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EIS study of organic coating on zinc surface pretreated with environmentally friendly products

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Abstract

The life time of many steel structure can be remarkably improved by protecting the steel with zinc layers. However, also the zinc coating can be involved by corrosion phenomena with the consequence that some steel surface is unprotected.

The reduction of the corrosion rate of zinc is therefore an important topic. These results can be obtained by introducing zinc alloys with lower corrosion rate (ZnNi, ZnFe, etc.) or by protecting the zinc surface with organic or inorganic layers able to reduce the corrosion rate.

In the past a very popular way to reduce the corrosion rate of zinc was the use of chemical conversion layers based on Cr^{6+} , able to increase the passivation tendency of the zinc (chromating). This procedure is quite effective also for improving the adhesion of organic coatings deposited on the zinc surface, but there is the important problem that the use of chromium salts is now restricted because of environmental protection legislation.

It is therefore very important to develop new zinc surface treatments environmentally friendly to improve the corrosion resistance of zinc and the adhesion with the final organic protective layer.

In this paper a characterisation of environmentally friendly conversion treatments based on Cr^{3+} for zinc surface will be reported in comparison with traditional based Cr^{6+} pretreatments on different zinc layers protected by organic coatings.

The samples were studied using EIS measurements, and the data analysis was mainly based on the discussion of the mathematical combination (ratio, product, etc.) of different parameters of the equivalent electrical circuit model.

This approach was found more useful, in order to compare the performance of different materials, in comparison to the simple discussion of the numerical values of the parameters, being these values generally influenced by random defects present in the samples, affecting the measured impedance.

The results showed that the performance (adhesion and corrosion protection) of good formulated Cr^{3+} based pretreatments are not far from the results, which it is possible to obtain with industrial Cr^{6+} pretreatments and therefore Cr^{3+} conversion layers can be considered an interesting alternative to the traditional ones.

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1. Introduction

The corrosion protection of steel structure is often obtained, in particular for outdoor applications, by using a duplex system: the combination of a zinc coating with an organic coatings [1]. In order to reduce the corrosion rate of the zinc

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layer and increase the adhesion between the two coatings, a pretreatment of the metal layer is necessary and this pretreatment generally consists in a chemical conversion layer [2].

A very common zinc surface pretreatment is the passivation in chromates bath, very efficient both in reducing the zinc corrosion rate and increasing adhesion [3].

Unfortunately the cancer-producing and toxic activity of Cr^{6+} , important component of the pretreatment bath and

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chemical conversion layer, is well known [4]. For this reason it is probable that in the next future this pretreatment will be abandoned, also under the pressure of legislative actions.

Many different pretreatments have been studied in the last decade in order to avoid the use of Cr^{6+} , in addition to the typical phosphating treatment: chromium free, including molybdates, permanganates, vanadates, and tungstates (pre-treatments with protecting mechanism similar to Cr^{6+} acting as passivating agents) [5,6], or adhesion promoters like fluozirconates, fluo-titanates, organosilanes, etc. [7,8].

A further possibility is to use pretreatments based on Cr^{3+} , which is not considered carcinogenic [9].

Many papers are available in the literature dealing with new pretreatments of zinc and their corrosion protection characterisation [10,11]; some works are also focused on studying the influence of the pretreatment in the complete duplex system (zinc coating, pretreatment and organic coating) [12].

The aim of this work is the comparison of traditional and new industrial pretreatments based on Cr^{6+} and Cr^{3+} on different zinc coatings and further covered by an organic waterborne primer. The comparison is obtained mainly by electrochemical impedance spectroscopy measurements and a new approach to the EIS data analysis is proposed, based on the combination of different parameters, able to give information on the duplex system performance.

2. Materials and experimental procedure

Materials with different metallic coatings were studied: hot-dip galvanised coatings and electrodeposited coatings.

The hot-dip galvanised coatings were deposited on steel sheets with the following chemical composition: C 0.04–0.11%, Si 0.02%, P 0.07%, Fe balance (low-silicon substrate). It is very important to maintain low the Si and P content because these elements can remarkably affect the microstructure and the thickness of the metal layer, producing metallic coatings with low performance [13].

The coating deposition (symbol H) was carried out at 450 °C in a bath of molten zinc containing Ni (\sim 0.5%), Pb (\sim 1%) and Bi (\sim 1%), immersion time about 2 min and extraction rate about 70 cm/min. The coating thickness is about 70 µm.

