

CORROSION BEHAVIOUR OF DUPLEX SAF2507 IN AQUEOUS ORGANIC ACID SOLUTIONS

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This paper reports on mass loss and electrochemical polarization behaviour of duplex SAF2507, in aqueous solutions of acetic acid, formic acid and their mixtures, in the presence of specific contaminants, such as sulphuric acid. The effect of temperature and redox couples was also investigated.

SAF2507 withstands corrosion in acetic acid solutions in a wide temperature and concentration range. The corrosion rate is higher in the more dissociated formic acid at the same concentration. Uniform corrosion with selective dissolution of the austenitic phase was observed in all tested solutions, the selectivity being strictly connected to solution aggressiveness.

The presence of sulphuric acid in organic acid aqueous solutions is severely detrimental to the corrosion resistance of the duplex: the corrosion rate increases almost linearly with H_2SO_4 concentration. Few tens of ppm of Fe^{3+} or Cu^{2+} improve the corrosion performance markedly, causing often the corrosion rate to decrease to very low values. The addition of H_2O_2 has a strong effect favouring the increase of the corrosion potential up to the passivity of duplex due to the possible formation of peracids.

KEYWORDS: stainless steel, electrochemistry, material evaluation, processes

INTRODUCTION

Thank to their high chromium and molybdenum contents, higher duplex grades like SAF2205 and SAF2507 are highly resistant to uniform corrosion in many industrial environments. Besides, they exhibit improved pitting corrosion resistance as a consequence of higher levels of nitrogen compared to austenitic steel grade. In the last decade, duplex applications in chemical and petrochemical industry increased even though not always supported by specific tests or research activities.

Organic acids constitute a broad family of chemicals of general formula $RCOOH$, where R is a hydrocarbon chain or ring, commonly met in chemical industry. Their corrosive action is not simple because of the high number of acids and because they are not used pure, but in mixture with other organic compounds or inorganic acids or salts. Generally speaking, carboxylic acid aggressiveness increases as the number of carbon atoms in the alkyl chain decreases: $C_4H_9COOH < C_3H_7COOH < C_2H_5COOH < CH_3COOH < HCOOH$.

The presence of contaminants makes the picture more complex, because they modify the oxidizing capacity of the acid mixture thus increasing the medium aggressiveness.

Among the organic acids, acetic and formic acids are most frequently used as chemicals or solvents in many industrial processes. Consequently, knowledge of their corrosion action is essential. Copper and its alloys are suitable materials to handle similar mixtures, since copper alloys do not directly displace hydrogen. Unfortunately, copper increasing costs and difficulty of supply make this choice sometimes unpracticable. The use of conventional and duplex stainless steels appears to be successful.

The corrosion behaviour of ferritic and austenitic stainless steels in organic acids is well documented, but relatively few works are devoted to duplex stainless steels. Besides, corrosion studies on duplex in organic acid solutions are scanty in comparison with similar studies in mineral solutions of remarkable industrial interest.

Scribner [1] reviewed the corrosion behaviour of stainless steels in organic acids reporting higher performance of higher grade duplex than the homologous of the AISI 300 series in both acetic and formic acid solutions.

Sekine et al. [2-4] worked extensively on the corrosion behaviour of stainless steels in acetic and formic acids. They concluded that the corrosion rate depends markedly on concentration and temperature, in turn closely connected with solution conductivity, water and oxygen content.

Chechirlian et al. [5] studied the influence of formic acid and sulphites on the corrosion behaviour of AISI 300 series in acetic acid. They observed that 20 ppm of sulphites are sufficient to depassivate AISI 304 in 50% acetic acid solution. The presence of Mo increases the critical concentration up to 200

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	C	Cr	Ni	Mo	N	Si	Cr _{eq}	Ni _{eq}	P.R.E.*
SAF2507	0.02	24.9	6.78	3.8	0.27	0.25	28.8	16	45.5

* according to P.R.E. = %Cr + 3,3x%Mo + 30x%N

▲
Tab. 1

Chemical composition % (wt) of SAF2507.

