Influence of thermal aging on SCC susceptibility of DSS 2304 in the presence of chlorides and thiosulphates

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In this paper, the effect of brief aging within the 650–850 °C temperature range on the resistance of DSS 2304 to stress corrosion cracking (SCC) was discussed. Slow strain rate tests (SSRT) were performed on both as-received and heat treated DSS 2304 in the standard NACE TM-0177 solution at pH 2.7 and 25 °C in the presence of 10^{-3} M $S_2O_3^{2-}$. High SCC susceptibility was detected with aging at 650 °C for 60 min, at 750 °C for 10 and 60 min and at 850 °C for 10 min, in good agreement with preceding results obtained for pitting resistance and degree of sensitization to intergranular corrosion. The SCC susceptibility is likely connected to chromium concentration levels in the depleted zones, which depend on the adopted aging times and temperatures.

KEYWORDS: DUPLEX STAINLESS STEELS, STRESS CORROSION CRACKING, SLOW STRAIN RATE TESTS, THIOSULPHATE

INTRODUCTION

Since some years the corrosion behaviour of lean duplex stainless steels (LDSS) is investigated at the "A. Daccò" Corrosion and Metallurgy Study Centre and the effects of brief aging treatments between 650 °C and 850 °C on pitting resistance and on the degree of susceptibility (DOS) to intergranular corrosion (IGC) were investigated on LDSS 2101, DSS 2304 and LDSS 2404 [1-3]. Aging of DSS 2304 between 650 and 850 °C, from 5 to 60 min, negatively influenced its pitting corrosion and IGC resistance. The critical pitting temperature (CPT) obtained in 0.1 M NaCl drastically decreased after aging at 650 °C for 60 min, but heat treatments of 5 and 10 min did not produce any effect. The sample treated at 750 °C for 10 min showed a CPT value 10 °C lower than that of the as-received one. The CPT value further decreased by extending the aging time to 60 min at the same temperature. At 850 °C, CPT decreased with only 5 min aging and did not show significant variations when the treatment time was increased up to 60 min. DOS to IGC measurements performed with Double Loop Electrochemical Potentiokinetic Reactivation (DL-EPR) method in 33% H_2SO_4 with 0.45% HCl at 20 °C, highlighted that DSS 2304 aged 60 min at 650 °C was the most susceptible to IGC, followed by that aged 10 and 60 min at 650 °C. Conversely, after aging at 850 °C from 5 to 60 min, DSS 2304 evidenced DOS values slightly lower than 1, which indicated a very low susceptibility to IGC [2]. These findings were related to the chromium impoverishment in regions adjacent to chromium carbides, produced after heat treatments at 650 and 750 °C. Instead, the lower influence of heat treatments at 850 °C on the alloy corrosion resistance was ascribed to partial chromium replenishment due to quick chromium diffusion.

The stress corrosion cracking (SCC) susceptibility of LDSS 2101 was also studied, both before and after heat treatments between 650 and 850 °C in standard NACE TM-0177 solution in the presence of thiosulphate ions ($S_2O_3^{2-}$) [4-6]. In fact, as proposed by Tsujikawa et al. [7], the use of $S_2O_3^{2-}$ in replacement of H_2S gas can minimize the health hazards in laboratory tests and therefore can reduce the costs to ensure safe working conditions [8]. As-received LDSS 2101 resulted susceptible to SCC in standard NACE TM-0177 solution in the presence of $S_2O_3^{2-}$ already at concentration of 10^{-4} M, at pH 2.7 and 25 °C [4]. SCC susceptibility significantly increased by increasing $S_2O_3^{2-}$ content. After brief heat treatments between 650 and 850 °C, the resistance to SCC of LDSS 2101 got worse at increasing aging temperature and time [5,6].

In this work, the SCC behaviour of heat treated DSS 2304 was studied in the standard NACE TM-0177 solution at pH 2.7 and 25 °C in the presence of $S_2O_3^{2-}$ at 10^{-3} M. These tests aim at filling a knowledge gap because very few data are reported in the literature about the SCC behaviour of

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lean duplex in environments containing hydrogen sulphide [9].