The electrodeposited coatings were produced on Q panel of mild steel after degreasing. Two different coatings were produced: the first one is pure zinc (symbol Z), the second one is a Zn–Fe alloy (Fe about 0.7%, symbol ZF), using the two cyanides free baths reported in Table 1. For both materials the coating thickness is about 17 μ m.

All the materials were further pre-treated and passivated in two industrial baths. The first bath is a traditional chromate treatment based on Cr^{6+} , working at room temperature, with 0.5% of nitric acid, 0.1–0.2 g/l of Cr^{6+} and additives; the time of permanence in the bath is 15 min (pretreatment symbol CrVI).

The second passivation treatment is based on Cr^{3+} , working temperature 50–55 °C, bath composition: 0.5% nitric acid, 0.1% Cr^{3+} and additives; the time of permanence in the bath is also 15 min (pretreatment symbol CrIII).

The samples were organic coated using an environmentally friendly product: Epoxyphenolyc unpigmented waterborne resin (Polifix[®]) by dipping of samples for 90 s, curing temperature 250 °C, curing time 15 min, final dry thickness $7 \pm 2 \,\mu$ m.

This coating should be considered as an example of a primer and it is a model system useful to evaluate the pretreatment influence on the adhesion and corrosion protection properties of the organic coating. Actually a thicker coating with higher barrier properties could hide the electrochemical behaviour of the interface for a long time [14].

The samples produced in this way were characterised microstructurally and morphologically by optical and electronic microscopy and they were analysed chemically by EDXS measurements.

The protective properties of the system were studied by electrochemical impedance spectroscopy measurements (EIS) obtained in a 0.3% Na₂SO₄ solution, which is a not aggressive environment. The EIS measurements were obtained at the free corrosion potential using a potentiostat and FRA equipment, signal amplitude 10 mV, frequency range 100 KHz–0.001 Hz and testing area about 15 cm². The electrochemical data were modelled using equivalent electrical circuits with the software Equivcrt [15].

The adhesion measurements in dry and wet conditions were obtained by pull-off technique (Sebastian IV instrument) and they are the average value of five measurements with the same failure mode (failure at the metal-coating interface) and neglecting all the measurements with coating de-cohesive failure. The wet adhesion measurements are obtained after immersion of the samples in distilled water for 24 h at room temperature.

3. Results and discussion

3.1. Pretreatments characterisation

After the pretreatment deposition, the samples have been observed by electron microscopy; two observed examples of

Table 1

Composition of the baths for the electrodeposition of zinc layers

Bath	Composition (g/l)	Temperature (°C)	Current density (A/dm ²)	Symbol
Zn alkaline	Zn 10-20 NaOH 110-190 additives	20–35	1.5–3	Z
ZnFe alkaline	Zn 15 Fe 0,03 NaOH 130 additives	22	2	ZF



Fig. 1. Surface morphology (SEM) of the CrVI pretreatment on electrodeposited zinc layer.

surface morphology are shown in Figs. 1 and 2. Fig. 1 is the surface morphology of a sample of electrodeposited pure zinc and is typical of this class of materials, for both the pretreatments CrVI and CrIII. The conversion layer is evident and is distributed on all surfaces. Typical cracks of the chromate layer are also visible. Fig. 2 instead is characteristic of the chemical conversion layer surface obtained on hotdip galvanised coatings. For both pretreatments it is difficult to see the chromate layer which is present only locally and apparently in not continuous way. Also the EDXS analysis showed a lower presence of Cr on hot-dip galvanised coatings in comparison with electrodeposited coatings. It is probable that the surface of the zinc coating obtained by hot dipping is more oxidised and less suitable for the pretreatment deposition and therefore the industrial surface preparation of the studied hot-dip samples is insufficient.



Fig. 2. Surface morphology (SEM) of the CrVI pretreatment on hot-dip galvanised layer.



Fig. 3. Impedance evolution for the sample ZCrVI (Nyquist representation).

The electrochemical characterisation of the materials without the waterborne coating was carried out. An example of evolution of the impedance diagram in Nyquist form is shown in Fig. 3. The equivalent electrical circuit able to model the impedance values is shown in Fig. 4. The circuit is based on two contributions: the impedance of the interface, the faradic reaction (charge transfer resistance R_{ct}) in parallel with the double layer capacitance (C_{dl}), and at highest frequencies a contribution associated to the chromate treatment layer (resistance and capacitance of the chemical conversion layer R_{Cr} and C_{Cr}). In the case of zinc dissolution, many authors noted a two steps process causing two different time constant related to the faradic reaction [16]. We have not observed this phenomenon in our test solution.

