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Assessment of the effect of surface finishing processes on the pitting resistance in saline environments of welded AISI 316L stainless steel

G. Masi, C. Chiavari, C. Martini, F. Pasini, S. Sessa, N. Gandolfi, M.C. Bignozzi

The stability of passive films of welded AISI 316L stainless steel, subjected to different surface finishing treatments, was investigated through anodic polarization measurements in 3.56 wt.% NaCl solution. The AISI 316L specimens, either hot or cold rolled and subsequently welded by TIG (Tungsten Inert Gas), were subjected to various surface finishing treatments (scarfing, mechanical polishing, brightening, pickling, passivation and electropolishing). All specimens were observed through optical and SEM-EDS microscopes, to highlight variations of microstructure and chemical composition of the heat affected zone (HAZ) caused by mechanical and chemical treatments. For each type of treatment, values of the open circuit potential (vs SCE) and pitting potential (vs SCE) were reported. It was observed that the scarfing process produces values of pitting potentials comparable to those obtained from untreated specimens. On the contrary, pickled specimens showed pitting potential values much lower than those treated with chemical passivation. The best pitting resistance performance were shown by the cold rolled series finished by brightening, where the values of pitting potential for both the BM and the HAZ were higher and comparable. The improved pitting resistance of brightened cold rolled samples was attributed to the beneficial role of brightening (due to the ability of this surface treatment to increase the surface chromium content and to form a compact and defect-free protective film), combined with microstructural features of the substrate such as the absence of martensite and the finer grain size.

KEYWORDS: AUSTENITIC STAINLESS STEEL, WELDING, SURFACE FINISHING, CORROSION, ELECTRON MICROSCOPY (SEM)

INTRODUCTION

Due to the high degree of hygiene and cleanliness that is required by applications related to packaging, namely for pressing machines which produce pharmaceutical tablets, it is necessary to use austenitic stainless steel for components, in order to allow full sanitization and avoid contamination due to corrosion products. In fact, austenitic stainless steels are listed in the European Regulations as Food Contact Materials (FCMs). The austenitic stainless steel AISI 316L usually shows a good inter-granular and pitting corrosion resistance against aggressive chloride solutions (with a PREN value ranging from 24 to 28) and a good weldability, since it does not require special post-weld heat treatments. The main problem affecting welded austenitic stainless steel is due to the possibility of localized corrosion, such as pitting, in the Heat Affected Zone (HAZ). In fact, the welded joint, being an element of structural discontinuity, can result in micro-structural variation and chromium-depleted areas, where the material does not behave as a stainless steel [1]. More specifically, in the HAZ, a welded joint shows micro-

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In the work of Garcia et al. [6], the anodic behavior of austenitic stainless steels such as AISI 316L and 304 was analyzed, through a specific minicell, in a 1M H₂SO₄ and 5N NaCl solution at 30°C, in different areas: in the welded metal, along the fusion line, in the heat affected zone and in the base metal, far from the welded joint. The worst corrosion resistance was given by the fusion line and HAZ; this is due to the fact that, in the fusion line and along the HAZ, a dendritic structure and grain coarsening were observed, respectively. These two kinds of microstructure make the protective film less uniform, in addition to a decrease of the mechanical properties.

During the welding process, in the temperature range between 550 and 850°C, sensitization (consisting of the precipitation of chromium carbides (such as Cr₂₃C₆, Cr₅C, Cr₇C₃) at grain boundaries) can occur, greatly decreasing the chromium content. The effects of the sensitization can have a lot of adverse implications for what concerns the mechanical and corrosion properties of stainless steels [7,8]. In order to reduce the harmful effects of sensitization, low carbon stainless steel can be used (marked with the final letter L), thus limiting carbide precipitation. Another way to decrease the sensitization degree, consists of pre-heating the material at 450°C, so that the steel can stay as shortly as possible in the 550-850°C temperature range. In a recent study, it was demonstrated, through cyclic anodic polarization curves that the pitting resistance of welded AISI 316L can be increased by a pre-heating at 450-650°C, thus reducing the current density by an order of magnitude [9].