EXPERIMENTAL PART

The tests were performed on DSS 2304 stainless steels (supplied by Outokumpu S.p.A. under annealed conditions), having the nominal chemical compositions (wt. %) reported in Tab. 1.

Tab. 1 – Nominal chemical composition (wt.%) of DSS 2304.

DSS	C	Mn	Cr	Ni	Mo	N	Fe
DSS 2304	0.02	-	23	4.8	0.3	0.10	bal.

Tensile samples with an overall length of 23 cm and a gauge portion of 20x5x1.5 mm were machined from a 1.5 mm thick steel sheet. The samples were aged for 10 and 60 min at 650, 750 °C and 850 °C and then air cooled. The resulting microstructures were observed by Zeiss EVO MA15 scanning electron microscope (SEM) in back-scattered electron (BSE), in order to reveal the presence of secondary phases.

The susceptibility to SCC was evaluated by SSRT, with a strain rate of $1x10^{-6}$ s^{-1}. After thermal aging, the samples were ground parallel to the stress direction down to 800 grit emery papers and screened by a two-component epoxy varnish, so leaving only the gauge portion exposed to the solution. SSRT were performed by inserting the sample in an electrochemical cell, which was filled by deaerated and thermostated 5% NaCl and 0.5% CH_3COOH solution (the basic standard solution NACE TM-0177 [10], without saturated H_2S gas) in the presence of 10^{-3} M $Na_2S_2O_3$, at 25 °C and pH 2.7. During each test, the stress - strain curve was recorded and the corrosion potential values (E_{COR}, versus Saturated Calomel Electrode (SCE)) were measured. Reference SSRT in air at 25 °C were also carried out. Each test was performed in triplicate.

The SCC susceptibility was evaluated by the ratio (R) between the percentage strain to fracture (ε_f%) in the test solution and that in air at 25 °C. R values equal to or higher than 0.8 were considered an index of immunity to SCC [11]. At the end of the tests, the gauge length section of the samples were observed with optical stereomicroscope and side surfaces were examined by OM, after polishing and etching with Beraha's reagent, with the purpose to analyse crack initiation and morphology.

RESULTS

Fig. 1 shows the microstructures of the short transverse sections of DSS 2304 sheets under both as-received conditions (Fig. 1-a) and aged for 60 min at 850 °C (Fig. 1-b). Elongated austenitic grains (lighter phase) were distinguishable in the ferritic matrix (darker phase). Due to the low molybdenum content in this alloy, no χ and σ secondary phases were detected after heat treatments [12]. Very small black precipitates were observed at the α/γ grain boundaries in the sample aged for 60 min at 650 °C and on all samples aged at 750 °C or 850 °C. At these higher temperatures, the particles grew up with time. The SEM-EDS examination by line-profile analysis on these larger particles indicated they were based on chromium carbides. Other authors reported the precipitation of chromium nitrides and carbides in DSS 2304 aged at 750 and 850 °C for about 45 min [13].