The more interesting data to discuss are the resistance of the chromate treatment R_{Cr} (giving information on the barrier properties of the chemical conversion layer) and the charge transfer resistance R_{ct} giving information on the kinetic of the corrosive process. An example of evolution of the resistance of the chromate treatment R_{Cr} on hot-dip galvanised steel is in Fig. 5. The pretreatment with Cr⁶⁺ seems to offer a higher protection, in comparison with the pretreatment CrIII.

This fact has a strong influence on the charge transfer resistance and therefore on the corrosion rate (Fig. 6). The



Fig. 4. Equivalent electrical circuit for the pretreated samples.



Fig. 5. Evolution of the conversion layer resistance (R_{Cr}) for the two pretreatments on hot-dip galvanised coatings.



Fig. 6. Evolution of the charge transfer resistance (R_{ct}) for the two pretreatments on hot-dip galvanised coatings.



Fig. 7. Evolution of the conversion layer resistance $(R_{\rm Cr})$ for the two pretreatments on pure zinc electrodeposited coatings.

sample H-CrVI shows higher R_{ct} values and therefore lower corrosion rate. In Fig. 6 it is possible to note an increase of the R_{ct} values, increasing the immersion time. This phenomenon can be due to the passivation action, in the case of CrVI, or to the accumulation of zinc corrosion products (acting partially as a barrier) in the pretreatments defects for CrIII.

Different is the situation in the case of electrodeposited zinc coatings. An example of the evolution of the pretreatment resistance in the case of pure zinc is shown in Fig. 7, where it is possible to note an opposite behaviour than in Fig. 5. The material with better barrier properties is the sample pretreated with the Cr^{3+} system, causing also higher value of charge transfer resistance (Fig. 8). This is a general result, confirmed by all the measured samples, even if sometimes the differences, in our opinion, are not sufficient to prove that the CrIII treatment is better than the CrVI (on electrodeposited zinc) but, at least, we can affirm that the performance are comparable.



Fig. 8. Evolution of the charge transfer resistance (R_{ct}) for the two pretreatments on pure zinc electrodeposited coatings.

The conclusions that can be obtained from this part of the work are that in the case of hot-dip galvanised coatings, the not perfect deposition of the chemical conversion layer, produced a pretreatment with low barrier properties, and therefore low corrosion protection in particular in the case of chemical conversion system (like CrIII) without inhibitive action, while in the case of CrVI there is a limited protection action which is due to the passivating properties of Cr^{6+} .

The situation is different in the case of electrodeposited zinc layers (pure Zn and ZnFe alloy). The good deposition of both the pretreatments causes, in the low aggressive environment used, good corrosion behaviour of the CrIII system, comparable or better than the behaviour of the materials passivated with the CrVI system.

3.2. Duplex system characterisation

Considering the unsatisfactory properties of the hot-dip galvanised coatings after pretreatment, we will present the



Fig. 9. Impedance evolution for the sample ZCrVI with organic coating.



Fig. 10. Equivalent electrical circuit for the organic coated samples.

EIS data of the organic coated samples, only for the electrodeposited zinc layers.

A typical evolution of the EIS spectra for the complete duplex system is shown in Fig. 9, while in Fig. 10 is shown the equivalent electrical circuit used to analyse the EIS data which includes, beside the previously discussed parameters, the impedance contribution of the organic coatings (coating capacitance C_c and coating resistance R_p).

We used a low thickness primer because the aim of the investigation was to study the influence of the pretreatments, and not the behaviour of the organic coating itself, and therefore a high impedance coating is not the best choice because it could shield the interface contribution, causing a very long testing time before to see any difference in the studied samples.

However, a low impedance coating with low thickness (like the epoxyphenolic waterborne we used), has intrinsic defects which can cause a high data dispersion when an impedance characterisation is carried out. The dimension of data scattering could be comparable with the variation between different samples and therefore the data analysis could be very difficult.

In order to solve this problem a first approach could be to increase the number of identical samples to test, in order to have values with a high statistical reliability [17], but this way is very time expensive. A second approach is to try to consider, instead of the absolute values, the ratio or the product of parameters. In this way it is possible to discuss parameters which are independent on the presence of defects.

For example, it is well known that the coating resistance R_p could be written in the following form [18]:

$$R_{\rm p} = (\rho d) / A_{\rm pores} \tag{1}$$

where ρ is the electrolyte resistivity, *d* the coating thickness, and A_{pores} the total area of the pores through the coating.

