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Influence of centerline intermetallic stringers on pitting corrosion resistance of superduplex stainless steel

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ABSTRACT

Superduplex stainless steel UNS S32750 / EN 1.4410 is commonly used in marine environment, petrochemical, oil and gas, chemical and desalination industries, requiring materials with superior corrosion and mechanical properties. Very few residual intermetallic particles may be present under the form of centerline stringers whose effects on corrosion properties are not well documented. A previous study demonstrated the negligible influence of the intermetallic phases in centerline stringers (typically < 0.1% over thickness) on the hydrogen embrittlement susceptibility of superduplex stainless steel [1]. The present study aims at highlighting the impact of centerline intermetallic stringers on pitting corrosion resistance.

Samples containing σ -phase only within segregated centerline area have been intentionally produced in the laboratory. After detailed microstructural characterization, ASTM G48 Method A tests and long term immersion tests have been conducted to demonstrate that very few intermetallic phases within segregated bands don't lead to a loss of pitting resistance. Then macroscopic and microscopic electrochemical investigations were performed on samples with centerline intermetallic stringers to highlight the weak points of microstructure regarding corrosion properties.

Key words: DX2507, UNS S32750, 1.4410, intermetallic phases, centerline stringers, pitting corrosion resistance

INTRODUCTION

Superduplex UNS S32750 is one of the most corrosion resistant grades within the duplex family, making it a competitive alternative material to nickel-based alloys, such as 825. Due to their high chromium and molybdenum content, superduplex stainless steel (SDSS) grades are more susceptible to intermetallic phase precipitation, such as σ -phase, than other grades. As such, particular care must be taken during the entire manufacturing process in order to mitigate deleterious phases precipitation. During solidification, conventional casting processes may induce a slight local modification to the chemical composition by solute partitioning. Although it is more or less the case for all metallic alloys, the consequences vary depending on the grades and final application of the alloy. For example, with the SDSS grade, segregated areas which are generally located close to mid-thickness for flat products, contain higher concentration of both austenite-formers (Ni, N...) and ferrite-formers (Cr, Mo...). This could cause a slight change in phase balance and a localized increase in pitting corrosion resistance. However, the higher chromium and molybdenum contents also make these regions more susceptible to intermetallic phase precipitation, such as σ -phase. Therefore, these phases may be present in the form of the so-called centerline intermetallic stringers, even in the case of proper solution annealing.

As part of the quality control process, it is important to evaluate the effect of these centerline intermetallic stringers on the in-use properties. A previous study demonstrated the negligible influence of the intermetallic phases in centerline stringers (typically < 0.1% over thickness) on the hydrogen embrittlement susceptibility of superduplex stainless steel [1].

Literature review [2 – 4] tends to indicate that σ -phase precipitation would indirectly impair corrosion properties through low alloyed austenite formation within segregated areas. The present study aims at highlighting the impact of centerline intermetallic stringers on pitting corrosion resistance in order to complete the overview of in use corrosion properties of superduplex stainless steels. After extensive optical characterization, samples containing centerline stringers have been selected and high magnification microstructural characterization were performed including TEM and AFM investigations. Standard corrosion tests were performed to evaluate the impact of intermetallic stringers followed by a complete study of local electrochemical behavior by microcell capillary technique. Only the main results are presented in the following paper to illustrate the pitting behavior of centerline stringers in severe environmental conditions.

MATERIAL AND EXPERIMENTAL PROCEDURE

As-received Materials

Two different coils from the same heat of S32750 were supplied:

- 2.1 mm thick cold-rolled & solution annealed (SA) sheet,
- 6 mm thick hot-rolled & solution annealed sheet.

The chemical composition of the S32750 is given in Table 1 and main microstructural characteristics are presented in Table 2. The average composition is measured by X-ray fluorescence (XRF). The ferrite fraction is determined by a Setaram sigmameter. The austenite spacing is measured in agreement to Recommended Practice DNV-RP-F112 with light optical microscopy (LOM) after Beraha etching.

