

CITRIC ACID AEROSPACE STAINLESS STEEL PASSIVATION: A GREEN APPROACH

M. Bragaglia^{1,3}, V. Cherubini^{1,3}, I. Cacciotti^{2,3}, M. Rinaldi^{1,3}, S. Mori^{1,3}, P. Soltani⁴, F. Nanni^{1,3},
S. Kaciulis⁴, G. Montesperelli^{1,3}

¹University of Rome “Tor Vergata”, Dept. Enterprise Engineering, Via del Politecnico 1, 00133 Rome, Italy

²University of Rome “Niccolò Cusano”, Via Don Carlo Gnocchi 3, 00166 Rome, Italy

³Italian Interuniversity Consortium on Materials Science and Technology (INSTM), Italy

⁴ISMN - CNR, P.O. Box 10, 00015 Monterotondo Stazione, Rome, Italy

ABSTRACT

Passivation is a common treatment to maximize the corrosion resistance of stainless steel. Nitric acid is generally used and involves several ecological problems, citric acid could be a promising and environmentally friendly alternative to nitric acid. In this work citric acid has been extracted from lemon waste using an eco-friendly procedure. The stainless steel samples have been treated in both nitric and citric acid (commercial and extracted) and corrosion tests have been performed. The results show how citric acid can be used as a substitute of nitric acid in passivation treatment.

INTRODUCTION

Stainless steels are widely used in the aerospace sector, because of their high mechanical properties and corrosion resistance. A clean and polished stainless steel element exposed to the air, spontaneously undergoes a surface chromium enrichment thus preventing further corrosion [1].

During machining process, after welding, or other processes, a microscopic amount of exogenous surface contamination may be transferred to the surface of the stainless steel workpiece [2]. If not removed, these foreign particles can reduce effectiveness of the original protective film allowing the pit initiation at these sites. In order to maximize the natural corrosion resistance and to remove contaminants from the surface, an acid cleaning of stainless steels, called passivation, is commonly employed in industry.

The primary aim of the surface treatments is to enhance the passive film protection by changing its composition, structure and thickness and/or by reducing weak points such as non metallic inclusions [3].

Passivation process is controlled by industry standards [4] and it is almost exclusively based on the use of a nitric acid mixture (HNO₃) [5].

Several authors have studied the effect of passivation treatment of stainless steels in nitric acid (HNO₃) [3-7]. The treatment has been shown to be effective in improving the corrosion resistance of standard austenitic stainless steels [3].

Barbosa also found that nitric acid passivation treatments remove sulphide inclusions from the surface and supposed this to be the main factor in their beneficial effect on pitting resistance of 316 stainless steel [1].

Shibata and co-workers carried out a detailed study of nitric acid passivation and concluded that the critical factor is the degree of chromium enrichment in the passive film [6].

The process is undoubtedly economic and leads to excellent results, but the use of nitric acid involves extremely serious ecological problems and chemical hazards. Actually, highly polluting nitrogen oxide (NO_x) vapours are released to the atmosphere during passivation by HNO₃, and high nitrate concentrations are dissolved in wash water and exhaust baths. Both types of pollutants require expensive treatment prior to disposal. Moreover, these disposal operations have no certainty about the obtainment of targets complying with the regulations in force [7].

In the recent past years, passivation treatment in citric acid (C₆H₈O₇) baths seems to be a successful greener passivation process. Citric acid is a biobased acid which exists in greater than trace amounts in a variety of fruits and vegetables, particularly in citrus fruits such as lemons and limes, comprising as much as 8% of the dry fruit weight [8]. Passivation in citric acid can be performed on a large number of stainless steel families, and it is considered environmentally friendly in every respect. However, it has not been clearly demonstrated if citric acid passivation is an adequate alternative to nitric acid passivation [9].

The aim of the present work is to propose a completely green sustainable stainless steel passivation procedure, using baths based on citrus fruit waste derived citric acid, as a promising alternative route to the currently

employed nitric passivation process. As a preliminary step, a green sustainable method for citric acid extraction, from citrus fruit waste, is attempted.

AISI 304 stainless steel samples were submitted to the passivation in both citric and nitric acid baths, in order to compare these two procedures in terms of effectiveness (potentiality of the citric acid based passivation) and processing time. The samples were also submitted to the passivation in extracted citric acid bath.

Corrosion tests were performed using potentiodynamic linear polarization test.

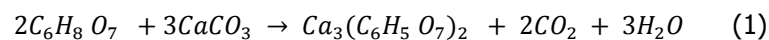
The samples were investigated before and after corrosion tests with optical microscopy (OM), scanning electron microscopy (SEM-EDS), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

Waste lemon Citric acid extraction

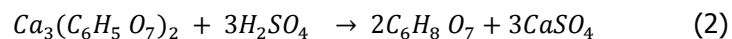
Waste from freshly squeezed lemons, consisting in lemon peels (flavedo) and endocarp, was collected and rinsed in deionized water under constant magnetic stirring for 24 hours. Then the solid phase was filtered using metallic filters with 500 μm and 320 μm meshes, in order to collect the liquid phase (extract). The liquid phase was also centrifuged using a MPW 351 centrifuge to remove other possible residual solid particulates. The amount of citric and other organic acid in the solution was quantified by means of titration with 0.1M NaOH solution, resulting about 10 g/l. In order to isolate citric acid from the obtained solution, the following procedure was set up and followed, on the basis of literature data [10].

