# Effect of cold rolling on pitting resistance in duplex stainless steels

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*Duplex Stainless Steels (DSS) are biphasic austeno-ferritic steels in which the best combination of mechanical and corrosion-resistance properties is achieved for almost equal volume fractions of the phases. These steels are classified according to their pitting corrosion resistance, assessed by the PREN index (Pitting Resistance Equivalent Number) which, although qualitatively, is widely employed as comparison. The present work is aimed to study the pitting resistance of four DSS grades (SAF 2101, 2304, 2205 and 2507) in the as-received conditions and after cold rolling at various thickness reductions (from 15% to 85%), to highlight the effects of cold working on the corrosion behaviour. The materials were potentiodynamically tested in artificial seawater (pH 7) and the corresponding Critical Pitting Temperatures (CPT) were determined. Cold deformation mainly affected the Lean DSS grades, whereas the high-alloyed DSS were stable, even after heavy deformations. These differences can be attributed not only to composition but also to the onset of diffusionless phase transformations induced by cold working, which make the materials more prone to corrosive attacks.*

**Keywords:** Duplex stainless steel - Pitting corrosion - Plastic deformation - Phase transformation

## INTRODUCTION

In the austeno-ferritic Duplex Stainless Steels (DSS), the presence of equal volume fractions of the phases provides the best combination of mechanical and corrosion-resistance properties. This microstructure is achieved by correctly balancing the composition, thus allowing for the stabilization of the phases at room temperature, especially of austenite. Moreover, after the forming operations, a mandatory solution-annealing treatment (solubilization) is performed in all DSS, in order to attain the biphasic microstructure and re-dissolve undesired compounds [1, 2].
DSS have superior resistance to localized corrosion attacks than austenitic grades and a better resistance against generalized corrosion than ferritics [1]. These steels can be classified according to their resistance to pitting corrosion, assessed by the PREN index, which is intimately related to the steel bulk composition and frequently used as comparison term between different grades. The PREN is defined as following:

$$PRE_N = Cr\ (\%) + 3.3 \cdot Mo\ (\%) + k \cdot N\ (\%)$$

where $k$ is a constant, for which 16 is the most widely used value. If DSS are tungsten-alloyed grades, the index is called $PRE_W$ and the contribution of W modifies the previous relation.

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$PRE_N$ (or $PRE_W$) has only a qualitative character, because it refers to the average alloy composition and does not consider the influence of phases morphology and microstructural inhomogeneities, such as a not uniform elements partitioning within the phases. However, by means of $PRE_N$ it is possible to classify DSS in four main categories: Lean ($PRE_N$ = 25–26), Standard ($PRE_N$ = 35–36), Super ($PRE_N$-$PRE_W$ = 40–42) and Hyper ($PRE_N$-$PRE_W$ > 45) DSS. In Lean DSS, the stabilization of austenite at room temperature and the phase balancing require the addition of N and Mn but, while nitrogen – together with Cr, Mo and W – favours the resistance to localized attacks, the presence of Mn can destabilize the protective layer in passive conditions.
The pitting resistance is significantly influenced by metallurgical parameters, such as inclusions or second phases, heat treatments, grains size and cold working, and the $PRE_N$ index does not account for these variables. Conversely, for a given chlorinated environment, each stainless steel can be characterized with a temperature below which pitting does not occur, even after indefinitely long times. This temperature is defined as the Critical Pitting Temperature (CPT) and, since reflected the real steel conditions, represents a parameter of highly interest. CPT is usually determined in chlorinated solutions, but its value was found to be independent of both chlorides concentration (range 0.01–5 M) and pH (range 1–7) [3, 4]. On the other hand, the surface roughness of the material can affect the CPT value [5], which decreases as roughness is increased.

| SAF grade | C | Si | Mn | Cr | Ni | Mo | Cu | P | S | N | $PRE_N$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **2101** | 0.028 | 0.69 | 3.82 | 21.72 | 1.13 | 0.10 | 0.34 | 0.028 | 0.0025 | 0.16 | 25 |
| **2304** | 0.030 | 0.56 | 1.43 | 20.17 | 4.29 | 0.18 | 0.16 | 0.027 | 0.0010 | 0.13 | 26 |
| **2205** | 0.030 | 0.56 | 1.46 | 22.75 | 5.04 | 0.19 | - | 0.025 | 0.0020 | 0.16 | 36 |
| **2507** | 0.015 | 0.24 | 0.83 | 24.80 | 6.89 | 0.83 | 0.23 | 0.023 | 0.0010 | 0.27 | 42 |

