

Resistance to localized corrosion of lean duplex stainless steels after brief thermal treatments.

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Lean duplex stainless steels are biphasic steels with a low nickel and/or molybdenum content, which represent an interesting and cost effective alternative to the employment of the most common austenitic stainless steels (such as AISI 304 and 316) or traditional more expensive duplex steels (such as DSS 2205). However, during production and welding operations, a relatively brief permanence (a few minutes or tens of minutes) in the critical temperature range between 650 and 950 °C, induces the formation of undesirable secondary phases (mainly chromium and molybdenum carbides and nitrides) which influence the alloy corrosion resistance. This paper compares the pitting corrosion resistance of three lean duplex alloys, LDSS 2101, DSS 2304 and LDSS 2404, before and after heat treatments of 10 min at 650, 750 and 850 °C and analyses the correlated pitting propagation modes. With this aim, critical pitting temperature (CPT) measurements were performed in 0.1 M NaCl solution. The results show that concerning the solubilized alloys their localized corrosion resistance is in good agreement with $PREN_{Mn}$ indications. Thermal treatments, and in particular that at 750 °C, reduce the pitting corrosion resistance of the alloys, mainly in the case of LDSS 2404 and 2101, due to the impoverishment in passivating elements (especially chromium and molybdenum) in regions close to precipitates. The heat treated DSS 2304 alloy shows a more limited reduction of its performances in comparison to the solubilized material and its CPT does not vary significantly with the treatment temperature. This phenomenon can be linked to the low nitrogen content of the alloy, which limits the volume of precipitates during heat treatments, allowing to reduce the extent of impoverishment in passivating elements.

KEYWORDS: STAINLESS STEEL – LEAN DUPLEX – THERMAL TREATMENT –
PITTING CORROSION – CRITICAL PITTING TEMPERATURE

INTRODUCTION

Duplex stainless steels (DSS) are steels with austeno-ferritic microstructure with a relevant applicative interest as they have a favourable combination of mechanical properties, weldability and high corrosion resistance in different environments. These characteristics make these alloys appropriate for different field conditions: from the paper industry to the petrochemical one, from the construction sector to that of nuclear energy production [1]. In the last 20 years, the research of new duplex alloys followed two main directions: from one side the improving of corrosion resistance by increasing the alloyed content of chromium, molybdenum and nitrogen (superduplex and hyperduplex stainless steels) and, from the other side, the market introduction of a new duplex family, called lean duplex stainless steels (LDSS) [2], still rather corrosion resistant, but more cost effective. The first lean duplex placed in the market was DSS 2304 (UNS 32304), with a low molybdenum content, which permitted both the prevention of detrimental secondary phases formation (χ and σ phases) during welding operations and production cost savings [1]. Subsequently, since the years 2000, the development of new lean duplex alloys focused on the reduction of nickel content, as this element, like molybde-

num, is significantly subject to market price fluctuations. With this aim, alloys were developed with nitrogen contents close to the element solubility limit and with high manganese levels, added to increase nitrogen solubility and to stabilize austenite phase. In this context, LDSS 2101 (UNS S32101) was introduced in the market with the aim of advantageously substituting the most frequently used austenitic stainless steels (AISI 304 e

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316), in field conditions where high mechanical properties and significant localized corrosion performance are required [3-6], but also carbon steels where maintenance costs are relevant [1]. In more recent years (year 2010), again in the field of low nickel and high manganese content duplex stainless steels, LDSS 2404 (UNS S82441) was developed. This alloy, containing higher chromium, molybdenum and nitrogen levels with respect to LDSS 2101 and DSS 2304, is expected to show a better localized corrosion resistance compared to the latter ones. In particular, the PREN (Pitting resistance Equivalent Number) value of LDSS 2404, and also its mechanical properties, are very similar to those of the traditional DSS 2205 (UNS S32205), with lower costs. Currently, DSS 2205 is widely used in aggressive environments, such as chemical and desalination plants and in the petrochemical industry, but it is also successfully used in architectural and civil engineering works, such as the Marina Bay pedestrian bridge in Singapore [7] or the Millenium Bridge in York [8]. In general, the possibility of reducing maintenance costs, guaranteeing the aesthetic appearance of the material for a very long time, lightening the structures by maintaining or even improving the mechanical resistance and, finally, the possibility of buying, transporting, welding and assembling more limited quantities of material, as a result of weight reduction, so allowing manpower cost savings, make LDSS a beneficial alternative to the use of the austenitic stainless steels and carbon steels most commonly used in construction field and civil engineering works [7]