Table 1
Composition of the superduplex stainless steel (wt%)

UNS	Fe	Cr	Ni	Mn	Mo	Si	N	PREN
S32750	Bal.	26.07	6.95	0.89	3.81	0.33	0.274	43.0

Table 2
Metallurgical characterization of superduplex stainless steel sheets

UNS	Process	Thickness (mm)	% Ferrite	γ spacing (μm)
S32750	cold rolled + SA	2.08	48.0	2.2 ± 0.5
	hot rolled + SA	6	52.6	3.4 ± 0.5

Selection of samples to obtain corrosion specimens with or without sigma phase precipitation

Superduplex stainless steels may contain very few intermetallic phases in segregated area (typically < 0.1 % over thickness). That's why a random sampling cannot guarantee all corrosion specimens will containing σ -phase stringers at mid-thickness. An extensive sampling coupled with LOM after NaOH electroetching was performed to provide two different kinds of corrosion specimens from each coil:

- specimens free from σ -phase specimens (Figure 1),
- specimens with qualitatively evaluated σ -phase presence within centerline stringers (segregated regions only), Figure 2.

For the 6 mm thick sheet (Figure 2 c & d), σ -phase content was quantitatively evaluated by image analyses on the worst field equal to 1.9 % at x500 that leads to a σ -phase content of 0.065 % (x500) on full thickness on the same sample.

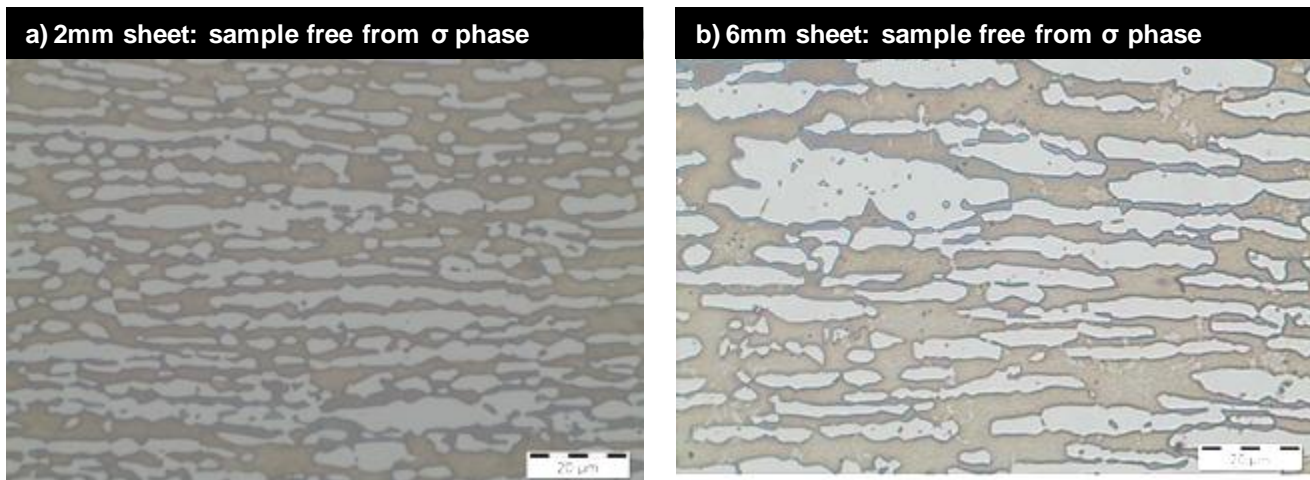


Figure 1: Selection of samples free from sigma phase for both sheets, light optical microscopy at mid-thickness
a) 2 mm cold rolled sheet, b) 6 mm hot rolled sheet

