JOURNAL OF APPLIED ELECTROCHEMISTRY **28** (1998) 1333–1341

Influence of the exposure of AISI 304L stainless steel at moderately high temperature on the susceptibility to crevice corrosion*

S. P. TRASATTI,[‡] E. CAMONA, F. MAZZA, E. SIVIERI

Department of Physical Chemistry and Electrochemistry, University of Milan, Milan, Italy
(E-maila: trasatti@icil64.cilea.it)

Received 11 November 1997; revised 13 July 1998

Stainless steels passivate in air by forming a very thin (a few nanometre thick) protective film of Fe and Cr mixed oxides. The nature and the protective properties of this film change if the stainless steel surface is previously exposed to elevated temperatures. Thermal treatment, chemical processes and mechanical manufacture to which stainless steel surfaces are normally subject, result in changes to the surface conditions, and therefore to modification of the corrosion resistance. Among the various forms of corrosion of stainless steels, crevice corrosion is undoubtedly the most common in industrial environments and one of the most insidious from an engineering point of view. In this work the effects of surface conditions, in particular as a consequence of exposure at moderately high temperature ranging between 150 and 300 °C, on the corrosion behaviour of type AISI 304L stainless steel have been investigated. The aim has been to verify if common treatments causing local heating, such as welding, even in remote regions, thermal stretching, grinding, exposure to superheated steam, or sterilisation processes can constitute aggravating circumstances in respect of crevice corrosion susceptibility.

Keywords: *crevice corrosion*, *stainless steel*, *thermal treatment*

1. Introduction

Stainless steels show excellent resistance to general corrosion in many environments due to the formation of a highly protective surface film [1]. However, in many cases, particularly in the presence of chlorides, stainless steels undergo localized attack, resulting in pitting, crevice corrosion and stress corrosion cracking, which are associated with the localised breakdown of the surface passive film [2].

Among the most crucial metallurgical factors determining the corrosion resistance of stainless steels, the alloying elements, the impurities in the steels and the surface conditions play a significant role [3–6]. The surface state of commercial stainless steels cannot be generated as sufficiently defined for the reproducibility of corrosion tests on a laboratory scale. For this reason samples are conditioned with abrasive papers or chemically or electrochemically pretreated. In some cases the mechanical preparation is followed by pickling and/or passivation. The preparation of the metal surface is crucial, especially on a mostly passive surface, in that the local collapse of the passive state is responsible for the onset of the localized corrosion attack [7]. The influence of surface pretreatment on the susceptibility to crevice corrosion has been investigated by a number of authors. Syderberger [8] studied the crevice corrosion of austenitic and austeno-ferritic stainless steels. His results suggest that the breakdown of passivity on surfaces with crevices is preceded by pitting corrosion, preferentially stimulated by inclusions of MnS. The beneficial effects of chemical attack or passivation as a pretreatment was interpreted as due to the removal of such inclusions from the steel surface. Ericsson *et al.* [9] investigated the resistance of AISI 316 stainless steel to pitting corrosion; chemically pretreated surfaces turned out to be the most resistant. Hultquist and Leygraf [10] continued the same work by determining the surface composition of the surface oxides. By means of Auger spectroscopy, they found a surface enrichment with chromium, higher for passivated samples. They concluded that the initial steps of crevice and pitting corrosion are of a different nature.

Crolet *et al.* [11] tried several chemical treatments to 'decontaminate' the steel surface. They concluded that a chemical pretreatment of pickling or passivation improves the resistance to pitting and crevice corrosion significantly.

The same conclusion was reached by Kain [12] with AISI 316 stainless steel in seawater. This author has also shown that electropolished surfaces exhibit the minimum susceptibility to crevice corrosion.

---

* This paper is dedicated to the memory of Professor Giuseppe Bianchi.
[‡] Present address: Henkel Surface Technologies, Caleppio di Settala (Mi), Italy.

Grubb [13] has shown the positive effect of pickling corrosion by removing the Cr-deficient layers which can form during annealing at high temperatures. Lu and Ives [14] have shown that crevice corrosion can be mitigated by inhibiting the cathodic process. This can be achieved by a pretreatment in solutions containing rare earth elements, or by ion implantation of cerium.

Surface finishing is therefore a very important factor: the smoother the surface, the higher the resistance to the two forms (pitting and crevice) of localized corrosion. However, a definite correlation between laboratory tests and industrial plant conditions has not yet been established. [15–17]

Bianchi and coworkers [3, 18] studied the influence of oxide films formed at various temperatures in air on the resistance of AISI 304L stainless steel to pitting corrosion in glycero-ethanolic solutions of $FeCl_3$. These authors have pointed out the importance of the surface preparation and a correlation between the electronic conductivity and ionic structure of the air-formed oxide films and the susceptibility to pitting corrosion.

Parts of industrial plants can frequently undergo overheating by some hundred degrees as a consequence of welding, in the HAZ, or grinding, as well as of exposure to hot gases, superheated steam etc. The thin coloured oxide layers thus formed on the metal surface are usually removed by chemical pickling since they are universally recognised to be deleterious for the corrosion resistance of the alloy. In contrast, the colourless films formed at lower temperature, being invisible, are not usually removed.

