

Determination of the acceptability conditions for a safe use of super duplex stainless steel through SSRT screening

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ABSTRACT

The present work mainly focuses on determining the limits of use of a UNS S32750 super-duplex stainless steel tube product in NACE standard solution A under 0.5 bar H₂S, at different temperatures between 23 and 80°C, and pH 2.8 to 6 through slow strain rate testing. The acceptability conditions for SCC/SSC resistance were compared to those obtained on plate products of UNS S32205 duplex and UNS S32707 hyper-duplex stainless steels using the same experimental technique. Two different plate products in UNS S32205 were tested, with two different thickness reductions upon manufacturing: a 17 mm thick plate and a 2 mm thick foil.

The super duplex stainless steel tube material UNS S32750 showed higher SCC and SSC resistance compared to the plate duplex stainless steel UNS S32205. It has been observed that both the duplex and super-duplex stainless steels are suffering from selective dissolution in low pH at 80°C, however, in different phases. Selective dissolution of austenite is observed in alloy UNS S32750 at 80°C when pH ≤ 3.5, whereas only ferrite dissolution is observed in UNS S32205 (as plate) at 80°C and pH 4.5. No SSC has been observed in UNS S32750 at lower temperature down to 23°C and at pH 2.8. However, dissolution in both phases has been evidenced in UNS S32205 (as foil) at temperature as low as 23 and 50°C and pH between 2.8 and 4.5. EBSD investigation has shown that the microstructural difference between the thin and thick plate products of UNS S32205 is most likely process-related. In addition, the UNS S32707 plate showed the highest resistance to SCC and SSC. No degradation has been observed for UNS S32707 in any of the conditions tested in this study.

Key words: SSRT, H₂S, pH, temperature, selective dissolution (SD), stress corrosion cracking (SCC), sulfide stress corrosion cracking (SSC), environmental assisted cracking (EAC)

INTRODUCTION

NACE^(*) MR0175 / ISO^(†) 15156-3¹ standard specifies H₂S partial pressure thresholds limits for a safe use of duplex stainless steels as a function of the Pitting Resistance Equivalent Number (PREN) of the considered material. Published results demonstrated however that these limits can be very conservative for low chloride contents and high pH conditions², and that there is often a temperature leading to a maximum cracking susceptibility^{3,4}. In case of depassivation, the material can also undergo localized corrosion in the form of selective dissolution (SD) of ferritic or austenitic phase^{5,6,7}. Susceptibility to SD depends, among other parameters, on environmental conditions with possible generation of cracks enhanced in the presence of H₂S⁸.

Recently, F. Ruel et al.⁹ investigated the effect of temperature and pH on the environmental assisted cracking resistance of duplex stainless steel UNS S32205 through Slow Strain Rate Tests (SSRT). The effect of these parameters on the material susceptibility was clearly established and the authors highlighted a higher cracking susceptibility in the temperature and pH conditions leading to selective dissolution of the ferrite phase.

Considering the lack of data regarding the acceptable service conditions of recently developed duplex stainless steels, a characterization program using SSRT was performed on both super-duplex UNS S32750 (Sandvik SAF 2507[®])^(‡) and hyper-duplex UNS S32707 (Sandvik SAF 2707 HD[™])^(§) alloys under 500 mbar H₂S. This study focuses on pH and temperature impact on susceptibility to environmental assisted cracking (EAC) including sulfide stress cracking (SSC) at room temperature, and stress corrosion cracking (SCC) at higher temperatures, by SSRT performed at different temperatures from ambient to 80°C and pH from 6 down to 2.8. As a reference, the super-duplex stainless steel was also compared with a duplex stainless steel UNS S32205 in the same testing conditions. The test methodology was the same as the one we used in the work published by F. Ruel et al.⁹.