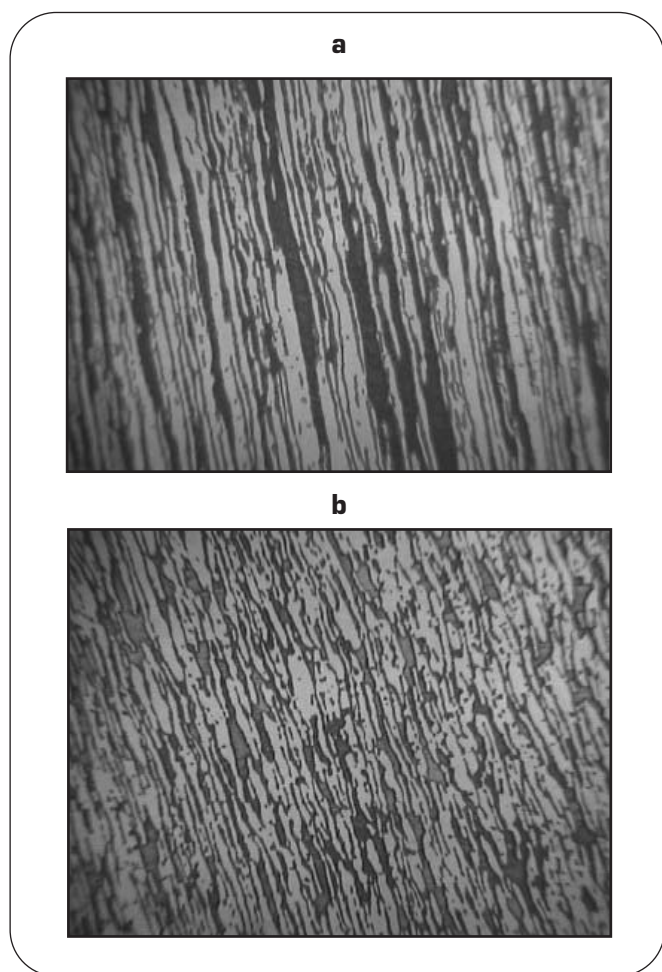
Composizione chimica (percentuale in peso) del SAF2507.

ppm for AISI 316 stainless steel, improving its corrosion performance also in formic acid.

Qi et al. [6] showed that traces of sulphuric acid ($\leq 1\text{wt}\%$) in esterification processes have detrimental effect on the corrosion resistance of AISI 300 series in acetic acid media, so much that these steels cannot be used in such conditions. The same authors stated that depolarizing ions, such as Cu^{2+}/Cu or $\text{Fe}^{3+}/\text{Fe}^{2+}$, are beneficial to restore a stable passive state, even though this process is temperature dependent.

Curtis [7] investigated the corrosion behaviour of SAF2205 and SAF2507 in organic acids, concluding that in the case of chloride contamination, acetic anhydride or formic acid, the best material is SAF2507.

The selective dissolution in a duplex stainless steel (DSS) is



▲
Fig. 1

Microstructure of SAF2507: a) axial; b) transverse (400X).

Microstruttura del SAF2507: a) assiale b) trasversale (400X).

expected to occur due to the difference in chemical composition of the constituent phases. However, the results reported in the literature are contradictory as to which phase dissolves at a more accelerated rate [8-12].

On the basis of the above considerations, an experimental work on duplex SAF2507 in organic acid aqueous solutions, in the presence of specific contaminants, such as metal redox couples ($\text{Fe}^{3+}/\text{Fe}^{2+}$ and Cu^{2+}/Cu) and sulphuric acid was carried out.

The following aims were pursued:

- (a) to bring an additional contribution to the scarce data available in the literature on this specific topic;
- (b) to investigate in more details the selective dissolution of duplex;
- (c) to scrutinize a few operational parameters, notably the acid nature and contaminant species;
- (d) to assess the possibility of improving the corrosion behaviour by addition of oxidant species.

EXPERIMENTALS

Materials

The material used in this study was a commercially available duplex stainless steel, SAF2507 (UNS S32750), whose chemical compositions is reported in Tab. 1. SAF2507 was in the form of 2 mm thick plates. SAF2507 electrodes for the electrochemical characterisation were machined from 10x10 mm rectangular bars.

For long-term exposure tests, 40x20x2 mm flat coupons were cut and a 3 mm hole was made to hang up the samples in the testing solutions with a glass hook.