The optimization of the mechanical properties and the corrosion resistance of duplex stainless steels, is obtained by ensuring a ferrite (α)/austenite (γ) ratio close to 1 and avoiding detrimental secondary phases formation [9]. However, during production and welding operations, or under high temperature conditions, excessive permanence in the critical temperature range between 650 and 950 ° C, can determine (depending on the chemical composition of the alloy) the growth of χ and σ phases and/or carbides and nitrides mainly of chromium. These phases can have a negative effect on the mechanical performances and localized corrosion resistance of the alloy [10].

The authors of this research study carried out several studies dealing with the resistance to localized corrosion and stress corrosion cracking of LDSS, before and after thermal treatments between 650 and 850 ° C [11-18]. In particular, it was found that aging for 5-30 min in the 650 - 850 ° C temperature range causes the formation of mainly chromium nitrides at LDSS 2101 grain boundaries, due to the high nitrogen content (0.22 wt%) of the alloy [13-15]. Instead, in DSS 2304 aging for up to 60 min in the same temperature range essentially determines chromium (and molybdenum) carbide precipitation, because the nitrogen content is much lower (0.1 wt%) [16,18].

These microstructural modifications tend to reduce the alloy localized corrosion resistance, as they can cause depletion in passivating elements (such as chromium and molybdenum) around the precipitates. This paper aims at comparing the effect of 10 min aging in the temperature range between 650 and 850 ° C on the microstructure and pitting corrosion resistance of LDSS 2101, DSS 2304 and LDSS 2404 in a 0.1 M NaCl solution. The different microstructures and phase compositions also affected the pitting attack morphology.

MATERIALS AND METHODS

The experimental tests were carried out on LDSS 2101, DSS 2304 and LDSS 2404 alloys (supplied by Outokumpu in the form of sheets under solubilized conditions) with the nominal chemical compositions shown in Table 1. In the same table, the PREN values of each alloy are showed. This index, specifically developed to predict the pitting corrosion resistance of stainless steels [19], is considered an easy way to estimate the corrosion resistance of stainless steels from their chemical composition and currently it is also applied to various DSS. [20]. Usually, the PREN is calculated on the basis of the Cr, Mo and N contents of the alloys, by using the formula $PREN = \% Cr + 3.3 \cdot \% Mo + 16 \cdot \% N$ [19]. The PREN values in Table 1 suggest that LDSS 2404 is the most pitting corrosion resistant alloy, due to its high Cr, Mo and N contents, while DSS 2304 and LDSS 2101 are expected to afford almost equivalent resistance to localized corrosion.

Tab. 1 – Nominal chemical composition (wt.%) and PREN values ($PREN = \%Cr + 3.3 \cdot \%Mo + 16 \cdot \%N$ [32]) of the studied lean duplex stainless steels.

DSS	C	Mn	Cr	Ni	Mo	N	Fe	PREN
LDSS 2404	0.02	3.0	24	3.6	1.6	0.27	bal.	34
DSS 2304	0.02	-	23	4.8	0.3	0.10	bal.	26
LDSS 2101	0.03	5.0	21	1.5	0.3	0.22	bal.	26

The electrodes for electrochemical measurements had a surface area of about 0.45 cm². They were cut from sheets of the three alloys. Some of them were thermally aged for 10 min at 650, 750 and 850 °C and then cooled in air. The microstructures, before and after the heat treatments, were documented by optical microscope (OM) observations, after metallographic etching with the Beraha's reagent, and by scanning electron microscope (SEM), using backscattered electrons (BSD). Finally, the elemental microanalysis with EDS microprobe were used to study the composition of the secondary phases formed during the heat treatments.