EXPERIMENTAL PROCEDURE

The test solution consisted in 50 g/L NaCl + 5 g/L CH₃COONa (sodium acetate) according to standard NACE TM0177 solution A¹⁰. This solution was selected in accordance with a previous study⁹ in order to allow comparison of the results. The solution was de-aerated during 1 hour in a separated reservoir by argon bubbling until residual dissolved oxygen level dropped below 10 ppb. The vessel used for the solution deaeration was connected to the test cell to allow its deaeration. Then the solution was heated when necessary and saturated with the test gas for 2 hours before solution transfer. During the deaeration and saturation process, the test cell was heated at the test temperature as well and a pre-load of few hundreds of newtons was applied on the specimen. The pH was adjusted once the solution reached the test temperature and was saturated with the test gas using additions of HCl (18%) to values from 6 down to 2.8, and even lower (2 and 1.5) for some tests. Very low pH was indeed necessary to generate a cracking susceptibility in some of the tested alloys. As soon as the solution was in contact with the specimen, tensile loading was started at a constant extension rate of 10⁻⁶ s⁻¹ (in/in/s).

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(‡) Trade name

(§) Trade name

Three temperatures were tested: 23, 50 and 80°C and the target H₂S partial pressure was 0.5 bar, balanced with CO₂, regardless of temperature. Different gas pre-mix were thus used for the different temperature to take the vapor pressure into account:

- 50%H₂S + CO₂ for the tests at 23°C (Water Vapor Pressure (WVP) = 0.032 bar)
- 57%H₂S + CO₂ at 50°C (WVP = 0.123 bar)
- 94%H₂S + CO₂ at 80°C (WVP = 0.474 bar)

Specimens were machined in the longitudinal direction from a seamless tube (UNS S32750) or a plate (UNS S32707 and UNS S32205) into standard cylindrical subsize NACE geometry (Figure 1). Specimens of UNS S32750 were taken from a final tube product, while the ones from UNS S32707 were taken from material manufactured at laboratory scale from 164 mm round bar down to 7 mm thick flat hot rolled material. This approach was selected in order to get material with enough thickness for cylindrical SSRT specimens with consideration of comparable geometry for S32750 and S32707. Both materials are in annealed condition. Whereas, commercial UNS S32205 plate was chosen as a reference for the comparison between three materials using cylindrical specimens and also to compare using uniaxial prismatic tensile specimens from thin foil of UNS S32205 (2 mm thick). The chemical compositions of the grades tested are given in Table 1 including PRE number and austenite spacing.

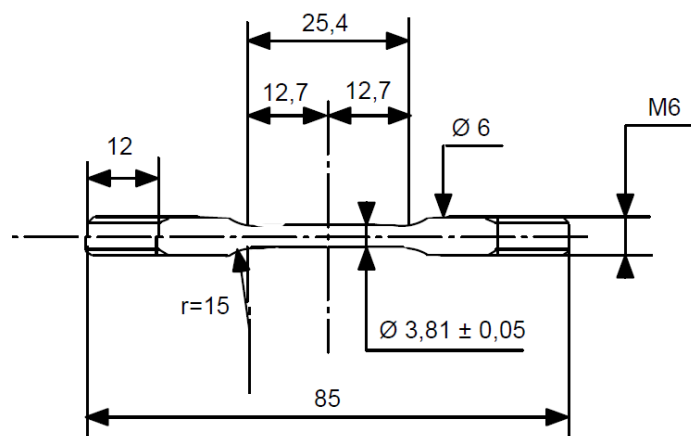


Figure 1: Standard subsize NACE geometry of the specimens tested

Table 1: Chemical composition of the materials used for testing, wt%

UNS	Product	Cr	Ni	Mo	N	PREN*	Austenite spacing
S32750	Tube, mm OD140*WT7.72	25.59	6.47	3.84	0.3	43	6.2±5.8 µm
S32707	Plate, hot rolled ~7 mm thick	27	6.5	4.8	0.4	49	12.4±10.3 µm
S32205	Plate, hot rolled 17 mm thick	22.8	5.3	2.9	0.2	36	6.2±4.2 µm
S32205	Foil, hot rolled 2 mm thick	22.8	5.5	3.1	0.2	36	1.7±1.3 µm

* Pitting resistance equivalent number, $PREN = \%Cr + 3.3 \times (\%Mo + 0.5\%W) + 16 \times \%N$

After machining, the gauge section of each specimen tested in corrosive environment was polished by SiC grit paper P1200, the ones tested as baseline in argon at room temperature and in glycerol at higher temperatures were prepared by grit paper P600 polishing. Several grit papers were used with a modification of the polishing direction after each paper change and final polishing step along longitudinal direction.