For electrochemical tests, parallelepipedal ($A=100\text{ mm}^2$, $H=15\text{ mm}$) specimens were machined.

Before each experiment, specimens were wet polished with abrasive papers down to 600 grit, rinsed in distilled water, degreased with anhydrous ethanol for 5 minutes, and dried in warm air.

For metallographic analyses, a few specimens were embedded in thermoplastic resin, polished with abrasive paper down to 1000 grit, and with diamond paste down to $0,25\text{ }\mu\text{m}$. Specimens were subjected to electrochemical etching in KOH 10 M at 1,5 V for 5 s. Typical microstructures for SAF2507 are shown in fig. 1, showing an equally distributed biphasic structure, about 50 α /50 γ , with no inclusions or defects of critical dimensions.

Testing procedure

Mass loss tests

Mass loss measurements were carried out mainly at the boiling temperature under atmospheric pressure in 1 L glass cell, where coupons were hung by means of a glass hook, with the option of full immersion or vapour exposure tests. The test cell was equipped with a water refrigerator to prevent fast evaporation of the solvent. Weight loss experiments lasted 6-72 h depending on the test solution. Surface area/solution volume

ratio was about $0,02 \text{ cm}^{-1}$. Temperature was controlled to $\pm 1^\circ\text{C}$ by a Vertex.

Electrochemical tests

The electrochemical behaviour in the testing solutions was investigated by means of polarization and corrosion potential vs. time curves.

Polarization curves were recorded potentiodynamically at 0.1666 mV s^{-1} using a Model 273A EG&G potenziostat/galvanostat. The temperature range was 20 to 110°C , controlled to $\pm 1^\circ\text{C}$ by a Vertex. Unless otherwise specified all curves were recorded under nitrogen.

A polarization cell of the type described in ASTM G5 specifications was used with a saturated calomel electrode (SCE) as a reference and two spirals of Pt as counter electrodes. The stability of the reference electrode was checked before and after each experiment.

Testing solutions

Solutions were prepared from analytical grade HCOOH , CH_3COOH , H_2SO_4 and LiClO_4 . Anhydrous LiClO_4 was used as a supporting electrolyte to reduce ohmic effects during polarization experiments. Doubly-distilled water was used in all cases.

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy was used to analyse the surface, using an M-probe apparatus (Surface Science Instruments). The source was monochromatic Al K α radiation (1486.6 eV). A spot size of $200 \text{ nm} \pm 750 \text{ nm}$ and a pass energy of 156.42 eV were used. The background was subtracted using Shirley's method [13].

RESULTS AND DISCUSSION

Mass loss tests

The corrosion rates of SAF2507 in sulphuric acid solutions are plotted against the acid concentration in Fig. 2.

The tests were carried out to get reference data. SAF2507 exhibits fairly uniform corrosion resistance up to 1% H_2SO_4 , then it deviates from linearity with progressive increase in corrosion rate up to 0.7 mm/y in 4% acid. Optical examination of specimen surfaces after the tests revealed a rough look typical of uniform corrosion. Metallographic analysis of cross sectioned specimens shows that corrosion proceeded selectively with respect to microstructure. A typical surface appearance of

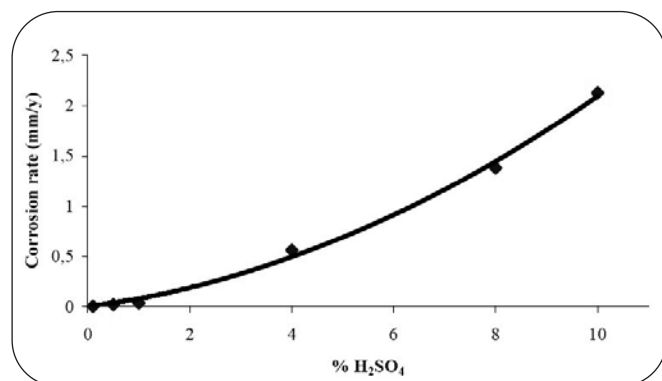


Fig. 2 Corrosion rate of SAF2507 in H_2SO_4 solutions. Velocità di corrosione del SAF2507 in soluzioni di H_2SO_4 .

