This is a postprint version of the following published document:

Álvarez, S., Bautista, A., Velasco, F. (2013). Influence of process parameters on the corrosion resistance of corrugated austenitic and duplex stainless steels. *Materials and Technology*, vol. 47, no. 3, pp. 317-321. Avalaible in http://mit.imt.si/Revija/izvodi/mit133/alvarez.pdf.

INFLUENCE OF PROCESS PARAMETERS ON THE CORROSION RESISTANCE OF CORRUGATED AUSTENITIC AND DUPLEX STAINLESS STEELS

Sandra M. Alvarez, Asunción Bautista, Francisco Velasco

Universidad Carlos III de Madrid, Materials Sci. and Eng. Dept – IAAB, Avda. Universidad 30, Leganés, Madrid, Spain
asuncion.bautista@uc3m.es

The main objective of this work is to study the influence of the forming process on two corrugated, lean, duplex stainless steels (DSSs): UNS S32001 and UNS S32304. Both grades have been recently proposed as alternative materials to the austenitic UNS S30403 grade for manufacturing reinforcement bars to be embedded in concrete structures, exposed to corrosive environments. Hot-worked (HW) corrugated bars of both DSSs are analyzed and their corrosion behaviour is compared with that of the HW and cold-worked (CW) corrugated bars of S30403.

The corrosion performance is characterized through cyclic polarization curves in 8 different solutions that simulate those contained inside the pores of concrete in different circumstances.

The obtained results justify a great interest in the studied lean DSS grades with respect to their use as reinforcements. Moreover, it is proved that the corrugated surface of a bar is clearly less corrosion resistant than the centre of the bar. The processing method of producing reinforcements influences not only the pitting susceptibility but also the pitting morphology.

Keywords: corrosion, stainless steel, reinforcements, processing, lean duplex

1 INTRODUCTION

The use of stainless-steel corrugated bars instead of carbon steel bars in those parts of reinforced concrete structures that are more exposed to corrosion is one of the most reliable strategies for assuring the durability of a structure.[1] Initially, austenitic grades were used with this objective.[2]

Duplex stainless steels (DSSs) have shown a good corrosion resistance in many media. With respect to the reinforced concrete exposed to aggressive environments, corrosion studies have shown advantages of the traditional UNS S32205 DSS reinforcements in comparison with the most common austenitic grades[3,4] and they started to be used for corrugated bars about ten years ago. Recently, two more economical DSSs have been proposed for their use in concrete,[5] not for replacing the S32205 reinforcements used in extremely aggressive conditions, but as an alternative to the corrugated bars of the austenitic UNS S30403 grade.

UNS S32304 DSS, considered in the present study, has a low Mo-content and it has been known for years. Since 2003 its use has been growing in desalinization industries, marine applications or production processes, replacing the austenitic UNS S31603 steel. UNS S32001 is the other DSS evaluated in this study. It is a very novel DSS grade, lower alloyed than S32304, with smaller Ni and Cr contents, i.e., cheaper.

There are scarce references about the corrosion behaviour of these lean DSS grades and most of the studies consider the environments very different form concrete. Special chemical characteristics of the solution inside concrete pores introduce factors that modify the protective ability of the passive layers on stainless steels. These characteristics are different from the ones shown by the materials that are exposed to the atmosphere or to other environments.[6] Most authors also agree that a higher alkalinity in a pore solution has a positive impact on the corrosion behaviour of stainless steel,[4–8] though the issue remains controversial.[9]

Moreover, to be used as reinforcements in concrete structures, the stainless steels must be hardened during the processing[10] and their surface must be formed into corrugations to assure a good adherence with the concrete. There are factors that many of the previous corrosion studies on stainless steels in simulated pore solutions have not considered, as they were carried out in stainless steels that were not formed as corrugated bars.[11–14] However, recent studies suggest that the forming process of corrugated bars can dramatically affect the corrosion behaviour of austenitic stainless steels in alkaline solutions with chlorides.[15]

2 EXPERIMENTAL WORK

Four different stainless-steel grades were considered in the study, two corrugated, lean, duplex stainless steels (DSSs): the UNS 32001 and UNS S32304 hot-worked (HW) corrugated bars and two austenitic UNS S30403, HW and cold-worked (CW) corrugated bars. The products were manufactured by Roldán S. A. (Acerinox Group, Spain). The diameters of the corrugated bars considered in the study as well as their chemical compositions can be seen in **Table 1**. The chemical compositions of the bars were experimentally determined with X-ray fluorescence (XRF), using a Spectre XEPOS equipment.