The purpose of the present work was to investigate the influence of these colourless oxides when grown in air at 150 to 300 °C on the resistance of AISI 304L stainless steel to crevice corrosion. The study was carried out by means of corrosion tests and electrochemical measurements on previously oxidised samples.

2. Experimental details

2.1. *Materials*

A 3 mm thick plate of AISI 304L stainless steel, of composition (wt %) Cr 18.09, Ni 10.05, Mn 1.38, Si 0.35, P 0.032, N 0.032, C 0.024, S 0.005 and Fe balance was cut into square samples of total 4 cm^2 surface area.

2.2. *Surface pretreatments of samples*

The following pretreatments were tested in the search for the best reproducibility:

(A) Polishing with abrasive paper down to 600 grit.
(B) Polishing as in (A) followed by immersion in 20% HNO_3 for 15 min.
(C) Polishing with abrasive paper down to 4000 grit followed by electromechanical cleaning for 1 min in a solution containing oxalic acid ($16\ g\,dm^{-3}$), tartaric acid ($80\ g\,dm^{-3}$), and γ-alumina ($2–3\ g\,dm^{-3}$) under anodic current (density $10–15\ A^{-3}\,cm^{-2}$) at a disc speed of 125 rpm.

Method C was chosen as the surface preparation method since it produced homogeneous fresh surface which allowed the growth of a homogeneous oxide surface layer. This enabled meaningful and reproducible results to be achieved in tests of resistance to crevice corrosion.

2.3. *Heat treatment*

Samples of 304L stainless steel already polished (described previously) were subjected to heat treatment in a continuous air stream at temperatures in the range 150 to 300 °C for 30 and 120 min. The samples were then cooled in a helium stream for 30 and 90 min, respectively, so as to quickly stop the oxidative process. Cooling in He was produced similar results with respect to the oxide growth as in air, but in a shorter time.

2.4. *Testing crevice corrosion susceptibility*

Two experimental approaches were used, the first electrochemical, the second chemical: measurement of the depassivation pH [19] and modification of the standard ASTM G 48–76 method [20], combined with a multiple crevice system [21].

2.4.1. Electrochemical test (depassivation pH) pH is a crucial parameter for the onset of crevice corrosion. Its effect can be evaluated from the change of the shape of polarization curves with pH. Samples were mounted on an electrode holder of the type described by Stern and Makrides [22] appropriately modified to hold thin sheet samples (Fig. 1). The edges of samples were protected by Teflon ribbon, since they were not prepared as the two faces of the samples.

Polarization curves were recorded potentiodynamically at $0.1666\ mV\,s^{-1}$ up to a potential of 0.1 V (passive state). Current was automatically recorded as a function of potential. A polarization cell of the type described in the ASTM G5-69 (964) specification with a saturated calomel reference electrode was used. A nitrogen stream was used to dearate the solutions which were kept at 25 °C.

The composition of the aqueous solution was 3.5% by weight NaCl; the pH was regulated to the desired value by means of 0.1 M HCl additions. Before each run, the samples were left in the solution at open circuit for 10 min. The electrodes were then subject to cathodic polarization starting from −0.6 V so as to establish conditions of better reproducibility. The susceptibility to crevice corrosion was expressed in terms of the pH at which the critical passivation current (i_{cr}) reached the value of $10\ \mu A\,cm^{-2}$ [23]. This

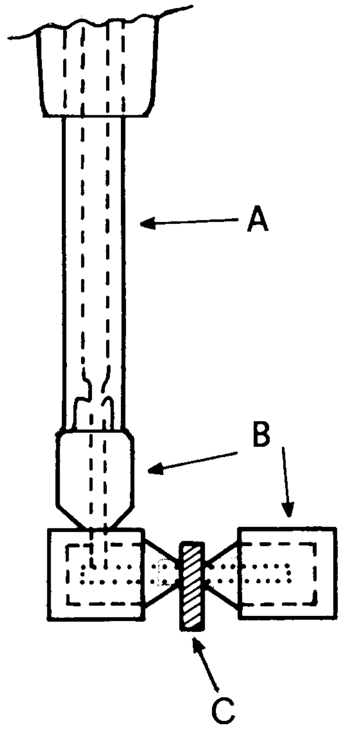

Fig. 1. Electrode holder for thin sheet samples used in electrochemical tests: (A) electrode mounting rod, (B) PTFE gaskets and (C) sample sheet.