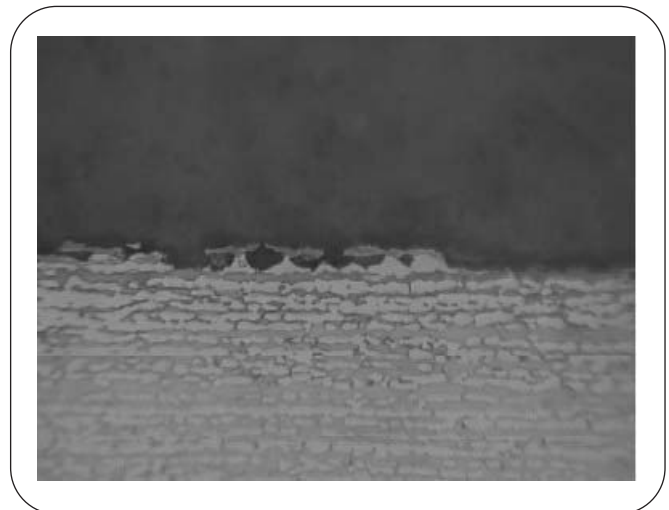


Fig. 3 Optical microstructure of SAF2507 after exposure in 6% H_2SO_4 (400X). Micrografia ottica del SAF2507 dopo esposizione in 6% H_2SO_4 (400X).

SAF2507 after exposure is reported in Fig. 3, showing the occurrence of selective dissolution of austenitic phase in 8% H_2SO_4 solution. It was apparently observed a dependence of the selective dissolution on the solution aggressiveness.

Typical corrosion rates of SAF2507 in formic acid solutions are shown in Fig. 4. The rate of attack increases slightly with increasing concentration, but more than the commonly accepted value of 0.1 mm/y, the corrosion rate of SAF2507 being typically one order of magnitude lower than that of AISI 304, and about half that of AISI 316 in the same conditions [9]. Corrosion morphology was uniform but a sort of selective dissolution of austenite was evident.

SAF2507 do not undergo corrosion in acetic acid in a wide range of temperature and concentrations, but in the presence of traces of sulphuric acid the situation changes dramatically. The effect of sulphuric acid on the corrosion rate of the duplex was checked in 80% acetic acid solution. This solution was chosen since corrosion rate becomes appreciable only at this concentration. Fig. 5 shows corrosion data for the duplex in boiling 80% AcOH solutions containing traces of sulphuric acid.

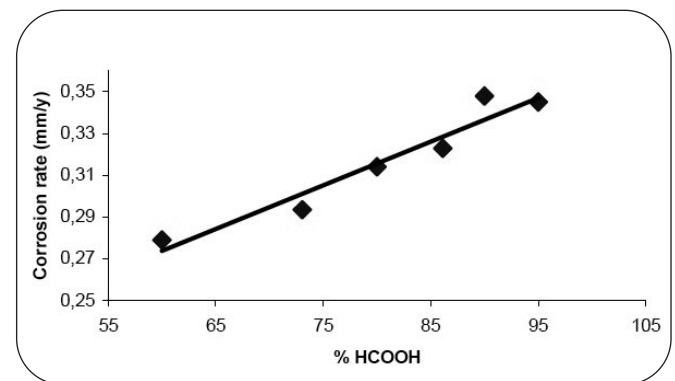


Fig. 4 Corrosion rate of SAF2507 vs. % HCOOH . Velocità di corrosione del SAF2507 vs. % HCOOH .

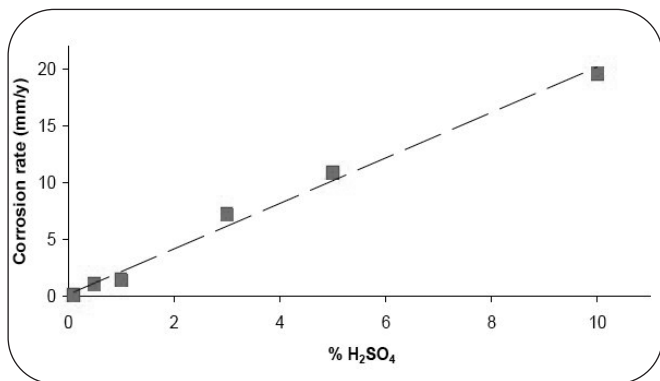


Fig. 5

Corrosion rate of duplex SAF2507 in 80% AcOH + %H₂SO₄.
Velocità di corrosione del SAF2507 in 80% AcOH + %H₂SO₄.

