

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.

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.

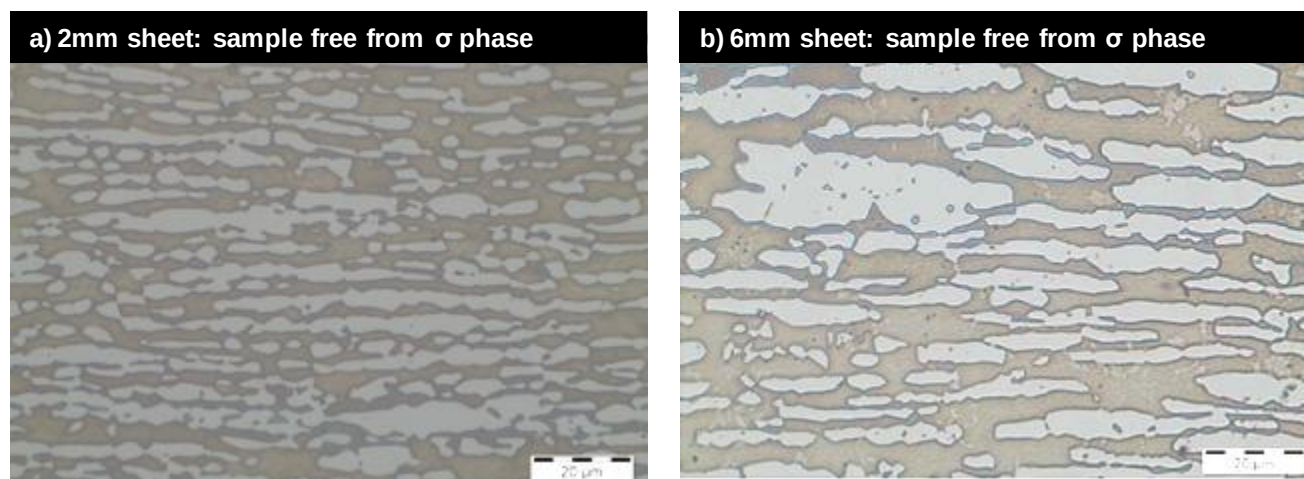


Figure 1: Selection of samples free from sigma phase for both sheets, light optical microscopy at mid-thickness

a) 2 mm cold rolled sheet, b) 6 mm hot rolled sheet

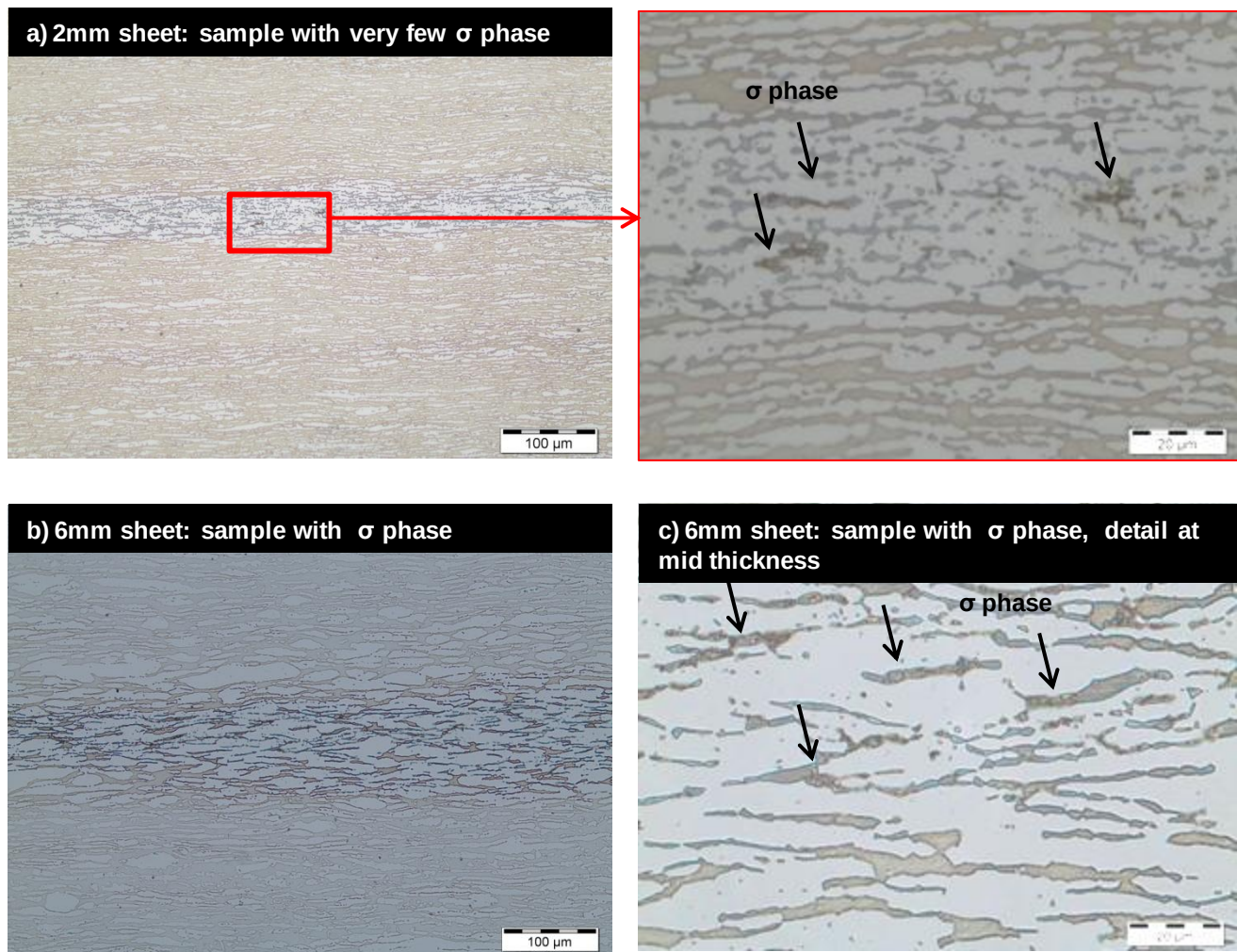


Figure 2: Selection of samples containing limited σ -phase within segregated bands
a) 2 mm cold rolled sheet, b) & c) 6 mm hot rolled sheet

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.