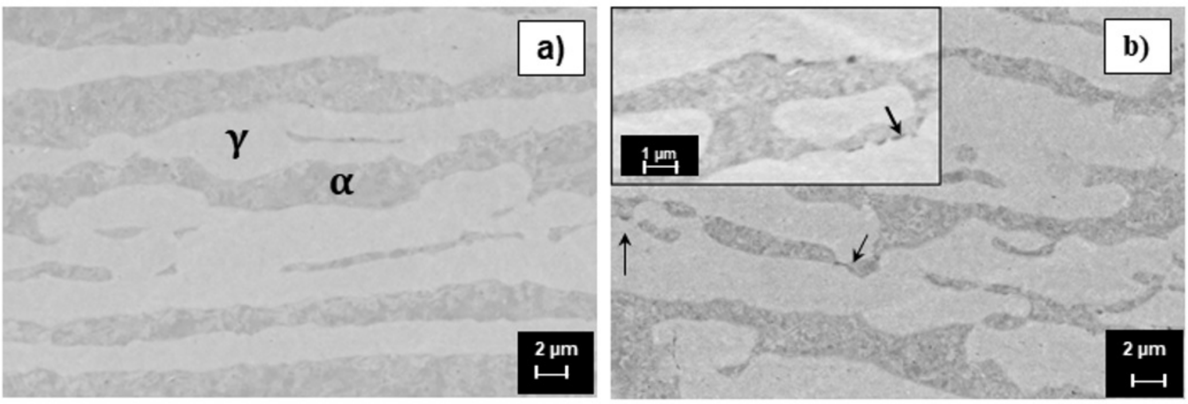

Fig. 1 - BSE-SEM micrographs of DSS 2304 cross sections as-received (a) and aged 60 min at 850 °C (b).

The stress - strain curves obtained with SSRT in air at 25°C on as-received and heat treated DSS 2304 (here not reported) evidenced that all aging treatments at 650 °C and the short ones at 750 and 850 °C did not modify the mechanical behaviour of the material. Instead, the long treatments at 750 and 850 °C determined a moderate increase in steel ductility (of about 10 %). This slight modification of the mechanical behaviour was induced by the subtraction of interstitial carbon atoms from solid solution, after precipitation of relatively large chromium carbide particles at the grain boundaries, after 60 min aging at the two higher investigated temperatures [6].

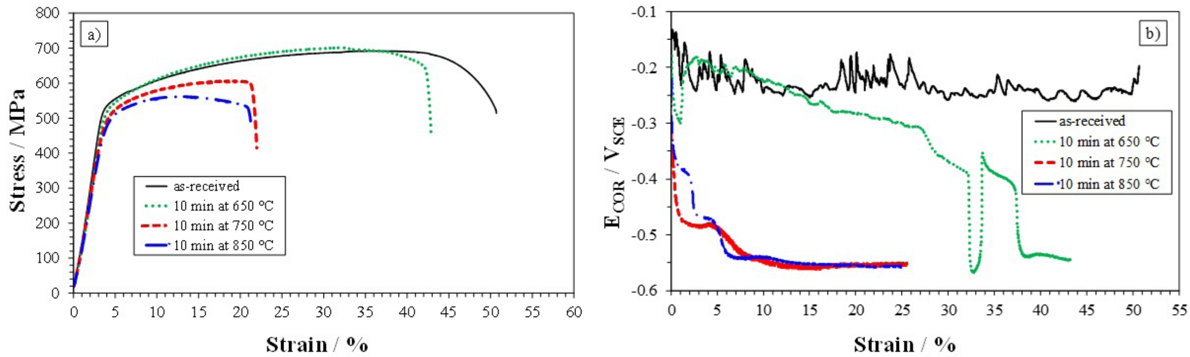

Fig. 2 - Stress – strain (a) and E_{COR} - strain (b) curves obtained with SSRT on DSS 2304, both as-received and after aging for 10 min within 650-850 °C range, in NACE TM-0177 in the presence of 10^{-3} M $S_2O_3^{2-}$.

Fig. 2-a and 2-b collect the stress - strain and E_{COR} – strain curves, obtained during SSRT performed in standard NACE TM-0177 solution in the presence of 10^{-3} M $S_2O_3^{2-}$, on both as-received and 10 min aged samples (T= 650, 750 and 850 °C).

They show that ε_f % of as-received sample was about 51 % (Fig. 2-a), almost equivalent to that obtained in air (52 %), while the heat treatments induced much smaller ε_f %. In fact, decreasing values of about 42, 22 and 21 % were obtained at progressively increasing aging temperature. During SSRT, E_{COR} values (Fig. 2-b) of the as-received sample remained around -0.2 V_{SCE}, that is in the passive potential range. The E_{COR} values of the sample aged 10 min at 650 °C had initially the same values recorded for the as-received sample, then, after a strain of about 15 %, slowly decreased reaching values of about -0.55 V_{SCE}, that are typical of active corrosion conditions, at the end of the test. Instead, the E_{COR} values of DSS 2304 aged for 10 min at 750 and 850 °C rapidly decreased already during elastic deformation and, after a plastic strain of only 5 %, reached about -0.55 V_{SCE}. At these quite negative E_{COR} values the $S_2O_3^{2-}$ conversion to reduced S-containing species, such as H_2S, is highly favored [14].