In the same way the equation of the double layer capacitance C_{dl} is

$$C_{\rm dl} = C_{\rm dl}^0 A_{\rm delam} \tag{2}$$

where C_{dl}^0 is the specific double layer capacitance (per unit of area) and A_{delam} the metal surface area in contact with the electrolyte.

The product of R_p and C_{dl} is

$$R_{\rm p}C_{\rm dl} = KA_{\rm delam}/A_{\rm pores} \tag{3}$$

which means that the product R_pC_{dl} is proportional to the ratio between the delaminated area at the interface and the area of defects in the coating (assuming constant, during the testing time the solution resistivity inside the pores ρ , even if there is the pretreatment dissolution, but we suppose that the small amount of water in the pores is quickly saturated, and therefore the resistivity is constant). If the product increases with the immersion time, the delaminated area is increasing faster than the area of coating defects and a loss of adhesion is occurring (the delamination will be proportional to the increase of the ratio R_pC_{dl}). Fig. 11 shows graphically this concept.

Figs. 12 and 13 show the evolution of the product R_pC_{dl} during 24 h of immersion for the four studied materials. It is important to note that the product never decreases, in agreement with Eq. (3), which is meaningless in the case of R_pC_{dl} decreasing with immersion time. Moreover, the changes in the R_pC_{dl} product are very limited. The maximum increase is about four times in the case of ZFCrVI. Applying Eqs.



Rp CdI = K A_{delam}/ A_{pores}

Fig. 11. Graphical representation of the approach using combination of elements of the equivalent electrical circuit.



Fig. 12. Evolution of the product R_pC_{dl} for the samples of ZF (ZnFe alloys electrodeposited) with organic coatings.

(1) and (2) it is possible to estimate the initial defect area in the order of $10 \,\mu\text{m}^2$ every square centimetre of coating, and therefore the maximum increase of delaminated area is about $40 \,\mu\text{m}^2$ every square centimetre. For this reason we can conclude that the term delamination is not very appropriate and it is probable better to speak, in our case, about a very limited, but measurable, loss of adhesion.

In Fig. 12 it is possible to note that there is a higher loss of adhesion in the case of ZFCrVI in comparison with ZFCrIII. This fact, in our opinion, is due to the higher solubility of the products containing Cr^{6+} . In fact, only by solubilisation the CrVI based pretreatment can act as passivating material and therefore a certain level of solubility is necessary. On the contrary the CrIII chemical conversion layer can be considered completely insoluble in water.

In Fig. 13 a comparison of the substrates (pure Zn and ZnFe alloys) is presented, with the same pretreatment (CrIII).

The sample ZCIII appears more stable than ZFCrIII. This fact is due to the slightly less homogenous surface of the

ZnFe alloys in comparison to pure Zn. In fact, even if the pretreatment coverage is the same, we have found (by EDXS) less Cr on ZF samples in comparison with Z samples and therefore we think that the ZCrIII is probably thicker and more uniform than ZFCrIII.

A further equation in the data analysis could be considered:

$$R_{\rm ct} = R_{\rm ct}^{\circ} / A_{\rm delam} \tag{4}$$

where R_{ct}^0 is the specific charge transfer resistance (per unit of area) and A_{delam} again the metal area in contact with the electrolyte.

The ratio in Eq. (5) is also proportional to the A_{delam}/A_{pores} ratio, like Eq. (3).

$$R_{\rm p}/R_{\rm ct} = K_1 A_{\rm delam}/A_{\rm pores} \tag{5}$$

There is however an important difference between Eq. (3) and (5). It is more difficult to estimate R_{ct}^0 than C_{dl}^0 because R_{ct}^0 is less constant during immersion. Actually R_{ct}^0 can change



Fig. 13. Evolution of the product $R_p C_{dl}$ for the samples Z and ZF with the CrIII pretreatment and organic coatings.



Fig. 14. Evolution of the time constant of the corrosion process $(R_{ct}C_{dl})$ for the ZFCrIII sample.

with time for many different reasons, for example the change of oxygen concentration on the metal surface.

If R_{ct}^0 is constant, also the product $R_{ct}C_{dl}$ (the time constant of the corrosion reaction) is constant (the product is independent on the area and it is equal to of $R_{ct}^0 C_{dl}^0$). Fig. 14 shows this product for the sample ZFCrIII. It is evident that the product is not constant and it is increasing with time (in the same time it was also observed a shift in the cathodic direction of the free corrosion potential, which is probably due to the oxygen concentration reduction close to the metal surface). For this reason, we consider better to use Eq. (3) for the evaluation of the interface stability.