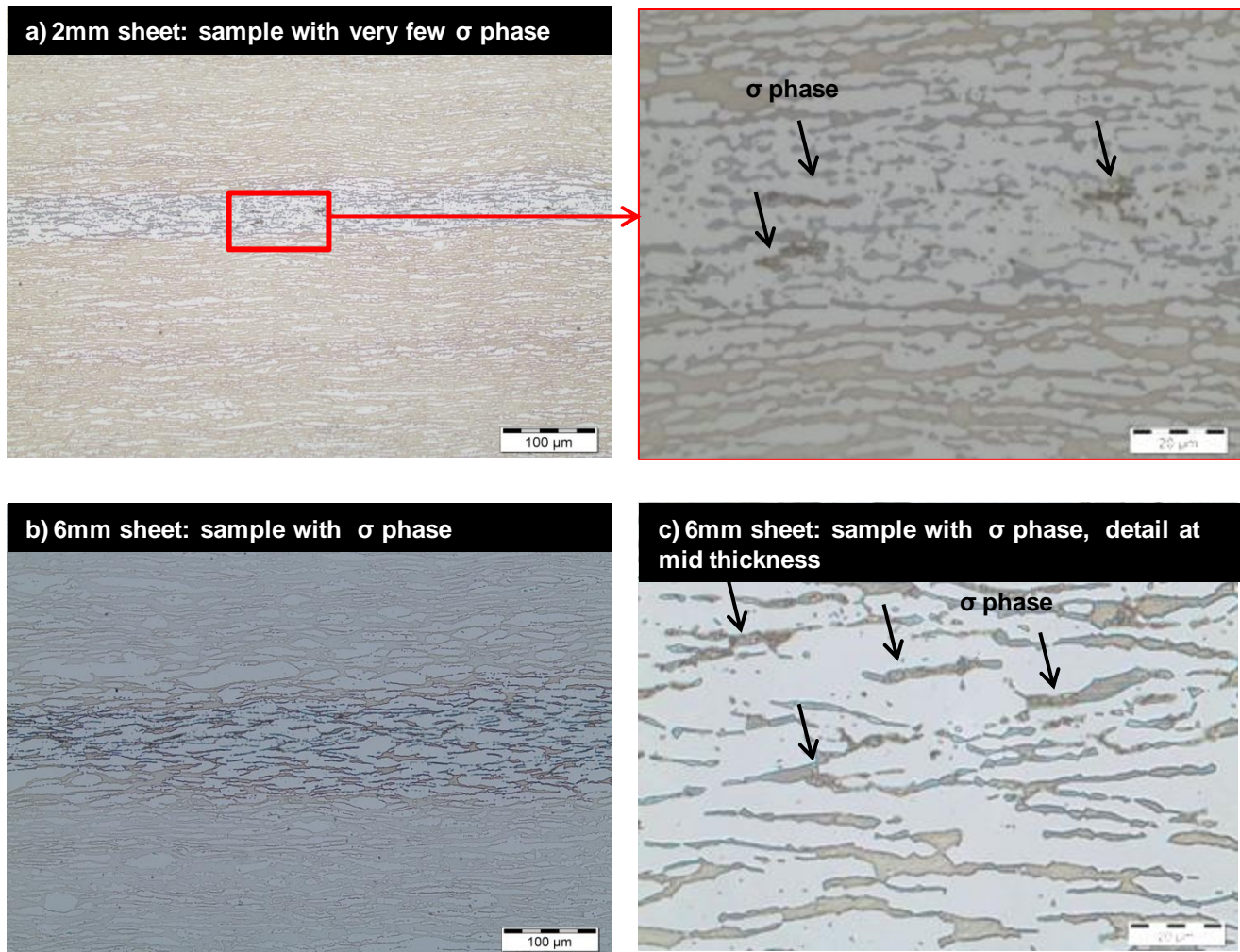


Figure 2: Selection of samples containing limited σ -phase within segregated bands
 a) 2 mm cold rolled sheet, b) & c) 6 mm hot rolled sheet

Experimental

Metallurgical characterization

Field Emission Scanning Electron Microscope (FE-SEM) coupled with Energy Dispersive X-ray spectroscopy (EDX) FE-SEM/EDX (JEOL 7600F) and Field Emission Transmission Electron (FE-TEM) coupled with EDX (JEOL JEM-2100) have been used to characterize σ -phase interfaces with ferrite and austenite. For TEM/EDX analyses, the spatial resolution is equal to 1.3 nm.

Pitting behavior through macroscopic characterization

Corrosion specimens 25 mm x 50 mm were cut. Prior to corrosion tests, one long edge of the specimen was polished and etched to check for the presence or absence of σ -phase precipitation. In case of σ -phase precipitation within centerline stringers, measurements were conducted at localized areas with σ -phase. This step enables to select 3 specimens (designated 1, 2, 3) with σ -phase precipitation and 3 specimens (designated 4, 5, 6) free from σ -phase precipitation. Then the etched edges were very lightly polished (120 grit abrasive paper) and ASTM G48 method A [5] tests were performed following ISO 17781 [6] requirements. Samples are exposed to a ferric chloride solution prepared with 111 g/L of FeCl_3 at the temperature of 50 °C and for a 24 hour exposure. This test aims at characterizing the pitting behavior and is widely used as quality control test in the oil & gas industry.

