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Corrosion of Conductor Rolls in an Electro galvanizing Line

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Abstract

Conductor rolls in continuous cold rolled steel strip horizontal acid electro galvanizing lines after some period of service suffer a surface deterioration that alters its color, aspect and eventually its roughness what is more deleterious to its good performance. The surface degradation finally produce a pattern on the roll surface that is transferred or copied to the electro galvanized strip surface originating quality defects that could make some level of rejections in high quality products. This process has been historically thought as an erosion-corrosion one. This work shows some interesting results that help in the understanding of the nature of this specific corrosion mechanism. It is also presented a new method capable of evaluate the corrosion resistance of new materials for construction of conductor rolls for this type of industrial process. Finally a comparison of the corrosion resistance of different alloys using this technique was made.

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Keywords: Corrosion, Stainless Steel, Conductor roll, Electro galvanizing, nickel alloys

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1. Introduction

Conductor rolls in steel strip acid electrogalvanizing lines always face a strong challenge regarding corrosion performance. Line stops for roll changes, regrinding, short roll operating life and eventually product rejection associated to the surface degradation of conductor rolls are all well known in the electrogalvanizing industry. This problem is critical when high quality products for exposed automotive use are produced. The selection criteria for conductor roll construction materials is usually based on some standards while very exigent for corrosion resistance evaluation of alloys against oxidant media, they do not represent the actual working conditions (R.W. Revie, 2000, L.L. Shreir, 1994, and ASM Handbook Vol. 13B and 13C). A cyclic anodic current treatment that accelerates the corrosive attack on stainless steel and other alloys has been proposed by R. Rebak, 1997 but this is not the real case of a conductor roll connected to the cathode of an electrochemical system either. Townsend et al., 1990, presented a more realistic cyclic connection and disconnection of zinc electrodes to stainless steel but with no in field validation of the correct electrochemical potentials.

In this work, the usual conventional parameters that characterize a corrosive system (corrosion potential, corrosion current, polarization curves) were measured and a surface electrochemical potential measuring system was designed. This system proved to be successful for the determination of the actual electrochemical potential of roll and strip surfaces during operation in the electrogalvanizing line without altering its normal production speed. In this way, the real corrosive condition of the rolls and the strip were evaluated. Besides, an electrochemical treatment that reproduces the actual industrial corrosive situation was designed: this allows corrosion resistance evaluation of different alloys that could be used for conductor rolls construction and moreover, the method could be easily adapted to different line configurations and process conditions.

2. Experimental

2.1. In situ conductor roll and steel strip electrochemical potential determination.

To evaluate the conductor rolls in real working conditions at one horizontal acid electrogalvanizing line, a system to determine conductor roll and steel strip electrochemical potentials was designed. A special saturated calomel reference electrode (SCE) was built to be used at the production line working media. A 1.5 meter long reference electrode holder helped to reach different positions along the roll length and diameter and strip width without changing the line speed. A rubber flap attached to the holder allowed the electrolyte accumulation for SCE tip immersion. Figure 1 shows how the electrochemical potentials were measured on the conductor rolls and the steel strip.

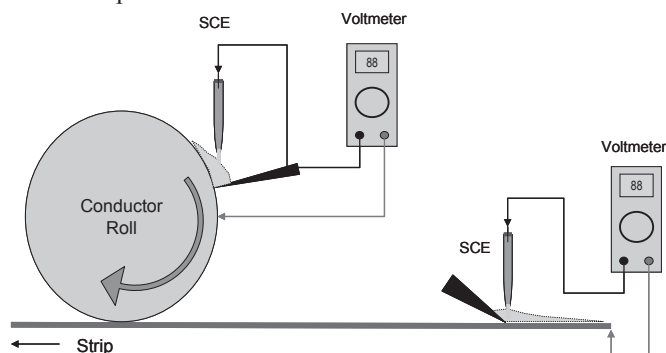


Figure 1. On line electrochemical potential measurement setup.

2.2. Working electrodes.

At present, the conductor rolls of the electrogalvanizing line are made of duplex stainless steel SAF 2205. A sample of a discarded conductor roll was cut. The lateral faces and back of a small block of 1 cm² section were isolated with acrylic polymer, the remaining face was polished with different abrasive papers and finally it was given a mirror finish with 1 μm diamond paste (Figure 2).