In addition to chemical and microstructural variations that involve the material near the welded joint, the generation of heat-tinted zones can take place during welding due to the formation, at high temperatures, of oxides of iron and other alloying element on the surface. In particular, these heat-tinted areas are characterized by a double layer, where the outer layer consists mainly of Fe₃O₄ and the inner layer of the spinel (FeCr)₃O₄ and mixture of iron, nickel and other oxides [7,10].

The formation of heat-tinted zones depends on several fac-

tors such as steel chemical composition, the thickness of Cr₂O₃ oxide, the surface finishing, the type of welding, the geometry of the welded joint and the thermal intake for fusion [10-14]. These heat-tinted zones, as well as chromium depletion zones, are characterized by lattice defects and by alloying element dilution, so the passive film is weaker and inhomogeneous in these areas, which become preferred sites for pits generation [15,16].

In the work of Kimbrel et al. [17], electrochemical tests were carried out in the heat affected zones of AISI 316L specimens with different levels of oxygen in the welding procedure; they found that an increase of oxygen content during the welding process extends the heat-tinted zones and lowers the corrosion resistance, by reducing significantly the pitting potential (E_{pit}) values.

The standard AWS D18.2 [18] (i.e. the weld discoloration chart for austenitic stainless steels) shows the different colors of heat-tinted zones for austenitic stainless steel, at different levels of oxygen (20÷12500 ppm) in the welding procedure: in the industrial practice a light yellow color (50 ppm of oxygen) is considered as the threshold condition in almost all corrosive environments.

The removal of surface oxides that may contaminate food, beverages or pharmaceuticals and the restoration of the protective passive layer through chemical and/or mechanical treatments, for improving the corrosion resistance, are mandatory. As chemical treatments, steps of degreasing, pickling, passivation and electro-polishing are usually considered; while, among the mechanical treatments, the best known are scarfing, polishing and brightening.

The preliminary degreasing phase consists of the removal of dirt and grease before any thermal, chemical and mechanical treatment; this step has the purpose to avoid superficial enrichment of carbon, which could trigger sensitization problems and it is carried out through alkaline solutions, emulsions, cleaning solvents or steam jets. After degreasing, the pickling treatment is carried out, in order to remove, mechanically (with rotating fiber brush) or chemically (with H₂SO₄ or HNO₃ + HF solutions), the oxide scales arising from the welding process and restore a more uniform protective film. Also the electrochemical pickling trough a voltage generator is widely used for industrial applications: a pole is connected to the material and the other to a torch, into which is mounted a bottle of electrolyte based on pho-

sphoric acid. As phosphoric acid is toxic and dangerous to the operator, in the work of Giovanardi et al. [19], an equally efficient and environmentally friendlier electrolytic solution was developed, based on citric and sulphamic acids.

The process called passivation is applied to restore the natural passive layer of stainless steel sand eliminate traces of less noble metals (typically iron) or other deposits. Passivation, as a general rule, always follows the pickling process. This method is used to prevent localized corrosion phenomena on stainless steel, in particular to avoid pitting and crevice corrosion. Before proceeding with the passivation treatment, it is important that the surface of the material is free from oxide scales and heat-tinted areas. Passivation usually consists of immersing the metallic component in nitric acid at 20-30 wt.% solution, for times varying between 10 and 30 minutes and temperatures from 20 up to 70 °C, depending largely on the material [20-23]. In addition to nitric acid solutions, chromic acid and chromates mixtures can be employed as well, but are rarely used because of their environmental impact.

In the work of O'Laoire et al. [24], through different analytical techniques, such as XRD, SEM and XPS, the effect of passivating solutions based on nitric and citric acid, was studied. It was reported that passivation treatments are able to generate chrome-enriched areas that can extend into the substrate for several microns. It was concluded that citric acid can create the more coherent and hence corrosion resistant passive films, even if the Cr₂O₃ layers generated by nitric acid passivation are thicker and deeper.

Surface roughness is an extremely important factor influencing contamination. Several papers have shown for stainless steels that with decreasing surface roughness, the resistance to pitting corrosion significantly increases [25, 26]. In Europe the surface finishes are classified according to EN 10088-2 [27]. In addition to the most common polishing processes with abrasive materials, a further method of mechanical polishing is brightening. After the step of chemical pickling, brightening consists of a mechanical polishing of the surface within tanks, filled with water and specific chemicals, with vibrating steel balls; the procedure ends with the drying of the material in machines containing heated corn sawdust.