The corrosion behaviour of different places (core and surface) of the corrugated stainless steels was characterized with cyclic polarizations curves, using an EG&G 263A galvanostat- potentiostat from Princeton Applied Research. Electrochemical measurements were carried out in the solutions that simulate those contained in the concrete pores in different conditions. Saturated $Ca(OH)_2$ solutions (pH ≈ 13), simulating non-carbonated concrete, with four different NaCl contents in mass fractions were used: (0, 0.5, 1 and 5) %. The saturated $Ca(OH)_2$ solutions, whose pH values decreased to about 9 due to CO_2-bubbling, were used to simulate the behaviour in carbonated concrete. Chloride contents of (0, 0.5, 1 and 5) % were also considered for carbonated solutions.

The testing procedure was based on the ASTM G61 Standard. Cyclic polarization curves were carried out using a three-electrode cell. A saturated calomel electrode (SCE) was used as the reference electrode and a stainless-steel mesh as the counter-electrode. Samples of the corrugated stainless-steel bars acted as working electrodes. The measurements were carried out after a 48-h exposure of the stainless-steel samples to the testing solution to assure the correct stabilization of the corrosion potential (E_{corr}). The sweeping rate was 0.17 mV/s. The potential was reversed when the current densities reached a value of 10^{-4} A/cm^2.

To study the corrosion behaviour of a corrugated surface, samples 2 cm of the real surfaces of the bars were exposed to the corresponding testing media. The corrosion behaviour of the non-corrugated materials was analyzed exposing the samples from the centres of the bars to the testing solutions. For the samples from the centres of the bars, an Avesta cell was used to assure the absence of crevices that could interfere with the measurements.

An analysis of the morphology of the attack after the polarization curves was carried out with scanning electronic microscopy (SEM) using a Philips XL30 equipment.

3 RESULTS AND DISCUSSION

The polarization curves of the corrugated surfaces and the centres of the stainless-steel bars clearly exhibit different shapes, as can be seen in **Figure 1**, where the curves corresponding to the non-carbonated solutions with 5 % NaCl are shown. For the samples without corrugations (**Figure 1a**), the pitting potential (E_{pit}) is well defined and corresponds with very sharp current increases. On the other hand, in the tests carried out on the real surfaces of the bars (**Figure 1b**), the current increase after E_{pit} is less pronounced. It must be pointed out that on certain materials exposed to particular testing conditions, no corrosion occurred during the test. This is the case, for example, of the centre of the HW S32304 bar in a non-carbonated solution with 5 % NaCl (**Figure 1a**), where the current increase does not correspond to any corrosion phenomenon but it is due to the water decomposition through reaction 1:

$$4OH^- \rightarrow 2H_2O + O_2 + 4e^- \quad (1)$$

In the case of a sudden current increase and the absence of hysteresis during the reverse cycle, the potential value confirms that no corrosion has taken place during the test.

The $E_{pit} - E_{corr}$ distance is widely considered to be a reliable way of measuring the resistance to localized corrosion. The E_{corr} values of all the systems considered in this study are very similar. The E_{pit} values plotted in

Table 1: Diameters of corrugated bars and experimentally determined chemical compositions of the studied stainless steels

Stainless steel	Diameter *d*/mm	Main alloying elements, *w*/%								
		S	Si	Mn	Cr	Ni	Mo	N	C	Fe
CW S30403	10	0.001 0	0.361	1.45	18.30	8.68	0.27	0.050	0.023	Bal.
HW S30403	16	0.001 2	0.298	1.42	18.37	8.74	0.27	0.055	0.026	Bal.
HW S32001	16	0.001 0	0.681	4.14	19.98	1.78	0.24	0.124	0.025	Bal.
HW S32304	16	0.002 0	0.651	1.54	22.70	4.47	0.26	0.153	0.017	Bal.

