Effect of multi-pass cold rolling on the corrosion properties of 2101 duplex stainless steel

edited by: L. Pezzato, C. Gennari, A.G. Settimi, I. Calliari, A. Kemény, I. Mészáros

Duplex stainless steels (DSS) are increasingly employed in the industry based on their combination of good mechanical properties and high corrosion resistance. These properties are achieved by stabilising quasi-equal volume fractions of the austenitic and ferritic phases at room temperature. The pitting resistance of a DSS is influenced by its chemical composition, presence of second phases, heat treatment, grain size, cold working, as-well-as surface roughness.

In this research, LDX 2101 (EN 1.4162) lean DSS is investigated at different grades of cold deformation (thickness reduction from 9% to 61%), obtained by multi-pass cold rolling. The effect of this type of cold-working method on the corrosion properties of the material was evaluated by means of potentiodynamic polarization tests at room temperature in 3.5 wt.% NaCl solution and of critical pitting temperature (CPT) evaluation in 1 M NaCl solution. The results of the corrosion tests were also linked with proper OM and SEM microstructural observation and with results of XRD tests. The results showed that the multi-pass cold rolling does not affect the corrosion properties of the investigated material with deformation steps that are <10%. Corresponding to this finding, the microstructural and phase analysis investigations proved that no strain-induced martensite was formed during the process.

The obtained results were also compared with single-pass cold-rolled properties of the material from a previous study pf the authors. As an effect of single-pass cold rolling, the same DSS (LDX2101) suffers a significant decrease of the CPT and destabilisation of the protective oxide layer with the thickness reduction. Therefore, this research shows that it is advisable to use multi-pass cold rolling instead of the single-pass method to reach high deformations without the deterioration of corrosion properties.

KEYWORDS: DUPLEX STAINLESS STEEL, MULTI-PASS PLASTIC DEFORMATION, CORROSION;

Luca Pezzato, Claudio Gennari, Alessio Giorgio Settimi, Irene Calliari
department Of Industrial Engineering, University Of Padua, Via Marzolo 9., I-35131 Padova, Italy
luca.pezzato@unipd.it

Alexandra Kemény
department Of Materials Science And Engineering, Faculty Of Mechanical Engineering, Budapest University Of Technology And Economics, Műegyetem Rkp. 3., H-1111 Budapest, Hungary; mta-Bme Lendület Composite Metal Foams Research Group, Műegyetem Rkp. 3., H-1111 Budapest, Hungary

István Mészáros
department Of Materials Science And Engineering, Faculty Of Mechanical Engineering, Budapest University Of Technology And Economics, Műegyetem Rkp. 3., H-1111 Budapest, Hungary

INTRODUCTION

Duplex Stainless steels (DSSs) are a category of high-alloyed steels characterized by a biphasic austeno-ferritic (c/a) microstructure obtained from a proper solution treatment after the forming operations. The presence of an equal volume fraction of the phases provides the best combination of mechanical and corrosion-resistance properties, making DSSs very interesting materials, especially for structural and special applications in aggressive environments. However, owing to the presence of the metastable austenitic phase and to the instability of ferrite at high temperatures, these steels are sensitive to diffusive and diffusionless phase transformations. (1–4) The eutectoidic decomposition of ferrite in the temperature range of 523 K to 1273 K (250 C to 1000 C) and its nitrogen-supersaturated condition are the main causes for precipitation of dangerous secondary phases. Further, the possibility of strain-induced martensite (SIM) formation from cold-worked austenite cannot be neglected if the phase is not adequately stabilized. (5) Both the fact can negatively affect the corrosion properties of the DSS. In particular the presence of secondary phases negatively affect the corrosion properties of the material due to the local depletion of Cr from the matrix (6) whereas the formation of the Strain-Induced Martensite (SIM) from the metastable austenite can substantially affect the pitting resistance of stainless steels (7), because the number of the active anodic sites in the surface are increased (8,9). Thickness, composition and uniformity of the passive layer are modified in different extent by plastic deformation (10,11) and the increasing in dislocation density favors the film dissolution, due to the presence of lower binding energy regions, if compared to a perfect crystal. In a previous work (12), the authors study the influence of single-pass cold rolling on the corrosion properties of different DSS, however a change in deformation mode influences SIM formation, causing a stress-state dependence of transformation kinetics. In the present work, the pitting resistance of 2101 DSS in as-received conditions and after multi step cold rolling is presented an compared with the ones previously obtained after single pass cold rolling with the aim to highlight the effects of different cold deformation modes on the corrosion behavior of lean duplex stainless steel.

MATERIALS AND METHODS

Chemical composition of 2101 steel is reported in Table 1.

