ESTIMATING THE COMPOSITION OF ZINC/COBALT ALLOY COATINGS WITH ENERGY-DISPERSIVE X-RAY FLUORESCENCE SPECTROSCOPY

J.M.Falcón Roque[1], I.V.Aoki[1], A.C.Neiva[2]*

[1] *Escola Politécnica da Universidade de São Paulo, Departamento de Engenharia Química; Av. Prof. Luciano Gualberto, travessa 3, 380, São Paulo, SP, Brasil*

[2] *Escola Politécnica da Universidade de São Paulo, Departamento de Engenharia Química; Av. Prof. Luciano Gualberto, travessa 3, 380, São Paulo, SP, Brasil; acneiva@usp.br*

Zn/Co alloy coatings electrodeposited on carbon steel were analyzed by EDXRF (Energy-Dispersive X-Ray Fluorescence) spectroscopy, in order to correlate their composition with deposition variables. The deposits were obtained potentiostatically at different cathodic potentials from three different plating baths with $ZnCl_2$, $CoCl_2.6H_2O$, KCl and H_3BO_3. EDXRF was performed with an Ital-Structures W-tube and a Si-drift Ketek detector. Two different approaches were used for estimating the Zn/Co ratio from the spectra. The first one consisted in obtaining absolute values by applying the Fundamental Parameters PyMCA software to fit the spectra, considering a double layer structure. The second one was based on directly on the areas of Co-KM3 and KL3-Zn peaks, correlated to compositions through calibration with reference samples. The technique was used to verify the effect of the solution composition, the potential and the charge on the deposit composition and thickness or density.

1. Introduction

Electrodeposited Zn has been used for a long time as a sacrifice corrosion protection for steel in the automotive industry. In the recent years, codeposited layers as Zn/Ni, Zn/Co and Zn/Fe [1] have received special attention as substitutes for pure Zn, due to their superior mechanical properties. The present work deals with EDXRF analysis of Zn/Co deposits in the scope of a corrosion study [2] which includes potentiostatic and galvanostatic depositions in several different conditions, electrochemical essays, XRD and SEM characterization, and corrosion tests. In the project, EDXRF was envisaged as a quick and non-destructive analytical method. In this paper, the focus will be the standardless determination of the deposit composition and of the layer thickness by a Fundamental Parameters software. For brevity, only the results from potentiostatic deposition will be presented, although galvanostatic deposition was also studied.

2. Methods

The deposits were obtained from plating baths with $ZnCl_2$, $CoCl_2.6H_2O$, KCl and H_3BO_3. Three different $[Zn^{2+}]/[Co^{2+}]$ ratios will be discussed: solution A, with ratio = 6, solution B, with ratio = 9, and solution C, with ratio = 12. For each solution, potentiostatic deposition was performed at three different cathodic potentials, ranging from -1150 mV to -1450 mV. The deposit was made on carbon steel with around 0.5% Mn.

EDXRF was performed with an Ital-Structures W-tube and a Si-drift Ketek detector, at open atmosphere. A 1.5mm Pb collimmator was used in the x-ray -tube. The measurements were made at 55kV and 0.3mA, for 300s, with the sample at 7mm from the detector. Most samples were small, with $2mm^2$ surface area. Scanning Electron Microscopy (SEM) with Energy-Dispersive X ray Analysis (EDXA) was also used for surface and section observation. PyMCA software [3] was used for simultaneously determine the peak areas and estimate the mass fraction of the elements by the Fundamental Parameters method. As the spectra have

contributions from both the Zn-Co deposit and the steel substrate, the multilayer option of the software was used. In this option, a structure of layers should be proposed, with defined compositions, densities and thicknesses. The software does not modify the values of density and thickness during the fitting process. It uses them for the calculations and then presents the resulting mass fractions of each proposed element in each layer. If density and thickness true values are unknown, one should guess a set of initial values for them and then, according to the results, make new trials in order to improve the fitting quality. The quality criterion, in our study, was obtaining mass fractions which add to 100% in both proposed layers. In the deposit layer d in the steel layer, then, one should obtain %Co + %Zn = 100% and %Fe + %Mn = 100%, respectively (carbon, which is not detected and has no influence on the spectra, can be disregarded).