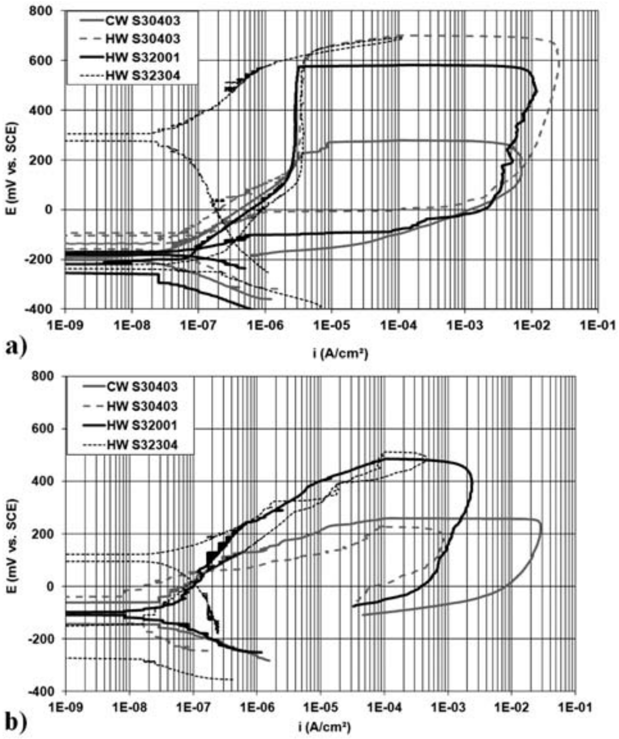

Figure 1: Polarization curves in non-carbonated $Ca(OH)_2$ solutions with 5 % NaCl: a) centres of the bars, b) corrugated surfaces

Slika 1: Polarizacijske krivulje v negazirani raztopini $Ca(OH)_2$ s 5 % NaCl: a) sredina palice, b) rebrasta površina

Figures 2 and **3** can be an adequate tool for comparing the corrosion behaviours of stainless steels in different conditions.

It is very interesting to find a significant decrease in the corrosion resistance of the bars due to the changes to the corrugations taking place during the forming process. **Figure 2** shows the difference between the E_{pit} values of the studied stainless steels in carbonated solutions, with the measurements carried out on the corrugated surfaces

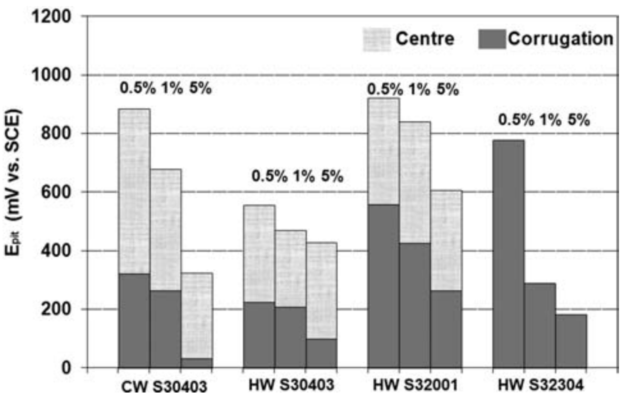

Figure 2: Differences between the E_{pit} measured in the centres of stainless-steel bars and on corrugated surfaces in carbonated $Ca(OH)_2$ solutions with different chloride contents