Electro-polishing is frequently used for surface finishing, too. In anti-acid plastic tanks containing phosphoric acid,

the material to be treated is connected to a titanium rack which acts as an anode, while the cathode is made of lead or copper plates. By applying a DC current through a voltage generator, elements such as Fe and Ni can be removed from the surface, obtaining a surface layer strongly rich in Cr and with less defects and lower mechanical stress [21, 26]. All the chemical and /or mechanical treatments mentioned above are often used together to ensure a high degree of stainless steel protection after the welding process. Even though these processes are well established from a technological point of view, to our knowledge no data are reported in the literature regarding the electrochemical guantification of their efficiency (also in combination among different processes) in increasing the pitting resistance of TIG-welded AISI 316L in 3.56 wt% NaCl solution. Therefore, the specific aim of the present work is to evaluate, through electrochemical tests, the influence of these mechanical and chemical treatments on the microstructure and the pitting resistance of both the HAZ and the base metal (BM). In fact, the protective properties of the passive film on stainless steel strongly depend on its chemical composition and microstructure, whose modifications, due to the welding process, could weaken the pitting resistance [1,2]. Therefore, the main aim of this study is the assessment of the relationships between the corrosion resistance and these microstructure variations, so as to identify the best surface finishing treatment, which is able to regenerate the protective film after the welding process.

MATERIALS AND METHODS

The tested specimens were AISI 316L SS TIG welded plates (250 x 250 mm²). AISI316L austenitic stainless steel has the following chemical composition (measured by Spark-Optical Emission Spectroscopy, weight %): C: 0.02; Mn: 1.35; Si: 0.40; Cr: 16.87; Ni: 10.05; Mo: 2.06; P: 0.03; S: 0.03; Fe: balance, corresponding to a PREN (Pitting Resistance Equivalent Number) of 25.

The preliminary thermo-mechanical treatment procedures were labeled as follows, according to EN 10088-2 classification [27]:

- 2B: cold rolled, heat treated, pickled and skin-pass rolled (thickness of the specimens: 4 mm);
- I: hot rolled, heat treated and pickled (thickness of the specimens:8 mm);

- BA: cold rolled and heat treated in an inert atmosphere (thickness of the specimens: 2 mm).
- All samples were then subjected to various processing technologies, named as follows:
- S: welding
- D: pickling
- P: passivation
- SC: scarfing
- L: mechanical polishing

- B: brightening
- E: electro-polishing.

In Table 1, all the specimens are listed, classified according to the surface finishing and chemical or mechanical treatment. The labels 2B, I, and BA are followed by sample number, which in turn identifies the treatments (e.g. 2B-03 means a 2B-type specimen which underwent a sequence of welding, pickling and passivation).

2B Series	l Series	BA Series	Treatment ^(a)
2B - 01	-01	BA - 01	S
2B - 02	/	BA - 02	S + D
2B - 03	I - 03	BA - 03	S + D + P
2B - 04	/	/	S + SC
2B - 05	l - 05	/	S + SC + L
2B - 06	/	/	S + SC + L + B
2B - 07	l - 07	/	S + SC + L + E + P

Tab.1 - 2B - I - BA series specimens with the corresponding sequence of chemical and mechanical treatments.

^(a)S: welding, D: pickling, P: passivation, SC: scarfing, L: mechanical polishing, B: brightening and E: electro-polishing.

The scarfing and mechanical polishing of the welded joints were obtained first by grinding with 120, 240, 400 and 600 grit abrasives and finally through diamond paste. The "Ecoinox" reagent (produced by Delmet Srl), composed of nitric acid (20-30%), ammonium difluoride (10-20%), a corrosion moderator (0.1-0.6 %) and water, was used as pickling agent.

For the passivation treatment, the "Passivating P" reagent (produced by Delmet Srl), composed of nitric acid (30-50%) and water, was used. For the brightening process, the reagent "Compound 1320" (produced by Metal Fin Snc) was used, consisting of nitrilotriethanol (20-25%), coconut amine ethoxylated (7-10%), citric acid monohydrate (7-10%), acid fat and salt of potassium (5-7%), iminodiethanol (1-3%), oleic fatty acid (1-3%), C8-18 amide (1-3%) and sodium dinaftenmetansulphonate(1-3%). Finally, for the electro-polishing bath, the reagent "LE 2000" by Delmet Srl was applied, consisting of sulphuric acid (30-50%), phosphoric acid (30- 50%) and water.