The presence of sulphuric acid increases the corrosion rate dramatically, suggesting a synergic effect between the two acids. Low levels of water and dissolved oxygen cause breakdown of the passive film even for solutions containing only 0.1% H₂SO₄, leading to unacceptable corrosion rates (higher than 0.1 mm/y). In 80% HCOOH solutions, sulphuric acid has the same effect with a more marked increase of corrosion rate. Since HCOOH is more dissociated than CH₃COOH, the corrosion rate is higher at the same concentration. At H₂SO₄ concentrations > 0,5% the effect of organic acids becomes negligible, corrosion being governed by the inorganic acid (Fig. 6).

The corrosion behaviour of the duplex in ternary solution mixtures (HCOOH/CH₃COOH/H₂SO₄) is shown in Fig. 7. The addition of up to 5% HCOOH at a 80% AcOH + 1% H₂SO₄ solution causes the corrosion rate of SAF2507 to increase to about 2.5 mm/y. Further addition has no effect up to 15% HCOOH.

Reduction of the H₂SO₄ content to 0.1% causes the corrosion rate to increase linearly with HCOOH content up to 12%, slightly decreasing for further addition. However the corrosion rate is always lower than 0.6 mm/y.

When AcOH is added to 80% HCOOH + 1% H₂SO₄, the corrosion rate vs. wt% varies linearly with a small slope: corrosion rate goes from 1.5 to 3.8 mm/y by increasing the AcOH content from 0 to 16%, respectively. This uncertain and unexpected behaviour can be explained in terms of conductivity

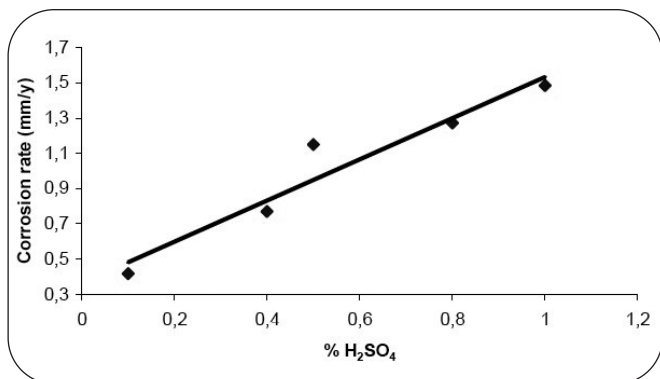


Fig. 6

Corrosion rate of SAF2507 in 80% HCOOH + %H₂SO₄.
Velocità di corrosione del SAF2507 in 80% HCOOH + %H₂SO₄.

change as water content decreases. Corrosion morphology was always uniform in ternary mixture solutions. The influence of temperature on the corrosion rate of SAF2507 in 80% AcOH + 1% H₂SO₄ is shown in Fig. 8. Temperature affects kinetics markedly, making the duplex unusable at temperatures > 90°C. An increase in temperature causes an increase in corrosion rate up to the boiling temperature, with an Arrhenius-like behaviour, even for SAF2507 in 80% AcOH + 0.1% H₂SO₄.

The corrosion rate in 80% AcOH + 0.1% H₂SO₄ is about one order of magnitude lower than in 1% H₂SO₄.

SAF2507 in 80% HCOOH + 1% H₂SO₄ exhibits similar behaviour with corrosion rates similar or slightly lower than in AcOH at temperatures > 90°C.