The method of citric acid extraction involved the precipitation of insoluble tri-calcium citrate by the addition of calcium carbonate to the lemon waste derived extract, followed by the dissolution of the obtained precipitate in 5% H_2SO_4 solution, in order to extract citric acid. Successful operation of the precipitation and acid extraction depends on citric acid concentration, temperature, pH and rate of calcium carbonate addition [11]. Calcium carbonate was added to the waste lemon derived extract solution at 80°C and under continuous magnetic stirring, obtaining a fine white precipitate of calcium citrate, according to the following reaction:



This reaction occurred in presence of an excess of calcium carbonate, in order to obtain the complete precipitation of calcium citrate and, thus, a the yield was 100 %. The reaction (1) strongly depends on the pH and temperature, in fact the dissolution of calcium carbonate at low pH values (less than pH=4) has been shown to be mass transfer limited, when calcium citrate precipitates during the reaction it may act as a diffusion barrier, which will slow the overall mass transfer process [12].

In order to use natural waste derived reagents, calcium carbonate was obtained starting from egg-shells. Collected egg-shells were cleaned in boiled deionized water, milled at 40 rpm for 300 minutes and dipped in 4% sodium hydroxide solution for several days in order to completely remove the organic component. The sodium hydroxide solution was replaced 3 times per day with fresh solution. The precipitate was vacuum filtered, washed with 1% HCl solution in order to remove possible excess of calcium carbonate [13], dried at 50°C and collected. Then the obtained precipitate was dissolved in 5% H_2SO_4 solution at RT until pH 3 was reached, in order to leave the citric acid in the liquid phase, occurring the following chemical reaction:



The liquid phase was then separated from the solid one, by filtering the obtained precipitate, and it was evaporated in controlled environmental conditions allowing the citric acid crystallization. Citric acid yield, at the end of extraction process was 38 %. Furthermore as anhydrous citric acid is hygroscopic, it is very important to avoid storage in areas of high temperature and humidity.

Passivation treatments

Circular specimens (diameter of 18 mm, thickness of 3 mm) were obtained from a commercial austenitic AISI 304 stainless steel threaded rod (C: 0.04, Cr: 18.1, Ni: 8.3, Fe: 73.56, all in %wt), using a low-speed diamond saw. The samples were polished using silicon carbide (SiC) paper and diamond suspension up to 3 μm , and finally washed in ultrasonic bath of ethanol [14].

Passivation treatments were carried out at a constant temperature of 55 °C in nitric acid (25% (v/v)) and in both commercial and extracted citric acid (8 wt%) baths, following the A967 and A380 ASTM standards, for 30 and 15 minutes, respectively. After passivation treatment, the samples were rinsed in distilled water and then neutralized in 5% NaOH solution at 75-80°C for 30 minutes followed by water rinse.

Characterisation of lemon waste and egg-shell derived powders

The obtained lemon waste and egg-shell derived powders were characterized by means of FT-IR and XRD, in order to verify the efficacy of the followed extraction protocols. The infrared spectra were recorded by means of a Spectrum 100 Perkin-Elmer model FT-IR spectrophotometer in the spectral range 400-4000 cm^{-1} (spectral resolution of 4 cm^{-1}), using KBr pellet.

X-ray diffraction (XRD, Philips X'Pert 1710) patterns were acquired in the following conditions: Cu K α radiation ($\lambda=1.5408 \text{ \AA}$), 40kV and 40mA, $2\theta = 10\text{--}80^\circ$, step size = 0.020°, time per step = 2 s, scan speed = 0.01°/s.

Characterisation of the unpassivated and passivated AISI 304 stainless steel specimens

The chemical composition of the AISI 304 stainless steel specimens were analyzed by XPS using a spectrometer Escalab MkII (VG Scientific, UK) equipped with five-channeltron detection system. The measurements were carried out by using the Al K α X-ray source, constant pass energy of 20 eV and small-area mode (diameter of about 1 mm) of electrostatic input lens. The XPS data were acquired and processed by using the Avantage v.5 software (ThermoFisher Scientific, UK). XPS depth profiles of the samples were performed at 2.0 keV energy of Ar $^+$ beam and a sputtering rate of about 0.1 nm/min.

The samples surface morphology after the passivation treatment was investigated by means of optical microscopy (Nikon Epiphot TM).

Field emission scanning electron microscopy (FEG-SEM, Zeiss *LEO Supra 35*), coupled with energy dispersive spectroscopy (EDS) (*INCAx-sight, Oxford instruments*), was performed to investigate the specimen surface after corrosion test and to evaluate the severity of corrosion.