***Table 1 – Chemical compositions [wt.%] and $PRE_N$ indexes of the investigated DSS.***

*Tab. 1 – Composizione chimica e relativo indice $PRE_N$ degli acciai Duplex in esame.*

After cold working, the occurrence of residual stress and the formation of the Strain-Induced Martensite (SIM) from the metastable austenite can substantially affect the pitting resistance of stainless steels, because the number of the active anodic sites in the surface are increased [6, 7]. Thickness, composition and uniformity of the passive layer are modified in different extent by plastic deformation [8, 9] and the increasing in dislocation density favours the film dissolution, due to the presence of lower binding energy regions, if compared to a perfect crystal [10]. Cold deformation induces lattice distortions and creates substructures inside the grains, thus increasing the crystalline disorder and the number of interfaces. This may affect the formation of a less effective passive film on the steel surface; moreover, the presence of distorted high-energy interfaces may provide further trigger points for the localized attack [11, 12].
In the present work, the pitting resistance of four DSS grades in as-received conditions and after cold rolling is presented, with the aim to highlight the effects of cold plastic deformation on the corrosion behaviour.

## MATERIALS AND METHODS

Chemical compositions and $PRE_N$ indexes of the four investigated SAF DSS grades (2101, 2304, 2205 and 2507) are reported in Table 1. The as-received materials were cold rolled at various deformation degrees (from 15% to 85% of thickness reduction) and mechanically polished. Since surface roughness can affect the material response to corrosive attacks and with the aim to correctly compare the results on various steel grades, the surfaces were polished to a finishing as uniform as possible (final polishing using 1 μm diamond paste suspension).
Anodic potentiodynamic polarization tests were performed for testing the corrosion behaviour of as-received and deformed DSS, using an AMEL 568 potentiostat and by immersing the samples in a pH 7 electrolyte solution composed by 35 g/l of NaCl in deionized water (artificial seawater). All tests were conducted at room temperature, using calomel as reference electrode and platinum as counter electrode; for all tests, a scanning rate of 0.8 mV/s was applied.
The determination of the CPT was carried out by following the ASTM G150 standard, using a potentiostat/galvanostat AMEL 7060. The system consisted in two cells, containing the same aqueous solution (1 Molar of NaCl) and electrically connected by a salt bridge; in the first cell, maintained at room temperature, the reference electrode (calomel) was immersed, whereas the counter-electrode (platinum) and the sample were placed in the second, a thermostated bath. The ASTM standard states the evaluation of the CPT by maintaining a constant potential of 700 mV and increasing the temperature of the thermostated cell at the rate of 1°C/min; the CPT is defined as the temperature at which a current of 100 $\mu A/cm^2$ is absorbed by the sample.

## RESULTS AND DISCUSSION

### *Microstructure*

The as-received samples possessed the hot-rolled and solubilized DSS structure, composed by a ferritic matrix containing the austenitic grains oriented toward the rolling direction. The phases were well balanced and next to the optimal 50/50 value, except for SAF 2101 having a ferrite content of about 75%.

