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Microstructural and Corrosion Properties of PEO Coated Zinc-Aluminized (ZA) Steel

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Abstract: Plasma Electrolytic Oxidation (PEO) is a surface treatment, similar to anodizing, that produces thick oxide films on the surface of metals. In the present work, PEO coatings were obtained on zinc-aluminized (ZA) carbon steel using as electrolyte a solution containing sodium silicate and potassium hydroxide, and working with high current densities and short treatment times in DC mode. The surface morphology resulted the typical one of PEO layers, with the presence of a lot of pores and micro-cracks. Considering the cross section, the thickness of the coating was strongly influenced by the process parameters, with different dissolution grades of the ZA layer depending on the current density and treatment time. The PEO layer resulted mainly composed by aluminum and zinc oxides and silicates. The corrosion resistance was remarkable increased in the samples with the PEO coating.

Keywords: Plasma Electrolytic Oxidation; PEO; Coatings; Steel; Zinc-aluminized; Corrosion

1. Introduction

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Steel is often employed in engineering applications thank to its high mechanical properties, good machining ability and low cost. Carbon steels in particular are often used in structural applications. Corrosion problems often affect carbon steels and the substitution with stainless steels is often not possible due to their higher cost. In order to overcome this problem a possible approach is the realization of proper surface treatments on the metal. Plasma electrolytic oxidation (PEO) of metals is an electrochemical process that produces an oxide ceramic layer on the surface of different metals. PEO is similar to traditional anodic oxidation but works with higher voltages and current densities. The high voltage (that has to be above the dielectric breakdown potential of the oxide layer) forms anodic micro-discharges that moving randomly over the processed surface produce the growth of the coating. [1,2] The corrosion and wear properties depend by current density, voltage, treatment time and electrolyte composition employed during PEO treatment. [3] The process has been widely studied on aluminum and magnesium alloys and many results are reported in literature especially about the increased corrosion and wear performances of light alloys after PEO treatment. Moreover, PEO offers the possibility to proper functionalize the surface by adding particles or specific compounds in the electrolyte. [4-6] In comparison to PEO on light alloys, the number of works regarding the application of this treatment on steels is quite low, and, in detail, some works on carbon steel and only one on low alloyed steel can be found. [7–11] These research showed that the quality of the coatings produced directly on steels, in term of adhesion, homogeneity and corrosion properties, resulted lower than the ones obtained on light alloys. One of the possibilities studied in literature to overcome this problem and to produce PEO coatings with good quality on ferrous metals is to perform, before the PEO, a pre-treatment. In particular, some works can be found regarding the realization of PEO coatings on aluminized steels. [12–14] The main problem regarding this approach

is that the aluminization of steels isn't a so common treatment. In order to use as pre-treatment an economic and common treatment, zinc-based pre-treatments could be used as possible substrates for PEO coatings. However, a preliminary research in literature showed that PEO coatings formed on pure zinc have high level of defects, as evidenced by Stojanovic *et al.* [15] and are slightly protective against corrosion, as stated Rocca *et al* [16]. In literature promising results were found for PEO coatings produced on zinc-aluminum alloys: in detail, Guangdong Bian *et al.* [17] found that the PEO method can produce continuous and dense coating on the ZA27 alloy using silicate, aluminate, and aluminate/borate electrolytes; and Guangyin Li *et al.* [18] showed that PEO coatings can effectively protect the ZA27 alloy from abrasive and adhesive wear and corrosion. Zinc-Aluminum coatings (ZA) are quite common in industrial applications to provide corrosion protection on steels. Considering this, the aim of this work was to study PEO process on steels with a ZA pre-treatment and to test the corrosion resistance of the obtained samples. This research represents an innovative use of PEO process, since no works in literature reported the obtainment of PEO coatings on zinc-aluminized steels.

2. Materials and Methods

Samples of carbon steel (0.16% C, 1.06% Mn, 0.09% Al, 0.03%Cr, 0.07% Cu) coated with commercial ZA coating (75% Al and 25% Zn) were used for the experiments. PEO treatments were performed using as electrolyte an aqueous alkaline solution with 20 g/L of Na2SiO3 and 10 g/L of KOH.