The pitting corrosion resistance was assessed by CPT (critical pitting temperature) measurements in 0.1 M NaCl solution. Before immersion of the working electrode, the solution was thermostated at 5 °C. Then, in order to increase the reproducibility of the measurements [21], the working electrode was cathodically polarized at -0.9 V_{SCE} for 5 min to reduce the air-formed surface oxide film. Subsequently, the electrode was left at the open circuit potential (E_{OCP}) for 30 minutes and finally it was

anodically polarized to + 0.75 mV_{SCE}, while the electrolyte temperature was increased by 1 °C / min [22]. The CPT was evaluated as that temperature at which the current exceeded 100 μA / cm² and the test was stopped when the current reached values of 250÷300 μA / cm². Each mean CPT value was determined as the average of 3 trials. The pitting corrosion morphology was observed by SEM with BSD electrons.

RESULTS

Microstructure

The microstructures of as-received LDSS 2101, DSS 2304 e LDSS 2404 samples are very similar. As an example, the microstructure of the short transversal section of DSS 2304, obtained with OM after Beraha's reagent etching, is shown in Figure 1. The image evidences the ferritic matrix (darker phase) embedding flattened austenitic islands (lighter phase), produced by sectioning the elongated austenitic grains (rolling direction perpendicular to the shown section).

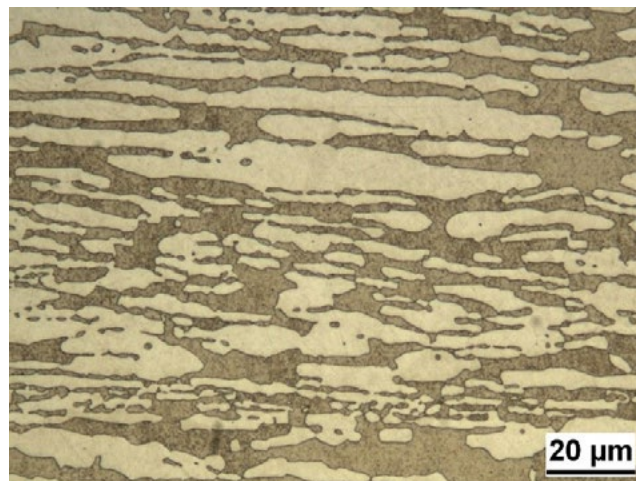


Fig. 1 – OM microstructure of the transversal section (perpendicular to rolling direction) of the as-received DSS 2304 (etching with Beraha's reagent).

As explained in the introduction, the chemical composition of the studied alloys determines the nature of the secondary phases which can grow during the thermal treatments, while the times and temperatures (between 650 and 850 °C) of aging influences their dimension and distribution at the grain boundaries. In general, with a 10 min heat treatment a more significant precipitation is detected by increasing the ageing temperature from 650 to 850 °C [13-16,18], so that the precipitates are better distinguished at the highest temperature. After 10 min at 850 °C, the microstructures of the three studied lean duplex alloys are shown in Figure 2. The precipitates, highlighted by red arrows, are more abundant in LDSS 2101 and 2404 than

in DSS 2304 and are localized at both α/α grain boundaries and α/γ interphases. These precipitates are mainly constituted by chromium nitrides in the case of LDSS 2101 and essentially chromium (and molybdenum) carbides for DSS 2304 [13-16,18]. In the case of LDSS 2404, Figure 3 presents the EDS elemental line analysis through these secondary phases which are evidently constituted by chromium nitrides. Therefore, the different volume fraction of precipitates in the alloy microstructures of Figure 2 is connected to the different N content in the alloys which is lower in 2304, where mainly carbides are formed, and higher in LDSS 2101 and 2404, where abundant nitride precipitation is observed.

