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Investigation on the Corrosion Behavior of Lean Duplex Stainless Steel 2404 after Aging within the 650–850 °C Temperature Range

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Abstract: This paper reports the effects of thermal aging between 650 and 850 °C on the localized corrosion behavior of lean duplex stainless steel (LDSS 2404). Critical pitting temperature (CPT) and double loop electrochemical potentiokinetic reactivation (DL-EPR) tests were performed. The localization of pitting attack and intergranular corrosion (IGC) attack after DL-EPR was investigated by optical (OM) and scanning electron microscopy (SEM) and by focused ion beam (FIB) coupled to SEM. Thermal aging caused the precipitation of mainly chromium nitrides at grain boundaries. Aging at 650 °C or short aging times (5 min) at 750 °C caused nitride precipitation mainly at α/α grain boundaries as a result of fast diffusion of chromium in this phase. Aging at 850 °C or aging times from 10 to 60 min at 750 °C also allowed the precipitation at the α/γ interface. Nitrides at γ/γ grain boundaries were observed rarely and only after long aging times (60 min) at 850 °C. Electrochemical tests showed that in as-received samples, pitting attack only affected the α phase. Conversely, in aged samples, pitting and IGC attack were detected close to nitrides in correspondence of α/α and α/γ grain boundaries depending on aging temperatures and times.

Keywords: duplex stainless steel; pitting corrosion; intergranular corrosion; CPT; DL-EPR; FIB-SEM technique

1. Introduction

Lean duplex stainless steels (LDSSs) are ferritic/austenitic steels characterized by a low nickel content, which makes them a cost-effective alternative to ordinary stainless steels (SSs) like SAE 304 and 316 [1]. LDSS 2404 is the most recent (year 2010) lean duplex developed by Outokumpu Company. This alloy, because of its higher Cr, Mo, and N concentration in comparison to the previously marketed lean duplex grades (UNS S32101 and UNS S32304), is expected to show a higher localized corrosion resistance [2,3]. Moreover, its mechanical properties and its pitting resistance equivalent number (PRE_N) are very close to that of the DSS 2205 duplex grade, which is successfully employed in several critical environments such as chemical, oil and gas, pulp and paper industries, desalination plants, and civil construction [1,4,5]. Thus, LDSS 2404 can be a good candidate for the same field of application as the DSS 2205, but more cost-effective.

Mechanical and corrosion properties in duplex stainless steels (DSSs) closely depend on microstructural characteristics including α/γ phase ratio and secondary phase formation during production or welding operations. In particular, in previous works [6–11], we found that short-term thermal aging between 650 and 850 °C negatively affected both localized and stress corrosion cracking (SCC) resistance of LDSS 2101 and DSS 2304. In 2101 grade, because of its high N alloyed-content

(0.22 wt.%), thermal aging from 5 to 30 min in the 650–850 °C range mainly induced chromium nitride formation at grain boundaries. Instead, in DSS 2304, which is characterized by a lower N concentration (0.1 wt.%), essentially chromium (and molybdenum) carbides formed with aging up to 60 min in the same temperature range. In both alloys, sigma (σ) phase formation was not detected after thermal aging, because of their low Mo concentration (0.3 wt.%), which slowed down the precipitation rate of this deleterious phase [12–14]. Precipitation of chromium compounds in the studied alloys led to formation of chromium-depleted areas adjacent to these secondary phases, which stimulated pitting corrosion initiation, induced sensitization to intergranular corrosion (IGC), and also susceptibility to SCC in chloride environments containing thiosulphate ions ($S_2O_3^{2-}$) [6,8,10]. In particular, the longest thermal aging at 650 and 750 °C resulted most deleterious for the resistance to localized corrosion on both LDSS 2101 and DSS 2304, while generally a recovery of the performances was observed after aging at 850 °C. This effect was due to a rediffusion of chromium from the grain bulk towards the depleted regions at the grain boundaries.