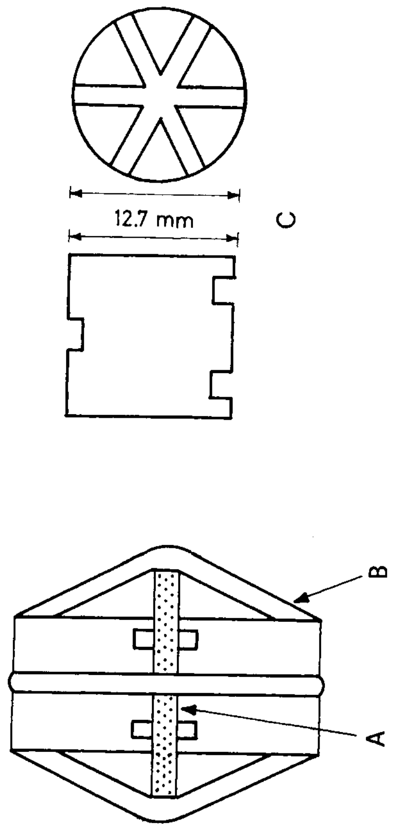

Fig. 2. Assembly system of samples in chemical tests: (A) sample, (B) O-ring and (C) PTFE cylinder.

criterion is to some extent arbitrary, but it is approximately equivalent to a corrosion penetration rate of 0.1 mm per year and may therefore be considered to represent the onset of a significant crevice corrosion rate.

2.4.2. Chemical test The chemical test used in this work was a modification of the standard ASTM 48–76 test in a 6% $FeCl_3$ solution combined with a multiple crevice system. The standard test was modified (i) because of the strong effect of $FeCl_3$ on the 304L stainless steel, which rendered the test nondiscriminating in evaluating the resistance of the oxidized samples to crevice corrosion, and (ii) because of the different size of the samples with respect to the standard recommendations.

The crevice system was realized using Teflon cylinders, treated with 2400 grit emery paper to increase the probability of onset [24], with three grooves producing six crevices so as to give some statistical significance to the method. The system sample/Teflon was assembled by means of Viton O-rings of 15.8 mm diameter (Fig. 2). Tests lasted two hours at 20 °C and the temperature was controlled by means of a Haake F3-CH thermocryostat. Three different samples were used in each experiment .

Crevice corrosion was evaluated on the basis of visual inspection of the sample and of a gravimetric analysis with a resolution of 0.001 g, after immersion for 15 min in 10% HNO_3 at 60 °C to eliminate the corrosion products. From the $FeCl_3$ tests information was obtained on the following items: (i) number of crevices, (ii) number of (eventual) pits, (iii) extent of crevice attack (%) and (iv) weight loss. For items (ii) and (iii), an image analysis technique was used by means of a Wild Heerbrougg Stereo and a Leica Q 500MC analyser. The image was first projected on a screen at 8× magnification, then digitized on the basis of the level of greys, and finally modified manually. The number of pits and the fraction of attacked area were obtained by means of the analyser.

XPS analyses were carried out on the surface, as well as at a depth of 18 nm, to determine the amount of Fe, Cr, and Ni in the oxide layer resulting from two of the most significant treatments (200 and 300 °C). A nonoxidized sample was used as reference. High resolution multiplexing was performed using an energy window of 568 to 594 eV and 701 to 736 eV for Cr and Fe, respectively. An MgK_α X-ray source was employed for all measurements, using a beam voltage of 15 kV at 400 W. The sample area analysed was approximately 3 mm^2.

3. Results and discussion

Surface preparation is one of the parameters which most influences the onset of crevice corrosion: for example, the pH of passivation (pH_p) depends critically on the surface state of the sample. The following results stress the criterion adopted in this work for surface preparation prior to oxidation treatments.

3.1. *Thermally nonoxidized surfaces*

3.1.1. Electrochemical tests. Figure 3 shows a typical family of polarization curves recorded at different pH between −0.6 and 0.1 V, for samples pretreated according to method C (cf. Section 2.2). Depassivation pH values (pH_d) were derived by plotting, for each family of curves, the height of the active peak (i_{cr}) (the 'nose') as a function of pH, and interpolating the plot at 10 μA cm^{-2}, a value deemed significant for a detectable onset of crevice corrosion. The depassivation pH referred to the various surface preparation types, as displayed in Fig. 4, are 3.6 for pretreatment A, 1.75 for B and 2.62 for C, as confirmed by similar tests not shown in this paper. The use of HNO_3 as a surface passivating and decontaminating solution results in a decrease in pH_d by about two units. Since a high susceptibility to corrosion is dependent upon a high pH_d an intermediate pH_d for sample C led to a decision to adopt such a pretreatment for preparation of sample surfaces prior to oxidation.

3.1.2. Chemical tests. Chemical tests provide the following information: (i) the number of crevices and (ii) extent of crevice attack. Scrutiny of the data in Table 1 shows that samples B behave quite differently from A or C. This indicates that treatment in HNO_3 is more discriminating than mechanical or electromechanical polishing. This is in agreement with Kain [12] and Crolet *et al.* [11]. The short duration (2 h) and the small ratio between cathodic and anodic areas ensure that the results reflect mainly the suscep-

Table 1. Chemical test results on samples (three for each treatment) subject to different surface treatments

Surface treatment	*Crevice attack (number of sites)*				*Extent attack /%*			
	1	*2*	*3*	*sum*	*1*	*2*	*3*	*mean*
A	11	8	8	27	5.04	2.86	2.65	3.51
B	2	5	2	9	0.43	1.6	0.24	0.75
C	5	7	9	21	2.42	2.26	4.38	3.02

