

Pitting corrosion resistance of UNS S32202 welds: bulk microstructure vs surface behavior

Veronica SCHEIBER, Pauline HUGUENIN, Jérôme BRIDEL,
Florent KRAJCARZ.
APERAM
Rue Roger Salengro BP 15
62330 Isbergues, France

Veronica SCHEIBER, Vincent VIGNAL
ICB UMR 6303 CNRS Université Bourgogne
Franche-Comté
BP 47870
21078, Dijon Cedex, France

ABSTRACT

Duplex stainless steel (DSS) provides a good alternative to austenitic stainless steel to build engineering designs thanks to excellent mechanical properties and corrosion resistance associated to their biphasic microstructure. Their microstructure changes during the welding. The influence of microstructure and elemental distribution on pitting corrosion resistance of different zones of the lean DSS UNS S32202 welded by Gas Tungsten Arc Welding (GTAW) was analyzed. The welded transversal cross section surface after polishing and the welded surface after pickling were studied. Comparing both surfaces, the welded surface is more resistant to pitting corrosion than welded transversal cross section surface, according to the electrical charge and the total mass loss. The High Temperature Heat Affected Zone (HTHAZ) surface after pickling has no pitting thanks to the presence of the superficial layer (DSS with a specific microstructure). However, the HTHAZ transversal cross section has the lowest pitting resistance. Its pit initiation sites could be associated to Cr₂N. Pit initiation sites in the molten zone (MZ) could be linked to oxide particles and Cr₂N for both surfaces. In all pits (in MZ and HTHAZ, for both surfaces) ferrite dissolves preferentially (austenite remains intact). Austenite is more resistant to pitting due to its higher nitrogen content than in ferrite.

Key words: UN S32202, 1.4062, Gas Tungsten Arc welds, pitting corrosion resistance, pickling, surface

INTRODUCTION

Duplex stainless steels (DSS) are an attractive alternative to conventional austenitic 300 series. They are becoming more and more present in industrial applications requiring high mechanical properties combined with good corrosion resistance. UNS S32202 is a lean duplex grade designed to guarantee

corrosion resistance superior to that of 304L in most environments and even equivalent to 316L in NaCl environment at room temperature. Its yield strength is twice as high as 304L and 316L allowing thickness and weight reduction in structural components. With low nickel content (2.5%) and no molybdenum addition, the impact of raw material price fluctuation is reduced. It makes UNS S32202 suitable for a high number of applications including public transportation, building & construction, water-systems, liquid storage and pulp&paper industry.

The optimized properties of DSS base metal are achieved when almost equal proportions of austenite and ferrite are present in the microstructure. During a welding operation, the ferrite / austenite phase balance in the MZ (molten zone) and HTHAZ (heat affected zone - high temperature) of lean duplex stainless steel welds can be significantly altered. This non-equilibrium microstructure is associated to the variation in grain size, chemical composition and secondary phase precipitation phenomena. This modified microstructure may affect the behavior of welded DSS under service conditions.

The proportion of each phase in the microstructure of welded joints depends on the local chemical composition, the maximum temperature reached and the cooling rate. The variation in the cooling rate has a particularly significant effect on the distribution of the phase ratio (between ferrite and austenite) in the HTHAZ as well as on the appearance of precipitates, such as Cr₂N, CrN or M₂₃Cr₆.¹ Despite the work undertaken to optimize grades and welding techniques, these metallurgical changes may affect the corrosion behavior of welded materials and may request some precautions.

During welding process, the combination between the maximum temperature reached and the local metal composition and the shielding gas provokes the formation of an oxide layer at the weld surface. Its thickness varies between zones. The formation of these thermal oxides can lead to the appearance of a sub-layer poor in chromium which may have a lower corrosion resistance than the non-welded alloy.^{2,3,4,5} Properties of thermal oxides and the sublayer depend on welding conditions. To guarantee the corrosion resistance of the weld it may be necessary to carry out a pickling operation. It has been shown that HF + HNO₃ solutions are a good option in terms of efficiency for pickling duplex stainless steels.^{4,6,7}

The present study aims to establish links between the microstructure of the different zones, including the pickled weld surface, and their corrosion behavior. This work is carried out using mainly a pulsed method called "Potentiostatic Pulse Technique" (PPT).⁸ Literature indicates that this method allows to generate a large number of small pits and thus to quickly characterize the first stages of pitting corrosion (initiation and early stages of propagation).^{8,9,10} After the PPT test it is possible to execute a statistical study of the pit size and to estimate a mean pits density per zone.