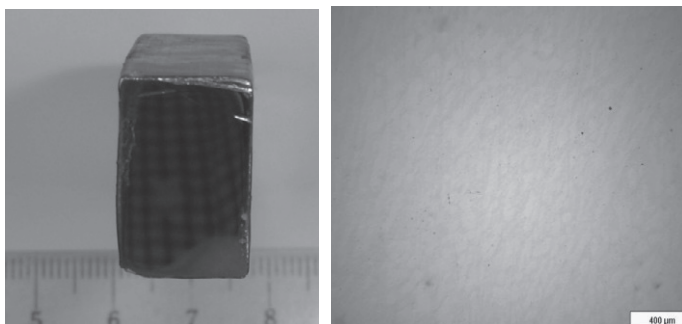


Figure 2. a) SAF 2205 working electrode; b) Same electrode surface microphotograph.

A selection of four different alloys from the literature [1-4] was done considering their corrosion resistance in aqueous acid non oxidant media. The commercial names and compositions are shown in Table 1, together with the same data for the SAF 2205 for comparison. Working electrodes of each of these alloys were made from 0.24 cm diameter rods included in epoxy resin following the same polishing procedure as with the SAF 2205 working electrode.

Table 1. Selected alloys and SAF 2205 chemical compositions.

	Ni	Cr	Fe	Mo	Nb/Ta	Cmax.	N	Cu	Comax.	W
SAF 2205	5	22	Bal.	3.2	--	0.03	0.18	--	--	--
Inconel C625	Bal.	20-23	5 max	8.0-10.0	3.5	0.1	--	--	1	--
Hastelloy C 276	Bal.	14.5-16.5	4.0-7.0	15-17	--	0.01	--	--	2.5	4.0
Hastelloy C22	Bal.	20-22.5	2.0-6.0	12.5-14.5	--	0.01	--	--	2.5	3.0
Alloy 20	32-38	19-21	Bal.	2.0-3.0	8xC-1	0.07	--	3.5	--	--

2.3. Electrochemical tests.

The electrochemical experiments were carried out in a conventional three-electrode cell operated with an EG&G Princeton Applied Research Potentiostat/Galvanostat (Mod. 273A) controlled with a personal computer with CorrWare2 software. The temperature was controlled at 50 ±0.5 °C; this value was representative of the industrial process. All potentials reported in this work are expressed in volts (V) with respect to SCE (+0.241 V vs SHE). A platinum foil of 10 cm² area was used as counter electrode. The working electrolyte was ZnSO₄ in aqueous solution (90 g/l Zn⁺²) at 1.6 pH.

2.4. In situ microscopy.

In situ characterization of the surface of the rolls was done with a portable USB digital microscope, with inbuilt 2.0 mega pixel digital camera, light control and variable magnification (200X maximum).

The microscope was connected to a portable computer and images were acquired with Digi View software.

3. Results and discussion.

3.1. Electrochemical potential and corrosion rate.

After stabilizing each one of the electrodes, the corrosion potentials (E_{CORR}) were measured. The polarization curves were also recorded and in Table 2 the results of polarization resistance (R_p), corrosion rate (C_R) and corrosion current density (I_{CORR}) are shown. The Stern Geary constant was fixed at 26 mV.

Table 2. Corrosion rate data.

Alloy	E_{CORR} (V)	R_p ($M\Omega$)	C_R (mpy)	I_{CORR} ($\mu A/cm^2$)	EW(g)*	δ (g/cm^3)
SAF2205	0.058	0.07	0.124	0.37	19.9	7.85
C625	0.240	0.08	0.120	0.33	24.0	8.44
C276	0.224	0.07	0.134	0.35	26.4	8.89
C22	0.236	0.06	0.166	0.44	25.6	8.69
A20	0.228	0.10	0.093	0.27	21.3	8.08

*EW = Equivalent weight according to ASTM G102

The electrochemical potential of all the conductor rolls (E_R) and the galvanized strip (E_{St}) in contact with them were measured for different operating conditions and for different electrogalvanized product specifications using the system described in 2.1. It is known that the rolls suffer a more severe superficial attack when the steel strip is coated with zinc on both faces than when it is coated only on one face. Thus, all registered data were split in two average values corresponding to each one of these two products (Table 3).

Table 3. Conductor roll and steel strip electrochemical potentials for one and two faces products.