Concerning the newly developed LDSS 2404, only a few research papers [2–4,15–20] deal with its corrosion behavior after thermal aging. In particular, Zhang et al. [2,18] studied the effect of isothermal aging at 700 °C for times ranging from 0.1 to 100 h on the pitting corrosion and IGC behavior of the 2404 grade. They mainly focused on long holding times, during which the σ phase grew significantly, leading to the formation of wide secondary austenite (γ_2) regions, significantly affecting the pitting corrosion and IGC resistance of this alloy. The same authors [15] studied the effect of a brief aging time (15 min) in the 600–950 °C temperature range on the pitting corrosion behavior of LDSS 2404. They determined that lower pitting corrosion resistance occurred at 800 °C, and then recovery was detected at higher tested temperatures.

Starting from the results of previous research studies carried out in our laboratory on LDSS 2101 and DSS 2304 [6–11,21–23], in this work the effects of brief (5, 10, and 60 min) thermal aging between 650 and 850 °C on the pitting and IGC corrosion behaviors of LDSS 2404 were investigated. With this aim, both electrochemical tests and scanning electron microscope (SEM) observations, coupled to energy-dispersive X-ray spectroscopy analyses (SEM-EDS), were performed also with the help of the focused ion beam coupled to SEM imaging (FIB-SEM) technique.

2. Materials and Methods

LDSS 2404 stainless steel was supplied by Outokumpu Company in the annealed condition. The alloy nominal composition (wt.%) is shown in Table 1, where the alloy pitting resistance equivalent number (PRE_N) is also reported.

Table 1. Nominal chemical composition (wt.%) and pitting resistance equivalent number (PRE_N) value of lean duplex stainless steel (LDSS) 2404.

Alloy	C	Mn	Cr	Ni	Mo	N	Fe	PRE_N *
LDSS 2404	0.02	3.0	24	3.6	1.6	0.27	bal.	34

* PRE_N (pitting resistance equivalent number) = % Cr + 3.3% Mo + 16% N.

Specimens with about a 15 mm × 15 mm surface area were cut from a 1.5 mm thick steel sheet. The specimens were thermally aged for 5, 10, and 60 min in air at 650, 750, and 850 °C and then air-cooled. The resulting microstructures were observed using a Zeiss EVO MA15 (Zeiss, Oberkochen, Germany) scanning electron microscope (SEM), coupled to an Oxford Aztec energy dispersive X-ray spectroscopy (EDS) system (Oxford, UK), on the transverse section (perpendicular to rolling direction) of the specimens.

Electrochemical Measurements

The electrodes were obtained by embedding LDSS 2404 samples in epoxy resin. The exposed surface (about 0.25 cm²) was prepared with emery papers down to 2500 grit, polished by a diamond colloidal suspension (from 6 to 1 μ m), rinsed by deionized water, and finally degreased using ethanol.

Critical pitting temperature (CPT) tests were carried out in 0.1 M NaCl solution by employing a potentiostatic polarization method. The solution temperature was held at 5 °C before the working electrode was immersed. First, the electrode was cathodically polarized at $-0.9 V_{SCE}$ (i.e., potential value expressed with reference to SCE, saturated calomel electrode) for 5 min in order to de-oxidize the surface and improve test reproducibility [24]. Then, it was allowed to stabilize at the open circuit potential (E_{OCP}) for 30 min. CPT was determined by raising the electrolyte temperature by 1 °C/min [25] at an applied potential of $+0.75 V_{SCE}$. CPT was defined as the temperature at which the current exceeded 100 μA , and the test was stopped when the current reached values of 250–300 $\mu A\ cm^{-2}$. Each mean CPT value was determined as the average of three trials. Pitting corrosion morphology was observed by Optical Microscope (OM) before and after chemical etching with Beraha's reagent (1000 mL deionized water, 200 mL 37 wt.% HCl, and 0.3–0.6 g $K_2S_2O_5$).