MATERIAL AND EXPERIMENTAL PROCEDURE

Alloy and samples

The studied alloy corresponds to a lean DSS UNS S32202. Its nominal chemical composition is (wt%) 0.020 C; 22.8 Cr; 2.5 Ni; 1.2 Mn; 0.40 Si; 0.24 Mo; 0.20 N. The partitioning of alloying elements in the constituent phases which was determined using the Electron Probe Microanalyser (EPMA) is shown in Table 1. The partitioning of alloying elements in the base metal (BM) was given as a reference. The pitting resistance equivalent number (PREN) of each zone was then calculated using expression (1).¹¹

$$PREN = wt.\%Cr + 3.3 \times wt.\%Mo + 16 \times wt.\%N \quad (1)$$

Table 1
Chemical composition of the lean duplex stainless steel UN S32202 (wt%).

Zone	% vol. α	Phase	Fe	Ni	Cr	Mn	Si	Mo	N	PREN
MZ	69.9	α	72.60	2.58	22.84	1.31	0.43	0.22	0.02	21.4
		γ	72.31	2.64	22.56	1.32	0.41	0.22	0.55	32.0
HTHA Z	66.5	α	72.48	2.48	23.06	1.30	0.44	0.23	0.02	24.1
		γ	72.21	2.68	22.63	1.34	0.42	0.21	0.52	31.6
BM	51.4	α	74.73	1.98	21.38	1.13	0.48	0.26	0.07	23.3
		γ	74.85	2.82	20.03	1.27	0.41	0.19	0.42	27.3

Coupons were cut from cold rolled, solution annealed and pickled sheets with a thickness of 1.3 mm. Samples on which microstructural and electrochemical characterizations were performed consist of two coupons welded by the Gas Tungsten Arc Welding (GTAW) technique (square butt joint), without filler metal. The welding conditions are 152 A; 11.2 V; 69 cm/min (speed) and 1.5 kJ/cm (heat input). Nitrogen was introduced in the shielding gas (Ar + 10% He + 2% N₂) and the backing gas (100 % N). The welding direction was the same as the rolling direction.

Sample preparation

Microstructural and electrochemical characterizations were carried out on two sets of samples:

- Welded transversal cross section surfaces, after polishing. Samples (500 mm x 1.3 mm) were embedded in an epoxy resin. They were ground with emery papers (from P1200 to P 4000) and polished using diamond pastes (6, 3 and 1 μ m).
- Welded surfaces, after pickling. These surfaces (8 mm x 45 mm) were brushed using a stainless steel brush for the removal of heat tint and then pickled in 20 % HNO₃ + 5 % HF aqueous solution at 60 °C for 5 minutes.

Microstructural characterizations

Welded transversal cross section surfaces were etched in a Behara solution (36 mg of K₂S₂O₅ in 22 ml of HCl diluted in 100 ml of distilled water) for 20 s, in order to highlight the two main phases (ferrite and austenite) in the different zones. The ferrite fraction was measured using an optical microscope GX71 Olympus[†] combined with an OLYMPUS[†] Image Analysis Software package thanks to grey scale threshold. In addition, welded transversal cross section surfaces were electrolytically etched in a 20 %vol. NaOH solution at 2 V at room temperature for about 15 s in order to locate ferrite emerging at the weld surface. This etching is currently used for duplex stainless steel microstructure characterization, where ferrite appears darker (blue and/or brown) than austenite (white).¹² After etching, surfaces were observed using an optical microscope Nikon eclipse LV 100 - S32.

Welded surface after pickling were analyzed using X-ray diffraction (XRD) in order to confirm the presence of ferrite and austenite at the surface. X-ray diffraction patterns were obtained using a Bruker D8 advance diffractometer[†] under Cu-K α radiation. Diffraction scans were performed at 40° < 2 θ < 140°, sampling every 0.02° (step size) and 4 s per step. The method Rietveld was used to determine phase content from XRD tests.