Anodic polarization curves were performed according to

ASTMG5-94 [28] and ASTMG61-86 [29] for tests in sulphuric acid and 3.56 wt.% NaCl solution. The electrochemical tests were carried out through a 50 mL "paint test cell", produced by Gamry Instruments. By this cell, it was possible to carry out the analysis directly on our test-plate, avoiding sampling procedures such as punching or laser cutting, which might modify the microstructure of the specimens and their response to corrosion. In addition, there was the advantage of selecting the test area (1 cm²) by applying adhesive masks directly on the sample surface. A saturated calomel electrode (SCE) was used as the reference electrode (RE), while a graphite bar was used as a counter electrode (CE). The tests were conducted at 25 ± 1°C and before carrying out the electrochemical measurements, the cell was blanketed in nitrogen flow, in order to reproduce the corrosive environment of the reference application. After degassing, the Open circuit potential (E_{OCP}) was recorder for about 50 min. The polarization curves were performed through an AMEL 7050 potentiostat, using a scan rate of 0.6 V/h starting from the open circuit potential (E_{OCP} vs RE) up to 1.6 V vs RE. The pitting potential E_{pit}, was determined for each scan and the values were reported as mean of 3 measurements.

Before and after each electrochemical test, the samples were inspected by optical microscope to determine the grain size and evaluate the presence of martensite or ferrite, intra-granular twins and sensitized areas. The specimens were grinded (120, 240, 320, 400 and 600 grit) and then polished with diamond suspensions (3 to 1µm). Chemical etching was carried out by the Beraha II reagent (consisting of an aqueous solution at 30 vol.% of HCl, 0.8-1.0 vol.% of potassium bi-sulphite and 4 vol.% of ammonium di-fluoride). The microstructure of welded samples was observed both by optical and scanning electron microscope (SEM/EDS: Zeiss EVO 50 SEM with Oxford Inca Energy 350 EDS microprobe).

The average grain size was evaluated through the Heyn Linear Intercept Procedure following the ASTM E 112-10 [30]. All the data are reported as mean values of 10 measurements ± the confidence interval (CI) with a level of confidence of 99% (Student's t and degrees of freedom equal to 3.25 and 9 respectively). For each measurement, the value of relative standard deviation (RSD %) was also shown, for evaluating the reproducibility of the data. Through the Heyn Linear Intercept Procedure, RSD% values close to 5 ÷7 %, were obtained.

RESULTS AND DISCUSSION Microstructure

Before electrochemical tests, the microstructures of base metal (BM) and heat affected zones (HAZ) of the samples of 2B and I series were analyzed and compared, after surface polishing and etching (Fig. 1). As regards the influence of the preliminary treatments, the average grain size values reported in Table 2 show that the specimens of the I series, having been hot rolled and having a double thickness compared to the 2B series, underwent a longer post-welding cooling time, with subsequent slightly more marked increase of grain size after recrystallization.

As regards the influence of welding, the comparison between the microstructures of the base metal and the HAZ for both series of samples (2B and I), shows that welding leads to a significant increase of grain size in the heat affected zone. Namely, welding increased the average grain size (Table 2) in the HAZ of about 40 - 45% compared to the microstructure of the base metal. Therefore, the influence of the welding on grain size is more remarkable than that of the initial rolling process (hot or cold).



Fig.1 - Comparison between BM and HAZ microstructure for 2B-07 and I-07 specimens (optical microscopy images). Corresponding grain size values are reported in Table 3. Tab.2 - Comparison between BM and HAZ average grain size for 2B-07 and I-07 specimens (corresponding opticalmicrographs are reported in Fig. 1)

Series	Average size ± CI 99% (BM) [μm]	RSD % (BM)	Average size ± CI 99% (HAZ) [μm]	RSD % (HAZ)
2B-07	21.62 ± 1.32	5.95	30.00 ± 2.02	6.56
I-07	23.75 ± 1.55	6.37	35.03 ± 1.71	4.76





A more detailed comparison between the microstructures of samples 2B-07 and I-07 was also performed through SEM. It is worth noting that the main differences were observed in the HAZ (Fig. 2), where only in hot rolled sample (I series) martensite was observed. In fact, hot rolling can induce a high cooling rate of the austenitic stainless steels, thus accelerating the kinetics of martensitic structure formation [31-32]. This fact justifies the remarkable presence of martensite both in the BM and in the HAZ of the I-series samples.