A second kind of immersion test has been used to simulate the long term exposure of superduplex at in-use standard conditions:

- specimens with a polished cross-section (diamond paste 1 μm) have been used to facilitate SEM examinations after immersion
- 80 g/L NaCl (~1.4 M NaCl)
- 50 °C
- pH = 4.5
- 6 month exposure

Electrochemical characterizations

All samples have been mechanically polished through 1 μm diamond paste. The different test locations have been chosen after electrochemical etching and light optical microscopy examinations and have been marked using micro-hardness tests. Samples were then polished for 2-3 minutes with diamond paste to eliminate the effect of etching. A standard electrochemical cell with 3 electrodes was used for global polarization curves. Local electrochemical polarization curves (polarization curve, critical pitting temperature - CPT) were performed using the electrochemical microcell technique in following conditions:

- capillary diameter of 330 μm ,
- 3 M NaCl, pH = 1 acidified with HCl.

For local CPT the applied potential was equal to 800 mV vs. Ag/AgCl and the heating rate was 10 °C/min until 40 °C and then 1 °C/min.

Sweep rate has been chosen equal to

- 1 mV/s for global electrochemical behavior.
- 4 mV/s for local polarization curves.

RESULTS

Microstructural characterization of σ -phase precipitation within segregated area

FE-SEM analyses confirmed by FE-TEM investigations shows evidence of the presence of a Cr and Mo-depleted phase within centerline intermetallic stringers (Figure 3, Figure 4). This phase has been identified as secondary austenite γ_2 [2]. It was reported to be preferential site for pit initiation [3,7]. Detrimental environment is not always specified but some authors report preferential initiation on secondary austenite in NaCl environments [7].

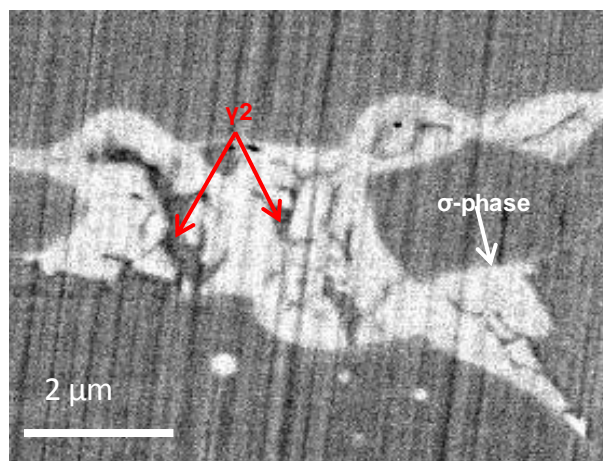


Figure 3: FE-SEM images of intermetallic stringers under the form of σ -phase and secondary austenite