Tab.1 - Chemical composition of 2101 DSS.

Fe%	C%	Si%	Mn%	P%	S%	Cr%	Mo%	Ni%	Al%	Cu%	N%
70,85	0,028	0,669	4,61	0,026	0,003	21,26	0,20	1,60	0,022	0,316	0,248

The as-received materials were cold rolled at various deformation degrees (from 9% to 61% of thickness reduction). The starting thickness of the sheet was 4 mm and each reduction were obtained with multi-pass mode with 0.25 mm of reduction for each pass. The samples after the various thickness reduction were polished with standard metallographic techniques (grinding with abrasive paper and polished with clothes and diamond suspensions) and the microstructure was studied by means of optical and electron microscope observation. The etched microstructures (Beraha's etching) were observed using a Leica Cambridge Stereoscan 440 scanning electron microscope (SEM; Cambridge Instruments Ltd., Cambridge, UK) whereas for OM observation a Leica DMR light optical microscope (OM; Leica Microsystems, Wetzlar, Germany) was employed. Austenite/ferrite ratio in the different samples was evaluated with XRD measurements using a siemens D500 diffractometer (Siemens Corporation, Cherry Hill, NJ) using Cu Ka radiation (step size of 0.05 deg and 5 seconds of counting time for each step). Vickers Micro-Hardness tests were performed on both the phases in the different samples. Corrosion resistance of the as-received material and of the samples after the cold deformation process was analyzed with potentiodynamic polarization tests (PDP) and critical pitting temperature tests (CPT). Potentiodynamic polarization tests were performed using an AMEL 2549 potentiostat and by immersing the samples in a pH 7 electrolyte solution composed by 35 g/l of NaCl in deionized water. All tests were conducted at room temperature, using calomel as reference electrode and platinum as counter electrode; for all tests, a scanning rate of 0.0005 V/s was applied. PDP tests were performed in triplicate to assure reproducibility and is reported one representative curve for each sample. The determination of the CPT was carried out by following the ASTM G150 standard (13), 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 thermostatic bath. The ASTM standard states the evaluation of the CPT by maintaining a constant potential of 700 mV and increasing the temperature of the thermostatic cell at the rate of 1°C/min; the CPT is defined as the temperature at which the anodic current exceeds 100 μA/cm².

RESULTS AND DISCUSSION

The as received sample (0% of thickness reduction) and the samples cold rolled with multipass rolling at 9, 24, 45 and 61% of thickness reduction were first of all observed at the OM and the results are reported in Fig.1. In all the samples both austenite and ferrite grains resulted elongated along the deformation direction. Increasing the thickness reduction, and in particular in the samples with 24, 45 and 61 % of thickness reduction, a fragmentation of the grains can be noted.

Fig.1 - OM micrographs of the samples with 0% (A), 9% (B), 24% (C), 45% (D) and 61% (E) of thickness reduction.

Considering the SEM micrographs, reported in Fig.2, can be noted in the images taken at lower magnification (sample 0% and 9%) the good balance between austenite and ferrite phases. Considering the more deformed samples (24, 45 and 61 %) the SEM images taken at higher magnification evidence the presence of slip bands that also intersected between each other's. This can be an indication of SIM formation but can also be due to deformation process.

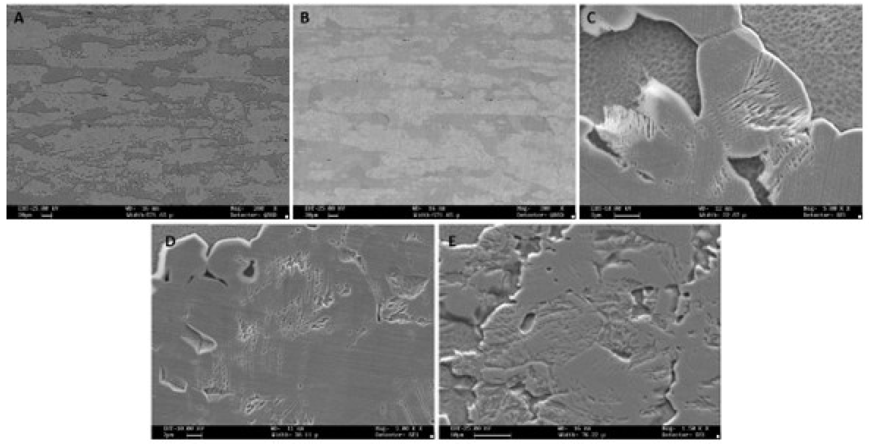

Fig.2 - SEM micrographs of the samples with 0% (A), 9% (B), 24% (C), 45% (D) and 61% (E) of thickness reduction.