Finally, the potentiodynamic curves were acquired on as received and passivated samples. The exposed sample area was 1 cm^2 . Potentiodynamic polarization curves were performed in 3,5 %wt NaCl by Solartron SI 1287 Electrochemical Interface. A potential scan was carried out from -40 mV (vs. Open Circuit Potential OCP) in the anodic direction, at a scan rate of 1.66 mV/s, until current density value of 100 $\mu\text{A}/\text{cm}^2$ was reached. A platinum foil and an Ag/AgCl electrode were used as counter electrode (SCE) and reference electrode (RE), respectively. Tests were performed at room temperature and holding the electrode for 1 h at OCP before tests. All the tests were run in triplicate.

RESULTS AND DISCUSSION

FT-IR and XRD analysis

The egg-shell derived calcium carbonate was analysed by means of FT-IR and XRD in order to demonstrate the complete removal of the organic compound and to identify the crystalline phase. In Figure 1 the FT-IR spectrum and the XRD pattern of the obtained powder were reported and compared with those of commercial calcium carbonate (*Sigma Aldrich*, crystalline phase: calcite).

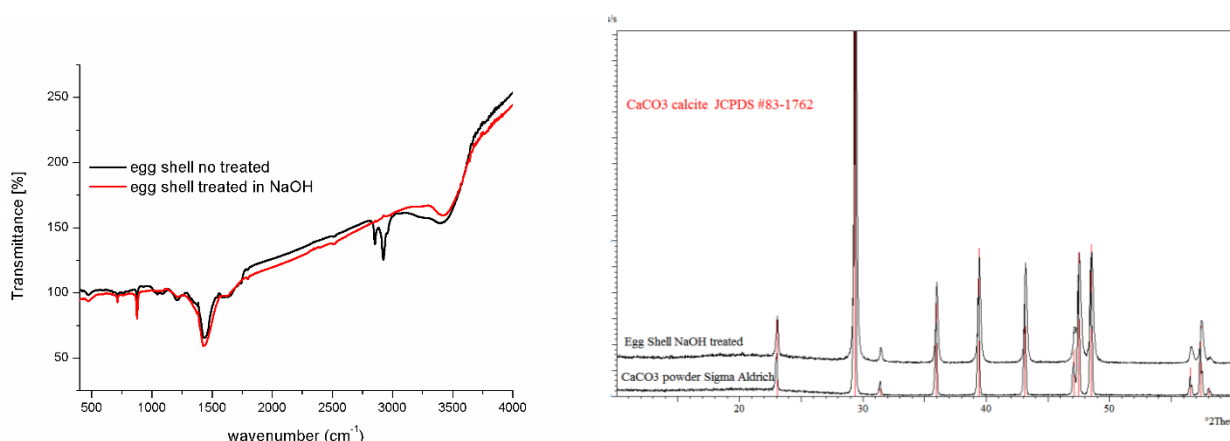


Fig. 1: FT-IR spectra of egg shell before and after the treatment in NaOH

Fig. 2: XRD patterns of egg shell derived calcium carbonate and commercial calcite

Both FT-IR and XRD (Figures 1 and 2) investigations confirmed the calcite phase, as expected, being among the CaCO_3 crystalline phases the calcite the most abundant form, widely distributed in the Earth's crust. The calcite FT-IR spectrum presents the characteristic vibrational modes (i.e. at 1442 , 876 and 714 cm^{-1} , ascribed to the *asymmetric stretching*, *out of plane bending* and *in-plane bending* of CO_3^{2-} groups, respectively [15] and the XRD pattern the calcite typical diffraction peaks (JCPDS 83-762). From the comparison with the FT-IR spectrum of the untreated egg shell it is interesting to note that there are absent the peaks associated to the organic component, i.e. at 2853 cm^{-1} (symmetric *stretching* of CH_2), at 2925 cm^{-1} (symmetric *stretching* of CH_3) and at 2959 cm^{-1} (asymmetric *stretching* of CH_3 and/or CH_2), testifying the efficacy of the occurred treatment (Figure 1).

The extraction of citric acid from the lemon waste was confirmed by both the FT-IR and XRD analyses. In Figure 3 the FT-IR spectrum of lemon waste derived calcium citrate is compared to commercial calcium citrate, presenting the typical calcium citrate vibrational modes: 1434 cm^{-1} (COO^- anti-symmetrical and symmetrical vibration) and 919 cm^{-1} (C-C vibration) [16, 17].