The EAC susceptibility in each condition was determined using SSRT with a constant extension rate of 10^{-6} s^{-1} (in/in/s) leading to a strain rate after the yield point of 10^{-6} s^{-1} considering the specimen geometry (gauge length 25.4 mm, Figure 1). For each condition, one specimen was strained to failure in an inert environment (argon or glycerol) at the test temperature and one specimen in the gas saturated solution at the same temperature but variable pH, the objective being to coarsely define the sensitivity domain of the materials and identify the embrittlement mechanisms involved.

After each test, the ultimate tensile stress (UTS), plastic elongation (E_p) and reduction of area ratio (RAR) of each specimen were determined and the EAC susceptibility was evaluated through the plastic strain-to-failure ratio estimated according to the following formula.

$$E_p R(\%) = \frac{E_{pE}}{E_{pA}} \times 100 \quad (1)$$

With:

- E_{pE} the plastic strain to rupture measured in the solution and,
- E_{pA} the plastic strain to rupture measured in the reference inert environment -i.e. argon or glycerol depending on the temperature.

RAR was calculated using the formula (2).

$$RAR(\%) = \frac{RA_E}{RA_A} \times 100 \quad (2)$$

With:

- RA_E the reduction in area in the solution and,
- RA_A the reduction in area in the reference inert environment.

Both reduction in area (RAR) and plastic elongation ($E_p R$) ratios were used to characterize sensitivity of the material to EAC. Ductility ratios of RAR and $E_p R$, higher than 70%, indicate high resistance of the material to SCC and SSC in the test conditions.

Additional investigation has been carried out using electron backscattered diffraction (EBSD) for microstructure characterization of the duplex stainless steel UNS S32205 samples taken from the plate and the foil in longitudinal cross-sections containing rolling and normal directions. The sample preparation involved grinding of embedded samples down to a fine finish obtained with 1 μm diamond paste and subsequently polished with colloidal silica. The polished specimens were subjected to EBSD data acquisition in Carl Zeiss** Field Emission Gun scanning electron microscope equipped with the Symmetry EBSD detector supplied by OXFORD Instruments††. The data acquisition was carried out at a detector speed of approximately 2000 Hz covering a total area of approximately $0.077 \times 0.0288 \text{ cm}^2$ with a step size of 0.3 μm . Post processing analysis was carried out with OIM analysis 8‡‡ software. For EBSD analysis, grain tolerance angle of 5° to differentiate two neighboring grains was applied. Phase maps and fractions, grain boundary densities of 1° - 15° and $>15^\circ$ grain boundaries, Kernel average misorientation (KAM) map and area weighted average grain size of ferrite phase were evaluated. Few of these parameters are briefly described below:

- KAM is a local misorientation parameter which is the average misorientation of a pixel with the neighboring pixels and also with a choice of excluding some pixels that exhibit higher misorientation angles. In this study, neighboring pixels higher than 5° misorientation angles were excluded. These regions of high KAM values indicate presence of residual strain or in other words the microstructure is not fully recrystallized.

** Trade name

†† Trade name

‡‡ Trade name

- The grain boundary density is estimated as total boundary length (cm) divided by the total scan area (cm²). This also indicates the extent of recrystallization. 1°-15° grain boundaries, considered as low angle grain boundaries (LAGBs), are predominant in deformed structures. On the other hand, >15° boundaries, known as high angle grain boundaries (HAGBs), are dominant in recrystallized structures.
- As austenite spacing corresponds to ferrite size, the grain size of ferrite is included in this study.

RESULTS

SSRT curves obtained on UNS S32750 at 23, 50 and 80°C, and at different pH-values in the solution derived from NACE solution A are plotted on Figure 2. No Environmental Assisted Cracking or Selective Dissolution was noted during the SSRT at 23 and 50°C, whereas a reduction of plastic elongation to failure is observed at 80°C for pH≤3.5. As expected, the lower the pH, the higher the EAC susceptibility. The mechanical properties extracted from all the SSRT curves are also gathered in Table 2.