Steel strip type	E_R	E_{St}
1 Face	-0.3	-0.7
2 Faces	-0.4	-1.4

The main preliminary concept that can be inferred from the previous results is that none of the alloys included in this investigation is appreciably corroded ($I_{CORR} \approx 10^{-7} A/cm^2$) at the considered temperature and electrolyte composition. The cathodic polarization of the conductor rolls during operation was also evident. In the case of the SAF 2205 it is 0.3 to 0.4 V cathodic against its corrosion potential and when the line is processing the two faces product, the conductor roll is more cathodic than with the one face product.

3.2. Potentiostatic treatment at operating electrochemical potential.

The SAF 2205 electrode was held at the two faces product E_R for 3 hours, time known to be enough to produce a clear evidence of corrosion on a new conductor roll in the line. After this potentiostatic experiment at 50 °C there was no evidence of corrosion on the electrode surface.

3.3. Potential cycling.

As the constant potential treatment did not produce any attack on the SAF 2205, it was decided not to apply it to the other alloys. Instead, an electrochemical experiment that represents in a better way what happens to the conductor roll surface was designed. Considering that a roll takes τ seconds to fulfill a complete revolution and that t_c is the contact time between the sheet and the roll, an asymmetric repetitive square wave potential (ARSW) signal like the one described in the scheme of Figure 3 is proposed. In this case, the electrode surface stay $(\tau - t_c)$ seconds at E_R and t_c seconds at E_{St} . So, each ARSW cycle represents electrochemically one revolution of a conductor roll.

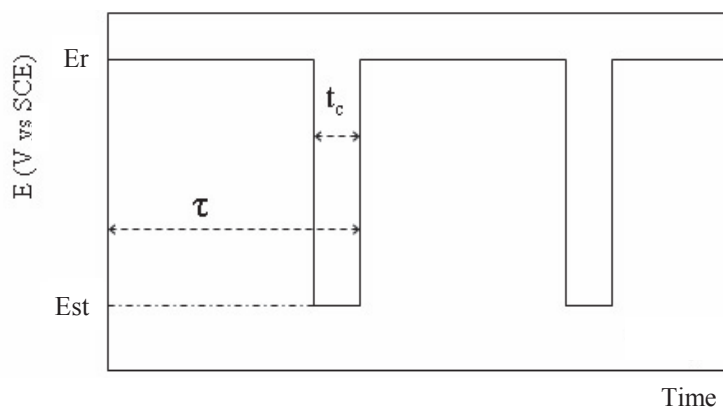


Figure 3. Asymmetric repetitive square wave potential signal.

The parameter τ is directly related to the line speed and roll diameter and t_c depends on the line speed and contact length between conductor roll and strip. It was possible to measure the roll-strip contact length accurately using a pressure sensitive polymeric film, and a length of 0.05 cm was taken as a representative average value for different roll pressures and diameters. Using the actual conductor roll diameter in the plant and the real line speed distribution of the production mix, it was possible to use $t_c=0.01$ seconds and $\tau=1.5$ seconds as representative average values. The resulting ARSW was applied to the SAF 2205 electrode for 30 minutes (1200 cycles) adjusting E_R and E_{St} to the values showed in Table 3. A strong corrosion pattern appeared (Figure 4), pitting (Figure 6) and eventually a very slight intergranular corrosion. When E_R and E_{St} corresponded to the processing of the two faces material, the attack was stronger and some corrosion products were observed on the electrode surface (Figure 4 b). This is similar to the observed phenomena on the conductor roll surface in the electrogalvanizing line. Based on these results, the ARSW signal was applied to the other alloys.

Figure 5 shows the images of Hastelloy C22 electrodes after both treatments. It is important to consider that neither in this case nor in the rest of the alloys any evidence of corrosion for one face ARSW was detected, but for the two faces condition a color change was observed. J. Gao et al, 2010 and Z. Y. Liu, 2011, showed some evidence of pitting of duplex stainless steel electrodes applying symmetric square wave potentiostatic signals but never at potentials more cathodic than E_{CORR} . In this case E_R for two faces material is even more cathodic than the active corrosion potential in 1N sulfuric acid of SAF 2205, J. H. Potgieter et al., 2008. However, the corrosion effect is more severe probably due to the austenite-ferrite anodic-cathodic polarization interaction, Tsai and Chen, 2007.