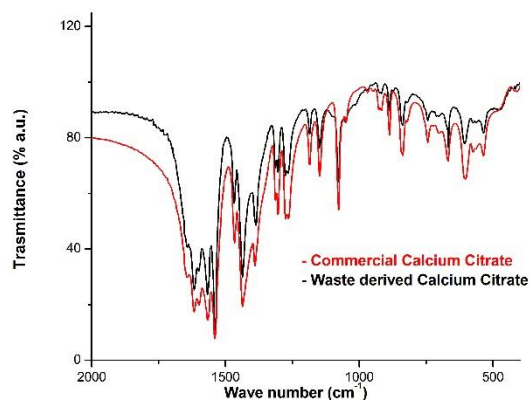


Fig. 3: FT-IR spectra of commercial and lemon waste derived Calcium citrate

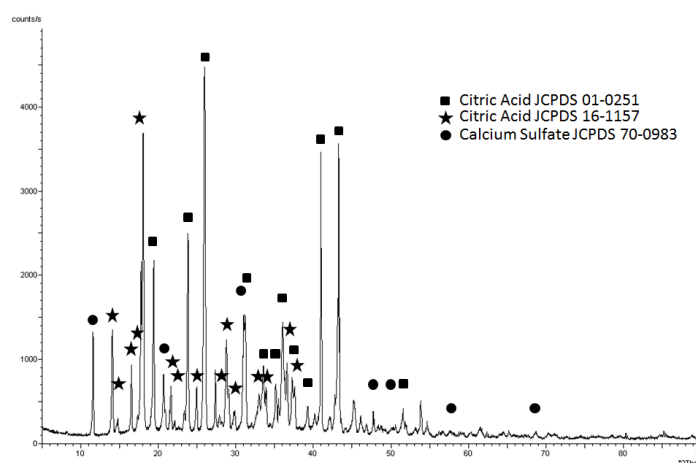


Fig. 4: XRD pattern of extracted citric acid

X-ray diffraction pattern of lemon waste extracted citric acid is shown in Figure 4.

XRD analysis confirmed the presence of citric acid; in details, two different anhydrate crystalline phases were detected (JCPDS 01-0251; JCPDS 16-1157), in agreement with literature [18]. Traces of calcium sulfate (JCPDS 70-0983) were also revealed.

Morphology of untreated and passivated specimens

The morphology of untreated, nitric, citric and lemon waste citric acid passivated sample was investigated by means of optical microscopy. As an example, the optical micrographs of as received sample and nitric acid passivated sample are reported in Figures 5 and 6, evidencing that the passivation treatment does not alter the morphology. In both samples it is possible to appreciate the presence of inclusions and second phase particles.

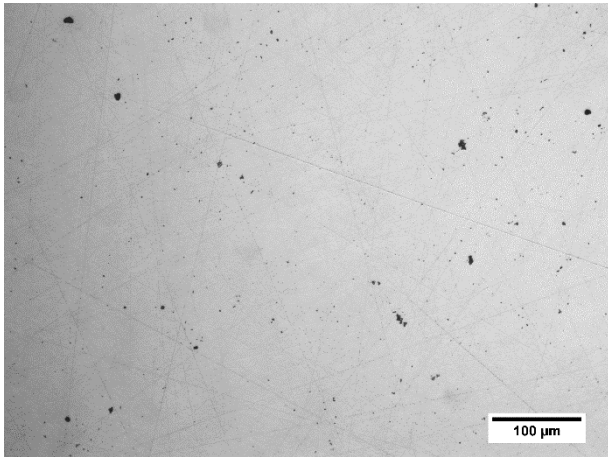


Fig.5: Optical micrograph of unpassivated sample

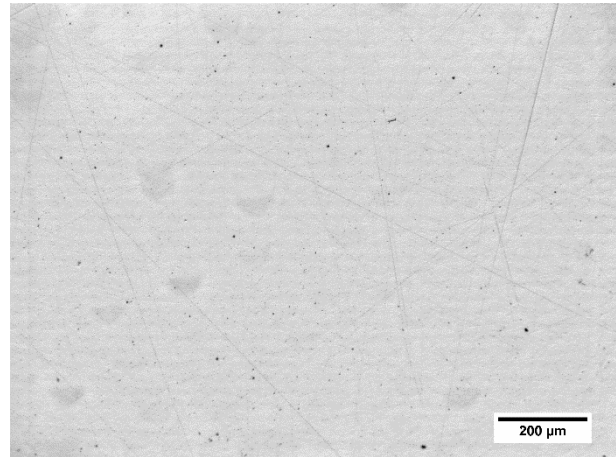


Fig.6: Optical micrograph of nitric acid passivated sample

Electrochemical test

The potentiodynamic polarization behaviour for the commercial and lemon waste derived citric acid passivated, nitric acid passivated and unpassivated AISI 304 stainless steel samples after 1 h in 3.5 %wt NaCl solution are shown in Figure 7. The potential value at which the current increases is called pitting potential (E_{pit}) i.e. the potential value at which pitting attack occurs. The higher E_{pit} , the less susceptible to pitting is the steel. The difference between E_{pit} and E_{corr} gives a measure of the tendency to pitting onset in the material; large differences indicate an improvement of the material resistance to pitting corrosion.

As expected, the curve related to untreated steel shows a partial passivation and a very narrow passivation range (Figure 7) since a passive film spontaneously grown after polishing. The passivation treatment largely increases the pitting potential, particularly and remarkably in the case of nitric acid.