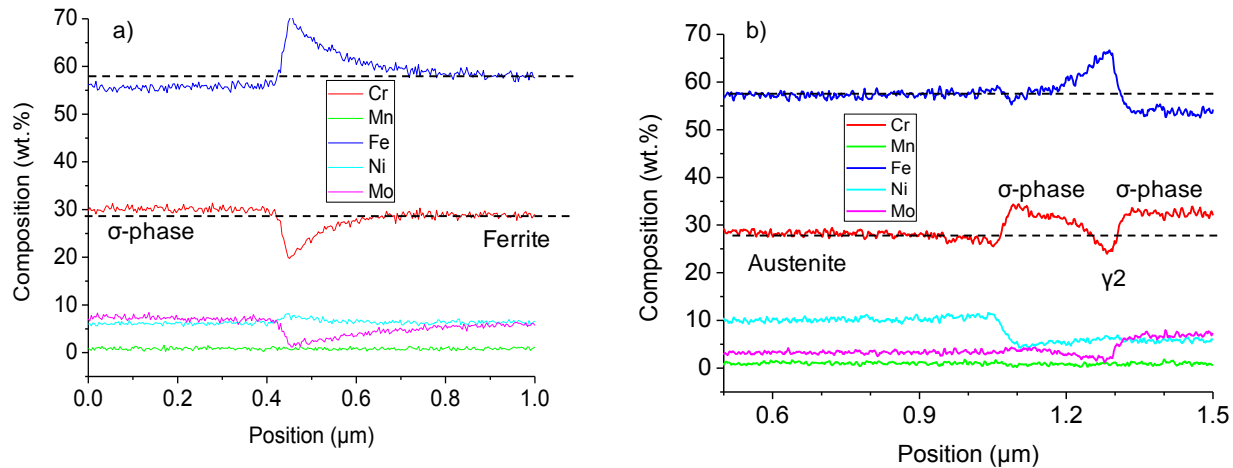


Figure 4: FE-TEM/EDX analyses of Cr, Mn, Fe, Ni and Mo across ferrite (a) or austenite (b) / sigma interface within centerline intermetallic stringers. Chromium-depleted area at ferrite/sigma interfaces.

TEM diffraction patterns confirm that σ -phase precipitated within the tetragonal structure with following lattice parameters $a = 0.87995\text{nm}$ and $c = 0.45442\text{ nm}$. TEM/EDX analyses of interfaces (Figure 3, Figure 4) enlighten that:

- no Cr-depleted zone is observed between σ -phase and austenite,
- Cr and Mo-depleted zone (about 200 nm) is observed between σ -phase and ferrite,
- secondary austenite inside intermetallic stringers exhibits lower Cr and Mo contents than austenite within segregated bands.

Pitting corrosion resistance in standard conditions

ASTM G48 method A [5] tests were performed following ISO 17781 [6] requirements in order to characterize the pitting behavior of samples with and without σ -phase in ferric chloride solution at 50°C .

After a 24 hour immersion, no pits are observed at 20 X magnification even for samples with σ -phase precipitation. Values of weight loss for all specimens are less than 1 g/m^2 (Table 3). So both acceptance criteria from ISO 17781 are met. However, relatively high values of weight loss are obtained that is directly due to the specimen preparations. Indeed, no pickling was performed prior to corrosion test. ISO 17781 states that this testing condition is more severe and that the test should be accepted if passing the acceptance criteria.

To conclude, a small amount of σ -phase within segregated regions does not impair pitting corrosion resistance even though it is present on the surface.

Table 3

Weight loss results on non-pickled specimens after ASTM G48 test A at 50°C with 24h exposure (ISO 17 781)

UNS	Process	Thickness (mm)	Sample	σ phase within intermetallic stringers	Weight loss (g/m ²)	Pits
32750	cold rolling + SA	2.08	1	Yes	0.64	No
			2	Yes	0.57	No
			3	Yes	0.36	No
			4	No	0.85	No
			5	No	0.69	No
			6	No	0.85	No

Then a long term immersion test at 50 °C, pH = 4,5 and 80 g/L NaCl was performed on a diamond polished specimen from hot-rolled and solution annealed S32750 with very limited σ -phase within centerline stringers.

After a 6 month exposure, no pit is observed. No dissolution of secondary austenite or σ -phase is observed with FE-SEM (see Figure 5). The results indicate that σ -phase remains in a passive state even after a long term immersion in standard environment.

The same trend has been observed after the ASTM G48 method A and long term immersion tests in very different environmental conditions: σ -phase remains passive and so this phase doesn't represent the weak point of microstructure.

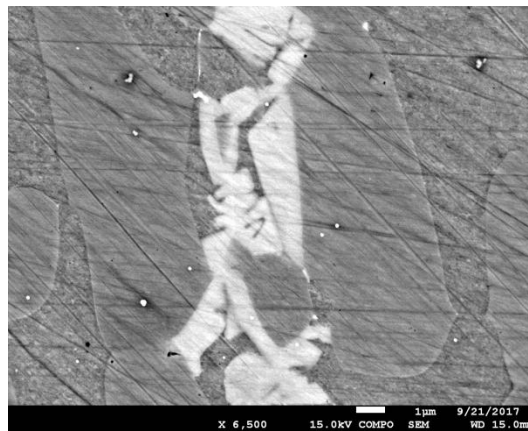


Figure 5: Example of FE-SEM examinations after long term immersion test. Stability of σ -phase at exposure surface in tested environment

Critical pitting temperature, low pH

First of all, preliminary tests have been performed to determine which conditions could be used to observe pit initiation and propagation within segregated bands that including a few σ -phase precipitates. Low pH conditions and high temperature are required. Further choice of temperature relies on local critical temperature (CPT) tests.