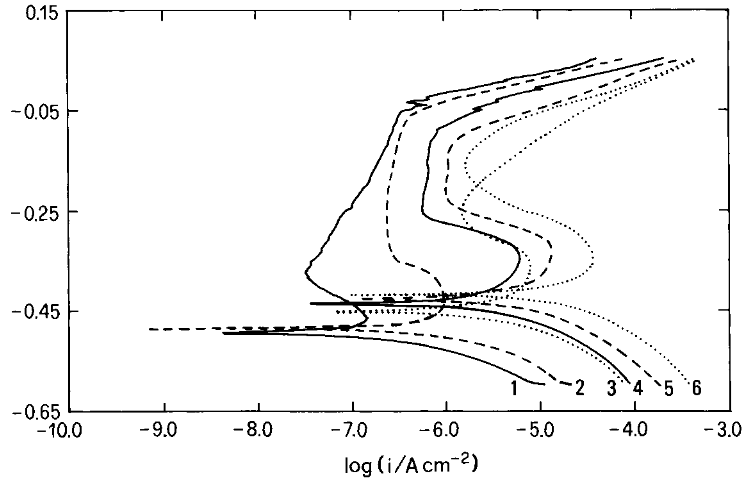

Fig. 3. Polarization curves of samples polished with emery paper down to 4000 grit followed by electrochemical cleaning as a function of pH: (1) pH 4.0, (2) pH 3.8, (3) pH 3.7, (4) pH 3.5, (5) pH 3.2, (6) pH 3.0.

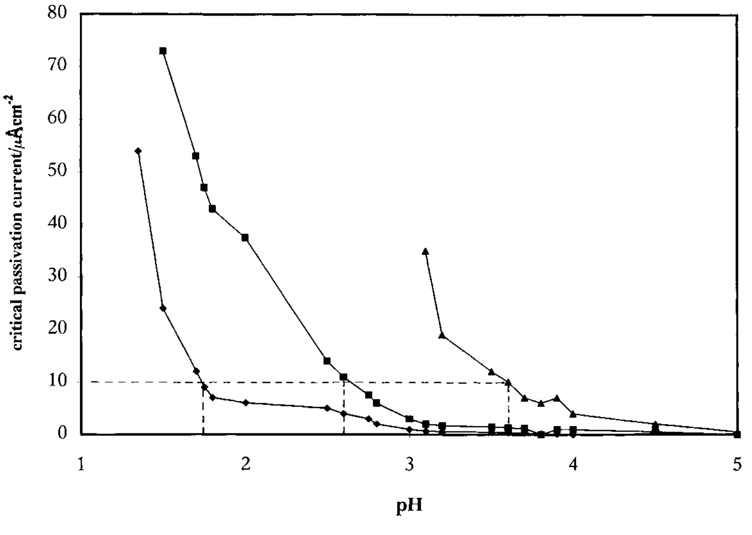

Fig. 4. Plot of the critical passivation current as a function of solution pH for samples pre-treated according to (1) method A, (2) method B, (3) method C (cf. Section 2.2). The identification of the depassivation pH (pH_d) is indicated.

tibility to the initiation step rather than the resistance to the propagation process of crevice corrosion.

On the basis of the results of both electrochemical and chemical tests it can be concluded that the surface preparation (using abrasive paper down to 4000 grit) and electromechanical cleaning (method C) can be properly used as a basis for the successive thermal treatments. In fact, sample A (polished with abrasive paper down to 600 grit) undergoes a marked localized corrosion, whereas for sample B (immersed for 15 min in 20% HNO_3 after the same mechanical treatment as for sample A) corrosion is inhibited by HNO_3. Therefore, to obtain meaningful and reproducible results, a surface treatment avoiding extreme conditions (either too much or too little corrosion) is necessary.

Observation by SEM of samples A and C has shown the absence of any sign of polishing on the surface of sample C. As for the effect of surface pretreatment on the results of thermal treatments, a perfectly smooth surface ensures a homogeneous growth of oxidation, as shown by Caplan *et al.* [25]. The experimental data obtained with sample C have been taken as a reference for the discussion of the results obtained with oxidized samples, and are summarized in Table 2.

3.2. *Thermally oxidized surfaces*

3.2.1. Electrochemical tests. Figure 5 shows a typical family of polarization curves recorded at various pH from −0.6 to 0.1 V for samples oxidised at 150 °C for 120 min. An increase in acidity results in a shift of the cathodic polarization curve toward higher currents (higher availability of H^+ ions). The influence of acidity is visible on the passivation process, in the sense that a decrease in pH produces an increase in the critical passivation current. The variation of E_{corr} as a function of pH is, in general, toward a more noble potential as pH decreases: this also indicates the important role of acidity in the equilibrium between metal surface and solution.

Table 2. Experimental data from electrochemical and chemical tests on sample prepared by method C

Quantity	*Value*
pH_d	2.62
Crevice attack (number)	21
Extent attack/%	4.58
Pits/cm^{-2}	17
Weight loss/mg	15.8

It is intriguing that while E_{corr} depends on pH for oxidized samples, this is not the case for E_{corr} of non-oxidized samples. A plausible explanation is that oxidized surfaces are subject to acid–base equilibria which establish pH-dependent surface potentials, while such equilibria are not operative with nonoxidized surfaces.