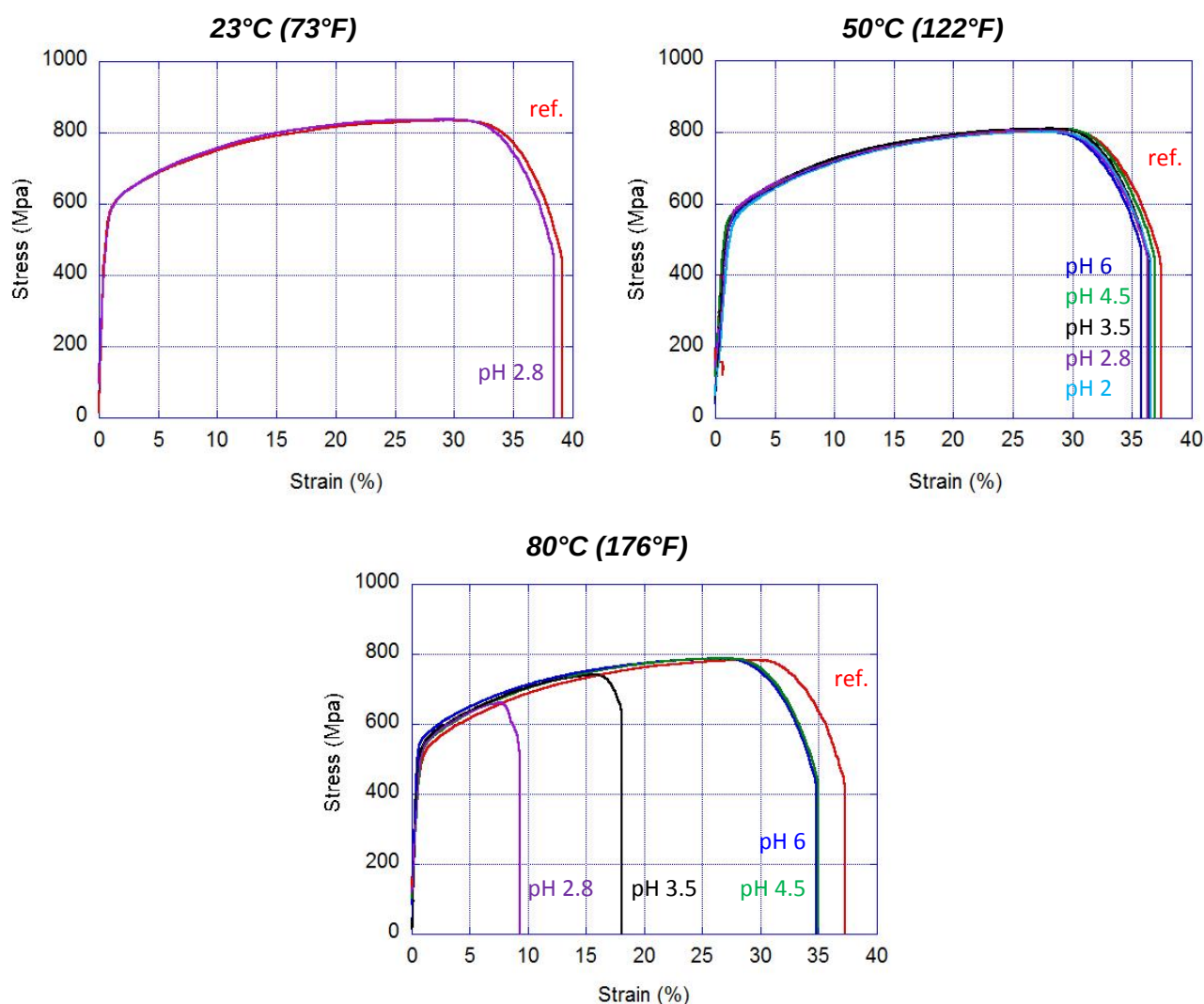


Figure 2: SSRT stress-strain curves of grade UNS S32750 at 23, 50 and 80°C, and different pH values under 0.5 bar H₂S