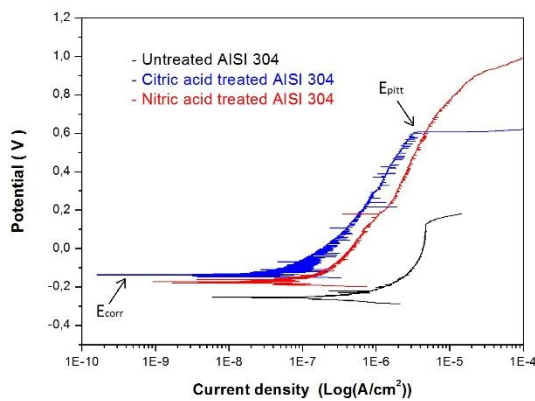


Fig. 7: Polarization curves of untreated, citric acid and nitric acid treated AISI 3014

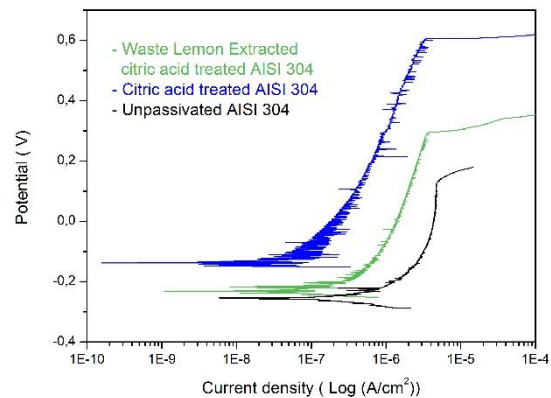


Fig. 8: Polarization curves of untreated, commercial and waste lemon extracted citric acid treated AISI 3014

Compared to untreated AISI 304, E_{corr} values of both commercial citric acid and nitric acid passivated sample shifted to a more positive region along with decreased i_{corr} values indicating slower corrosion rates.

Concerning the sample passivated with lemon waste derived citric acid, although it behaved better than unpassivated sample, in terms of i_{corr} and a sharp E_{pitt} , its E_{corr} value shifted to a more negative region along with increased i_{corr} value, indicating higher corrosion rates with respect to commercial citric acid treatment. At same time, the passive region range ($E_{pitt}-E_{corr}$) of the specimen passivated with lemon waste extracted citric acid was about 0.1 V lower than commercial citric acid treated sample (Figure 8).

Potentiodynamic polarization curves for the Citric acid passivated, Nitric acid passivated and waste extracted citric acid passivated samples in 3.5% NaCl solution after 24 h are compared in Figure 9. The behavior for the nitric acid and the citric acid passivated sample are almost identical.

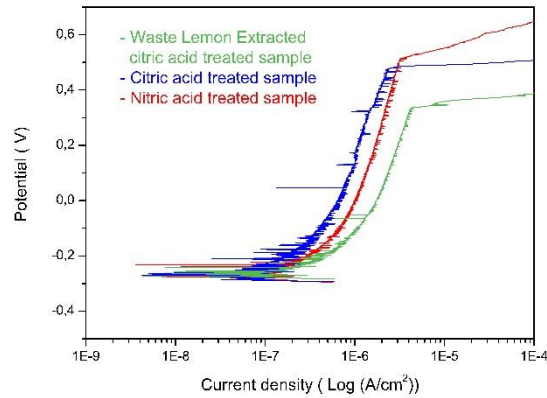


Fig. 9: Polarization curves of nitric acid, commercial and waste extracted citric acid treated AISI 3014 after 24h

The polarization curve of the HNO_3 passivated sample shows a clear decrease of E_{pitt} value while, for both commercial and lemon waste extracted citric acid passivation treatments, the polarization caused an ennoblement of the pitting potential since E_{pitt} value increases. This result indicates that the chromium oxide passivation film grown on nitric acid treated sample was not completely chemically stable and suggest that even if as stated in literature the most effective treatment involves a solution of 20 ± 25 wt% nitric acid [2] the passivation condition could be optimised changing the temperature value and/or the process time.

The lower value of E_{pitt} for the lemon waste extracted citric acid passivated sample could be due to the presence of calcium sulphate into the passivation bath which may influence the passivation film growth.

The E_{corr} , E_{pitt} , I_{corr} and $E_{\text{corr}} - E_{\text{pitt}}$ values (obtained from Tafel-type fit) are summarised in Table 1.

Table 1: E and I are in Volts and μA

	E_{corr}	I_{corr}	E_{pitt}	$E_{\text{pitt}} - E_{\text{corr}}$	E_{corr}	I_{corr}	E_{pitt}	$E_{\text{pitt}} - E_{\text{corr}}$
			1 h				24 h	
Unpassivated	-0.131	3.6	0.259	0.39	-0.077	5.12	0.243	0.32
Nitric acid	-0.182	0.312	0.854	1.036	-0.241	0.667	0.504	0.745
Commercial citric acid	-0.112	0.099	0.540	0.652	-0.287	0.641	0.443	0.730
Waste citric acid	-0.230	0.702	0.293	0.523	-0.26	0.900	0.338	0.598

XPS and depth profiling

The measured photoemission spectra allowed to evaluate the composition and the thickness of the passive film on untreated, nitric acid passivated, commercial and lemon waste-derived citric acid passivated samples. Typical XPS spectra of Cr $2p_{3/2}$ and Fe $2p_{3/2}$ regions, recorded for the sample treated with waste-derived citric acid, are shown in Figures 10 and 11.