A typical plot of the critical passivation current as a function of pH is shown in Fig. 6 for a sample oxidized at 300 °C for 30 min. The location of the depassivation pH is also shown. The values of depassivation pH for the various thermal treatments are collected in Table 3.

As the oxidation temperature is increased, the pH_d value decreases for both oxidation times. At the highest temperatures there is a trend toward an increase in pH for the longer times. This can be understood in terms of Cr migration being a function of temperature as well as of exposure time. Comparison with the initial pH (2.62) suggests that treatment at relatively high temperature improves the resistance to crevice corrosion, and that an increase in temperature produces a similar effect as that of a surface treated with nitric acid.

3.2.2. Chemical tests. Optical microscope images of three samples subjected to different pretreatments are shown in Fig. 7; this illustrates the influence of thermal treatment on the development of localized (crevice and pitting) corrosion. The number and size

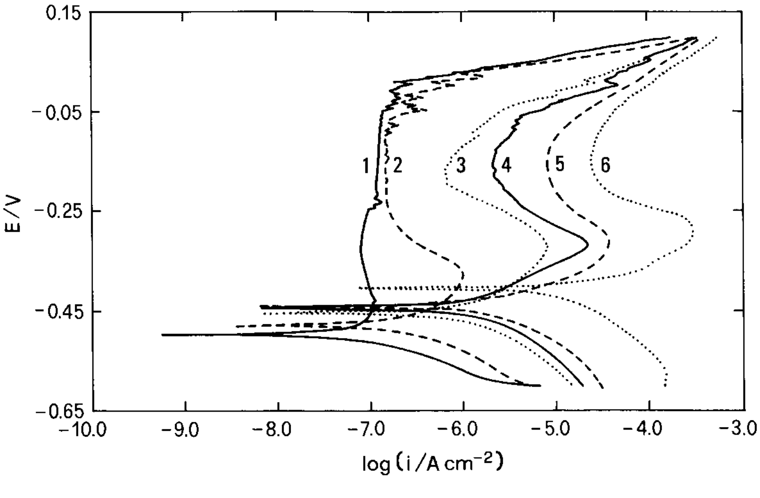

Fig. 5. Polarization curves of samples heated in air at 150 °C for 120 min as a function of pH: (1) pH 4.0, (2) pH 3.0, (3) pH 2.0, (4) pH 1.8, (5) pH 1.5, (6) pH 1.0.

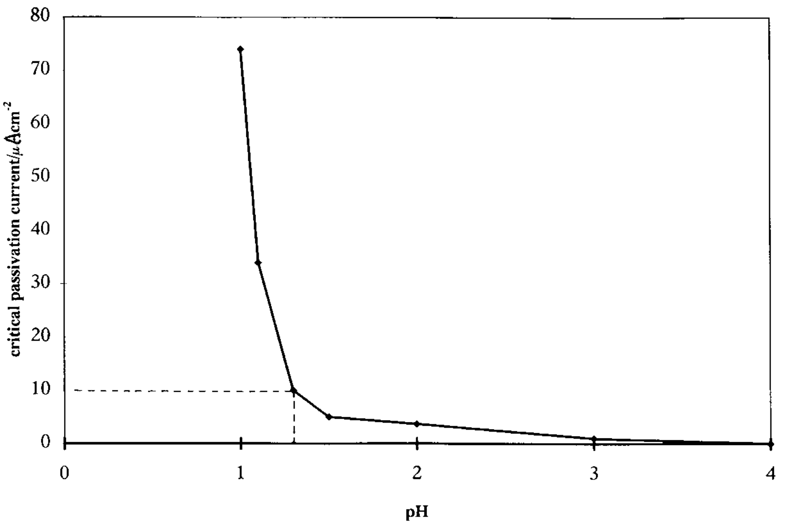

Fig. 6. Plot of the critical passivation current as a function of solution pH for a sample heated in air at 300 °C for 30 min. The depassivation pH (pH_d) is indicated.

Table 3. Depassivation pH of samples thermally oxidized as a function of the treatment time

Temperature/°C	pH_d *(30 min)*	pH_d *(120 min)*
150	2.25	1.98
200	1.6	1.5
250	1.5	1.89
300	1.3	1.35

of pits increase as the oxidation temperature is increased, whereas the extent of crevice attack decreases. Table 4 summarizes the experimental results. The values are obtained as the mean of three independent tests, except for the crevice attack, whose values are the sum of the three experiments (cf. data in Table 1). Comparison with the data in Table 2 shows that electrochemical and chemical tests lead to similar results. Thermal treatment at 250–300 °C gives the formation of an oxide layer less resistant to localized corrosion, so that heavy pitting occurs on the external surface and decreases the intensity of the attack within the crevice. The propagation of the attack is measured by weight loss, which obviously encompasses crevice attack and pitting. Weight losses are rather similar with the exception of those for the treatment at 300 °C: at the two exposure times opposite values are observed, that is, the highest and the lowest weight loss.