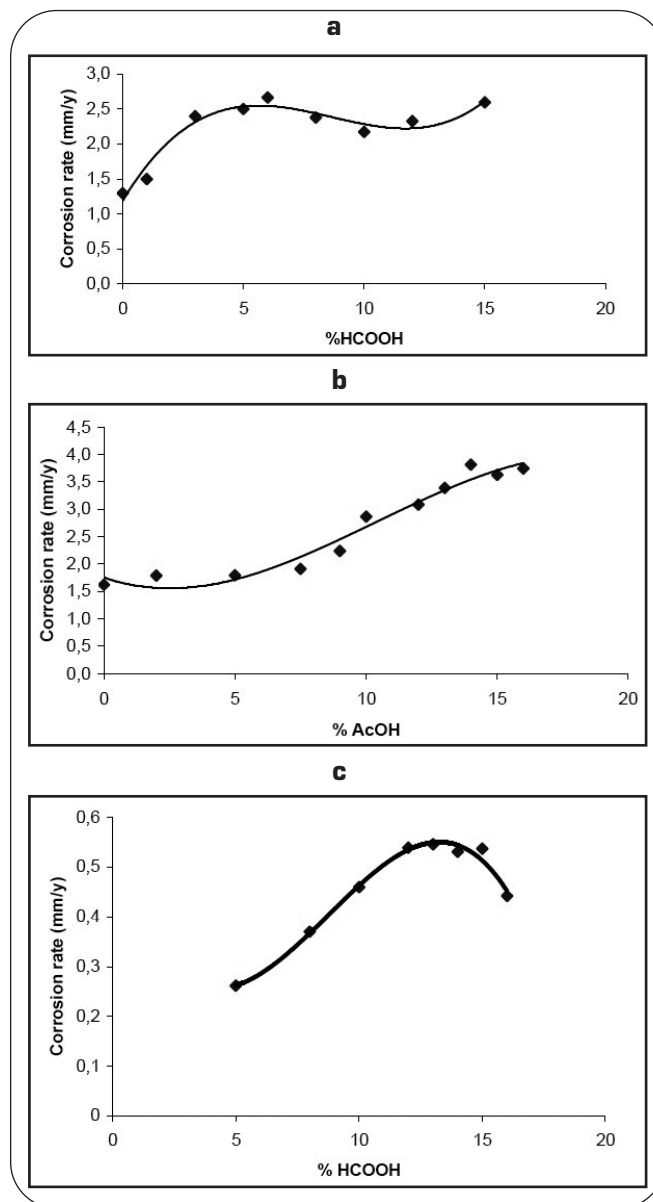


Fig. 7

Corrosion rate of SAF2507 in: a) 80% AcOH + 1% H₂SO₄ + % HCOOH; b) 80% HCOOH + 1% H₂SO₄ + % AcOH; c) 80% AcOH + 0.1% H₂SO₄ + % HCOOH.
Velocità di corrosione del SAF2507 in: a) 80% AcOH + 1% H₂SO₄ + % HCOOH; b) 80% HCOOH + 1% H₂SO₄ + % AcOH; c) 80% AcOH + 0.1% H₂SO₄ + % HCOOH.

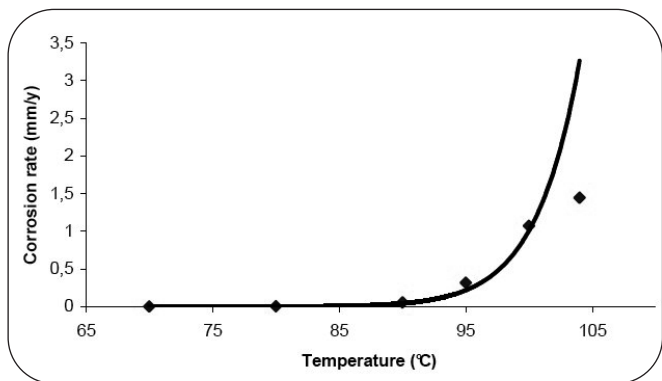


Fig. 8

Corrosion rate of duplex SAF2507 in 80% AcOH + 1% H₂SO₄ as a function of temperature.
 Velocità di corrosione del SAF2507 in 80% AcOH + 1% H₂SO₄ in funzione della temperatura.