According to literature [19, 20, 21] both the oxide and the metallic states of Fe and Cr were detected indicating the presence of thin passive film covering the metal phase. The atomic percentage of these elements for untreated, commercial, lemon waste-derived citric acid passivated and nitric acid passivated samples are reported in Table 2. There is a big difference of Cr surface content directly after passivation treatment, since the Cr content redoubles, while the content of Fe (representing metallic Fe and its oxides) decreases.

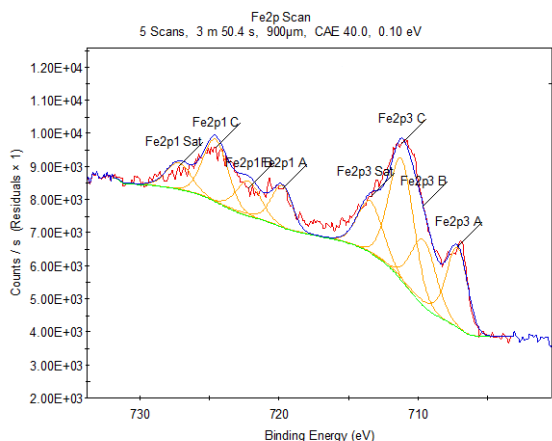


Fig. 10: Deconvolution of Fe 2p spectrum for the waste citric acid passivated sample

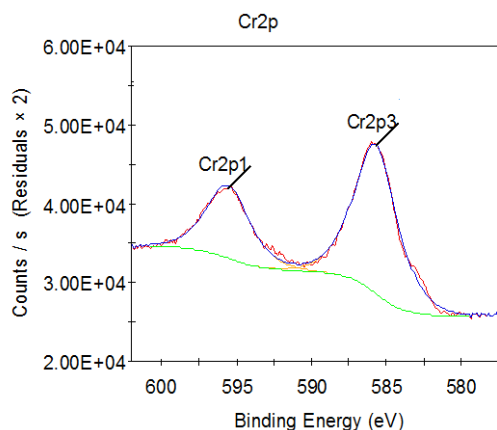


Fig. 11: Cr 2p spectrum for the waste citric acid passivated sample

Table 2: XPS quantification of differently treated samples.

Peak	Bond	Unpassivated		Nitric acid		Commercial citric acid		Waste citric acid	
		BE (eV)	Atomic %	BE (eV)	Atomic %	BE (eV)	Atomic %	BE (eV)	Atomic %
Cr2p_{3/2}	Cr ₂ O ₃	576.5	4.5	576.6	7.2	576.6	8.8	576.7	9.2
Fe2p_{3/2} A	Fe(0)	707.1	3.6	707.0	2.2	707.1	4.8	707.0	2.7
Fe2p_{3/2} B	FeO	709.6	3.1	709.6	1.0	709.3	1.5	709.6	1.1
Fe2p_{3/2} C	Fe ₂ O ₃	711.2	5.8	711.2	1.4	711.2	1.3	711.2	1.2

The surface content of Cr in the sample treated with nitric acid is lower than in the samples treated with citric acid, but comparing the electrochemical results it is clear that the sample treated with nitric acid behaves better than the ones treated with citric acid.

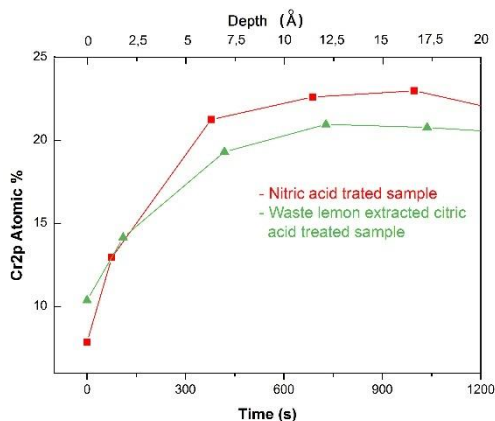


Fig. 12: XPS depth profiles for the samples passivated with nitric acid and waste citric acid.

The XPS depth profiles of Cr 2p for the samples treated with nitric acid and waste citric acid are reported in Figure 12. After a sputtering time of 700 s (depth of ~12 Å), the sample treated with nitric acid contained

about 23% of Cr, whereas the one treated with citric acid contained of about 19%. This value corresponds to the nominal value of 18% in stainless steel after a longer sputtering time, indicating that the oxide layer in the sample treated with nitric acid is thicker than in other specimens and explaining the better corrosion behaviour.

Scanning Electron Microscopy (SEM-EDX)

The electrochemical results were confirmed by observation at SEM of the samples after corrosion tests. SEM micrographs of treated and untreated samples after corrosion tests are shown in Figure 13-15. As expected, the untreated sample presented some corrosion pits, with an average size of 1-3 μm , on its surface (Figure 13). On the other hand, it is interesting to note that the pits on the treated specimens were smaller than pits on unpassivated steel (less than 1 μm) and less visible on the samples. Furthermore the pit edge of the untreated sample was irregular (Figure 13), whereas the treated samples showed round pits with smooth edges (Figure 14-15), in agreement with literature [25].