Local critical pitting temperature is determined using micro capillary technique at the applied potential of 800 mV vs Ag/AgCl in 3 M NaCl, pH = 1 (HCl), Figure 6. For the matrix far from segregated band (black curve), some transients are observed that means that no stable pit is obtained. Then a gradual increase of current density is observed from around 70°C. Two kinds of behavior are observed within segregated bands (Figure 6):

- behavior similar to the matrix (see green curve),
- rapid increase of the current density from the temperature of 70-75°C (red & magenta curves).

These differences are directly linked with the local density of σ -phase within intermetallic stringers.

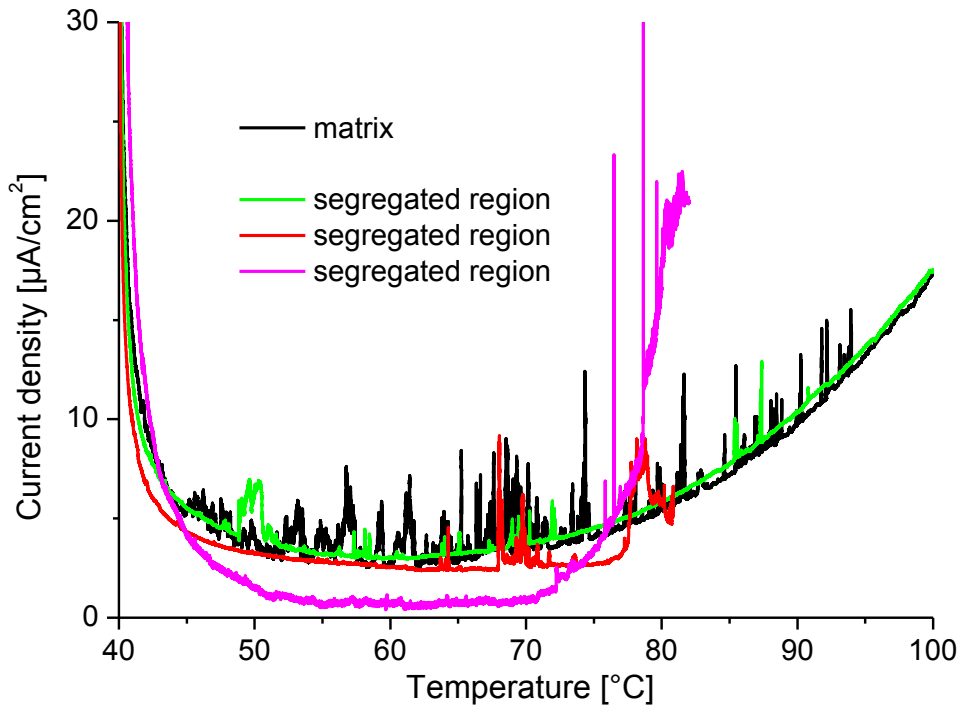


Figure 6: Active behavior from 70-75 °C in 3 M NaCl, pH = 1 acidied with HCl

These preliminary electrochemical test demonstrates that the critical pitting temperature of segregated band containing σ -phase in 3 M NaCl, pH = 1 (HCl) is within the range of 70-75 °C so the temperature of 80 °C is selected for both global and local corrosion characterizations.

Corrosion behavior at 80 °C, low pH

The global corrosion behavior was characterized at 80 °C in the same environment for 6 mm thick S32750 (hot rolled + solution annealed), Figure 7. This electrochemical test aims to observe the propagation of active sites; this is why severe conditions were chosen in terms of temperature, pH and chloride content. Furthermore the tests are performed on the cross section of the sample (after polishing) to investigate the behavior of centerline stringers.