A field-emission type scanning electron microscope (FE-SEM) JEOL 6400F[†] with an integrated energy-dispersive X-ray spectroscopy (FE-SEM/EDS) was used in order to determine the chemical composition and the morphology of phases (austenite and ferrite) in both samples.

[†] Trade name

Mechanical characterizations

Hardness measurements

In order to determine the hardness of the weld, the tests were performed with a Buehler 5114[†] Microindentation Vickers Hardness Tester. The experiments were carried out with a load of 500 g-Force (objective x 10) by around 15 s. A hardness profile was obtained through all regions. Hardness measurements were only carried out on the welded transversal cross section after polishing to avoid the effect of different imperfections present in the welded surface after pickling, such as residual oxides, and roughness.

Electrochemical characterizations

Pitting behavior through macroscopic characterization

Corrosion specimens (25 mm x 50 mm) were cut. Prior to corrosion tests, edges were polished (220 grit abrasive paper) and samples were pickled in 5 %vol. HF and 20 %vol. HNO₃ solution at 60°C for 5 minutes. Then ASTM A 1084A method C was performed following ISO 17781 requirements.^{13,14} Samples are exposed to a ferric chloride solution prepared with 5 %wt. FeCl₃ + 1% NaNO₃ at the temperature of 25 °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.

Potentiostatic pulse technique (PPT) test

The corrosion behavior of both welded surfaces (welded transversal cross section surface, after polishing and welded surface, after pickling) was studied using the PPT method in a 0.5 M NaCl aqueous solution, pH = 3 (acidified by HCl), aerated solution, at 35 °C.¹⁰ Prior to PPT tests, surfaces were observed thoroughly using optical microscopy (OM (2D et 3D images)) and field emission scanning electrical microscopy (FE-SEM) to identify pre-existing imperfections.

As underlined in the literature, preliminary experiments were performed to define optimized test parameters.¹⁰ The optimized conditions were: a potential of -0.6 V vs SCE (cathodic domain) for 2 s, followed by a potential of 1 V vs SCE was applied for 5 s (pitting). This procedure was repeated during 10 cycles. PPT tests were carried out under aggressive conditions (acidic solution, applied potential in the anodic domain of 1 V vs SCE) in order to activate all potential pitting initiation sites. It can be underlined that under classical field conditions most of the pitting initiation sites remain passive.

A PGSTAT128 AUTOLAB[†] potentiostat and a classical three-electrode cell were used in the experiments. The counter electrode was a platinum grid (30 mm x 30 mm) and the reference electrode was a saturated calomel electrode (SCE).

After electrochemical tests, the samples were observed thoroughly using an optical microscope (OM (2D and 3D images)) and a field emission scanning electron microscope (FE-SEM) to determine the occurrence, location and morphology of pits.

RESULTS AND DISCUSSION

Microstructural characterizations

Welded surface, after pickling

The welded surface after pickling is shown in figure 1(a) and (b). As a consequence of mechanical brushing and chemical pickling, the MZ surface displays some cavities and folds (figure 2(a)). Grain boundaries are never etched. Only a few shallow pits with a diameter less than ~ 400 nm were found

[†] Trade name

mainly near the boundary between the MZ and the HTHAZ (figure 2(b)). A variation in chromium content (between 18 and 25 wt.%) is detected in different sites of the MZ from EDS (46 points analyses). This chromium variation could be associated to the heterogeneous dissolution of the sub-layer depleted in chromium (the more the sub-layer is dissolved, the higher the chromium content is) and secondly to the coexistence of austenite and ferrite in the superficial layer.

Apart from cavities and folds, some oxide particles are detected at the MZ surface (MgO, CaO, AlTiO, Al₂O₃, AlCaO, ...) (figure 2(c)). They are formed either during the alloy manufacturing process or welding process. Furthermore, some precipitates are observed in the center and at the edges of the MZ, as shown in figure 2(d). Based on literature, these precipitates may be Cr₂N located in ferrite grains.¹⁵⁻¹⁶ They are formed during the welding process as a result of decrease in nitrogen solubility in the ferrite upon cooling and insufficient nitrogen diffusion process from the ferrite grains to the austenite grains. This assumption will be confirmed by field emission transmission electron microscopy (FE-TEM) analyses. Rare residual oxides (size ~ 10 µm) are found by means of FE-SEM.