Double loop electrochemical potentiokinetic reactivation (DL-EPR) measurements were conducted in 33 wt.% H_2SO_4 solution, at 20 °C, with controlled addition of HCl (0.3, 0.6, 0.9, and 1.2 wt.%) acting as depassivator [26]. The LDSS samples were cathodically polarized at $-0.6 V_{SCE}$ for 3 min in order to improve reproducibility. After 10 min stabilization under free corrosion conditions, the potential was cycled from E_{OCP} to $+0.3 V_{SCE}$ and then to E_{OCP} again, under a scan rate of 2.5 mV/s. According to the standard [27], the active dissolution in the depleted zones is proportional to the ratio I_r/I_a , where I_r is the peak current in the reverse scan (peak reactivation current) and I_a is the peak current in the anodic scan (peak activation current). The degree of susceptibility (DOS) to intergranular corrosion was estimated by the $(I_r/I_a) \times 100$ percent ratio ($I_r/I_a\%$) [28]. Below an I_r/I_a percent of about 1, the corrosion rate calculated by weight loss is reported to be negligible, while above 1 the change in DOS is strongly reflected in weight loss values [29]. Moreover, if I_r/I_a percent is higher than 5, the samples could fail the Streicher, Strauss, and Huey tests [27].

After the DL-EPR tests, the morphology and the extent of IGC attack was observed with both OM and SEM. Moreover, a morphological characterization of IGC attack propagation inside the alloy was performed by the FIB-SEM technique (FEI STRATA DB 235M, Hillsboro, OR, USA). This dual-beam equipment combined a field emission gun SEM (FEG-SEM) imaging (2 nm resolution) with a focused ion beam (FIB) milling (Ga^+ ions), which allowed investigation of the local corrosion attack and the material microstructure in the exact position of interest. In the FEG-SEM chamber, each sample was tilted at 52°, and a preliminary in situ platinum deposition was performed in order to protect the area of interest during ion milling.

3. Results

3.1. Microstructure

Figure 1 presents the microstructure of the transverse section of as-received LDSS 2404. The micrograph (obtained by OM after etching with Beraha's reagent) showed elongated austenitic (γ) grains (lighter phase) in the ferritic (α) matrix (darker phase).

Figure 2 shows some LDSS 2404 microstructures obtained with SEM with backscattered electrons (BSE) after different thermal aging. A short aging at 650 °C did not produce relevant microstructural modifications (images not showed), while after 60 min at 650 °C (Figure 2a) black particles along α/α (quite voluminous and continuous, indicated by blue arrows) and α/γ (very fine, indicated by red arrows) grain boundaries could be detected. After 5 min of aging at 750 °C, the precipitates were already evident at α/α grain boundaries (Figure 2b), and by prolonging the aging time to 10 min (Figure 2c) they became detectable also at α/γ interface, even if they remained very fine. Then, with aging of 60 min at 750 °C (Figure 2d) the black particles became more voluminous and discontinuous at both α/α and α/γ grain boundaries. Moreover, growth of the sigma (σ) phase was detected, as a new brighter intermetallic phase was observed at the α/γ interface. The average results of SEM-EDS semi-quantitative analyses obtained on this phase after the heat treatment of 60 min at 750 °C are reported in Table 2. Small precipitates of σ phase with the same composition were also observed after

60 min treatments at 850 °C. This composition was in good agreement with those reported in the literature [17].

Figure 1. Optical microscopy (OM) microstructure of the transverse section (perpendicular to rolling direction) of the as-received LDSS 2404 (etching with Beraha's reagent).

Figure 2. SEM (at backscattered electrons—BSE) micrographs of LDSS 2404 aged for: 60 min at 650 °C (a), 5 min (b), 10 min (c) and 60 min (d) at 750 °C, and 5 min (e) and 60 min (f) at 850 °C.