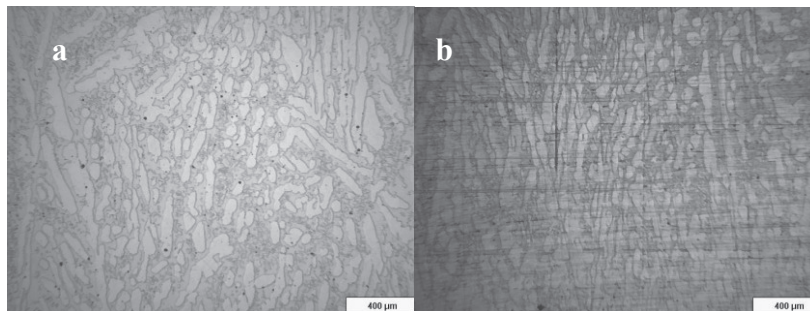


Figure 4. a) ARSW treatment for one face and b) two faces product for SAF 2205 electrode.

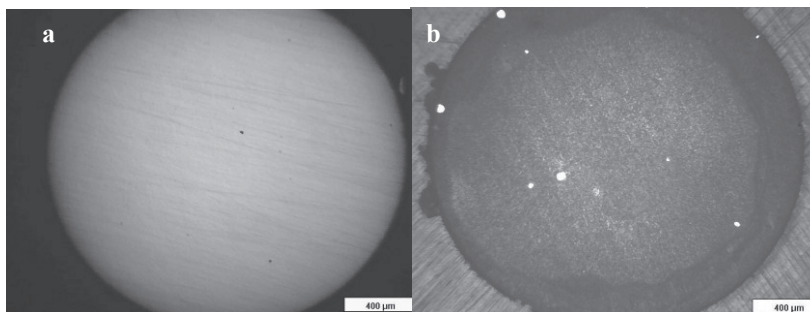


Figure 5. a) ARSW treatment for one face and b) two faces product for Hastelloy C22 electrode.

3.4. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX).

Figure 6 shows the SEM micrographs of SAF2205 electrode surface after ARSW treatment for the two faces product. The etching of the crystalline grain structure and the existence of pits are clearly confirmed.

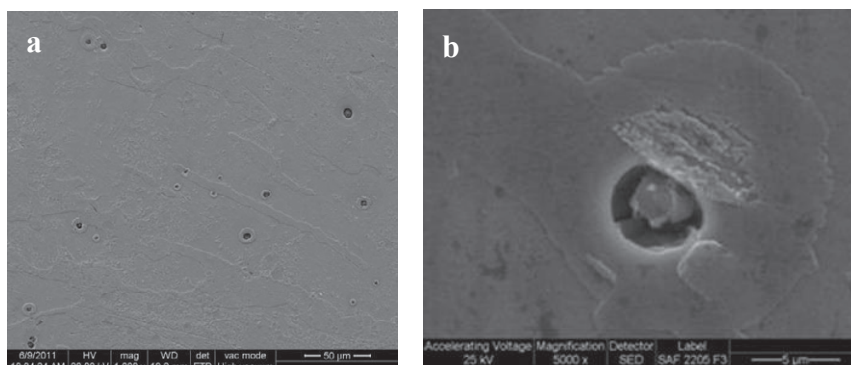


Figure 6. SEM micrographs of SAF2205 after ARSW two faces treatment. a) 1000X, b) 5000X.

Zn crystals on the surface were detected by EDAX analysis. Regarding the other alloys, it was confirmed that the ARSW treatment for the one face condition did not alter the surface of the electrodes and that the color changes observed for the two faces treatment was due to the presence of Zn crystals.

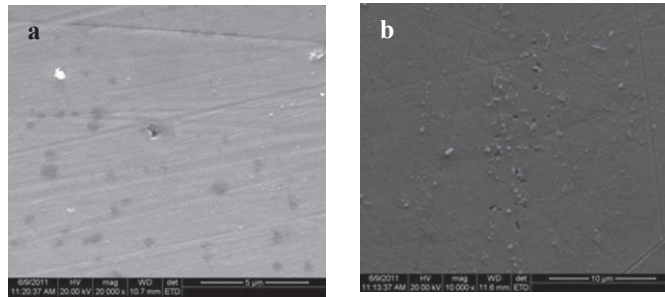


Figure 7. SEM micrographs a) C625 (20 000X) y b) C276 (10 000X) after ARSW for two faces treatment.