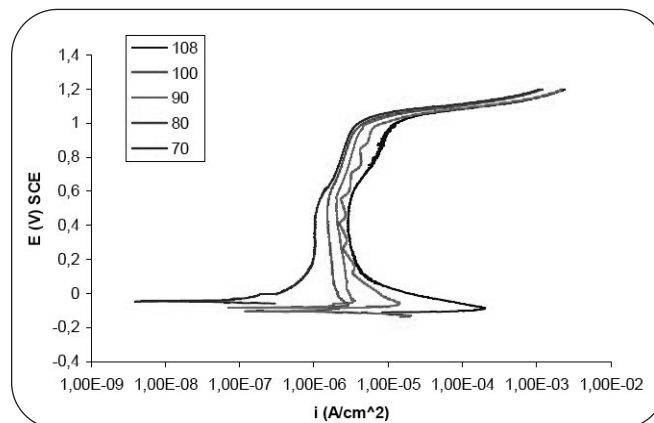


Fig. 8

Corrosion rate of duplex SAF2507 in 80% AcOH + 1% H₂SO₄ as a function of temperature.
 Velocità di corrosione del SAF2507 in 80% AcOH + 1% H₂SO₄ in funzione della temperatura.

The low stability of the SAF2205 passive film in organic acid aqueous solutions containing sulphuric acid in the absence of oxidizing species, was also confirmed by a few tests under continuous nitrogen purging to remove dissolved O₂. Results showed that corrosion increased markedly: the absence of dissolved oxygen did not allow the formation of a stable passive film, presumably replaced by a non protective salt film, as deduced from the opaque look of the coupons, covered by green-yellow layers, likely chromium and nickel compounds. The attack exhibits uniform corrosion morphology with preferential dissolution of the austenitic phase. The need for oxidant conditions was investigated by adding metal ions in the higher oxidation state (eg. Fe³⁺ and Cu²⁺). A few tens of ppm was sufficient to make the duplex passive even in the most aggressive environments.

Electrochemical experiments

The anodic behaviours of SAF2507 are quite similar in all aqueous organic acid solutions, showing the existence of two passive regions tending to become one as temperature increases. The curves show a wide passive range and the breakdown potential does not change significantly with temperature. Typical anodic potentiodynamic polarization curves for SAF2507 in 80% HCOOH + 1% H₂SO₄ at different temperatures in the range 70-108°C (boiling temperature) are reported in Fig. 9. No distinctive active-to-passive transition region is observed until temperatures close to the boiling point are tested. In these operating conditions, enhanced anodic current density was observed in the active-to-passive transition region. The results are consistent with those of mass loss, as SAF2507 in 80% CH₃COOH + 1% H₂SO₄ corroded uniformly only close to the boiling temperature. The anodic behaviour in 80% AcOH + 0,1% H₂SO₄ was similar but shifted to lower current density by about an order of magnitude. At temperatures lower than 90°C, SAF2507 exhibits a wide passive region. Only a small active peak is visible at 90°C. In contrast, at temperatures higher than 90°C, a pronounced active region appeared around E_{corr} + 100 mV. In particular, the value of the critical passivation current density (i_{cr}) goes from 10⁻⁶ A/cm² to about 10⁻⁴ A/cm² with increasing temperature from 70 to 108°C (boiling temperature).

A sharp increase in current occurred at about E_{corr} + 1300 mV, possibly due to either oxidation of Cr³⁺ in the passive film to Cr⁶⁺ species, or oxygen evolution, or a combination of both. Localized corrosion was not observed on the electrode surface by optical examination after each polarization experiment. To obtain data about the composition of surface oxide films, some specimens were subjected to potentiostatic aging for 30 min at two potentials, E₁ = 350 mV and E₂ = 850 mV, placed in the two diverse passive range, respectively. This is to facilitate the formation of oxide film over the surface of both SAF2507. Potentiostatic experiments were carried out in 80% HCOOH + 1% H₂SO₄ at 70°C. Surface films were analysed by XPS that revealed the presence of chromium oxide (Cr₂O₃), silicon oxide (SiO₂) and iron oxide (Fe₂O₃) as reported in recent studies [15,16]. Data reported are in tab. 2. The findings indicate that iron enrichment occurred in the passivated film of SAF2507 "aged" at E₁. However it should be noted the presence of nitrogen in the passivated film of SAF2507 at E₁, disappearing at E₂. This observation is not in agreement with previous studies which observed nitrogen enrichment of the oxide/metal interface. No significant variation in the Si/Fe ratio was observed, indicating the same level of silicon in the passivated film in every condition. The presence of the S2s peak in all conditions reveals the participation of sulphur species in the formation of the oxide film.