Table 2. Average scanning electron microscope energy-dispersive X-ray spectroscopy (SEM-EDS) semi-quantitative analysis in the bright phase particles detected in samples heat treated at 750 °C for 60 min (Figure 2d). As a comparison, the average α and γ phase compositions in the same sample are also reported.

wt. %	Si	Cr	Mn	Ni	Cu	Mo	Fe
σ	0.67 ± 0.05	29.50 ± 0.19	2.77 ± 0.13	2.23 ± 0.13	0.08 ± 0.12	3.72 ± 0.18	bal.
γ	0.35 ± 0.03	23.92 ± 0.27	3.05 ± 0.25	4.06 ± 0.22	0.51 ± 0.07	1.34 ± 0.01	bal.
α	0.42 ± 0.03	25.47 ± 0.12	2.77 ± 0.02	2.94 ± 0.19	0.40 ± 0.03	1.81 ± 0.07	bal.

C, N, V not detectable.

At 850 °C, formation of precipitates at both α/α and α/γ grain boundaries was already significant after 5 min of aging (Figure 2e). Then, by prolonging the holding time to 60 min, they grew in volume and became less continuous. Moreover, at this long aging time, rather continuous black particles also became detectable at γ/γ grain boundaries (indicated by green arrows in Figure 2f), and small amounts of σ phase were detected (not shown). Similarly to what was observed in another high-nitrogen LDSS alloy [6], all line profile analyses performed on the precipitated particles at the α/γ interface and at α/α and γ/γ grain boundaries evidenced the presence of chromium and nitrogen peaks with very small amounts of molybdenum. A carbon peak was usually quite small or absent (Figure 3). This pointed out that the performed thermal treatments led essentially to the precipitation of chromium nitrides [15].

Figure 3. SEM-BSE microstructure of the transverse section of LDSS 2404 and EDS profile-line analysis (white segment through the particles at the α/γ interface) of chromium, nitrogen, molybdenum, and carbon.

These results indicated that the localization and morphology of precipitated nitrides depended on the diffusion rates of chromium (and molybdenum) and nitrogen in α and γ . Concerning the diffusivity of chromium, Williams and Faulkner [30] determined the average chromium diffusion data for chromium concentrations in steels in the range 14 to 28 at.% for both a ferritic stainless steel (AISI 446) and an austenitic stainless steel (AISI 301) in the temperature range 800–1000 °C. At 850 °C (the highest temperature considered in our study), chromium diffusion coefficients of $9.7 \times 10^{-13} \text{ cm}^2/\text{s}$ in γ and $2.6 \times 10^{-11} \text{ cm}^2/\text{s}$ in α (about 30 times higher than in γ) can be calculated from their data. Willis et al. [31] showed that chromium diffusion coefficients at 550 °C in γ ($D_{\text{Cr-}\gamma} = 2.2 \times 10^{-17} \text{ cm}^2/\text{s}$) were about two orders of magnitude lower than in α ($D_{\text{Cr-}\alpha} = 2.0 \times 10^{-15} \text{ cm}^2/\text{s}$). Also, for diffusion coefficients of nitrogen, differences of two or three orders of magnitude were obtained in γ ($D_{\text{N-}\gamma}$) and α ($D_{\text{N-}\alpha}$) structures dependent on the temperature (e.g., $D_{\text{N-}\gamma}$ varied from 2.7×10^{-10} to $1.3 \times 10^{-8} \text{ cm}^2/\text{s}$ and $D_{\text{N-}\alpha}$ from 2.7×10^{-7} to $1.7 \times 10^{-6} \text{ cm}^2/\text{s}$ in the range from 650 to 850 °C [32]). Due to much faster diffusion in α , a 5 min treatment at 750 °C produced precipitation essentially at α/α grain boundaries, while at longer treatment times (10 and 60 min), precipitation occurred also at α/γ interfaces. After long thermal treatments (60 min) at the highest temperature (850 °C), nitrides were detected also at γ/γ grain boundaries, and diffusion rates in α and γ increased, so favoring the formation of large discontinuous nitride particles.

3.2. Critical Pitting Temperature (CPT) Test

Figure 4 shows the average CPT values, determined in 0.1 M NaCl solution on LDSS 2404 electrodes, after aging at the three tested temperatures for different holding times. Aging at 650 and 750 °C created a reduction of pitting corrosion resistance, in comparison to the as-received sample (CPT value of 49.7 °C), particularly after the longest aging time (60 min). On the contrary, in agreement with previous results on LDSS 2101 and DSS 2304 [7,10], at 850 °C a recovery of pitting resistance in comparison to the corresponding aging at 750 °C was obtained.