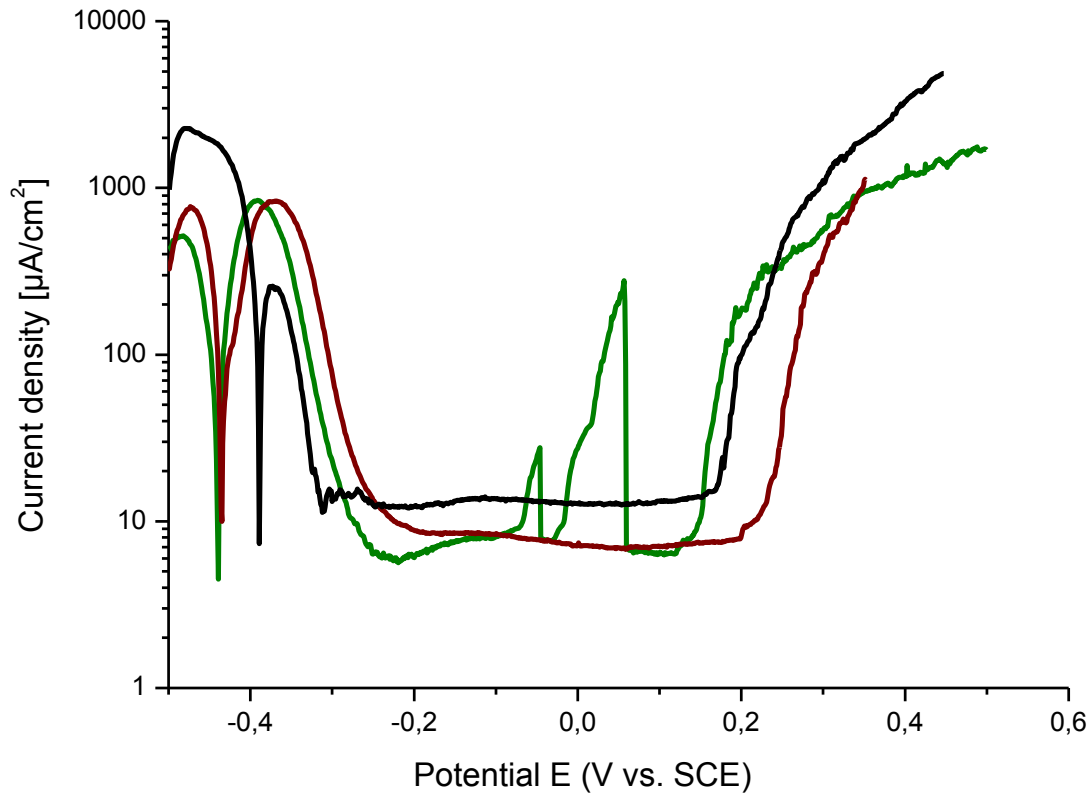


Figure 7: Global polarization curves of sample with centerline stringers at 80 °C in 3 M NaCl, pH = 1 acidified with HCl (1 mV.s⁻¹)

At low pH acidified with HCl, a large passive plateau is observed in the anodic domain in the case of sample with centerline stringers (Figure 7) for all tests. Some current transients are noticed which correspond to metastable pits (green curve). After potentiodynamic test, the surface was examined with SEM (Figure 8). Pits initiate mainly on the matrix, *i.e.* out of the centerline intermetallic stringers, consistent with inclusion dissolution. In centerline stringers, secondary austenite dissolution is observed and pits initiate in ferrite from these resulting crevices. However, the size of pits within intermetallic stringers remains limited compared to those initiating from inclusions.

To conclude, the global behavior of the sample with centerline stringers is ruled by pit propagation within the matrix far from centerline stringers. Inclusions represent the weakest points on surface for both samples.

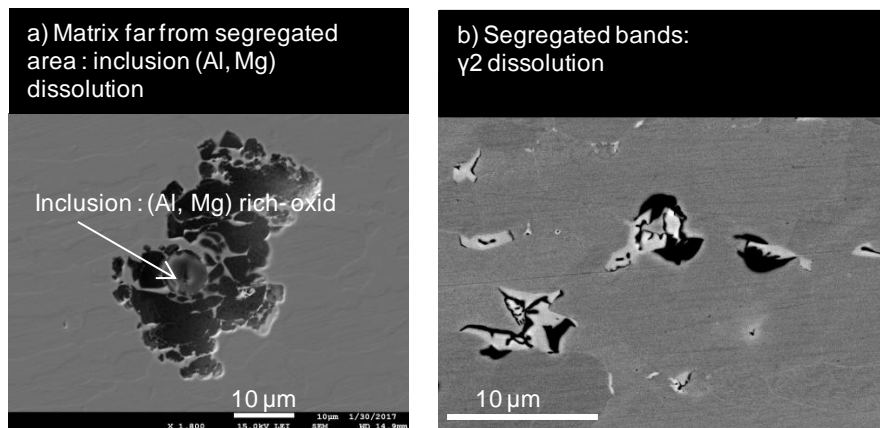


Figure 8: FE-SEM examinations after potentiodynamic test in 3M NaCl, 80°C, pH = 1 acidified with HCl a) Matrix, b) Segregated bands