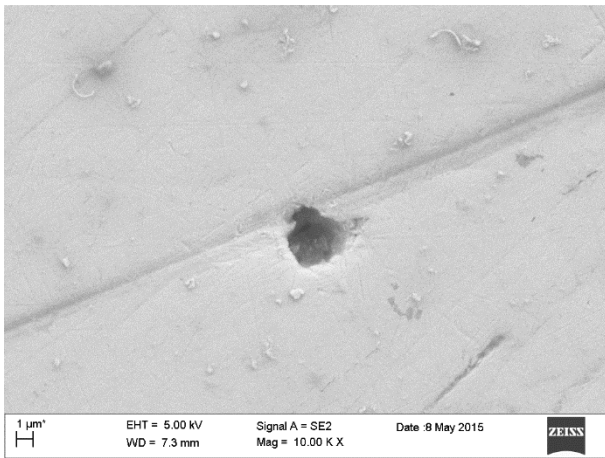


Fig. 13 Unpassivated sample SEM morphology after corrosion test

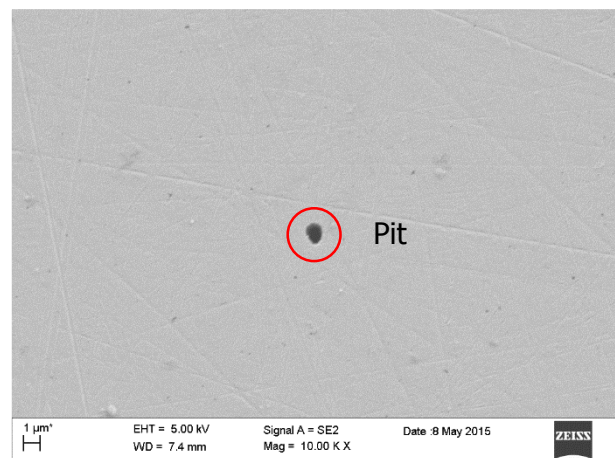


Fig. 14 Citric acid passivated sample SEM morphology after corrosion test

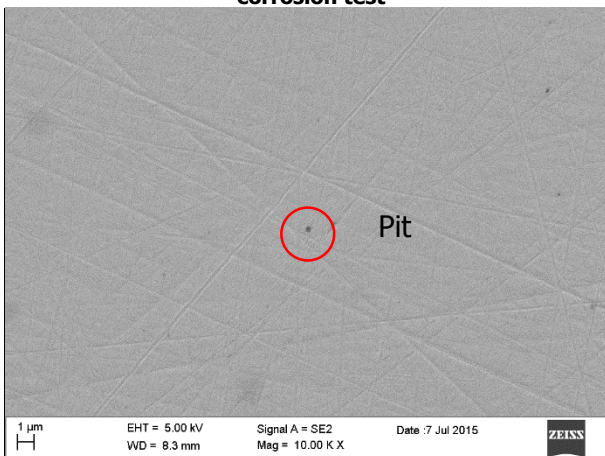


Fig. 15 Extracted citric acid passivated sample SEM morphology after corrosion test

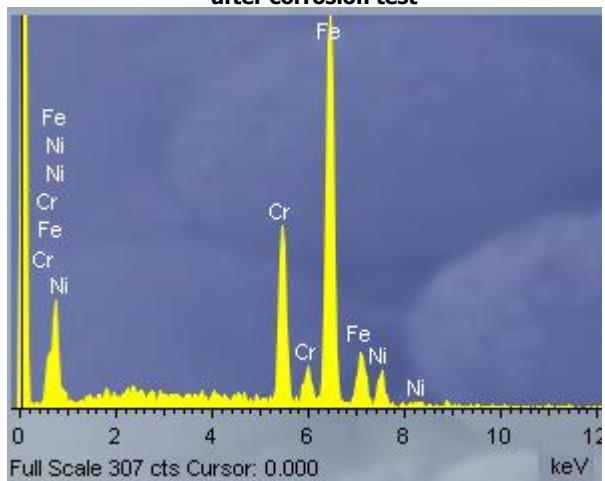


Fig. 16 EDX spectrum of citric acid passivated sample after corrosion test

Pitting corrosion arises where passivity is lost at localized spots on the metal surface, usually under the action of aggressive anions, among which chloride is the most commonly encountered aggressive anion causing pitting corrosion. Moreover, as well known, the evolution of corrosion pits on stainless steel immersed in chloride solution occurs in three distinct stages: nucleation, metastable growth and stable growth [22]. Several studies have shown that pits can initiate from oxide inclusions and it has already been demonstrated that manganese sulphide inclusions play a critical role and pitting events are found to occur at, or close to, such second-phase particles [1, 2]. Chemical changes in and around sulphide inclusions have been postulated as a mechanism for pit initiation [23, 24]. Lower number and smaller pits indicate that the citric acid passivation

works as well as nitric acid passivation in removing free iron and sulphide inclusion. EDX analysis (Fig. 16) confirm the presence of stainless steel elements such as Fe, Cr, Ni. The EDX spectrum is almost identical for all the samples.