PEO process was performed with a TDK-Lambda DC power supply of 400V/8A capacity. During the treatment, the substrate was the anode and a carbon steel mesh was the cathode. The electrolyte was maintained at ambient temperature with a thermostatic bath. The treatments were performed in DC galvanostatic mode, letting the potential free to vary, working at high current densities for short treatment times. Different current densities and different treatments times were tested. In detail, current densities of 1.1, 1.7 and 2.3 A/cm² were employed. For each current density, two different treatment times were used: 2 and 3 min. The samples, after the treatment, were washed with deionized water and ethanol, then dried with compressed air.

For all the samples, morphology, composition, thickness, and corrosion resistance of the coatings were evaluated. The samples were compared with the ones with only the ZA coating.

The treated samples were cut in the cross section and mounted in epoxy resin, then polished with standard metallographic technique (grinding with abrasive papers from 320 to 1200 grit and polishing with clothes and diamond suspension 6 and 1 μ m). Both the surface and the cross-section of treated samples were examined with a Cambridge Stereoscan 440 scanning electron microscope, equipped with a Philips PV9800 EDS, in order to evaluate morphology, thickness and elemental composition of the coating. To better evaluate the distribution of the elements along the cross section also EDS elemental mapping was performed. The phase composition of the most significant sample was performed with X-ray diffraction (XRD) using a Siemens D500 X-ray diffractometer, using Cu K α radiation with a step scan of 0.05 and a counting time of 5 s in an angular range between 20 and 80°.

The corrosion performance of the coatings was determined firstly by potentiodynamic polarization tests (PDP), and then by electrochemical impedance spectroscopy (EIS) at ambient temperature.

The PDP tests were performed in a solution containing 0.1 M Na₂SO₄ with an AMEL 2549 Potentiostat. A saturated calomel electrode was employed as reference electrode (SCE) and a platinum electrode as counter electrode, with a scan rate of 0.5 mV s⁻¹. Considering the insulating nature of the PEO layer PDP was employed only for qualitative evaluation of the corrosion performances, whereas quantitative considerations was performed with EIS measurements. [5]

The EIS measurements were carried out with the same cell and electrolyte employed in potentiodynamic polarization, at the value of the open circuit potential and in a frequency range between 10⁵ Hz and 10⁻² Hz, with a perturbation amplitude of 10 mV. A Materials Instrument Spectrometer coupled with the 2549 Potentiostat was used to record EIS measurements and the Z-

View software was employed for the fitting of impedance data. All the electrochemical measurements were performed in triplicate, in order to assure the reproducibility of the results. In order to better understand the corrosion behavior, some samples were observed at SEM after potentiodynamic polarization test (test stopped at the same current density) and the corrosion products were analyzed with EDS.

3. Results

3.1. Microstructural characterization

The surfaces and the cross sections of the samples were analyzed at SEM and the results are reported in Fig. 1 (surfaces) and Fig. 2 (cross sections).



Figure 1. SEM images (backscattered electrons mode) of the surfaces of the samples: a) 1.1 A/cm² - 2 min; b) 1.1 A/cm² - 3 min; c) 1.7 A/cm² - 2 min; d) 1.7 A/cm² - 3 min; e) 2.3 A/cm² - 2 min; f) 2.3 A/cm² - 3 min.

From the analysis of the surfaces of the samples resulted the typical morphology of PEO coatings with the presence of nodular structures and with the evidence of a lot of pores and micro-cracks of different dimensions, coming from the discharge phenomena. In the sample treated at 1.1 A/cm² for 2 min (A) the presence of some uncoated zones, highlighted by white circles, can be observed, indicating that the PEO layer was not completely formed on the surface. In detail, these uncoated zones are the lighter in the SEM micrographs. Increasing the treatment time up to 3 minutes a more uniform coating was produced, characterized by the presence of nodular structures as observable in (B). Considering the samples treated at 1.7 A/cm² (C and D), in both the samples the coating covered

all the surface. Comparing the two samples, an increase in the tretament time produced an increase of the nodular structures on the surface. The sample treated at 2.3 A/cm^2 for 2 min (E) was characterized by a smoother surface with the presence of less but larger volcano-like pores, in comparison with the other samples. The coating seemed also more compact that the one obtained on other samples. The sample treated at 2.3 A/cm^2 for 3 min (F) was instead characterized by the presence of many small pores and low number of nodular structures, even if the surface was not as smooth as the one obtained at 2 min.