In order to evaluate the presence of sensitized microstructures, EDS analysis of both series of samples were performed. A comparison of the EDS results obtained in the grain boundaries and in the grain core for I-series samples did not show any detectable enrichment in chromium content (Table 3) at the grain boundary. The morphological effect of thickened grain boundary observed through optical metallographic analysis (Fig. 1) may be simply due to chemical etching.

Tab.3 - Comparison of EDS results for grain core and boundaries of I-series samples (weight %).

Element	% C	% O	% S	% Cr	% Fe	% Ni
Boundaries	1.3±0.3	4.4 ± 0.2	2.5 ± 0.4	15.9 ± 0.4	64 ± 1	10.4 ± 0.2
Core	1.2 ± 0.1	4.4 ± 0.2	2.7 ± 0.3	16.4 ± 0.3	62 ± 1	10.3 ± 0.4

ANODIC POLARIZATION CURVES

For each welded specimen, treated with different surface finishing procedures, measurements of open circuit potential (E_{OCP} vs SCE) were conducted both on the bare metal (BM) and in the Heat Affected Zone (HAZ): the measured E_{OCP} values are listed in Table 4. Anodic polarization curves were also recorded and the pitting potential (E_{pit} vs SCE) was used as a parameter to evaluate the pitting corrosion resistance. All pitting potential values are reported in Table 4 and, for HAZ areas, a visual comparison is illustrated in the histograms of Fig. 3.

Free corrosion potential measurements (E_{OCP} vs SCE), both recorded on BM and HAZ zones, showed significant differences among chemical and mechanical treatments. Considering the samples not treated after welding (S), the open-circuit potential values (E_{OCP} vs SCE) measured in the BM area are between 100 and 200 mV higher than those measured in the HAZ. The obvious reason of this shift of potential towards more negative values is the damage of the passive film, which occurred in the HAZ zone, due to welding.

For cold-rolled samples (the 2B-series in particular), the pickling procedure (D) strongly affects the behaviour of the HAZ, shifting the potential of more than 200 mV towards more positive potentials, while the following passivation treatment (P) does not ennoble further the HAZ area. For these samples, the difference between E_{OCP} values of BM and HAZ is almost eliminated.

Conversely, for hot-rolled samples (I-series), a full set of surface finishing treatments, consisting of passivation, scarfing, mechanical polishing, electro-polishing (S+-SC+L+E+P) must be performed in order to obtain E_{OCP} values, in the HAZ, comparable to those of BM (-0.143 V vs SCE), on welded samples.

2B Series (Cold rolling, Thickness 4 mm)							
No	Code	Treatments	Е _{осР} ВМ vs SCE (V)	E _{ocP} HAZ vs SCE (V)	E _{pit} BM vs SCE (V)	E _{pit} HAZ vs SCE (V)	
1	2B-01	S	-0.155 ± 0.004	-0.344 ± 0.003	+0.530 ± 0.008	+0.019 ± 0.006	
2	2B-02	S + D	-0.114 ± 0.008	-0.094 ± 0.005	+0.516 ± 0.021	+0.454 ± 0.009	
3	2B-03	S + D + P	-0.118 ± 0.005	-0.119 ± 0.008	+0.481 ± 0.016	+0.552 ± 0.015	
4	2B-04	S + SC	-0.127 ± 0.010	-0.210 ± 0.013	+0.447 ±0.012	+0.142 ± 0.008	
5	2B-05	S + SC + L	-0.117 ± 0.005	-0.147 ± 0.007	+0.512 ± 0.015	+0.505 ± 0.010	
6	2B-06	S + SC + L + B	-0.130 ± 0.009	-0.186 ± 0.005	+0.589 ± 0.009	+0.620 ± 0.013	
7	2B-07	S + SC + L + E + P	-0.139 ± 0.012	-0.238 ± 0.021	+0.593 ± 0.011	+0.526 ± 0.022	

Tab.4 - EOCP and Epit vs SCE values for BM and HAZ of all the samples studied in 3.56wt% NaCl solution.