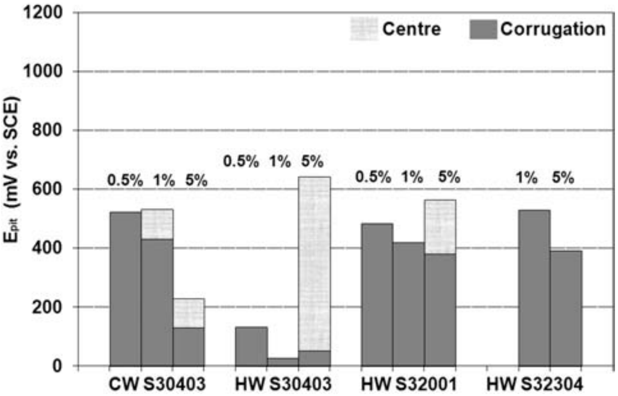

Figure 3: Differences between the E_{pit} measured for the centres of stainless-steel bars and for the corrugated surfaces in non-carbonated $Ca(OH)_2$ solutions with different chloride contents. Conditions without the plotted E_{pit} values correspond to tests where no corrosion takes place.

or in the centres of the bars. As in some cases the definition of E_{pit} is not easy, the potential, at which the anodic current reaches the value of 10^{-4} A/cm^2, has been chosen as the criterion for determining this parameter.

The marked difference between the E_{pit} values, corresponding to the corrugated surface and to the other regions of a bar, emphasises the effect of the process parameters. It would be risky to extrapolate the results of the stainless steels processed in the way different from that of the corrugated bars to the performance in concrete, though it has been often done in literature. These data confirm the trend observed in the recently published work on more traditional austenitic stainless steels.[15] The minor corrosion resistance of a corrugated surface of stainless steel has been explained with a more deformed microstructure and a higher stress concentration in the corrugation than found in the centre of the bar.[15] Different grain sizes and grain morphologies of the corrugations and of the centres of the bar were studied previously for the reinforced bars considered in our earlier work,[16] and the obtained results proved that the corrugations exhibit a highly deformed microstructure with a reduced grain size.

In the carbonated solutions without chlorides, no corrosion was detected for any of the studied stainless steels. Moreover, the centres of the HW S32304 bars proved to be immune to corrosion during the polarization tests carried out independently of the chloride content of the carbonated solution. However, during the polarization of the corrugated surfaces of HW S32304 in the presence of chlorides, current increases corresponding to a corrosive attack were detected, even with 0.5 % NaCl.

For the other three studied stainless-steel grades, a localized corrosion always occurred during the polarization tests in the carbonated solutions with chlorides.

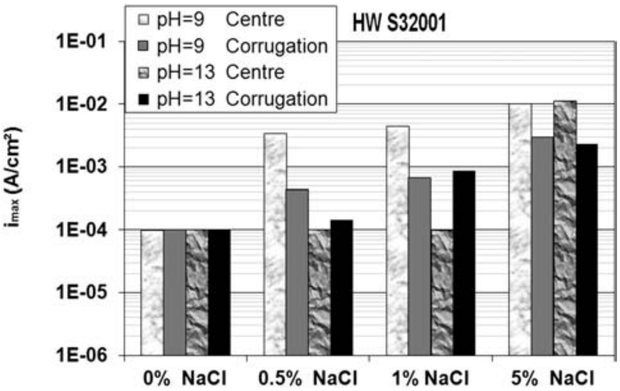

Figure 4: Differences between the i_{max} values obtained with the polarization curves for the centres and the corrugated surfaces of duplex HW S32001 bars in carbonated and non-carbonated $Ca(OH)_2$ solutions with different chloride contents