Figure 2. SEM images (backscattered electrons mode) of the cross sections of the different samples: a) 1.1 A/cm² - 2 min; b) 1.1 A/cm² - 3 min; c) 1.7 A/cm² - 2 min; d) 1.7 A/cm² - 3 min; e) 2.3 A/cm² - 2 min; f) 2.3 A/cm² - 3 min.

Considering the cross sections of the samples (Fig. 2), resulted that increasing the current density produced a progressive thinning of the thickness of the ZA layer (the internal grey one, named 1 in the figures) and a thickening of the PEO layer (the dark and porous layer on the top, named 2). This can be correlated with the oxidation of the ZA layer during PEO process and, consequently, an increase in the current density induced a higher oxidation rate. From the reported microgrpahs was observed the presence of some dark grey zones in the ZA layer. In the sample treated at 1.1 A/cm² for 2 min (Fig. 2A) the formation of the PEO layer was not complete, whereas after the treatment for 3 min (Fig. 2B) the PEO coating formed above all the surface. The samples treated at 1.7 and 2.2 A/cm² showed a remarkable reduction in the thickness of the ZA layer, if compared with the samples obtained at 1.1 A/cm². Moreover, longer treatment times, at these current densities, induced the

formation of thicker layers with a higher porosity in upper layer. A summary of the thickness of the PEO layers an of the ZA layers for the various samples is reported in Tab. 1.

Table. 1. Summary of the thickness of ZA and PEO layers for the different samples, evaluated from SEM observation.

	Thickness of the ZA layer (µm)	Thickness of the PEO layer (µm)		
1.1 A/cm ² 2 min	24.5	7-Not Uniform		
1.1 A/cm ² 3 min	20	10		
1.7 A/cm ² 2 min	15	22		
1.7 A/cm ² 3 min	11	30		
2.3 A/cm ² 2 min	12	25		
2.3 A/cm ² 3 min	7	40		

In order to study the composition of the different layers, EDS micro-analysis was performed on the cross section of the samples treated at the higher and the lower current density. The semiquantitative results are reported in Tab. 2.

Table. 2. EDS semi-quantitative results (v	wt%) on the various samples
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	Al%	Si%	Zn%	0%
1.1 A/cm ² 2 min light grey areas in the inner layer	74.5	-	25.5	-
1.1 A/cm ² 2 min dark grey areas in the inner layer	65.4	-	15.1	19.5
1.1 A/cm ² 2 min outer layer	60.5	3.9	16.0	19.6
1.1 A/cm ² 3 min light grey areas in the inner layer	75.8	-	24.2	-
1.1 A/cm ² 3 min dark grey areas in the inner layer	66.8	-	13.1	20.1
1.1 A/cm ² 3 min outer layer	17.7	39.2	4.0	39.1
2.3 A/cm ² 2 min light grey areas in the inner layer	74.2	-	25.8	-
2.3 A/cm ² 2 min dark grey areas in the inner layer	64.8	-	16.8	18.4
2.3 A/cm ² 2 min outer layer	13.9	32.8	-	53.3
2.3 A/cm ² 2 min light grey areas in the inner layer	75.1	_	24.9	-
2.3 A/cm ² 3 min dark grey areas in the inner layer	64.6	-	16.0	19.4
2.3 A/cm ² 3 min outer layer	17.5	29.4	2.0	51.1

Considering the results reported in Tab. 2, it can be noted that the light grey areas in the inner layer are composed by only Zn and Al, that is the ZA layer. The dark grey zones in the inner layer were constituted by Al, Zn and O, suggesting that oxidation phenomena occurred. In all the samples the external layer represented the actual PEO layer, with the main presence of silicon and aluminum oxides, in accordance with the composition of the electrolyte and substrate.

To further investigate the distribution of the elements in the layers, also EDS elemental mapping was performed on the more significant and representative sample, the one obtained at 2.3 A/cm² for 2 minutes. The results are reported in Fig. 3. From the analysys of the elemental mapping it can be observed that the PEO layer (the outer layer) was mainly composed by silicon and aluminum oxides, whereas the inner layer (the ZA layer) was composed by aluminum and zinc.

XRD analyses was also performed on the sample obtained at 2.3 A/cm² for 2 minutes. The XRD pattern is reported in Fig. 4. It can be noted the presence of the peaks of aluminum and zinc coming from the ZA layer, due to the penetration of X-rays under the PEO layer. The PEO layer resulted mainly composed by SiO₂, in accordance the composition of the electrolyte that was a silicate-based one.