I Series (Hot rolling, Thickness 8 mm)							
Νο	Code	Treatments	E _{ocP} BM vs SCE (V)	E _{ocP} HAZ vs SCE (V)	E _{pit} BM vs SCE (V)	E _{pit} HAZ vs SCE (V)	
1	1-01	S	-0.143 ± 0.008	-0.355 ± 0.007	+0.143 ± 0.016	-0.215 ± 0.011	
2	1-03	S + D + P	-0.181 ± 0.005	-0.243 ± 0.011	+0.443 ± 0.012	+0.539 ± 0.016	
3	l-05	S + SC + L	-0.194 ± 0.006	-0.223 ± 0.004	+0.573 ± 0.024	+0.532 ± 0.014	
4	l-07	S + SC + L + E + P	-0.116 ± 0.008	-0.143 ± 0.006	+0.508 ± 0.015	+0.434 ± 0.017	

BA Series (Cold rolling, Thickness 2 mm)								
No	Code	Treatments	Е _{осР} ВМ vs SCE (V)	E _{ocP} HAZ vs SCE (V)	E _{pit} BM vs SCE (V)	E _{pit} HAZ vs SCE (V)		
1	BA-01	S	-0.216 ± 0.005	-0.295 ± 0.010	+0.519 ± 0.013	-0.052±0.012		
2	BA-02	S + D	-0.048 ± 0.004	-0.196 ± 0.007	+0.541 ± 0.021	+0.492 ± 0.016		
3	BA-03	S + D + P	-0.030 ± 0.008	-0.147 ± 0.005	+0.433 ± 0.018	+0.556 ± 0.015		

The effectiveness of a post-weld treatment can be studied in a more meaningful way through the values of the pitting potential, also because this mechanism of localized corrosion is the main phenomenon for stainless steels in presence of chloride ions, especially along the heat affected zone of a welded joint. In general, the worst pitting resistance for the untreated samples are shown by the hot-rolled series (I), where the value of pitting potential for BM settles around +0.15V vs SCE (in opposition to the cold rolled series, whose E_{pit} is around +0.50 V vs SCE), so showing a passivation range of less than 300 mV. This is likely due to the microstructural changes such as grain growth induced by the hot-rolling that can weaken the protective film, which is supposed to be still present on the BM surface after welding [6]. For I series, in HAZ after welding, E_{pit} settles around -0.21V vs SCE, so showing a very short passivation range, of around 50 mV, indicating an almost complete removal of the passivation film by the welding.

On the contrary, for the cold-rolled, welded and unfinished samples (2B series) the passivation range in the HAZ is short, but more extended than for the I-series of about 250mV. The different behaviour of HAZ areas for 2B- and I-series can be explained on a microstructural basis, specifically by considering the higher presence of martensite in the I samples, as previously discussed and shown in Fig. 2, which is known to be responsible for the lower corrosion resistance to chlorides [1].



Fig.3 - E_{Dit} vs SCE values for HAZ specimens of the three series

As an example, a comparison between the anodic polarization curves measured on BM and HAZ areas, relative to samples welded and not finished (S, 2B-01) and finished with S+-SC+L+B sequences (2B-06) is shown in Fig. 4.

The curve relative to the HAZ changes drastically by comparison to the BM area (passivation range of about 0.7 V), showing two short passivation ranges with very low E_{pit} (-0.200 V vs SCE and 0.019 V vs SCE).

Considering only the scarfing treatment (S+SC), i.e. removal of the external weld bead, only a limited effect on the resistance to pitting in the HAZ (+ 0.14 V vs SCE) was observed for 2B series, as scarfing is not capable of regenerating the passive film and remove defects from the surface. On the contrary, for all series, treatments such as pickling, passivation, mechanical polishing, electropolishing and polishing increase the pitting potential of the heat affected zone and balance it to that of the base metal (+0.5 ÷ +0.4V vs SCE). This is evident in Fig. 4, showing the influence of surface finishing on anodic curves for the 2B series (cold rolled samples). The anodic curves measured for the BM area do not vary significantly as a function of surface finishing, whilst those of HAZ change drastically. In particular, the pickling treatment gives pitting potential values for the heat affected zone slightly lower than those obtained through passivation (by \approx 100mV vs SCE), mechanical polishing (by \approx 0.05 V vs SCE) and electropolishing (by \approx 0.07 V vs SCE).