Figure 4. Average CPT values and standard deviations determined in 0.1 M NaCl solution on LDSS 2404 electrodes as a function of aging temperatures and at different aging times.

In Figure 5, the micrographs of the as-received LDSS 2404 electrode after CPT test, before and after etching with Beraha's reagent, evidenced that pits developed in the α phase and selectively grew within this phase. α phase was less corrosion-resistant than γ because of its low nitrogen content [33].

Figure 5. Micrograph of as-received LDSS 2404 electrode after critical pitting temperature (CPT) test in 0.1 M NaCl solution before (a) and after etching (b) with Beraha's reagent.

After aging for 10 min at 750 °C (Figure 6) or 60 min at 850 °C (Figure 7), pits started and spread corresponding to Cr-, Mo-, and N-depleted areas around precipitates. In the case of the samples aged 10 min at 750 °C, larger pits started and spread at α/α' grain boundaries (blue arrows in Figure 6) because of the slower growth of precipitates and no passivity impairment at α/γ .

Figure 6. Micrograph of LDSS 2404 electrode aged for 10 min at 750 °C, after CPT test in 0.1 M NaCl solution before (a) and after etching (b) with Beraha's reagent.

Figure 7. Micrograph of LDSS 2404 electrode aged for 60 min at 850 °C, after CPT test in 0.1 M NaCl solution before (a) and after etching (b) with Beraha's reagent.

Instead, 60 min aging at 850 °C preferentially induced a localized attack at the α/γ interface (red arrows in Figure 7), likely because of the relatively fast Cr replenishment at α/α boundaries.

3.3. Double Loop Electrochemical Potentiokinetic Reactivation (DL-EPR) Test

In order to determine susceptibility of alloys to IGC, the optimal concentration of the depassivator (HCl) to be added to the sulphuric acid solution was evaluated. With this aim, preliminary tests were performed on both as-received and all 60 min-aged LDSS 2404, with HCl concentrations of 0.3, 0.6, 0.9, and 1.2 wt.%. In Table 3, the I_r/I_a % values obtained under the different conditions are reported.

Table 3. I_r/I_a % ratios and standard deviations in 33 wt.% H_2SO_4 solution with different HCl concentrations, at 20 °C. Double loop electrochemical potentiokinetic reactivation (DL-EPR) tests performed on LDSS 2404, both as-received and 60 min-aged at 650, 750, and 850 °C.

HCl Concentration (wt.%)	I_r/I_a %			
	As-Received	60 min 650 °C	60 min 750 °C	60 min 850 °C
0.3	0.03 ± 0.003	0.8 ± 0.04	0.06 ± 0.002	0.02 ± 0.003
0.6	0.03 ± 0.002	3.6 ± 0.2	2.2 ± 0.4	0.16 ± 0.04
0.9	0.04 ± 0.003	5.2 ± 0.06	13.0 ± 0.07	1.0 ± 0.04
1.2	0.3 ± 0.02	7.5 ± 0.08	20.6 ± 0.05	4.6 ± 0.03

The HCl concentrations of 0.3 and 0.6 wt.% were not sufficiently high to obtain reliable activation and reactivation peaks (e.g., I_r of the samples heat-treated for 60 min at 650 and 750 °C was around 0.1 mA/cm²), and also I_r/I_a % was not clearly differentiated. With 0.9% and 1.2% HCl concentrations, activation and reactivation peaks became more easily distinguishable (e.g., I_r of the sample heat-treated for 60 min at 750 °C was around 2 mA/cm² or 5 mA/cm² at HCl concentrations of 0.9 or 1.2%, respectively). However, the 1.2% HCl concentration produced an increase in I_r/I_a % of the as-received samples of one order of magnitude in comparison to lower HCl concentrations. This behavior was due to the concomitance of IGC and a significant attack on α and γ phases of both as-received and aged samples [34], which affected all final I_r/I_a % values. Therefore, the 0.9% HCl concentration was selected as the optimal depassivator concentration, which ensured good compromise between a sufficiently aggressive attack and good selectivity.