Figure 3. SEM-EDS elemental mapping performed on the cross section of the sample obtianed at 2.3 A/cm² for 2 minutes.



Figure 4. XRD analysis of the sample obtianed at 2.3 A/cm² for 2 minutes.

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3.2. Corrosion resistance

The corrosion resistance of the samples was preliminarily evaluated by potentiodynamic polarization tests, in a solution containing sulphates. The results are reported in Fig. 5.



Figure 5. Potentiodynamic polarization curves for the different samples (test solution: 0.1 M Na₂SO₄).

Firstly, it is possible to see that the samples treated at 1.7 and 2.3 A/cm² for 3 min were characterized by a lower corrosion resistance if compared with the ZA sample, in accordance with the SEM observation that showed high porosity on these samples. The sample characterized by the higher corrosion resistance was the sample treated at 1.1 A/cm² for 3 min. Moreover, also the samples 1.1 A/cm² for 2 min and 2.3 A/cm² for 2 min showed better corrosion performances if compared with the ZA sample. Hovewer, considering the insulating nature of the PEO coating, no quantitative considerations can be performed from potentiodynamic polarization.

In order to deeply study the corrosion behavior of the samples also EIS tests were performed and the results in term of Nyquist plot are reported in Fig. 6. The experimental data coming from EIS were fitted with the software Z-view, using the equivalent circuits reported in Fig. 7. In detail, the circuit in Fig. 7A was used for the sample with only the ZA coating, whereas the circuit in Fig. 7B for the PEO treated samples. This circuit is the typical one used to fit data of PEO treated samples, where are present an inner barrier layer, that gives the major protection against corrosion, and an external porous layer. [11] The ZA layer under the PEO coating was not considered in the equivalent circuit since this layer, for its conductive nature, acts with the substrate as one unique electrochemical unit, under the PEO layer. Considering more in detail the meaning of the different elements in this circuit: R₁ represents the resistance of the electrolyte, whereas the two paralles R₂-CPE₁ and R₃-CPE₂ consider the two different interfaces formed between the eletrolyte and the external porous layer, and between the electrolyte and the inner barrier layer, respectively. As the measured capacitance is not ideal, CPE₁ instead of capacitances were used in the equivalent circuits. The fitting results of the experimental data are reported in Tab. 3. A good fitting quality was obtained considering the low reported values of chi squared.





Figure 6. Nyquist plot coming from EIS tests, global results (A) and detail of the samples with low resistance (B) (test electrolyte: 0.1 M Na₂SO₄).



Figure 7. Equivalent circuits employed to fit EIS data for the ZA coated sample (A) and for the PEO treated samples (B)

Analyzing the Nyquist plots reported in Fig. 6A resulted that the sample treated at 1.1 A/cm² for 3 min and the one treated at 2.3 A/cm² for 2 min were characterized by improved corrosion resistance in comparison with all the others samples. In fact, considering the width of the semicircle and the interesection with the X-axis as qualitative evaluation of the polarization resistance R_P , an increase of more than one order of magnitude in the polarization resistance of these two samples in comparison with the others can be noted. Observing the Nyquist plots of all the other samples (Fig. 6B) an increase in the polarization resistance of all the PEO treated samples in comparison with the only ZA one was recorded.

	7.4	1.1 A/cm ²	1.1 A/cm ²	1.7 A/cm ²	1.7 A/cm ²	2.3 A/cm ²	2.3 A/cm ²
	LA	2 min	3 min	2 min	3 min	2 min	3 min
$R_1[\Omega cm^2]$	31.17	15.06	50.21	50.48	50.24	40.24	50.35
$R_2[\Omega cm^2]$	-	341.76	8006	51.24	15.12	1668	100.12
R ₃ [Ωcm ²]	77.45	1827	12253	3241	908.42	10241	1023
Q_1 [FHz ¹⁻ⁿ]	-	3.1 x 10-4	3.6 x 10-6	4.8 x 10 ⁻⁴	3.6 x 10-6	1.7 x 10 ⁻⁵	1.5 x 10 ⁻⁴
Q_2 [FHz ¹⁻ⁿ]	5.1 x 10 ⁻⁵	5.2 x 10-4	3.7 x 10-4	3.8 x 10-4	3.7 x 10-4	9.3 x 10-5	5.1 x 10-4
n 1	-	0.46	0.91	0.79	0.98	0.63	0.51
n 2	0.66	0.78	0.52	0.59	0.51	0.44	0.61
Chi-squared	0.001	0.002	0.0006	0.02	0.0006	0.002	0.003

