the hysteresis loop and pointed out the wideness of the ranges of perfect/imperfect passivity. 470LI showed the highest Erip, the widest range of perfect passivity and the range of imperfect passivity at higher potential than the other steels (0.2V/SCE and. 0.55 V/SCE). 316L, 460LI and Steel1 indeed showed the range of imperfect passivity at lower potentials. Both the position and wideness of the range of perfect passivity allow to foresee the behaviour of the material in case of breakdown of the passivity film in the in-filed application.

Evaluation of Pitting corrosion resistance in alkali detergent solutions

Several measurements have been performed in two different alkaline cleaning solutions at different temperatures (RT, 55°C).

None of the tested materials showed susceptibility to pitting when exposed to the two solutions. The analysis of the specimen surfaces confirmed that localized corrosion in both environments was not present for all analyzed materials.

Evaluation of Pitting corrosion resistance in solution of H_2O_2 35% in volume at 70°C.

None of the tested materials showed susceptibility to pitting when exposed to 35% hydrogen peroxide solution at 70°C.

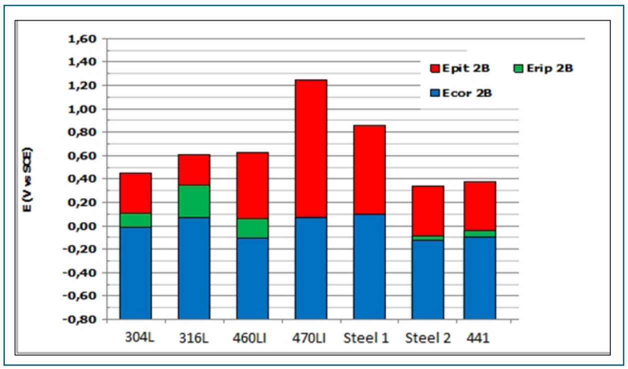

Fig. 3 - Resume of passivity range of stainless steel characterized – 2B finishing

Fig. 3 - Istogramma riassuntivo dei range di passività nella finitura superficiale 2B.

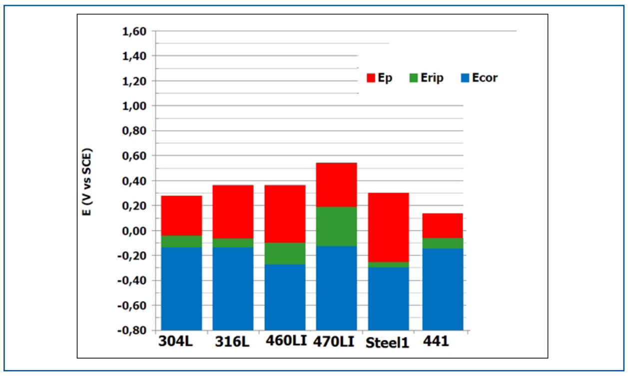

Fig. 4 - Resume of passivity range of stainless steel characterized – satin polish finishing

Fig. 4 - Istogramma riassuntivo dei range di passività nella finitura superficiale satinata.

On 2B finishing specimens, AISI 316L showed a range of perfect passivity wider than the other steels. Steel 470LI did not show susceptibility to pitting and, for this reason the unclosed hysteresis loop was not considered.

Crevice corrosion resistance test

In Figure 5 the results of the immersion corrosion test for both 2B finishing and satin polished specimens are reported. It can be observed that the CCT value found out for every steel, seem to be independent from the surface finishing because values and trends of the CCT for the two surface finishing were comparable.

These results consider the corrosion attack on both sample sides, sometimes the crevice has been observed only on one side, in other on both sides. This test could be not suitable to evaluate crevice corrosion resistance of the steels analyzed because of the different surface finishing of the two sides of the specimens.

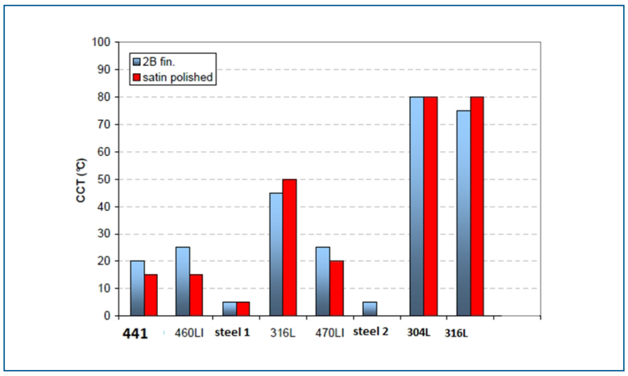

Fig. 5 - CCT of all steels in both surface finishing

Fig. 5 - CCT di tutti gli acciai caratterizzati a confronto nelle due finiture 2B e satinata.

In terms of crevice corrosion the Superferritic 470LI showed CCT of about 20-25°C in the tested conditions: less aggressive than the one suggested by the ASTM G48-F standard. Austenitic stainless steels AISI 304L and AISI 316L showed, as expected, better crevice corrosion resistance with an higher value of CCT (AISI 316L ~45 °C); this is due to the presence of elements that increase its re-passivation behaviour. The lower CCT value showed by 470LI should be considered in case of specific applications that require an high crevice corrosion resistance.

CONCLUSIONS

Chemical composition and surface quality of the steels characterized for both surface finishing appeared comparable with reference values.
Electrochemical tests in NaCl pointed out the effect of the surface finishing, because, for the same steel grade, the higher surface roughness of the satin polished specimens lowered the critical pitting potential respect to the 2B finishing specimens. Among the analyzed steels, 470LI showed the highest resistance to pitting in the test conditions for both 2B and satin polished finishing; in particular 470LI satin polished showed the highest pitting potential and the widest range of perfect passivity than the other steels.
The results of electrochemical tests in alkaline detergents and in hydrogen dioxide didn't show any susceptibility to pitting for the whole steels analysed.
In conclusion, the characterisations carried out on the steels analyzed, showed interesting performances of superferritic stainless steels (470LI) and so it could be experimented in Tetra Pak packaging machines as alternative to austenitic steels.

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Comportamento a corrosione di acciai superferritici ed austenitici in applicazioni alimentari

Parole chiave: Corrosione - Acciaio inossidabile – Impieghi alimentari

Il settore alimentare attualmente fa ampio uso degli acciai inossidabili convenzionali, AISI 304 e AISI 316, per l'elevata resistenza a corrosione che mostrano nei confronti di alcuni ambienti specifici, soprattutto nelle fasi di pulizia e sanificazione. Tra le possibili alternative che varie acciaierie propongono, nel presente lavoro sono stati scelti acciai inossidabili superferritici mettendoli a confronto con i comuni austenitici. Il lavoro di caratterizzazione qui presentato è volto a definire, tramite prove di corrosione eseguite nell'ambiente di lavoro e condizioni operative specifiche, se alcuni acciai ferritici/superferritici possano essere considerati, sotto la prospettiva di resistenza a corrosione, equivalenti agli austenitici ed essere quindi loro possibili sostituti. Per ognuno dei materiali selezionati sono state caratterizzate due differenti finiture superficiali. Sono state eseguite prove potenziodinamiche a temperatura ambiente in NaCl 0.5M e in detergente schiumogeno alcalino; a temperatura di 55°C in detergente alcalino; a temperatura di 70°C in ambiente di perossido di idrogeno al 35%. Sono state eseguite, inoltre, prove di crevice. I test hanno permesso di definire i limiti di esercizio e applicazione degli acciai ferritici/superferritici e di definire opportune condizioni operative per cui essi possano essere considerati sostituti equivalenti di acciai austenitici.