In Figure 8, the current density vs. potential DL-EPR curves obtained in the selected test solution (33 wt.% H_2SO_4 with 0.9 wt.% HCl solution, at 20 °C) on both as-received and 60 min aged samples are reported. Due to the biphasic microstructure of DSS, two peaks were distinguishable in the anodic scan: the first around $-0.28 V_{SCE}$ was related to the active–passive transition of α , and the second around $-0.2 V_{SCE}$ was related to that of γ . As a result of the properly selected DL-EPR test conditions (i.e., HCl concentration, solution temperature, and scan rate), only one significant reactivation current peak was detected in the reverse scan because of the passive to active transition of only the intergranular regions depleted in chromium and other passivating elements.

As an example, Figure 9 shows the microstructures obtained after DL-EPR tests on an as-received sample and on a sample aged at 650 °C for 60 min, and it clearly evidences IGC attacked only on the thermally aged sample. All DOS values collected under these DL-EPR test conditions are reported in Figure 10. Aging times of 5 and 10 min at 650 °C did not affect resistance to IGC. Instead, a 60 min aging at 650 °C determined a high increase in I_r/I_a % parameter (I_r/I_a % = 5.2%). A treatment at 750 °C for 10 min was sufficient to cause a very high susceptibility to IGC (I_r/I_a % = 4.4%), and by prolonging the treatment till 60 min, more than a double I_r/I_a % (up to 13%) was obtained.

Figure 8. Current density vs. potential curves recorded on as-received and 60 min at 650, 750, and 850 °C aged LDSS 2404 electrodes, by DL-EPR tests in 33 wt.% H_2SO_4 solution, with 0.9 wt.% HCl, at 20 °C.

Figure 9. Optical microscopy (OM) micrographs acquired on LDSS 2404 electrodes as-received (a) or aged 60 min at 650 °C (b), after DL-EPR tests in 33 wt.% H_2SO_4 solution, at 20 °C, with 0.9 wt.% HCl addition.

Figure 10. I_T/I_a % determined for as-received and aged LDSS 2404, by DL-EPR tests in 33 wt.% H_2SO_4 solution, at 20 °C, with 0.9 wt.% HCl addition.

Aging at 750 °C produced the highest sensitization to IGC in LDSS 2404. In contrast, a temperature of 850 °C determined a very low susceptibility to IGC (I_r/I_a % around 1%) at all aging times, in spite of the formation of relatively large precipitates (Figure 2f) [35].

The DL-EPR attack observed by SEM (Figure 11) was localized at both α/α (blue arrows) and α/γ (red arrows) grain boundaries after aging 60 min at 650 (Figure 11a) and 750 °C (Figure 11b), meaning that under these conditions, impoverishment in passivating elements close to chromium nitrides was present at both grain boundaries. After aging 60 min at 850 °C (Figure 11c), DL-EPR reactivation occurred essentially at α/γ interfaces, but in this case the IGC attack appeared shallow despite the formation of large precipitates. The EDS line profile analysis performed across the precipitates grown at the α/γ interface in the sample aged at 750 °C for 60 min (Figure 11b) revealed peaks related to Cr, N, Mo, and C, confirming the formation of chromium nitrides but also chromium and perhaps molybdenum carbides (likely of the $M_{23}C_6$ -type [36]). Moreover, in the sample aged for 60 min at 850 °C, SEM-EDS semi-quantitative analysis on a bright region at the α/γ interface (Spectrum 4 in Figure 11c) confirmed the formation of σ phase.

Figure 11. SEM (at secondary electrons) micrographs on LDSS 2404 electrodes aged 60 min at 650 (a), 750 (b), and 850 °C (c), after DL-EPR tests in 33 wt.% H_2SO_4 solution, at 20 °C, with 0.9 wt.% HCl addition. EDS profile-line analysis (black segment through the particles at the α/γ interface in (b)) related to chromium, nitrogen, molybdenum, and carbon elements.