From the analysis of the fitting results (Tab. 3), it was confirmed that all the PEO treated samples were characterized by improved corrosion performances compared to the ZA sample, as evidenced by the increased values of polarization resistance (R₂ and R₃) that were one or two order of magnitude higher in the PEO treated samples. Considering the different PEO treated samples and comparing the values of R₂ and R₃ it can be noted that the samples treated at 1.1 A/cm² for 3 minutes and treated at 2.3 A/cm² for 2 minutes showed values of R₃ one order of magnitude higher than the other PEO treated samples. This can be correlated with the higher homogeneity and lower porosity of these samples, as resulted by SEM obervations.

In order to study the corrosion products formed on the surfaces after corrosion tests, two samples, after potentiodynamic polarization, were observed at SEM with backscattered electrons (BSE) and EDS analysis were performed. In detail, were analysed the sample treated at 2.3 A/cm² for 2 min and the one treated at the same current density but with longer treatment time (3 min), which was characterized by lower corrosion properties. The results of both SEM observation and EDS spectra are reported in Fig. 8.



Figure 8. SEM-BSE images (backscattered electrons) of the surface of the samples after potentiodynamic polarization test with corresponding EDS spectra: (A) and (C) sample treated at 2.3 A/cm² for 2 min; (B) and (D) sample treated at 2.3 A/cm² for 3 min.

From the SEM-BSE images, it is possible to observe that on the surface of the sample treated at 2.3 A/cm² for 2 minutes (Fig. 3A) only small amount of corrosion products were present, whereas in the sample treated for 3 minutes (Fig. 8B) several compounds coming from corrosion (the grey areas) were clearly visible. This fact was also confirmed by EDS analysis carried out on the surface of the samples that showed the presence of sulphates only in the sample treated at 2.3 A/cm² for 3 min (Fig. 8D). Therefore, SEM observations of the surfaces after corrosion confirmed the previosly reported corrosion data, with improved performances of the sample treated at 2.3 A/cm² for 2 min in comparison with the one treated 2.3 A/cm² for 3 min. The corrosion products were mainly composed by sulpahtes, in accordance with the electrolyte composition.

4. Discussion

PEO coatings were successfully produced on ZA steels using as electrolyte a solution containing potassium hydroxide and sodium silicates. The possibility to obtain coatings with acceptable homogeneity and low defect level had to be ascribed to the presence of aluminum in the ZA layer, in fact PEO coatings produced on pure zinc were characterized by high level of defects and are not protective against corrosion. [15,16] The morphology of the coatings was rich of pancake and nodular structures, in accordance with the results of other authors regarding PEO coatings produced on bulk ZA alloys [17,18]. The increase in the current density employed in the treatment produced a thinning of the ZA layer and a thickening of the PEO layer due to the increase of the oxidation rate. The increase in coating thickness played an important role in the corrosion behavior due to the barrier effect given by the coating. However, high current density applied for long treatment times can be detrimental for corrosion protection due to the coarse and very porous microstructure, as already found in literature on other substrate such as ZK60 alloy [19]. Also, Bala Srinivasan et al. [20] found that high current density increased the number of defects and micro-cracks and that a compromise between growth rate and quality of the microstructure has to be found. The results of the present work were in agreement with these considerations, in particular it was found that the better results in terms of corrosion resistance were obtained either with low current density and long treatment time (sample treated at 1.1 A/cm² for 3 min) or with high current density and short treatment time (sample treated at 2.3 A/cm² for 2 min).

5. Conclusions

The present work demonstrated the possibility of producing PEO coatings on zinc-aluminized steels. The better conditions in order to maximize the corrosion resistance resulted 1.1 A/cm² for 3 min and 2.3 A/cm² for 2 min. In this way a homogeneous coating, mainly composed by aluminum and silicon oxide, was formed on the top of the ZA layer. Considering that ZA treatment is a common treatment on carbon steel, the use of ZA layer as pre-treatment layer may represent a promising way to produce PEO coating of good quality on steels.

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