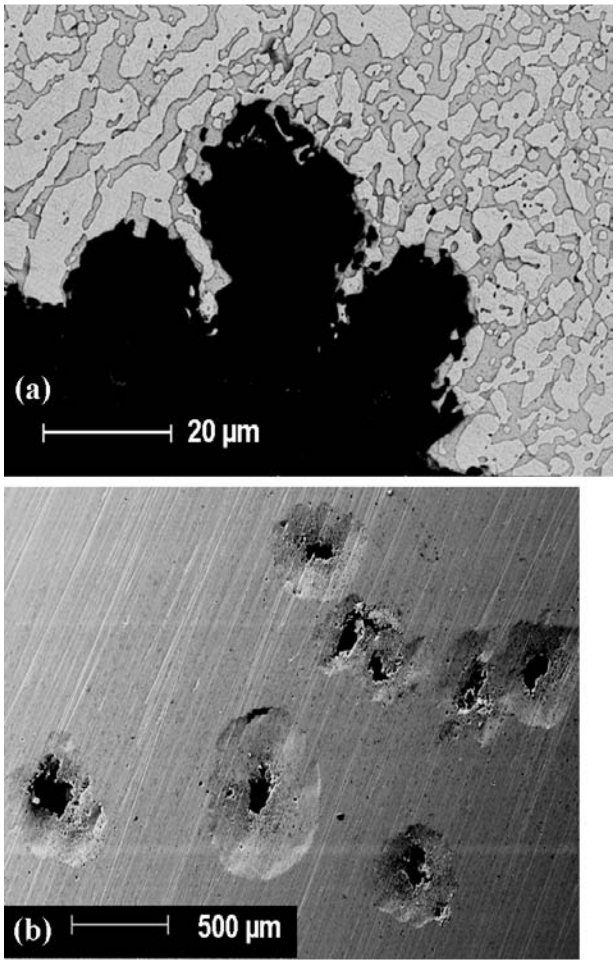

Figure 5: Images of different morphologies of the attacks that appear on the centre of a bar and on the corrugated surface. The pits after the polarization of HW S32001 in non-carbonated $Ca(OH)_2$ solutions with 5 % NaCl: a) corrugated surface, b) center of the bar.

For all the materials the E_{pit} of the corrugated surface is much lower than the E_{pit} of the centre of a bar.

As expected, in all the cases an increase in the chloride content of the solution causes a decrease in the resistance to localized corrosion, i.e., a decrease in E_{pit}.

In **Figure 3**, the E_{pit} values detected in non-carbonated solutions are plotted. It can be seen that, at a higher pH, it is more difficult to cause corrosion during the test. In the solutions without chlorides, no corrosion occurs in any of the cases and the centre of HW S32304 is immune to the attacks in the testing media with chlorides, as reported for pH $\approx$ 9. Besides, no corrosion occurs during the polarization in the solutions with 0.5 % NaCl on the centres of the other studied bars. In the case of the 1 % NaCl testing solution, no corrosion was found on the centres of HW S30403 or HW S32001.

The corrugated surfaces of the bars prove again to be much more prone to corrosion. For this type of samples, the only condition where no pitting is detected is HW S32304 with 0.5 % NaCl. The important influence of the microstructural changes occurring in the surfaces of the corrugated bars during the forming process is again clearly proved.

If the results from **Figures 2** and **3** are used to compare the corrosion behaviours of different grades, it is demonstrated that HW S32304 is clearly more corrosion resistant than any of the studied austenitic grades. Despite the volatility of the prices in the market, it can be considered that a S32304 grade can cost about 9 % less than a S30403 grade. This result justifies the great interest in this DSS grade that is seen as an alternative for the traditional austenitic grade used in these applications, as S32304 has a better performance and it is somewhat more economical. The DSS S32001 grade can be estimated to be about 15 % cheaper than the austenitic S30403. The results of the corrosion tests carried out indicate that the corrosion resistance of both grades are quite similar, or that the corrosion resistance of the cheap, new DSS grade is even better.

In addition to E_{pit}, another interesting parameter, which can be obtained from the polarization curves, is the maximum intensity (i_{max}) reached during the measurements. All the curves are programmed to reverse the potential sweep when a current intensity of 10^{-4} A/cm^2 is reached. When no corrosion occurs, i_{max} is 10^{-4} A/cm^2, as the current quickly decreases when the applied potentials decrease. When pits are formed during the anodic polarization, the current still increases as the potentials start to decrease due to the important autocatalytic effect of the localized corrosion. The higher the i_{max}, the more dangerous is the pitting morphology. As an example, the values of this parameter for sixteen tested conditions of HW S32001 were plotted in **Figure 4**. If the conditions, under which no corrosion takes place, are not considered (0 % NaCl and the centre of the bar for 0.5 and 1 % NaCl at pH ≈ 13), it can be seen that the samples from the centre of the bar, though less susceptible to corrosion than the corrugated surfaces, suffer from a more aggressive attack than when it occurs on the surface. The same conclusion is reached if the results for the other four studied materials are analyzed. It can also be seen in **Figure 4** that chlorides have an important influence on the increase of i_{max}.