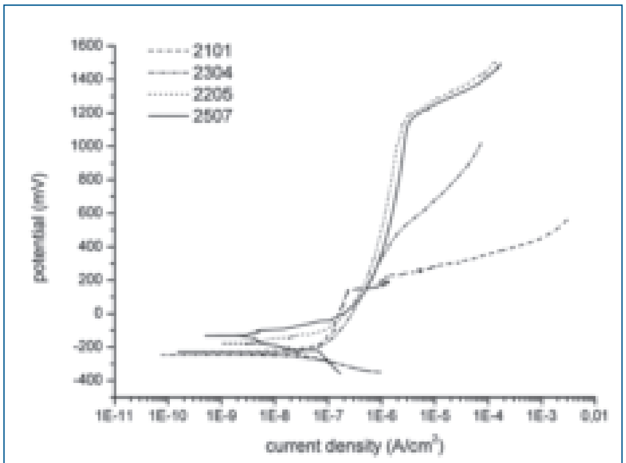


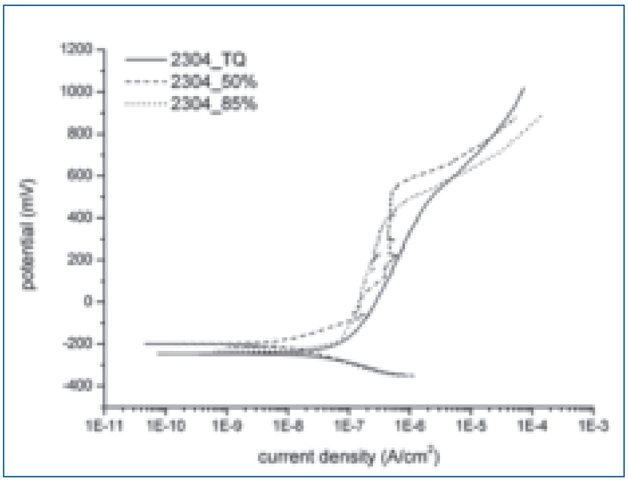

***Fig. 1 – Anodic polarization curves of the as-received materials.***

*Fig. 1 – Prove di polarizzazione anodica sui materiali allo stato di fornitura.*

### *Potentiodynamic tests at room temperature*

As expected, the as-received SAF 2205 and 2507 DSS exhibited excellent corrosion behaviours, significantly higher than SAF 2304 and 2101 (Fig. 1). In fact, although the absorbed current densities in passive condition were roughly comparable for all steels, the corrosion potential increased with $PRE_N$ index, and the potentials range of the passive behaviour was considerably wider for the high-alloyed grades, exhibiting a breakdown potential significantly higher than Lean DSS.
Respect to SAF 2101, a better overall behaviour of 2304 was registered. Free corrosion potentials and currents were similar for the two Lean DSS, but in SAF 2304 a greater stability in passive conditions was observed. Although in 2304 the highest content of Cr and Mo resulted in a negligible increasing in terms of $PRE_N$, the presence of higher amounts of such elements provided this steel an enhanced resistance to pitting corrosion, owing to their effect on the passive film stability. Furthermore, the higher content of Mn in SAF 2101 may be responsible for a further destabilization of the passive layer at potential next to breakdown.
Cold working did not substantially alter the pitting resistance of SAF 2304, 2205 and 2507, the oxide film was stable and the tests did not reveal significant variations by increasing the deformation degree. In the two high-alloyed grades, the corrosion curves at the various thickness reduction were superimposed each other, underlining the very high stability in aggressive environments, even after heavy plastic deformation whereas, in SAF 2304, only a slight decreasing in the transpassivity potential was observed at the highest deformation degree (Fig. 2a).
The corrosion behaviour of SAF 2101 was different. Although the plastic deformation implied a progressive decreasing in the breakdown potential, the passive film was stable up to 50% of deformation (Fig. 2b). Conversely, the highest thickness reductions caused a great destabilization of the protective layer, highlighted by a progressive rising in the absorbed current density as the scanning potential was increased. In this steel, the lower pitting resistance, coupled with the microstructural damage induced by cold working, determined an easy achievement of the critical conditions for the oxide layer breakage.

a)




b)

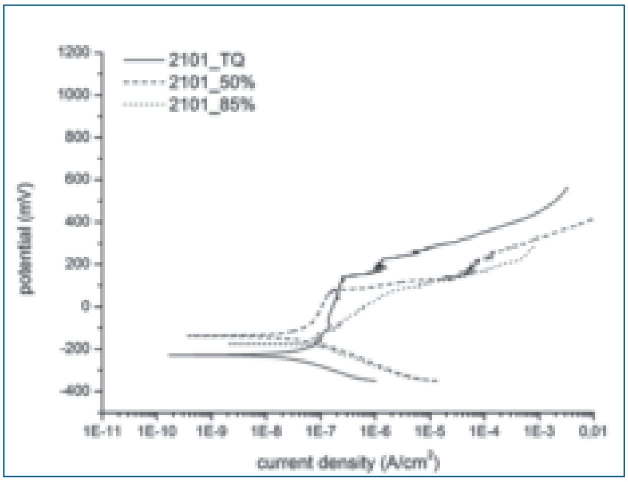



***Fig. 2 – Anodic polarization curves of the cold rolled materials: a) SAF 2304 and b) SAF 2101.***

*Fig. 2 – Prove di polarizzazione anodica a seguito di laminazione a freddo: a) SAF 2304 e b) SAF 2101.*

| SAF grade | 2101 | 2304 | 2205 | 2507 |
|---|---|---|---|---|
| CPT [°C] | 13 | 27 | 54 | 85 |