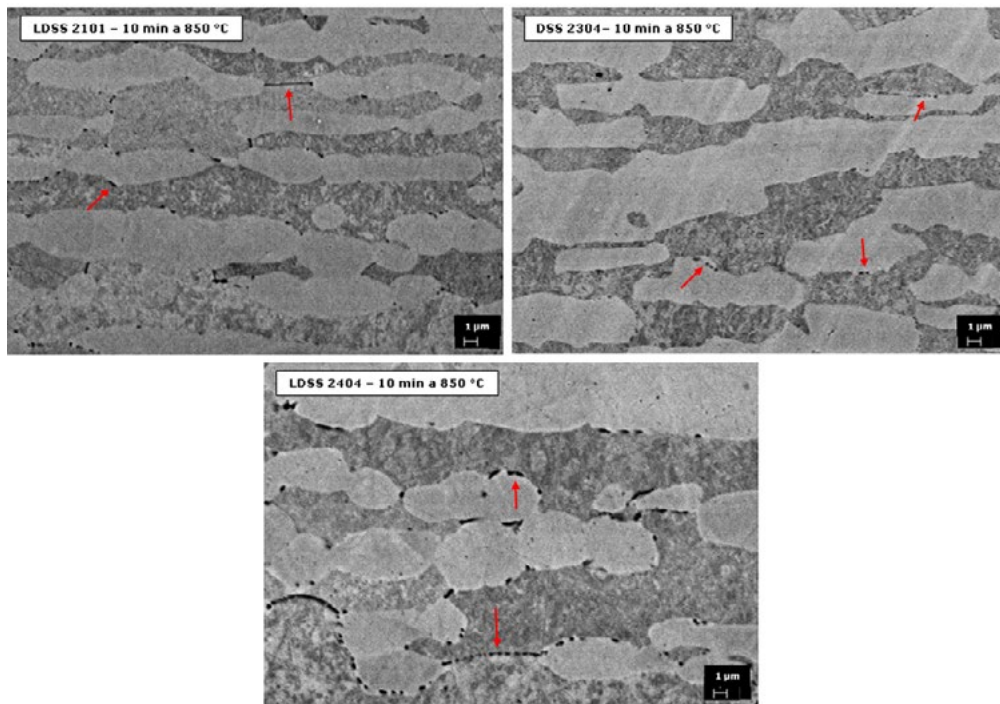


Fig. 2 – SEM-BSD microstructures of the transversal sections of LDSS 2101, DSS 2304 e LDSS 2404, after aging of 10 min at 850 °C.

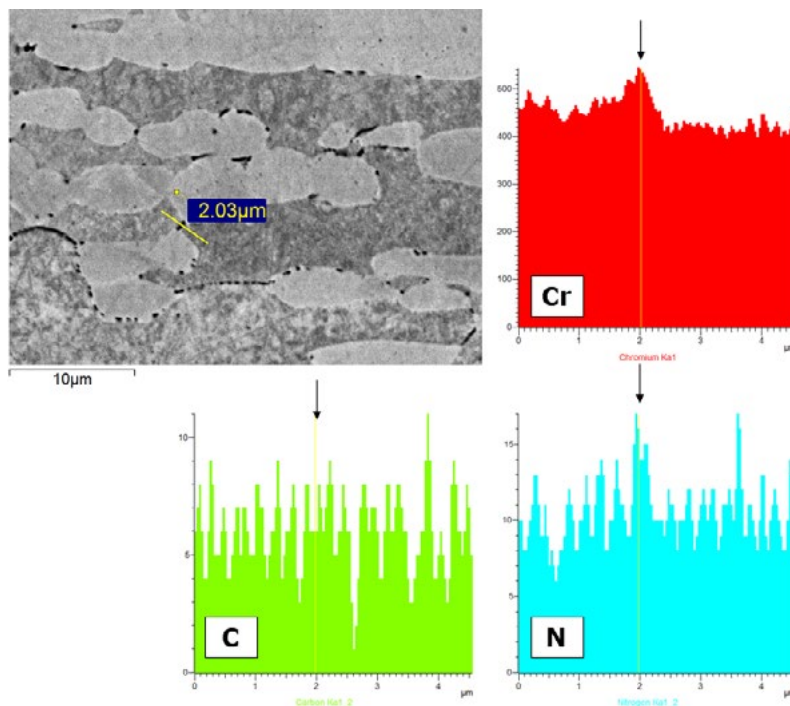


Fig. 3 – SEM-BSD microstructure of the transversal section of LDSS 2404 and EDS profile-line analysis of chromium, carbon and nitrogen.

CPT results

Figure 4 shows the current density/temperature curves recorded on as-received and 850 °C aged LDSS 2101, DSS 2304 and LDSS 2404 electrodes, during polarization at $+0.75 V_{SCE}$ in 0.1

M NaCl solution, while the histogram comparing all the average CPT values obtained from the current density/temperature curves, is reported in Figure 5.