An observation of the morphology of the pits after the polarization curves confirms the idea deduced from the i_{max} values. As it can be seen in **Figure 5**, the polarization causes small, shallow pits widely distributed on the most deformed regions of the surface of the corrugation. In the centre of the bar, polarizations cause scarce, but much bigger pits that can be much more dangerous.

4 CONCLUSIONS

The susceptibility to pitting corrosion on the corrugated surface of corrugated stainless steel is always much higher than in the centre of the bars of the same material. The forming process clearly decreases the corrosion resistance of stainless steel used as a reinforcement material in concrete structures.

The attack that appears on the corrugated surfaces of stainless steels during an anodic polarization is less localized and less dangerous than the attack that appears in the centres of the bars.

The new lean DSSs for reinforcing bars are very interesting options for substituting the traditional austenitic S30403 bars. S32304 clearly exhibits a better corrosion behaviour being also somewhat cheaper. S32001 is highly interesting from an economic point of view and its corrosion results are similar, even slightly better, than those of S30403.

5 REFERENCES

[1] U. Nürberger (Ed.), Stainless steel in concrete, State of the art report, Publication n° 18, Institute of Materials, London, 1996

[2] L. Bertolini, P. Pedeferri, Corrosion Reviews, 20 (**2002**), 129–152

[3] A. Bautista, G. Blanco, F. Velasco, A. Gutiérrez, S. Palacín, L. Soriano, H. Takenouti, Materiales de Construcción, 57 (**2007**), 17–32

[4] A. Bautista, G. Blanco, F. Velasco, Cement and Concrete Research, 36 (**2006**), 1922–1930

[5] S. M. Alvarez, A. Bautista, F. Velasco, Corrosion Science, 53 (**2011**), 1748–1755

[6] A. Bautista, G. Blanco, F. Velasco, A. Gutiérrez, L. Soriano, F. J. Palomares, H. Takenouti, Corrosion Science, 51 (**2009**), 85–792

[7] M. Kouril, P. Novak, M. Bojko, Cement Concrete Research, 40 (**2010**), 431–436

[8] L. Bertolini, F. Bolzoni, T. Pastore, P. Pedeferri, British Corrosion Journal, 31 (**1996**), 218–222

[9] L. Freire, M. J. Carmezim, M. G. S. Ferreira, M. F. Montemor, Electrochimica Acta, 55 (**2010**), 6174–6181

[10] Guidance on the use of stainless steel reinforcement, Technical report N° 51, The Concrete Society, London, 1998

[11] M. Kouril, P. Novak, M. Bojko, Cement Concrete Composites, 28 (**2006**), 220–225

[12] L. Veleva, M. A. Alpuche-Avilés, M. K. Graves-Brook, D. O. Wipf, Journal of Electroanalytical Chemistry, 578 (**2005**), 45–53

[13] B. Elsener, D. Addari, S. Coray, A. Rossi, Electrochimica Acta, 45 (**2011**), 4489–4497

[14] S. Fajardo, D. M. Bastidas, M. Criado, M. Romero, J. M. Bastidas, Construction and Building Materials, 25 (**2011**), 4190–4196

[15] E. C. Paredes, A. Bautista, S. M. Alvarez, F. Velasco, Corrosion Science, 58 (**2012**), 52–61

[16] S. M. Alvarez, A. Bautista, F. Velasco, S. Guzman, Proceedings of the 7th European Stainless Steel Conference, Como, Italy, 2011