Fig. 3-a and 3-b collect the stress - strain and E_{COR} – strain curves obtained during SSRT performed in NACE solution containing 10^{-3} M $S_2O_3^{2-}$ on both as-received and 60 min aged samples (T = 650, 750 and 850 °C).

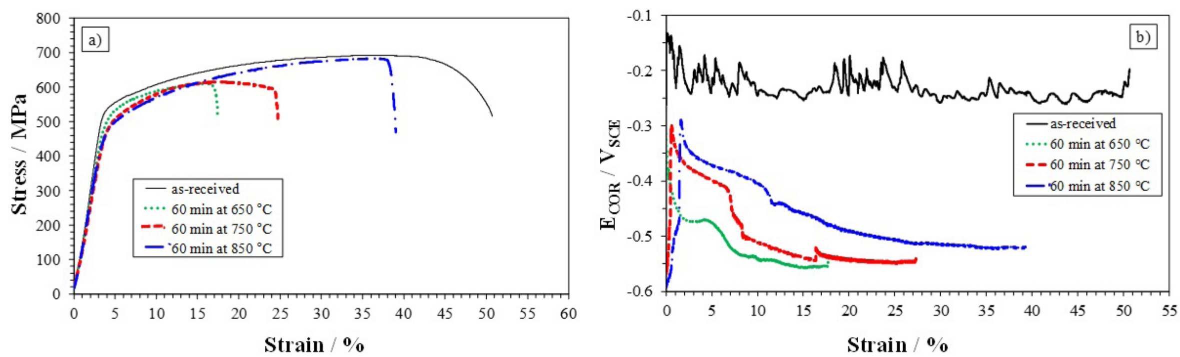

Fig. 3 - Stress – strain (a) and E_{COR} - strain (b) curves obtained with SSRT on DSS 2304, both as-received and after aging for 60 min within 650-850 °C range, in NACE TM-0177 in the presence of 10^{-3} M $S_2O_3^{2-}$.

Also in this case, the ductility of heat treated samples was much lower than that afforded by the as-received sample, but ε_f % increased by increasing heat treatment temperature. In fact, values of 18 %, 25 % and 39 % were obtained after long aging treatments at 650, 750 and 850 °C, respectively. Thus, 60 min aging at 650 °C resulted the most SCC susceptible heat treatment in $S_2O_3^{2-}$ solution. This result is also supported by E_{COR} values (Fig. 3-b), which shifted very rapidly to -0.55 V_{SCE} in the case of the sample aged 60 min at 650 °C, while the decay was slower in the case of samples heat treated at 750 and particularly at 850 °C, for the same time.

At the end of SSRT, all samples aged for 10 and 60 min between 650 and 850 °C showed a brittle type fracture and badly corroded surfaces with many secondary cracks as those observable in the macrograph of Fig. 4-a. In contrast, as-received samples evidenced a ductile type fracture with necking both in air and in NACE solution with $S_2O_3^{2-}$. The micrographs of the longitudinal sections of samples failed by SCC evidenced that in all cases, small pits were present (Fig. 4-b), clearly operating as crack initiators [15]. Then the cracks propagated in the ferrite phase and/or following ferrite/austenite grain boundaries (Figure 4b).