	Cr/Fe	Si/Fe
SAF2507 at E ₁	0.61	1.30
SAF2507 at E ₂	1.38	1.41

Tab. 2

Atomic ratio of Cr/Fe and Si/Fe in the passivated film, determined by XPS after 30 min in 80% HCOOH + 1% H₂SO₄ (SAF2507).
 Analisi XPS: rapporto atomico Cr/Fe e Si/Fe nel film di passività, dopo polarizzazioni di 30 min in 80% HCOOH + 1% H₂SO₄.

CONCLUSIONS

In aqueous solution of acetic acid SAF2507 duplex stainless steel do not undergo corrosion in a wide range of acid concentration and temperature. SAF2507 is not subject to severe corrosion in formic acid up to 40% of concentration at the atmospheric boiling temperature. The presence of sulphuric acid changes the situation completely with a dramatic decrease of the corrosion performance in both acids.

A few tens of ppm of iron (III) or copper (II) was sufficient to make the duplex passive even in the most aggressive environments, although the choice of counterions is important. The occurrence of selective dissolution of austenitic phase, more pronounced with increasing of the solution aggressiveness, was observed in all experiments. Based on the results of this work, it can be concluded that, although SAF2507 is recommended for mildly oxidizing conditions, the addition of suitable depolarizing substances enables the transition from active to passive state to be efficiently controlled.

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ABSTRACT

COMPORAMENTO A CORROSIONE DEL DUPLEX SAF2507 IN SOLUZIONI ACQUOSE DI ACIDI ORGANICI

Parole chiave: acciaio inossidabile, elettrochimica, valutazione materiali, processi

In questo lavoro, il comportamento a corrosione del duplex SAF2507 in soluzioni acquose di acido acetico e acido formico è stato studiato in presenza di specifici contaminanti, quali l'acido solforico. L'effetto della temperatura e di coppie redox è stato altresì investigato.

I risultati evidenziano come il SAF2507 non sia soggetto a fenomeni di corrosione in soluzioni di acido acetico, in un ampio campo di concentrazioni e temperature. La velocità di corrosione, a parità di concentrazione, risulta più elevata in acido formico (Fig. 4), osservazione giustificata dalla più alta costante di dissociazione e dalle superiori caratteristiche di conducibilità.

In tutte le soluzioni studiate si è osservata una morfologia di corrosione uniforme, con evidenza di dissoluzione selettiva della fase austenitica (Fig. 3); la selettività dell'attacco appare strettamente connessa all'aggressività della soluzione.

La presenza di acido solforico in soluzioni di acido organico causa una drastica riduzione delle prestazioni a corrosione del duplex, la cui velocità di

degrado cresce quasi linearmente all'aumentare della concentrazione di H_2SO_4 (Fig. 5 e 6).

L'aggiunta di alcune decine di ppm di ioni Fe^{3+} o Cu^{2+} aumentano notevolmente la resistenza a corrosione, comportando in molti casi la riduzione della velocità di corrosione a valori prossimi a zero.

L'aggiunta di acqua ossigenata ha un marcato effetto sulla resistenza della lega, favorendo un aumento del potenziale di corrosione fino a valori tipici dello stato di passività, probabilmente per la formazione di peracidi.

Il comportamento elettrochimico del SAF2507 è stato valutato registrando le curve di polarizzazione nell'intervallo di temperature 70°C-temperatura di ebollizione. Le curve di polarizzazione anodica in 80% HCOOH + 1% H_2SO_4 sono ad esempio mostrate in Fig. 9.

Non si osserva alcuna evidente transizione attivo-passiva fino a che non viene superata la temperatura di circa 90°C.

Il comportamento in CH_3COOH è analogo, caratterizzato però da correnti inferiori di un ordine di grandezza.

L'analisi XPS della superficie di alcuni campioni polarizzati per 30 min, rispettivamente a $E_1 = 350$ mV ed $E_2 = 850$ mV, in 80% HCOOH + 1% H_2SO_4 a 70°C, ha evidenziato (Tabella 2) un arricchimento in ferro e la presenza di azoto nel film "invecchiato" al potenziale E_1 , mentre in entrambi i film di passività si è riscontrata la presenza di zolfo.