***Table 2 – Critical Pitting Temperatures (CPT) of the as-received DSS.***

*Tabella 2 – Temperature critiche di pitting (CPT) dei Duplex in esame nelle condizioni di fornitura.*

### *Critical Pitting Temperatures (CPT)*

The determination of the critical pitting temperature allows ascertaining a very useful parameter in the materials evaluation for applications in chlorinated environments. The rising in temperature introduces an additional variable for the assessment of the DSS resistance in an aggressive environment, which must be added to the contribution introduced by plastic deformation. As the temperature increases, the passive layer becomes thinner and more prone to localized attack, due to oxide dissolution rate higher than the growth rate of a new protective layer [13]. Other authors [14] has shown that the passive film becomes thicker and more porous at high temperatures, and thus less protective. In any case, the higher the temperature the weaker the protective properties of the passive film.
SAF 2304, 2205 and 2507, in the as-received conditions, exhibited CPT values approaching the upper limits of the expected ranges whereas, in SAF 2101, the CPT was very close to the lowest limit for its category (Table 2). In this latter steel, although an increase of ferrite content may lead to an improved performance of the austenitic phase, the content of Cr and Mo, characterizing the stability of the passive layer, is lower than in other grades. Moreover, the presence of a high amount of Mn can contribute to the pitting resistance worsening.

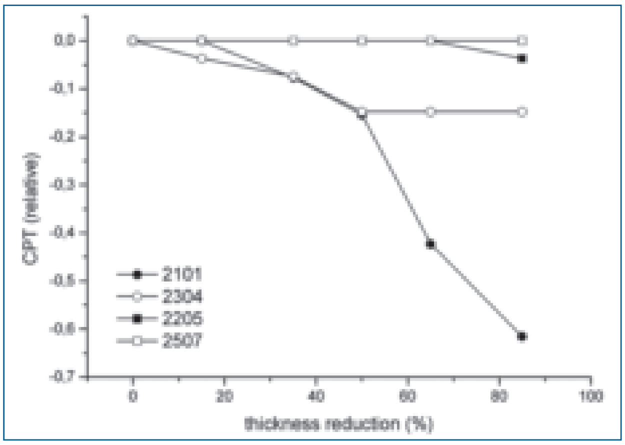



***Fig. 3 – CPT relative variation as a function of the deformation degree.***

*Fig. 3 – Variazione relativa della CPT all'aumentare della deformazione.*

In SAF 2507, cold rolling did not cause any change in CPT (Fig. 3), while in SAF 2205 only a decreasing of 4% was registered at the highest deformation degree. The corrosion resistance of these grades was very high, owing to the greater content of Cr, Mo and N which ensures an adequate stability of the passive layer, and of Ni and N as austenitic phase stabilizer. However, the slight reduction in CPT observed in SAF 2205 could be addressed not only to the disorder induced by plastic deformation, but also to the occurrence of the martensitic transformation [15].
The situation was different in Lean DSS, with SAF 2101 more affected by cold working. This steel is more prone to SIM formation, since the content of the strongly austenite-promoting elements (Ni and N) is very low and therefore the phase is not sufficiently stable at room temperature. Austenite is also the weakest phase against pitting and the occurrence of SIM would further compromise its corrosion behaviour. Here, SIM was found to continuously form for deformations exceeding 20–30% of thickness reduction [16], determining the observed progressive decreasing in CPT (Fig. 3).
In SAF 2304, the situation was rather similar to that of 2101 (Fig. 3). For this steel, the intermediate deformations caused a lowering in CPT of about 15%, while higher thickness reduction no more altered the CPT values. In this steel, the greater microstructural stability determined a smaller effect of plastic deformation than in SAF 2101, and the observed reduction at lower strains can be probably addressed to microstructure-related factors. However, the formation of SIM in SAF 2304 cannot be excluded and its behaviour in corrosive environments could be attributed to the formation of this new phase, although the verification of this hypothesis requires further study.