The hardness of the bulk and of the single phases (austenite and ferrite) was evaluated through Vickers microhardness tests and the values were obtained from an average of four total measurements and the results are reported in Fig.3. As can be observed the micro-hardness increases as the degree of deformation increases, or as the thickness of the various samples decreases. This behavior is related to the increase in the work hardening of the material during the deformation process.

Also, austenite/ferrite ratio was analyzed with X-ray diffraction method and the results are reported in Tab.2 but no significant trend between the relative quantity of the phases and the grade of deformation can be found.

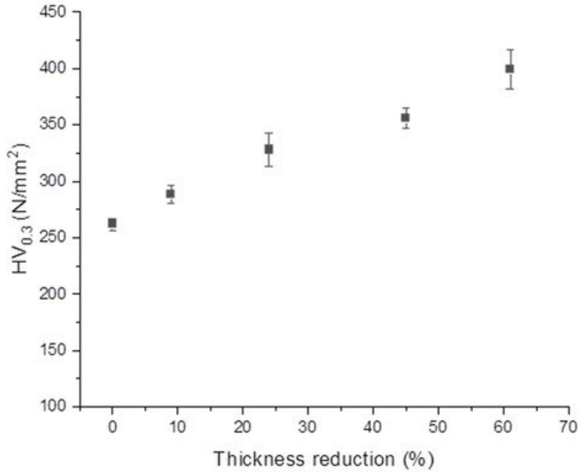

Fig.3 - Micro-Hardness values recorded in the whole material in the samples with the various thickness reduction.

Tab.2 - Ferrite and austenite content evaluated through XRD method.

Sample	Ferrite Content %	Austenite Content %
0%	56	44
9%	50	50
24%	62	38
45%	68	32
61%	58	42

The corrosion resistance of the different samples was analyzed by means of PDP tests and CPT tests and the results are reported in Fig.4 and Tab.3. From the observation of the PDP curves cannot be observed a significant difference in the corrosion behavior of the samples with the different deformation grades. In fact, all the curves are substantially overlapped, with very similar values of corrosion potentials and corrosion current densities (see Tab.3 for the values) and also similar passive regions. Pitting potential for the as received sample and for the deformed samples is in the range 0.1-0.2 V Vs SCE, in accordance with previous work of the authors (6) and with the literature (14). The presence of pits was clearly observable on the samples surfaces after the test. Also, CPT values, recorded accordingly to ASTM G150 standard and reported in Tab.3, does not vary significantly with the deformation grade and remain in all the samples in a range between 13 and 16 °C that are the standard for 2101 DSS. (6) Generally the presence of SIM remarkably reduces the corrosion properties of the material, so this result, together with the absence of a clear trend in the austenite/ferrite ratio, can be considered as an important indication of the fact that SIM probably is not formed in 2101 DSS with multi-pass cold rolling. In order to experimentally confirm the absence of SIM more advanced characterization technique (i.e. Neutron Diffraction) should be done. This result is the opposite of what was previously found by the authors with single pass cold rolling (5), this evidencing that the type of deformation plays a key role. In particular with single pass cold rolling was found a reduction of almost 50% of the CPT with 60% of cold deformation whereas with multi-pass cold rolling the CPT at 61% of thickness reduction was the same of the as received material.

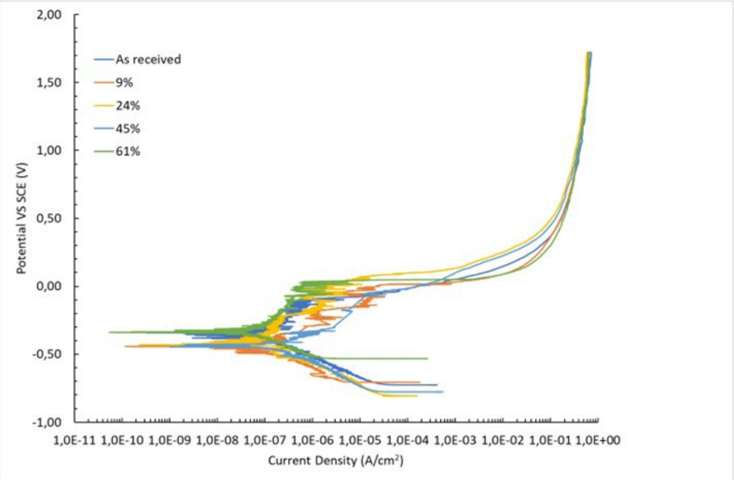

Fig.4 - Potentiodynamic polarization plots recorded in 3.5% NaCl solution for the samples with the different thickness reduction.

Tab.3 - Values of the corrosion potential, corrosion current density and of the critical pitting temperature for the samples with different thickness reduction.