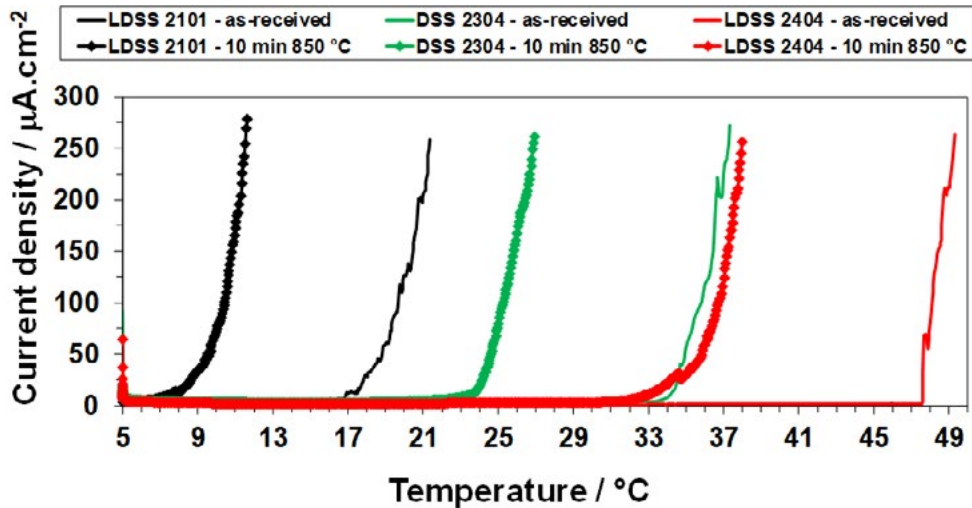


Fig. 4 – Current density vs. temperature curves obtained in 0.1 M NaCl solution on LDSS 2101, DSS 2304 and LDSS 2404 both as-received and aged 10 min at 850 °C.

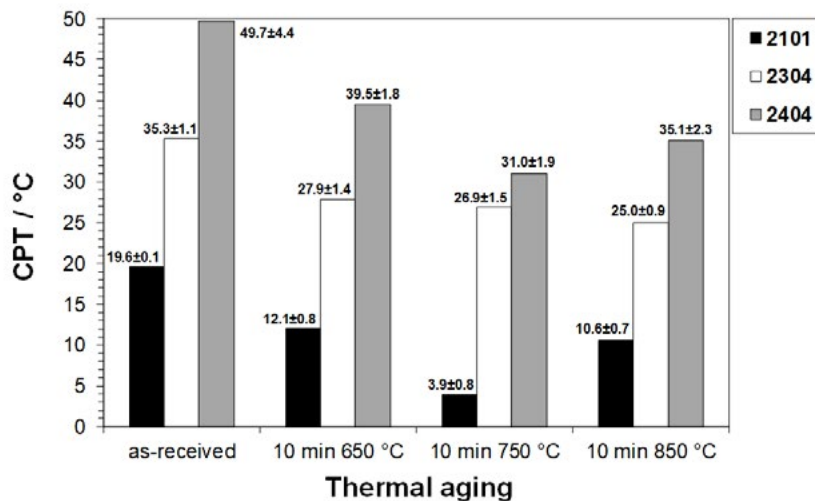


Fig. 5 – Average CPT values and standard deviations determined in 0.1 M NaCl solution for LDSS 210, DSS 2304 and LDSS 2404, before and after thermal aging for 10 min at 650, 750 and 850 °C.

Concerning the as-received alloys, LDSS 2404 presents the highest CPT value, i.e. for this grade a higher solution temperature is necessary to induce pitting corrosion at an applied potential of $+0.75 V_{SCE}$. This suggests, in agreement with the high alloy PREN value (Table 1), that LDSS 2404 has a higher resistance to pitting corrosion in comparison to 2101 and 2304 grades. However, even if the PREN values of DSS 2304 and

LDSS 2101 are equivalent (Table 1), the average CPT of LDSS 2101 is significantly lower (of about 15 °C) than that of DSS 2304. This result is in agreement with SCC susceptibility data of these as received alloys [17] and is likely linked to the significant Mn content (5 wt.%) in LDSS 2101, which negatively affects the resistance to pitting corrosion of stainless steels, according to some authors [23,24]. Therefore, an alternative