Fig.4 - Anodic polarization curves for BM and HAZ of as-welded (2B-01) (a) and welded then surface finished (2B-06) cold rolled AISI 316L specimens (b).

More specifically, it is evident that the brightening treatment (B) in addition to S+SC+L sequence of operations makes E_{nit} vs SCE higher of about 100 mV in both areas (HAZ and BM); the difference for pitting potential between base metal and heat affected zone falls within the experimental error band and the values are higher than all other treatment. Therefore, the mechanical treatment of brightening gives the best results in pitting resistance towards saline environment, relative to the HAZ areas of the welded joint. For the sample I-07, which was treated through electropolishing, measured pitting potentials are about 0.1V vs SCE lower than those recorded for the brightening treatment. The reasons of this particular behavior could be ascribed both to (i) the fact that the brightening treatment may increases the chromium content inducing the formation of a protective film more compact and free from surface defects and (ii) to the decrease of roughness induced by brightening [25].

CONCLUSIONS

The different stability of the passive films, formed both on base metal (BM) and heat affected (HAZ) zones of TIG-welded AISI 316L stainless steel, surface finished by different techniques, was investigated in 3.56 wt.% NaCl solutions.

Anodic polarization curves showed that the decrease of corrosion resistance in the HAZ compared to the BM, is strongly reduced by all re-passivation treatments.

Among all the investigated finishing processes, the best resistance to pitting corrosion is given by the operational sequence consisting of scarfing, mechanical polishing and brightening, which proved to be even better than the electropolishing procedure. Concerning the different thermo-mechanical treatments applied before welding, cold rolled samples (2B- and BA-series) have shown pitting potential values basically higher than those obtained by hot rolling (I-series). Metallographic analysis clearly showed that cold rolled samples have finer grains, while the hot rolled samples showed the presence of martensite which gives a lower pitting resistance compared to austenite, since it is more mechanically stressed. In all series, sensitization is not observed, due to the fact that the very low content of C (0.03% wt) has drastically reduced the sensitization phenomena.

These results demonstrate that, in applications related to packaging machines for the pharmaceutical industry, where TIG-welded AISI 316L is widely used for high resistance to pitting in chloride enriched environments, it is essential to carry out post-weld treatments. For parts exposed to aggressive chloride-containing environments, the best corrosion resistance is achieved by using cold rolled sheets, surface-finished by brightening as the last finishing step. Further experimental tests are required for investigating the pitting corrosion resistance of these materials in a more representative environment closely simulating service condition.

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REFERENCES

- [1] ASM, Metal Handbook, Corrosion, ASM International, 1994, Vol.13.
- [2] Smith JJ, Farrar RA. Influence of microstructure and composition on mechanical properties of some AISI 300 weld metals. Int Mater Rev 1993; 38:25-51.
- [3] Lu BT, Chen ZK, Luo JL, Patchett BM, Xu ZH. Pitting and stress corrosion cracking behaviour in welded austenitic stainless steel.
 Electrochim Acta 2005; 50:1391-1403.
- [4] Cui Y, Lundin CD. Evaluation of initial corrosion location in E316L austenitic stainless steel weld metals. MaterLett 2005;59:1542-1546.
- [5] Kokawa H, KuwanaT. Realationship between grain boundary structure and intergranular corrosion in heat affected zone of type
 304 stainless steel weldments. TransJpn Weld Soc 1992; 23:11-19.
- [6] Garcia C, Martin F, de Tiadra P, Blanco Y, Lopez M. Pitting corrosion of welded joints of austenitic stainless steels studied by using an electrochemical minicell. CorrosSci 2008; 50:1184-1194.
- [7] Ahmad M, Shoaib KA, Shaikh MA, Akhtar JJ. Identification of surface carbides and spinels in welded austenitic stainless steels. J Mater Sci 1994; 29:1169-1173.
- [8] Weiss B, Stickler B. Phase instabilities during high temperature exposure of 316 austenitic stainless steels. Metall Trans 1972;
 3:851-866.
- [9] ZareiRejani HR, Torkmani H, Sharbati M, Raygan S. Corrosion resistance improvement in gas tungsten arc welded stainless steel joints through controlled preheat treatment. Mat Des 2012; 34:51-57.
- [10] Brajkovic T, Suraga I, Simunovic V. Influence of surface treatments on corrosion resistance of Cr-Ni steels. Eng Rev 2013; 33:129-134.
- [11] Juraga I, Esih I, Simunovic V. Effect of the welding procedure on the pitting susceptibility of stainless steel. Proc. 15th Int. Corrosion Cong, ICC (International Corrosion Council, Granada, Spain) 2002, 712.
- [12] Patterson RFA, Flyg J. Influence of weld oxides on the corrosion of 316L stainless steel. Proc. EUROCORR, EFC(European Federation of Corrosion) 2005, 644.