## CONCLUSIONS

DSS exhibit excellent resistance to corrosion in a wide range of corrosive media, particularly against pitting attacks. The performances of the as-received SAF 2101, 2304, 2205 and 2507 in artificial seawater (pH 7) were very satisfactory and the excellent behaviour of 2205 and 2507, also after cold-working, makes them preferred for applications in heavily chlorinated environments, where the higher cost is justified by their extraordinary pitting resistance.
On the contrary, the performances of SAF 2101 were significantly lower, making it not suitable for applications in highly corrosive environment, especially if subjected to cold deformation. In 2101, the presence of high Mn contents and the formation of the martensitic phase after cold working caused a significant destabilization of the passive layer and a global deterioration of the corrosion behaviour. The corrosion-resistance features in SAF 2304 were instead intermediate between SAF 2101 and the higher-alloyed grades, having breakdown potential close to that of 2101 but with a passive layer more stable, even after plastic deformation.
As expected, the CPTs confirmed the potentiodynamic tests. SAF 2507 exhibited the greatest microstructural stability, also after heavy cold deformation. In SAF 2205, only a slight decrease in CPT was observed at the highest thickness reduction, probably caused by the onset of a little amount of martensite. Conversely, in Lean DSS, cold rolling caused a reduction in CPT but, while in SAF 2304 this deterioration was mild (15%), a marked reduction was observed in SAF 2101, reaching the 25% of the initial value at the highest deformation degree. In both cases, the reduced corrosion resistance can be attributed not only to compositional factors and to the disorder induced by plastic deformation, but also to the formation of the Strain-Induced Martensite.

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## Effetto della laminazione a freddo sulla resistenza al pitting negli acciai inossidabili duplex

**Parole Chiave:** Acciaio inossidabile duplex - Corrosione per vaiolatura (pitting) - Deformazione plastica - Trasformazione di fase

Negli acciai inossidabili austeno-ferritici (Duplex), la migliore combinazione di proprietà meccaniche e di resistenza alla corrosione si ottiene in corrispondenza di uguali frazioni volumetriche delle fasi. Dato l'elevato contenuto di elementi in lega, i Duplex sono sensibili alla precipitazione di fasi secondarie nell'intervallo 300–600°C ed inoltre la fase austenitica può essere soggetta a trasformazione martensitica indotta da deformazione plastica a freddo. Dopo le operazioni di formatura, tutti i Duplex sono sottoposti a solubilizzazione e spegnimento in acqua, con lo scopo di conferire la caratteristica struttura bifasica e di ridisciogliere eventuali fasi secondarie formatesi durante il ciclo produttivo.

I Duplex vengono classificati in base alla loro resistenza alla corrosione per vaiolatura (pitting), valutata mediante l'indice PREN (Pitting Resistence Equivalent Number) che, seppure di carattere qualitativo, viene utilizzato come termine di confronto. Un parametro di maggior interesse è invece la Temperatura Critica di Pitting (Critical Pitting Temperature o CPT), definita come la temperatura sotto la quale il fenomeno del pitting non si verifica, anche dopo tempi indefinitamente lunghi e che, a differenza del $PRE_N$, tiene conto delle reali condizioni microstrutturali dell'acciaio.

Il presente lavoro si propone di studiare la resistenza al pitting di quattro categorie di Duplex (SAF 2101, 2304, 2205 e 2507) nelle condizioni di fornitura e a seguito di laminazione a freddo a varie riduzioni di spessore (da 15% a 50%), con lo scopo di mettere in luce gli eventuali effetti sul comportamento a corrosione. I risultati hanno evidenziato che la deformazione plastica condiziona il comportamento a corrosione delle sole categorie più basso-legate (SAF 2101 e 2304) ed in special modo quello del 2101, per il quale si è registrata una drastica diminuzione delle CPT alle più alte deformazioni. Al contrario, le categorie più alto-legate (SAF 2205 e 2507) sono risultate essere più stabili, anche a seguito di deformazioni molto spinte. Le differenze osservate possono essere imputate alla più elevata instabilità microstrutturale dei Duplex meno legati e al possibile insorgere di trasformazioni di fase generate della deformazione plastica, che rendono il materiale più sensibile all'attacco corrosivo.