CONCLUSIONS

In this work citric acid has been extracted in an eco-friendly way from natural waste derived reagents, such as lemon waste and egg-shell.

Stainless steel samples have been successfully passivated in both commercial, waste extracted citric acid and nitric acid baths and their electrochemical behavior has been compared in order to demonstrate the potentiality of the citric acid based passivation.

The citric acid passivation treatment significantly increases the corrosion resistance due to a high Cr content in the passive film. Citric acid passivation is almost effective as well as nitric acid passivation.

Thus, the proposed citric acid passivation can be considered a promising completely green sustainable alternative to the traditionally used stainless steel passivation treatments.

REFERENCES

- [1] M. A. Barbosa, *Corrosion science*, 23 (1983), p. 1293-1305.
- [2] J.S. Noh, N.J. Laycock, W. Gao, D.B. Wells, *Corrosion science*, 42 (2000), p. 2069-2084.
- [3] D. Wallinder, J. Pan, C. Leygraf, A. Delblanc-Bauer *Corrosion Science* Volume 41, Issue 2, 1 February 1998, Pages 275–289.
- [4] ASTM A967 "Standard specification for chemical passivation treatments for stainless steel parts".
- [5] ASTM A380 "Standard practice for clearing, descaling, and passivation of stainless steel parts, equipment, and systems".
- [6] T. Shibata, T. Haruna, T. Nakamura. *Proceedings of International Symposium on Plant Aging and Life Prediction of Corrodible Structures*, NACE, Houston, TX, 1997, p. 641
- [7] S. R. Schulte, *PF Online (Products Finishing Magazine)*, <http://www.pfonline.com/articles/nitric-acid-passivation-and-ehsimpact>, (2011).
- [8] K. L. Penniston, S. Y. Nakada, R. P. Holmes, and D. G. Assimos. *Journal of Endourology*. March 2008, 22(3): 567-570. doi:10.1089/end.2007.0304.
- [9] D. Yasensky, C. Larson, J. Reali, United Space Alliance, (2011).
- [10] M.H. AlKhalidi, H.A. Nasr-El-Din, S. Mehta, A.D. Al-Aamri. *Chemical Engineering Science* 62 (2007) 5880 – 5896.
- [11] M. Berovič and M. Legiša. *Biotechnology annual review*. February 2007.
- [12] C. N. Fredd and H. S. Fogler. *Journal of colloid and interface science* 204, 187–197 (1998) Article no. CS985535.
- [13] M.H. AlKhalidi, H.A. Nasr-El-Din, H. Sarma. "Impact of calcium citrate precipitation on the reaction of citric acid-calcite" *The 2008 Annual Meeting*. 2008.
- [14] M. Bragaglia, G. Montesperelli, R. Montanari. *La metallurgia italiana* Volume 107, Issue 5, 1 May 2015, Pages 23-29.
- [15] [Engin B., Demirtas H., Eken M., Temperature effects on egg shells investigated by XRD, IR and ESR techniques, *Radiation Physics and Chemistry*, Vol. 75, 2006, p. 268–277.]
- [16] S. P. M. C. Souza, E. G. Araújo, F. E. Morais, E. V. Santos, M. L. Silva, C. A. Martinez-Huitle, N. S. Fernandes. *Braz. J. Therm. Anal.* Vol. 2 No. 1 (2013) 17 – 22.
- [17] M. H. Khaskheli, S. T. H. Sheraz, H. M. Ujan, S. A. Mahesar. *Turk J Chem* 36 (2012), 477 – 483, tubiak doi:10.3906/kim-1108-26].
- [18] H. Groen, Heriot-Watt Kevin J. Roberts *J. Phys. Chem. B* 2001, 105, 10723-10730
- [19] L. Wegrelius and B. Sjöden. *Outokumpu Stainless Acom 4-2004*].
- [20] M. Aronniemi, J. Sainio, J. Lahtinen. *Surface Science* 578 (2005) 108–123].
- [21] I. Ciancaglion, R. Donnini, S. Kaciulis, A. Mezzi, R. Montanari, N. Ucciardello, G. Verona-Rinati. *Surf. Interface Anal.* 2012, 44, 1001-1004.
- [22] P. C. Pistorius and G. T. Burstein. *Physical Sciences and Engineering*, Vol. 341, No. 1662 (Dec. 15, 1992), pp. 531-559.
- [23] M. P. Ryan, D. E. Williams, R. J. Chater, B. M. Hutton & D. S. McPhail. *Nature* 415, 770-774 (14 February 2002) | doi:10.1038/415770a.
- [24] J. Stewart and D. E. Williams *Corrosion Science*, Vol. 33, No. 3, pp. 457-474, 1992.

[25] X.B. Tian, S.C.H. Kwok, L.P. Wang, P.K. Chu. *Materials Science and Engineering A326* (2002) 348–354.