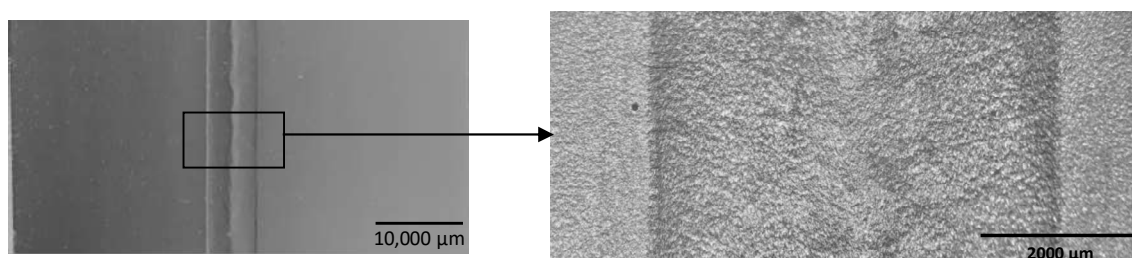


Figure 1: (a) Macroscopic image and (b) optical micrograph of the welded surface after pickling.

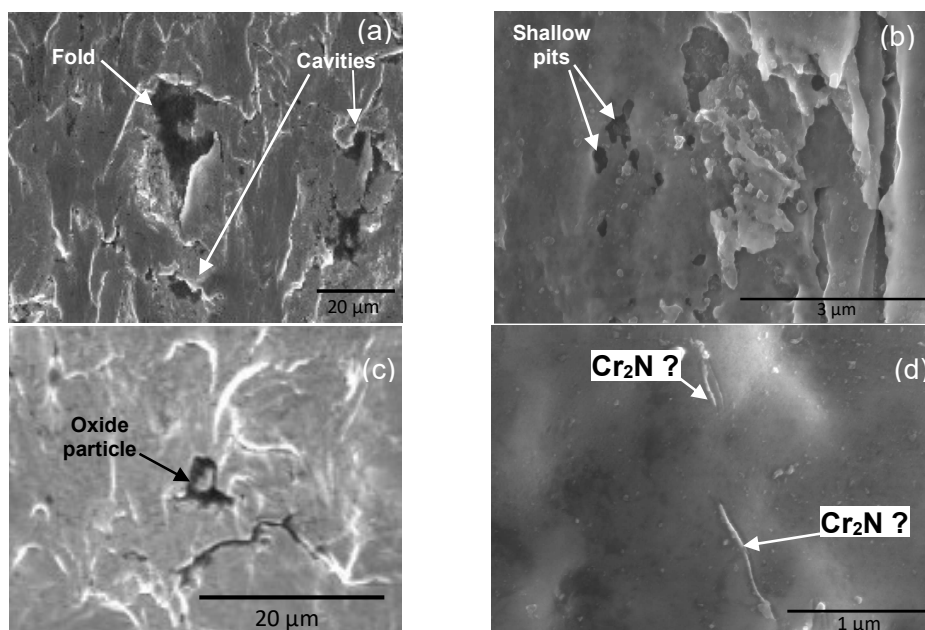


Figure 2: FE-SEM images of the MZ topography (a) folds and cavities in the MZ surface after pickling, (b) shallow pits in the MZ surface after pickling, near the boundary between the MZ and the HTHAZ, (c) oxide particle (MgO) and (d) small precipitates in the MZ surface after pickling, near the boundary between the MZ and the HTHAZ.

In some sites of the HTHAZ surface, grain boundaries are revealed corresponding to over-etched sites, figure 3(a). In these sites, shallow and small pits (diameter less than ~ 500 nm) may be observed (figure 3(b)). In addition, residual surface oxides (equivalent diameter of ~ 15 µm, figure 3(a)) and oxide particles (mainly Al₂O₃ and a few CaO, (figure 3(c)) are found at the surface. Residual surface oxides