Some tendency for weight loss to increase with the temperature of the thermal treatment is evident. The treatment at 300 °C for 120 min shows the highest number of pits per cm^2; that is, such a treatment makes the resistance to corrosion worse. A similar conclusion was achieved by Bianchi *et al.* [18], who pointed out that the p-type conductivity of these films indicated the possibility of anionic migration through the oxide lattice creating conditions of pit nucleation. In the present case the nucleation of crevice corrosion should occur with a similar mechanism, but the increase in attack intensity is more evident for pitting corrosion than for crevice corrosion. The preferential attack of pitting corrosion relative to crevice corrosion may be due to the easier pitting nucleation on the alloy surface than within the crevices by the action of the cathodic process.

If the values of the experimental parameters for both oxidation times are compared as a function of the oxidation temperature, the following trend are identified:

(i) An increase in temperature results in a decrease in the number of crevices, while the percentage crevice attack first decreases, then increases again; the most remarkable differences between the oxidation at 30 and 120 min are observed at 150 °C.
(ii) The number of pits increases with temperature and with the oxidation time.
(iii) The weight loss first is almost constant. An increase is then visible especially for the samples oxidized for longer times.

3.3. *XPS analysis*

Figure 8 compares the Fe (2p) spectra for unoxidized samples (a) and for samples oxidized at 300 °C for 30 (b) and 120 (c) min. Figure 9 shows the Cr (2p) spectra for unoxidized samples (a) and for samples oxidised at 300 °C for 30 min as received (b) as well as sputtered a depth of 18 nm. A complete analysis of the surface composition for as-received samples, as well as for sputtered samples at a depth of 18 nm, has revealed that:

(i) on the surface of samples oxidized at 200 and 300 °C there is a prevalence of FeO and FeOOH, Cr and its oxides being below the detection limits of the instrument. In contrast for untreated samples Cr oxides, typical of stainless steels, are detected. For samples exposed for 30 min the amount of FeO increases with temperature, whereas for the samples treated for 120 min the proportion between the two oxides remains practically constant.

(ii) at a depth of 18 nm, the amount of Fe decreases with increasing temperature, while Fe oxides increase in percentage (mol %), and the same behaviour is observed for Cr and Cr_2O_3.

Finally, the XPS analyses have confirmed the prevalence of Fe on the surface of samples oxidized for 30 min, whereas a mixture of Fe and Cr oxides is present below the surface layer as proved by ion etching at an 18 nm thickness of sample. At room temperature the stainless steel surface is covered by a film of Cr + Fe mixed oxide, presumably Fe(Fe, $Cr)_2O_4$, whereas on the surface of treated

Table 4. Samples oxidized at temperatures between 150 and 300 °C *

Temperature/ °C		*150*	*200*	*250*	*300*
Crevice attack (number)	30 min	13	10	13	8
	120 min	24	10	10	14
Extent of attack (%)	30 min	0.92	0.64	1.55	1.4
	120 min	3	0.44	1.04	2.14
Number of pits/cm^{-2}	30 min	17	26	54	38
	120 min	44	33	36	145
Weight loss/mg	30 min	6.03	5.2	9.6	3.17
	120 min	6.47	6.57	5.6	11.57

* Mean of three independent tests.