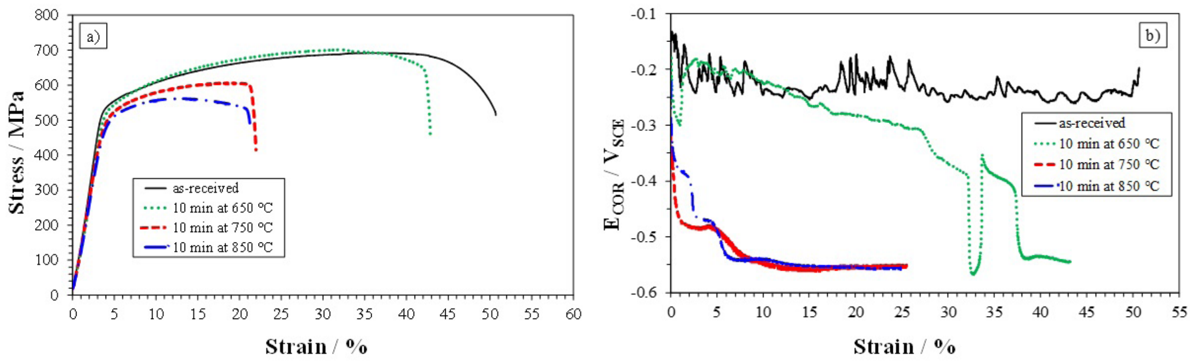

Fig. 4 - Macrograph (a) and micrograph (b) of DSS 2304 aged for 10 min at 850 °C after SSRT in NACE solution containing 10^{-3} M $S_2O_3^{2-}$ (in b) long transverse section, parallel to load direction).

Tab. 2 collects R values obtained from SSRT results, for both as-received and heat treated DSS 2304. The influence of heat treatment on SCC susceptibility in NACE solution containing $S_2O_3^{2-}$ is more or less the same after short aging at 750 and 850 °C (R = 0.42 and 0.41, respectively), but it is significantly less marked after 10 min at 650 °C (R = 0.83). By extending the aging time, an increase in SCC susceptibility was observed only at 650 °C (R = 0.36), while the susceptibility decreased at both 750 (R = 0.45) and particularly at 850 °C (R = 0.69).

Tab. 2 – R values obtained from SSRT in NACE TM-0177 in the presence of $S_2O_3^{2-}$ at 10^{-3} M on DSS 2304, both as-received and heat treated for 10 and 60 min between 650 and 850 °C.

Heat treatment conditions	As-received	650 °C		750 °C		850 °C	
		10 min	*60 min*	*10 min*	*60 min*	*10 min*	*60 min*
R	0.98	0.83	0.36	0.42	0.45	0.41	0.69

DISCUSSION

SCC susceptibility results are quite in agreement with previous findings concerning the measurements of CPT values and DOS to IGC, obtained on DSS 2304 samples under the same conditions here investigated [2]. The high SCC susceptibility and the low resistance to pitting and IGC induced by heat treatments with specific time-temperature combinations (60 min at 650 °C, 10 and 60 min at 750 °C and 10 min at 850 °C) are likely related to the formation of dechromized areas in the proximity of chromium carbide particles, precipitated during heat treatments. In these regions, pits tend to form, acting as crack initiators. Afterwards, cracks propagation occurs preferably in ferrite grains and along ferrite/austenite grain boundaries [16].

The most severe heat treatment consists in 60 min aging at 650 °C. It significantly reduces the SCC resistance of DSS, likely due to the achievement of very low chromium levels in narrow areas. As a consequence, easy surface activation occurs, as proved by the quite negative E_{COR} values (-0.55 V_{SCE}) reached very quickly during the elastic deformation step

in the tensile test (Fig. 3-b). At these low potential values, $S_2O_3^{2-}$ reduction to H_2S is possible and easily occurs, suggesting that a contribution of hydrogen penetration stimulated by sulphide species to SCC cannot be excluded [7,8].
During the 60 min heat treatment at 850 °C, there is time enough for chromium replenishment in depleted regions, so reducing the alloy SCC susceptibility. Under this aging condition, the sample undergoes a slower activation.

CONCLUSIONS

Heat treatments of 10 and 60 min in the temperature range between 650 and 850 °C increased SCC susceptibility of DSS 2304 in NACE TM-0177 solution containing 10^{-3} M $S_2O_3^{2-}$.
The SCC susceptibility was likely connected to chromium depletion in the vicinity of chromium carbide precipitates, whose extent depended on aging times and temperatures.
An aging of 60 min at 650 °C significantly reduced SCC resistance, while a recovery was observed by increasing heat treatment temperature.

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