Special care was necessary in these fittings due to the overlapping of the main Co peak (KL3, 6.930 keV) with the Fe-KM3 peak (7.058 keV), and also with the escape peak of Zn-KL3 (6.899 keV). Even being attenuated by the deposit layer, the Fe-peaks from the steel are stronger than the Co peaks. Due to this overlapping, the fitting software sometimes overestimates or underestimates the Co-K peaks. This can be visually verified by comparing the experimental data with the fitted curve of the Co-KM3 peak (7.65keV), which is not overlapped.

As this less intensive Co peak is not overlapped, it allowed a second, simpler, quantification method to be used: Co-KL3 and Co-KM3 were fitted independently and only the Co-KM3 area was used in the calculations. This is usually a bad practice, because these peaks are not physically independent, but in this case it is useful in order to avoid the problems created by the overlapping, especially at very low Co-contents. In this case, of course, calculating the mass fractions by the Fundamental Parameters software would be nonsense. Therefore, the mass fractions were estimated from calibration curves based on Zn-Co reference samples. In the scope of this project, some Zn-Co deposits analyzed by SEM-EDXA were considered as references.

3. Results and discussion

3.1 Composition and layer thickness from EDXRF

Figure 1 shows the spectrum of a sample deposited at -1450mV from solution A. One can observe the overlapping of Fe-KM3 (7.058 keV), Co-KL3 (6.930 keV) and the escape peak of Zn-KL3 (6.899 keV). The presented fitting was obtained by assuming a Co-Zn-layer thickness of 8.64 μm. This value came from the optimization of the internal coherence of the fitting results. Several different layer thicknesses were iteratively tried from 5 to 30 μm, with an arbitrary value of photon flux ($F_{arbitrary}=2.60 \cdot 10^7$ photons/s). For any trial, the Zn-Co-layer composition obtained could be adjusted to totalize 100% by changing the photon flux to a corrected value, $F_{correxted}=(\%Co + \%Zn) \cdot F_{arbitrary}$. But the value %Fe + %Mn in the substract should also add to 100%, and this will only happen for a single layer thickness value, which is then assumed as correct. Even if the assumed value of photon flux is arbitrary, a correct thickness should lead to $\%Co + \%Zn = \%Fe + \%Mn + \%Cr=F_{corrected}/F_{arbitrary}$. So, the Zn-Co-layer thickness assumed in the fitting was changed in the new trials simply in order to minimize the difference between %Co + %Zn and %Fe + %Mn . Figure 2 shows these values for the last four incorrect trial values of Zn-Co-layer thickness in the iterative process, and for the final value 8.64 μm, assumed as correct. One observes that the results are very sensitive to small changes in the thickness. The 8.64 μm thickness lead to %Co + %Zn = %Fe + %Mn + %Cr = 0.2722, then the correct flux could be assumed as $F_{corrected}=2.60 \cdot 10^7 \cdot 0.2722=7.08 \cdot 10^7$ photons/s, leading to Co = 11.7% and Zn = 88.3% as the

final result (in the final steps, the Zn-Co-layer composition assumed in the fitting was also modified iteratively to meet the obtained composition).