After a slight pickling in 1N sulfuric acid at room temperature for a few seconds, it was possible to study the surfaces free from Zn. After a detailed analysis of the pickled electrode surfaces and at higher magnifications, it was possible to find a slight evidence of corrosion effects in the alternative alloys. For example, the mild pitting observed on C625 and C276 alloys is shown in figure 7. Comparing the intensity and density of the corrosion attack produced by the two faces product ARSW, it was possible to make a relative ranking of the alloys according to their corrosion resistance: $C22 > C625 \geq C276 \approx A20 \gg SAF 2205$

3.5. In situ microscopy of worn roll.

In order to characterize the surface of a conductor roll that presented the mentioned defect after a complete production batch, some digital in situ micrographs were obtained. The general appearance of the roll is shown in figure 8. A severe attack was observed on the conductor roll surface and moreover, it was also verified that the intensity and pattern produced on the SAF 2205 electrode surface after the ARSW treatment and the surface of the discarded conductor roll were almost the same (Figures 9a and 9b).

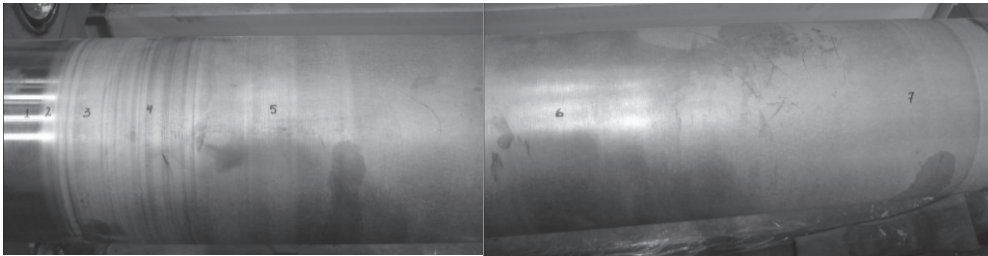


Figure 8. Photograph of worn roll.

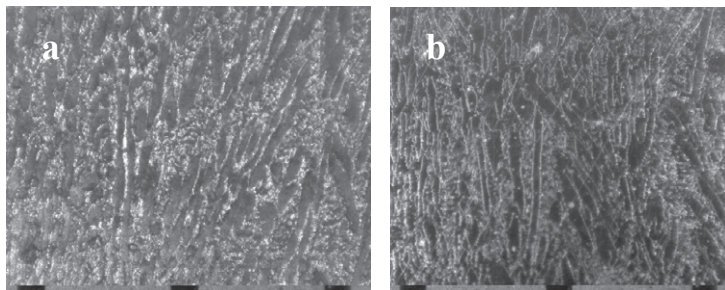


Figure 9. a) In situ image of spent roll surface 200X; b) SAF 2205 electrode after ARSW two faces treatment 200X.

4. Conclusions.

The corrosion process of SAF 2205 duplex stainless steel conductor rolls in acid electrolyte during the production of galvanized steel strip is mainly a dynamic electrochemical process originated by the cyclic variation of the electrochemical potential at the surface of the roll when it rotates and periodically touches the steel strip surface either covered or uncovered with zinc. The electrochemical potentials were measured with accuracy and reproducibility for the first time in an electrogalvanizing line during operation without altering its normal production regime. The results obtained in this work show that erosion does not play an important role in the overall degradation process taking into account that ARSW treatment by its own generates the same degradation pattern on the SAF 2205 electrode surface as the one the real process produces on the conductor roll surface.

The obtained knowledge explains why the roll surface is corroded only where it touches the steel strip surface without the occurrence of an erosion process. It also explains the difference in defect intensity when the line is processing one face or two faces galvanized product. Although it might be necessary to make some additional in situ measurements in the galvanizing line, it could be predicted that an increment in the total galvanizing current that passes through the conductor roll would not modify the actual corrosion process and characteristics (hypothetical consideration for a production increase). A new electrochemical method for evaluation of materials for conductor roll fabrication has been developed. It is easy adaptable for each specific production mix, pass line, conductor roll diameter, line speed, electrolyte composition and contamination. From the different alloys studied in this work (SAF 2205, Inconel C625, Hastelloy C276, Hastelloy C22, Alloy 20) it was established that the most corrosion resistant for this specific application is the Hastelloy C22.

Acknowledgements

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