In order to obtain information on adhesion properties, which are independent on the impedance data, we performed pull-off measurements in wet and dry conditions.

The results are in Table 2.

The results are consistent with the EIS characterisation. The better adhesion values (dry and wet and for both the pretreatments) are obtained on pure Zn coatings, while lower adhesion reduction, passing from dry to wet conditions, is measured on samples pretreated with CrIII, in comparison with CrVI. Apparently there is a lower stability of the chemical conversion layers on pure zinc (higher percentage of adhesion reduction passing from dry to wet), but it is only due to the higher dry adhesion, being the wet adhesion in any case higher for pure zinc substrates than the wet adhesion of ZnFe alloys.

Table 2	
Adhesion measurements (pull-off technique)	

Sample	Dry adhesion (kg/cm ²)	Wet adhesion (kg/cm ²)	Percentage of reduction
Zn/Fe-Cr(VI)	521	466	10.5
Zn/Fe-Cr(III)	524	494	5.7
Zn-Cr(VI)	734	501	31.7
Zn-Cr(III)	725	536	25.7

4. Conclusions

The zinc coatings pretreated with Cr^{3+} shows corrosion protection properties comparable with the same materials passivated with Cr^{6+} in the case of electrodeposited zinc layers, while in the case of hot-dip galvanised coatings the pretreatments are very defective and the coverage is partial.

Considering the organic coated samples, when there is a large EIS data dispersion, like in our case because of the low thickness of the organic coating, the mathematical combination (ratio or product, see Eqs. (3) and (5)) of the parameters of the equivalent electrical circuit can give useful results.

The pure zinc electrodeposited samples showed better adhesion (both CrIII and CrVI pretreatments).

The pretreatment based on CrIII seems to have a higher stability (less loss of adhesion) in humid environment in comparison with CrVI based samples.

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References

- J.F.H. van, Eijnsembergen Duplex System, Elsevier, Amsterdam, 1994.
- [2] Z. Wicks, F.N. Jones, S.P. Pappas, Organic Coatings: Science and Technology, Wiley, New York, 1994.
- [3] C. Gabrielli, M. Keddam, F. Minouflet-Laurent, K. Ogle, H. Pierrot, Electrochim. Acta 48 (2003) 1483.
- [4] Toxicological Profile for Chromium, Agency for Toxic Substances, US Public Health Service, Report no. ATSDR/TP-88/10, July 1989.
- [5] E. Almeida, L. Fedrizzi, T.C. Diamantino, Surf. Coat. Technol. 105 (1998) 97.

- [6] E. Almeida, T.C. Diamantino, M.O. Figueiredo, C. Sà, Surf. Coat. Technol. 106 (1998) 8.
- [7] P. Puomi, H.M. Fagerholm, J.B. Rosenholm, K. Jyrka, Surf. Coat. Technol. 115 (1999) 79.
- [8] W. Yuan, W. Van Ooij, J. Colloid Interface Sci. 185 (1997) 197.
- [9] T. Bellezze, G. Roventi, R. Fratesi, Surf. Coat. Technol. 155 (2002) 221.
- [10] P. Puomi, H.M. Fagerholm, J.B. Rosenholm, K. Jyrka, Surf. Coat. Technol. 115 (1999) 70.
- [11] L. Fedrizzi, F. Deflorian, G. Boni, P.L. Bonora, E. Pasini, Prog. Org. Coat. 29 (1996) 89.

- [12] N. Tang, W.J. van Ooij, G. Gorecki, Prog. Org. Coat. 30 (1997) 255.
- [13] F. Porter, Zinc Handbook, Marcel Dekker, New York, 1991.
- [14] J.H.W. DeWit, in: P. Marcus, G. Oudar (Eds.), Corrosion Mechanisms in Theory and Practice, Marcel Dekker, New York, 1995, p. 581.
- [15] B. Boukamp, Solid State Ionics 20 (1986) 31.
- [16] X.G. Zhang, Corrosion and Electrochemistry of Zinc, Plenum Press, New York, 1996.
- [17] F. Deflorian, L. Fedrizzi, S. Rossi, P.L. Bonora, Mater. Sci. Forum 289–292 (1998) 337.
- [18] F. Deflorian, S. Rossi, L. Fedrizzi, P.L. Bonora, J. Appl. Electrochem. 32 (2002) 921.