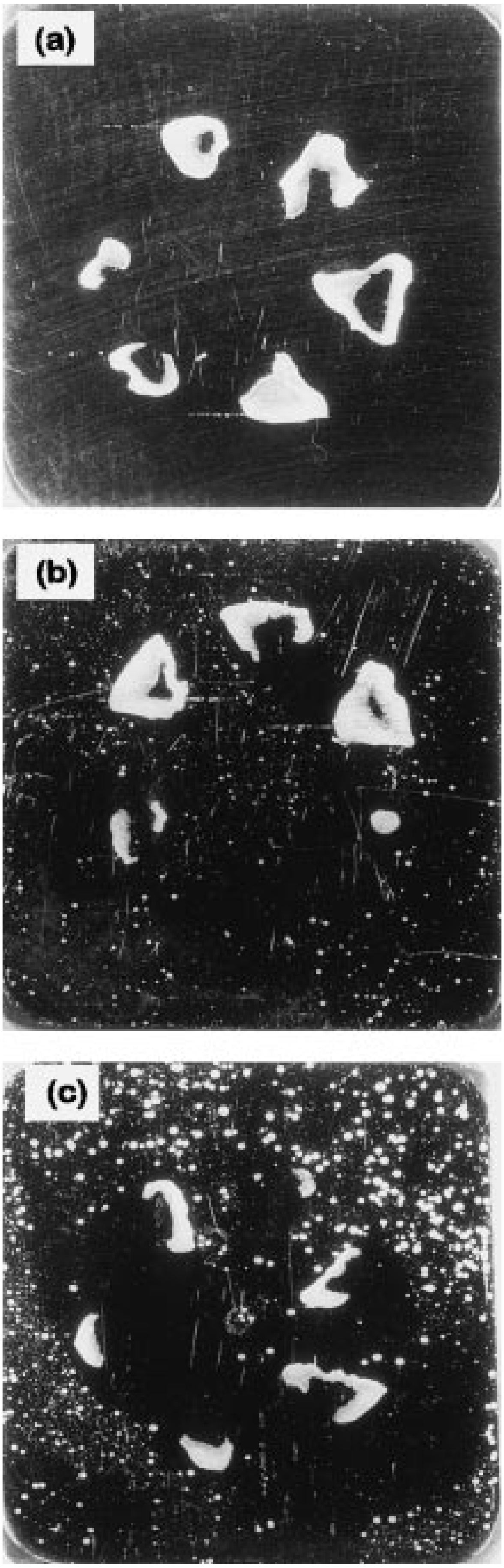

Fig. 7. Crevice and/or pitting corrosion development after chemical testing; (a) unoxidized, (b) oxidized at 250 °C for 120 min, (c) oxidized at 300 °C for 120 min (4×). *Large spots*: crevice corrosion attack; *small spots*: pitting corrosion.

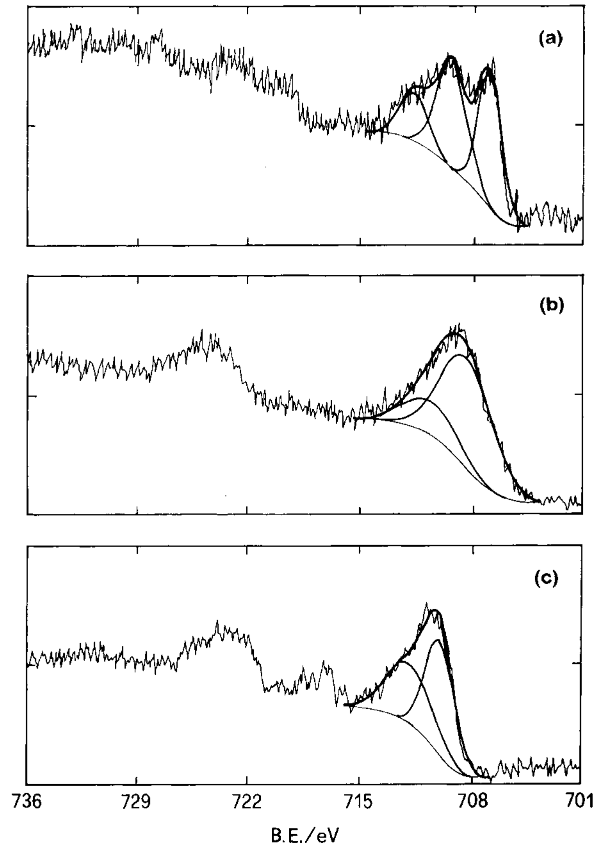

Fig. 8. High resolution XPS spectra of Fe(2p) for as received samples (a). Non-oxidized; (b) oxidized at 300 °C for 30 min; (c) oxidized at 300 °C for 120 min.

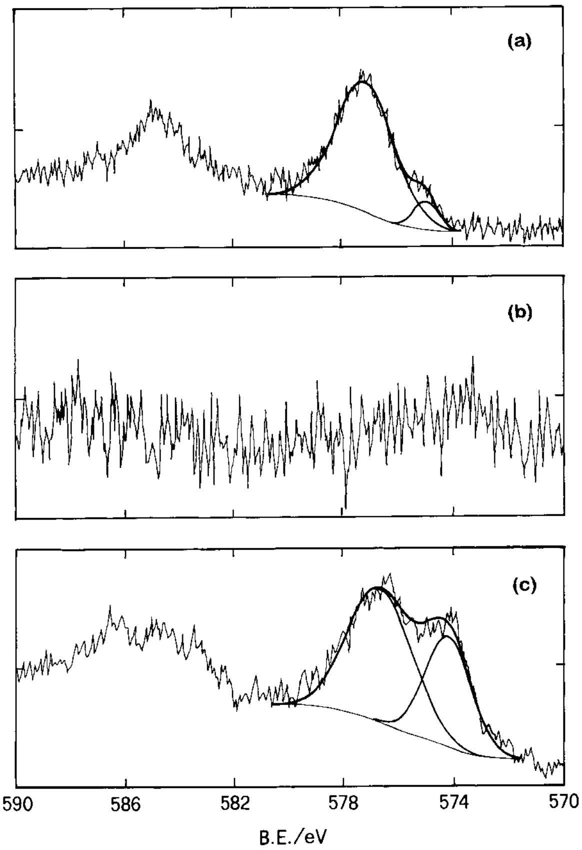

Fig. 9. High resolution XPS spectra of Cr(2p) for samples: (a) nonoxidized, as received; (b) oxidized at 300 °C for 30 min, as received; (c) same as (b), sputtered to a depth of 18 nm.

samples the oxide layer is externally rich in Fe, while internally it consists of Fe + Cr.

The double oxide structure is presumably associated with the higher mobility of Fe ions in the layer of natural passivity (n-type semiconductor) existing on stainless steel. The rapid diffusion of Fe through the oxide film produces a Fe concentration gradient at the metal–oxide interface.

4. Conclusions

(i) Mechanical pretreatment and the chemical nature of the surface of samples are critical factors affecting susceptibility to localized corrosion.