PREN formula has been proposed including the detrimental effect of Mn on localized corrosion resistance. The modified PREN formula ($PREN_{Mn} = \%Cr + 3,3\%Mo + 30\%N - 1\%Mn$) correctly evidences that LDSS 2101 ($PREN_{Mn} = 24$) is less resistant to pitting corrosion than DSS 2304 ($PREN_{Mn} = 27$) and much less resistant than LDSS 2404 ($PREN_{Mn} = 34$). In the latter alloy, the negative effect of the high Mn content (3% by weight) is counterbalanced by the higher content of Cr and especially Mo (1.6% by weight), which is particularly useful for increasing the pitting corrosion resistance of stainless steels [24].

After the aging at 650 °C, a decrease in CPT values of about 8-10 °C was observed for all three alloys. By increasing the treatment temperature to 750 °C, a further worsening of the localized corrosion resistance (CPT lowered of about 8 °C) was detected for LDSS 2101 and LDSS 2404, whereas the average CPT of DSS 2304 remained fairly constant with respect to that obtained after aging at 650 °C. This effect is likely related to the low nitrogen content in this alloy which limits the volume of precipitates during the thermal treatments (Figure 2), so allowing to reduce the phenomena of passivating element depletion at the grain boundaries.

After the thermal treatment at the highest temperature (850 °C), LDSS 2101 and LDSS 2404 alloys show an improvement in pitting corrosion resistance, with CPT values increased by about 6 °C compared to those obtained after ageing at 750 °C. This effect is most likely due to the rediffusion of chromium and molybdenum in impoverished areas, linked to the higher diffusion rate of these atoms at the higher temperature. On the other hand, DSS 2304 aged at 850 °C presents a CPT value quite comparable with those obtained at 650 and 750 °C. In this alloy, a partial recovery of the corrosion resistance at 850 °C was only detected after longer treatment times (60 min) [18], suggesting that in DSS 2304 Cr and Mo rediffusion are likely characterized by slower diffusion kinetics.

As far as the pit morphologies are concerned, Figure 6 collects the BSD-SEM micrographs obtained on the low-N DSS 2304 (Figure 6a,c) and on one of the high-N alloys (LDSS 2404, Figure 5b,d) at the end of the CPT tests (after reaching a more or less constant maximum current of 250-300 $\mu A / cm^2$). Each Figure exhibits the pit morphologies developed on the alloys under both as-received and 750 °C aged conditions. The pitting morphology of LDSS 2101 is quite similar to that on LDSS 2404. The as-received DSS 2304 (Figure 6a) shows a large pit with no evidence of preferential propagation into the ferrite phase. Instead, in the as-received LDSS 2404 (Figure 6b) and also in LDSS 2101, the pit seems to propagate mainly in the ferrite phase, which, in these alloys, is less corrosion resistant than the austenite one [25]. This is reasonable, because the high nitrogen content of these alloys, is mostly concentrated in the austenite phase, so determining a marked difference in PREN values of the austenite and ferrite phases. The 650 °C treatment reduced the pitting corrosion resistance of all as-received alloys, meaning that chromium- and molybdenum-depleted areas originated in the proximity of the precipitates during the thermal treatment. However, the pit morphologies (not presented in this paper) remained quite similar to those in the corresponding as-received samples (Figures 6a,b), likely due to a limited secondary phase formation which determined small variations in alloyed element distribution.

The pit morphologies changed after 750 and 850 °C thermal treatments. As examples, Figures 5c and d obtained on DSS 2304 and LDSS 2404, respectively, after 750 °C ageing, show that the pits strictly propagated along α/γ (mainly) and α/α grain boundaries, close to chromium- (and molybdenum-) rich precipitates, suggesting the presence of more continuous precipitates than at 650 °C, inducing passivating element depletion at intergranular regions.