Local electrochemical behavior at 80 °C, pH = 1, HCl

Local polarization curves at 80 °C have been recorded thanks to a micro-capillary in segregated bands covering centerline-intermetallic stringers and within the matrix (far from centerline stringers). Indeed the diameter of the micro-capillary is 330 μm which is far larger than the thickness of centerline stringers. Local electrochemical behaviors are then compared to global electrochemical behavior of the sample (Figure 9):

- The current in the passive region is higher in segregated bands than in the matrix which demonstrates that segregated bands are more reactive than the matrix. This result is interpreted as a consequence of σ -phase precipitation within intermetallic stringers,
- The current in the passive region for the global behavior is the result of contributions from the matrix and segregated bands,
- The increase of current after passive plateau obtained in all cases for very high potential is interpreted as the result of water electrolysis. Phase dissolution bands may also happen, in particularly within segregated bands.

No current transient is observed for the local matrix behavior, so it may be assumed that transients observed for segregated bands are responsible of transients observed on global curve.

No corrosion damage after tests with micro-capillary are observed with LOM. These local scale results are consistent with previous ones at macro-scale.

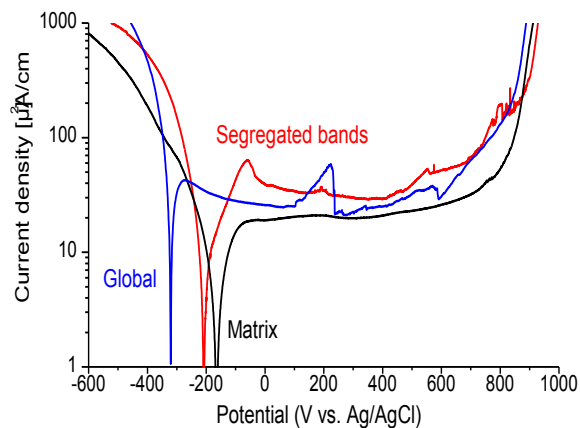


Figure 9: Comparison of local and global polarization curves at 80 °C, 3 M NaCl, pH = 1 acidified with HCl, 6 mm thick S32750 with few σ -phase within centerline intermetallic stringers

CONCLUSIONS

During solidification, conventional casting processes may induce a slight local modification to the chemical composition by solute partitioning that can lead to intermetallic phase precipitation, such as σ -phase, within segregated area. That is why a limited fraction of these phases may be present under the form of the so-called centerline intermetallic stringers. The present study aims at highlighting the impact of centerline intermetallic stringers on pitting corrosion resistance.

The limited fraction of intermetallic stringers at mid-thickness makes impossible a random sampling. First part of the study consisted in producing two kinds of specimens: specimens free from σ -phase precipitation and specimens with evidenced σ -phase precipitation within centerline stringers. Extensive sampling and optical characterization have been used to select appropriate specimens.

Standard tests have been performed on samples selected for the presence of limited σ -phase precipitation within segregated bands. Results demonstrate that sites containing σ -phase and secondary austenite remain passive for long duration in ASTM G48 method A environment [5] or in a solution with 1.4 M NaCl, pH = 4.5 at 50 °C.

Global electrochemical characterizations evidence that inclusion particles are the main weak point of S32750 stainless steels. Very aggressive conditions (80°C, 3 M NaCl, pH = 1) have been required to activate sites containing σ -phase. In the case of centerline stringers, secondary austenite is preferentially dissolved whereas σ -phase remains stable even for very severe conditions, limiting pit propagation. Preferential dissolution of secondary austenite leads to crevices under high activation potential and eventually to pit propagation within ferrite which is probably promoted by a Cr-depleted area within ferrite.

These results demonstrate that when centerline intermetallic stringers are detected in the range of the ISO 17781 requirements for cold-rolled or hot rolled solution annealed UNS S32750 superduplex steel, their presence does not impair localized corrosion properties in tested conditions.

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