(ii) Mechanical plus electrochemical treatment ensures the best reproducibility since it avoids local work-hardening and any mechanical disturbance modifying the susceptibility to localized corrosion.

(iii) Heat treatment at moderately high temperatures (150 to 300 °C) in air substantially modifies the nature of the passive film, thus creating conditions which favour nucleation and development of localized corrosion.

(iv) XPS analysis shows that an increase in oxidation temperature decreases the amount of surface chromium (Cr, Cr_2O_3), with consequent growth of a nonprotective film of iron oxides (FeO, FeOOH). This effect is already evident at 200 °C. Cr-deficient films favour the susceptibility of the alloy to pitting corrosion rather than crevice corrosion. This aspect has been especially pointed out by the chemical tests in $FeCl_3$ solutions .

(v) The even greater pitting development observed on the specimen thermally treated at 300 °C results in a lower development of crevice corrosion. This is mostly evidenced by the chemical tests where the whole cathodic process due to Fe^{3+} to Fe^{2+} reduction must be considered as mostly involving pitting rather than crevice corrosion. Actually, the geometrical constrictions within the crevices and the n-conductivity of the surface oxide film favour the nucleation and development of pitting corrosion instead of crevice corrosion.

(vi) In contrast, the above aspect is not so evident in electrochemical tests. In fact, localized corrosion, which proceeds on the open surface, is depressed by the presence of a thermally modified layer (decrease in depassivation pH). This indicates definite difference between chemical and electrochemical tests, despite these being both recommended by present international standards.

(vii) The above points suggest that caution should be adopted during and after operations such as brazing, welding, lapping, sterilization etc.

(viii) Removal of oxide films is necessary even from surfaces which have undergone modest temperature increases (150 to 300 °C), so as to restore the natural state of passivity which is fair less susceptible to the initiation of localized corrosion than crevice corrosion or pitting.

Acknowledgement

This work was partially supported by CNR (National Research Council) Rome, Italy.

References

[1] T. Shibata and G. Okamoto, *in* ‘Passivity of Metals’, edited by R. P. Frankenthal and J. Kruger, (The Electrochemical Society, Princeton, NJ, 1978), p. 646.
[2] Z. Szklarska-Smialowska, *in* ‘Pitting Corrosion of Metals’, (NACE, Houston, TX, 1986), p. 301.
[3] G. Bianchi and S. Torchio, *Metall.Ital.* **7** (1970) 261.
[4] J. T. Burwell and J. Wulff, *Trans. Am. Inst. Min. Met. Eng.* **135** (1969) 486.
[5] J. Wulff, *ibid.* **145** (1971) 486.
[6] A. J. Sedriks, *Corrosion* **45** (1989) 510.
[7] G.E. Coates, *Mates. Perform.* **7** (1990) 61.
[8] T. Syderberger, *Werkst. Korros.* **32** (1981) 119.
[9] R. Ericsson, L. Schon and B. Wallen, Proceedings of the 8th Scandinavian Corrosion Congress (Helsinki, 1978), p. 312.
[10] G. Hultquist and C. Leygraf, *Corrosion* **36** (1980) 126.
[11] J. L .Crolet, L. Seraphin and R. Tricot, *Mem. Scie. Rev. Metall.* **74** (1977) 647.
[12] R. M. Kain, Proceedings of Corrosion ’96, Research topical symposia (NACE, Houston, TX, 1996), p. 401.
[13] J. F. Grubb, Proceedings of the International Conference on Stainless Steels, Iron and Steel Institute of Japan (Tokyo, Japan, 1991), p. 944.

[14] Y. C. Lu and M. B. Ives, Proceedings of Corrosion '96, Research topical symposia (NACE, Houston, TX 1996), p. 385.
[15] W. Oldfield, NiDi, Technical series N.10 016.
[16] T. S. Lee and K. L. Money, *Mates.Perform.* **8** (1984) 28.
[17] S. P. Trasatti and F. Mazza, *Br.Corros. J.* **30** (1995) 275.
[18] G. B. Bianchi, A. Cerquetti, F. Mazza and S. Torchio, 'Localized Corrosion' (NACE, Houston,TX 1971), p. 399.
[19] J. L. Crolet, J.M. Defranoux, L. Seraphin and R. Tricot, *Mem. Sci. Rev. Metall.* **71** (1974) 797.
[20] 'Standard test methods for pitting and crevice corrosion resistance of stainless steel and related alloys by the use of ferric chloride solution', ASTM Designation G 48–76, (1980) p. 178.
[21] D. B. Anderson, in 'Galvanic and Pitting Corrosion', ASTM STP 576 (1976) p. 231.
[22] M. Stern and A.C. Makrides, *J. Electrochem. Soc.* **106**, (1959) 376.
[23] J. W. Oldfield and W. H. Sutton, *Br. Corros. J.* **13** (1978) 104.
[24] R. M. Kain, proceedings of 'Corrosion' 91, paper n:508, (NACE, Houston, TX, 1991).
[25] D. Caplan, A. Harvey and M. Cohen, *J. Electrochem. Soc.* **108** (1961) 134.