- [13] Rastogi PK, Shah BK, Sinha AK, Kulkarin PG. Effect of oxide film on pitting susceptibility of 304 austenitic stainless steel. Br Corros
 J 1994; 29:78-80.
- [14] Keans JR, GE Molli GE. Reducing heat tint effects on the corrosion resistance of austenitic stainless alloy. Mater Perform 1994;
 33:57-61.
- [15] Sunil Kumar B, Kain V, Banerjee K, Maniyar PD, Sridhar S, Kumar J, Kumar. Effect of oxidation on corrosion behaviour of austenitic stainless steel 304L welds. Adv Mater Res 2013; 79:598-605.
- [16] Tuthill AH, Avery RE. Heat tints on stainless steel can cause corrosion problems. Mater Perform 1999; 38:72-73.
- [17] Kimbrel K. Determining acceptable levels of weld discoloration on mechanically polished and electropolished stainless steel surfaces. Pharm Eng 2011; 31:28-36.
- [18] AWS D18.2. Weld discoloration chart. Guide to weld discoloration levels on inside austenitic stainless steel tube, 1999.
- [19] Giovanardi R, Poli G, Pasquali L, Montecchi M, Filippetti M, Orlando G. Electrochemical method for pickling and passivation of austenitic stainless steel welds. Corros Eng Sci Technol 2012; 47:54-60.
- [20] Crookes R. Pickling and passivation stainless steel. Materials and applications series, 2nd ed: Euro Inox., 2007, 4.
- [21] Kosmac A. Electropolishing. Materials and applications series, 1st ed: Euro Inox., 2010, 11.
- [22] ASTM A380/A380M. Standard practice for cleaning, descaling and passivation of stainless steel parts, equipments and systems.
 2013.
- [23] ASTM A967/A967M. Standard specification for chemical passivation treatments for stainless steel parts. 2013.
- [24] O'Loire C, Timmins B, Kremer L, Holmes JD, Morris MA. Analysis of the acid passivation of stainless steel. Anal Lett 2006; 39:2255-2271.
- [25] Alar V, Barsic G, Runje B, Alor Z. The influence of the surface finishing on the electrochemical behaviour of austenitic and superaustenitic stainless steels. Material wiss Werkst 2012; 43:725-732.
- [26] Lee SJ, Lai JJ. The effects of electropolishing (EP) process parameters on corrosion resistence of 316L stainless steel. J Mater Process Technol 2003; 140:206-210.
- [27] EN 10088-2. Stainless steels Part 2: Technical delivery conditions for sheet/plate and strip of corrosion resisting steels for general purposes. 2005.
- [28] ASTM G5-94. Standard reference test method for making potentiostatic and potentiodynamic anodic polarization measurements. 2011.
- [29] ASTM G1-86. Standard test method for conducting cyclic potentiodynamic polarization measurements for localized corrosion susceptibility of iron-, nickel-, or cobalt-based alloys. 2009.
- [30] ASTM E 112. Standard Test Methods for Determining Average Grain Size. 2013
- [31] Raabe D. Texture and Microstructure Evolution during cold rolling of a strip cast and of a hot rolled austenitic stainless steel. Acta Mater 1997; 45:1137-1151.
- [32] Ferreira de Dafè SS, Sicupira FL, Silva Matos FC, Silva Cruz N, Rezende Moreira D, Brandao Santos D. Effect of Cooling Rate on (ε, α') martensite formation in twinning/trasformation-induced plasticity Fe-17Mn-0.06C steel. Mater Res 2013; 16:1229-1236.