Sample	Ecorr (V)	Icorr (A/cm²)	T PIT (°C)
0%	-0.34	1,90x10⁻⁷	14
9%	-0.44	1,50 x10⁻⁷	16
24%	-0.43	2,50 x10⁻⁷	13
45%	-0.46	2,20 x10⁻⁷	15
61%	-0.34	1,50 x10⁻⁷	13

CONCLUSIONS

The cold plastic deformation of a lean DSS 2101, introduced by multi-pass cold rolling, did not affect the corrosion properties of the material. This can be related with the fact that probably deformation-induced martensite does not form with the multi-pass process. This fact is also confirmed by the XRD measurements, that does not evidence a clear correlation between deformation grade and austenite/ferrite ratio, and by the microstructural analysis that evidence only a slight fragmentation and elongation of the phases along the rolling direction.

The results of this study were compared with the ones of another study of the authors in which the effect of single-pass rolling deformation on 2101 DSS was studied. In this case, the material undergoes a significant decrease in corrosion resistance, due to the formation of SIM during the deformation process.

Therefore, this work proves that it is more advantageous to use a multi-pass cold rolling rather than the single pass method to produce cold deformation on 2101DSS, as the first method does not negatively alter its corrosion properties.

ACKNOWLEDGEMENTS

Ing. Marco Frigo from Outokumpu is kindly acknowledged for providing the material for this study.

REFERENCES

[1] Alvarez-Armas I, Degallaix S. Duplex Stainless Steels [Internet]. Hoboken, New Jersey Usa: Wiley-VCH Verlag; 2009. 464 p. Available from: https://www.wiley.com/en-us/Duplex+Stainless+Steels-p-9781848211377

[2] Gunn RN. Duplex Stainless Steels Microstructure, Properties and Applications [Internet]. Cambridge UK: Woodhead Publishing; 1997. 204 p. Available from: https://www.sciencedirect.com/book/9781855733183/duplex-stainless-steels

[3] Nilsson JO. The physical metallurgy of duplex stainless steels. In: In Proceedings of the Duplex Stainless Steels 97: 5th World Conference. Maastricht; 1997. p. 73–82.

[4] Nilsson JO. Super duplex stainless steels. Mater Sci Technol (United Kingdom). 1992;8(8):685–700.

[5] Breda M, Brunelli K, Grazzi F, Scherillo A, Calliari I. Effects of Cold Rolling and Strain-Induced Martensite Formation in a SAF 2205 Duplex Stainless Steel. Metall Mater Trans A Phys Metall Mater Sci. 2015;46(2):577–86.

[6] Pezzato L, Lago M, Brunelli K, Breda M, Calliari I. Effect of the Heat Treatment on the Corrosion Resistance of Duplex Stainless Steels. J Mater Eng Perform [Internet]. 2018;27(8):3859–68. Available from: https://doi.org/10.1007/s11665-018-3408-5

[7] Gennari C, Lago M, Bögre B, Meszaros I, Calliari I, Pezzato L. Microstructural and corrosion properties of cold rolled laser welded UNS S32750 duplex stainless steel. Metals (Basel). 2018;8(2):1–17.

[8] Randak A, Trautes FW. Uber den EinfluB der Austenitstabilitiit von 18 / 8-Chrom- Nickel-Stahlen auf die Verformungseigenschafien und auf das Korrosionsverhalten dieser Stahle "). Mater Corros. 1970;21(2):97–109.

[9] Elayaperumal K, De PK, Balachandra J. Passivity of Type 304 Stainless Steel-Effect of Plastic Deformation. Vol. 28, Corrosion. 1972. p. 269–73.

[10] Phadnis S V., Satpati AK, Muthe KP, Vyas JC, Sundaresan RI. Comparison of rolled and heat treated SS304 in chloride solution using electrochemical and XPS techniques. Corros Sci. 2003;45(11):2467–83.

[11] Naval F. Effects of tensile and compressive stresses on the passive layers formed on a type 302 stainless steel in a normal sulphuric acid bath. Vol. 30, Journal of Materials Science. 1995. p. 1166–72.

[12] Breda M, Pezzato L, Pizzo M, Calliari I. Effect of cold rolling on pitting resistance in duplex stainless steels. Metall Ital. 2014;106(6):15–9.

[13] ASTM-G150 Standard Test Method for Electrochemical Critical Pitting Temperature Testing of Stainless Steels and Related Alloys-2018 Edition

[14] Huang TS, Tsai WT, Pan SJ, Chang KC. Pitting corrosion behavior of 2101 duplex stainless steel in chloride solutions. Corrosion Engineering, Science and Technology. 2018; 53:9-15

TORNA ALL'INDICE >