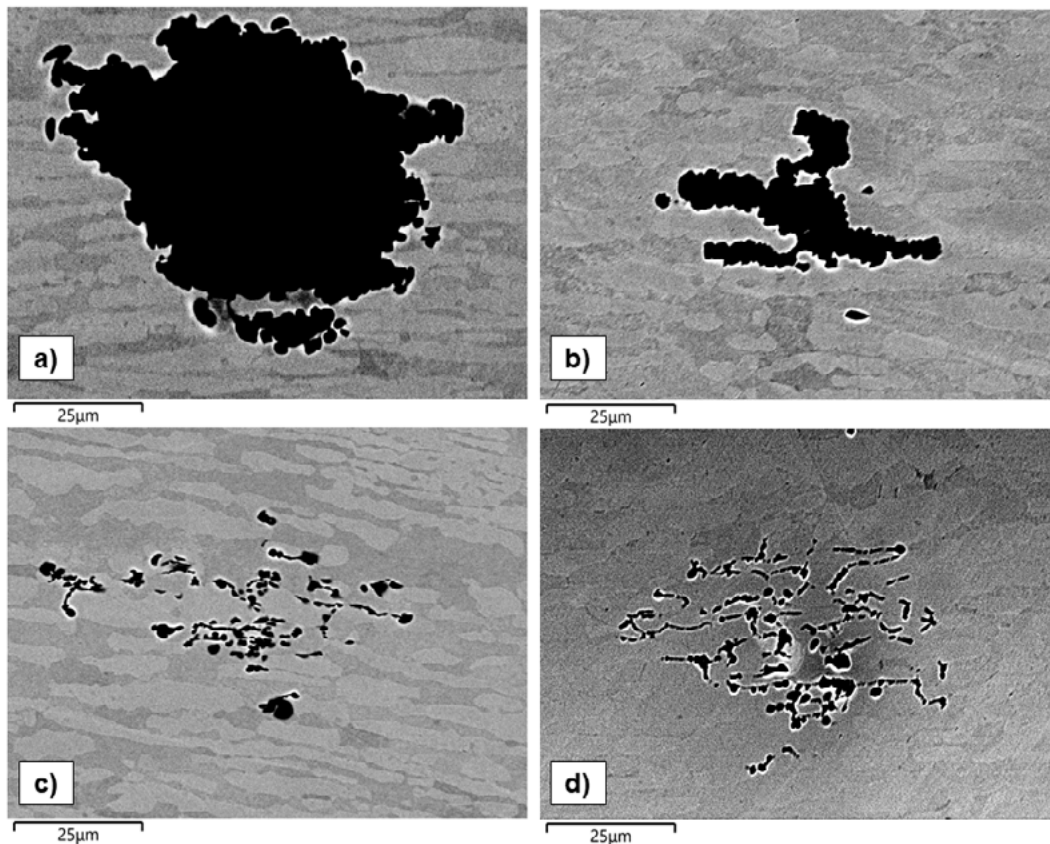


Fig. 6 – SEM-BSD images obtained after CPT tests on the transversal sections of DSS 2304 (left) and LDSS 2404 (right) as-received (a and b) and aged 10 min at 750 (c and d).

CONCLUSIONS

- In the absence and in the presence of thermal treatments, LDSS 2404 alloy exhibits a higher localized corrosion resistance in comparison to DSS 2304 and LDSS 2101 alloys. LDSS 2101 is the most susceptible to localized corrosion due to its significant Mn content.
- Brief thermal treatments (10 min) between 650 and 850 °C determine the formation of secondary phases at α/α and α/γ grain boundaries: mainly chromium nitrides in the case of LDSS 2101 and LDSS 2404 and chromium and molybdenum carbides in the case of DSS 2304. The Cr and Mo depletion in the areas adjacent to these precipitates causes a reduction in pitting cor-

rosion resistance compared to the as-received samples.

- By increasing the treatment temperature from 650 to 750 and then to 850 °C, LDSS 2101 and LDSS 2404 show an initial increase and then a decrease in the susceptibility to pitting corrosion. Instead, the same heat treatments determine a worsening of DSS 2304 pitting resistance which is more or less independent of the temperature in the 650-850 °C range.
- On as received LDSS 2101 and 2404, pits mainly propagate in the ferrite phase, while on DSS 2304 they propagate in both ferrite and austenite phases. This pit morphology changes after heat treatments at 750 and 850 °C and becomes essentially intergranular.

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