Figures 12–14 show the FEG-SEM images obtained at 60 min at 650, 750, and 850 °C aged samples, respectively, after DL-EPR test as well as before and after FIB milling. The red rectangle (Figures 12a, 13a and 14a) evidenced the area protected by platinum during ion milling, and the yellow arrow indicated the milling surface (Figures 12b, 13b and 14b). The red arrows in these Figures connected the corresponding corrosion attacks on the sample surfaces and on FIB sections. The images obtained at higher magnifications on the sample aged 60 min at 650 °C showed that the IGC attack at α/α grain boundaries (indicated by the arrow in Figure 12c) was quite rounded and not very deep; conversely, the attack between α/γ phases (indicated by the arrows in Figure 12d) propagated deeply from the surface exposed to DL-EPR solution. This indicated that, although at α/α grain boundaries near chromium nitrides, passivity was locally impaired inducing localized attack, a limited Cr depletion occurred, likely because of sufficiently fast chromium diffusion in the α phase from both sides of the precipitates. Instead, at α/γ sites where one-sided diffusion occurred, the impoverishment in passivating elements was more marked.

Figure 12. Field emission gun (FEG)-SEM images obtained on LDSS 2404 aged 60 min at 650 °C, after DL-EPR test, and before (a) and after (b–d) focused ion beam (FIB) milling.

Figure 13. FEG-SEM images obtained on LDSS 2404 aged 60 min at 750 °C, after DL-EPR test, and before (a) and after (b,c) FIB milling. In (d) SEM-BSE tilted image of intergranular corrosion (IGC) attacks evidenced with the yellow rectangle in (b).

DL-EPR produced a deep large crater at α/γ phase boundaries also on the sample aged at 750 °C for 60 min (indicated by the arrow in Figure 13c). In this case, the attacks at the α/γ interface were also documented by SEM in BSE at high magnification with the sample tilted at 80° (Figure 13d). Figure 13d clearly shows that, after the DL-EPR test, the γ phase remained in relief and was less attacked in comparison to the α . In the area evidenced by a blue rectangle on the left, a limited localized attack was detected at both sides of the γ (filled by platinum on the left side of the γ phase). On the right side of the phase, the figure clearly shows that the localized attack initiated in γ , confirming the negative influence of low chromium diffusion rates in this phase. In the area evidenced by the green rectangle, the IGC attack propagated in-depth around chromium-rich precipitates, growing through both α and γ regions.

In the samples aged for 60 min at 850 °C (Figure 14c), all localized α/γ IGC attacks were rounded and shallow, suggesting that an almost complete recovery of chromium levels occurred under this thermal aging condition.

Figure 14. FEG-SEM images obtained on LDSS 2404 aged 60 min at 850 °C, after DL-EPR test, and before (a) and after (b,c) FIB milling.

4. Conclusions

1. The brief thermal aging performed in the 650–850 °C range on LDSS 2404 determined the formation of mainly chromium nitrides at grain boundaries.
2. Localization and distribution morphologies of these precipitates depended on thermal aging conditions. Aging at 650 °C or short aging times (5 min) at 750 °C caused nitride precipitation mainly at α/α grain boundaries because of fast diffusion in this phase. Aging at 850 °C or aging times from 10 to 60 min at 750 °C also allowed precipitation at the α/γ interface. Nitrides at γ/γ grain boundaries were observed rarely and only after long aging times (60 min) at 850 °C.
3. At 650 and 750 °C, the susceptibility to pitting corrosion of LDSS 2404 increased by prolonging the aging time and was higher at 750 °C. Instead, at 850 °C a partial recovery of pitting resistance was detected. The effects of thermal treatments on DOS to IGC were in good agreement.
4. Pitting corrosion attack and IGC attack after DL-EPR were mainly localized at α/α grain boundaries (particularly at low aging temperatures and short aging times) or at α/γ interfaces (mainly at high aging temperatures and long aging times).

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