For the fittings of the spectra from deposits obtained from solution A, the densities assumed for the Zn-Co-layer were estimated from the weighted average densities of pure hexagonal Zn and pure hexagonal Co (the assumed composition, as mentioned, was iteratively changed according to the resulting composition). For solutions B and C, the thicknesses so obtained were compared to the measured values in sections observed in the SEM, thus allowing a correction to be made in the densities. A factor of around 0.95 was found for them, corresponding to an apparent density from 6.87 for 95%Zn to 6.80 for 99%Zn. The resulting thicknesses for solutions B and C, and also for the non-corrected values of solution A, are shown in Figure 3 as function of the charge. Although deposition potentials were different for each charge, reasonable linear correlations were found for each solution. The Co-richest solution (A) gave rise to lower thicknesses, and vice-versa, what can be explained by the higher density of hexagonal Co. If all the depositions conditions except the charge were constant, one should expect the thickness to be directly proportional to the charge. One observes, however, that the inclination is positive, as expected, but that the lines do not cross the axis origin. This can be explained because, as already mentioned, the different depositions for each solution were made with different potentials, thus leading to different layer compositions, as will be seen is section 3.3.

3.2 Comparison with SEM-EDXA results, confidence and reproducibility

The %Zn/%Co ratios obtained by SEM-EDXA in surface observation are compared to the EDXRF values in Figure 4. For low Co-contents, one observes some dispersion, which can be attributed to the poorer Co-K fitting in EDXRF due to Fe-K overlapping (which does not happen in SEM, due to its smaller depth of analysis). But we should consider also that the EDXA quantification process should be very affected by the porosity and surface roughness of the deposits (which is different for each deposition condition) and that the EDXA analysis depth corresponds only to around 5 to 20% of the layer thickness, and therefore may be not representative of the average composition. The same SEM-EDXA compositions were used to establish correlation constants for the second quantification method, based on reference samples. For this calibration, a graph similar to Figure 4 was obtained, leading to the equation %Co/%Zn = 5.7038 (Co-KM3$_{area}$/Zn-KL3$_{area}$) + 0.0103. R^2 obtained for this correlation was 0.9477, which is poorer than that obtained for the Fundamental Paramenters results (0.9726). Also, it is observed that the constant 0.0103 is pretty high, as the curve should be expected to cross the origin. Anyway, this second method is much quicker, because depends on just one software fitting, and can be used for control purposes.

For deposits obtained at -1450mV from solution A, the Co-K peak areas are large, typically around 100000 counts, and the sigma/area ratios for them were in the range of 0.2%. For deposits obtained from the Co-poorest solution C and higher potentials (-1350mV, for instance), the peaks are much smaller, typically around 1200 counts, and the sigma/area ratios increased to around 12%. On the other side, the Co-K/Zn-K area-ratios for five different depositions in the same nominal conditions presented standard deviations from 3% for high Co contents to 9% for low Co contents.

3.3 Deposit composition as function of the deposition variables

Figure 5 shows the %Co/%Zn ratios obtained for different deposition potentials for solutions A, B and C. One observes that more negative potentials lead to Co-richer deposits, as expected from the voltametric results for the two ions [2]. One observes, as also expected,

that Co-poorer solutions give rise to Co-poorer deposits. This effect is much stronger from solution A to B than from solution B to C, as can be seen in the inset of Figure 5.

4. Conclusions

It was observed that EDXRF is a quick and reliable technique for compositional analysis of Zn-Co deposits on steel, and that a standardless Fundamental Parameters method can be used to determine the composition and the thickness or the density of the deposited layer by using the multilayer option of PyMCA. To reach coherent results with this method, a series of trial fittings should be done in order to optimize a quality criterion, which in this case was choosen as the totalizing to 100% of the mass fractions of both Zn-Co layer elements and steel-substrate elements.

Using the multilayers option instead of a monolayer model is important because, although Fe-K peaks are enhanced by Co-KM3, Zn-KL3 and Zn-KM3 peaks (which are above Fe-K absorption edge energy), no corresponding attenuation effects should be expected on Co-KM3, Zn-KL3 and Zn-KM3 peaks (except by tertiary fluorescence), because these characteristic x rays are generated in the external layer and reach the detector without interacting with Fe atoms.

On the other side, it was also observed that a purely mathematical quantification method based on calibration by reference samples also leads to reasonable results in the composition range of the analyzed samples, and is adequate for control purposes.

The technique was successfully used to verify the effect of deposition variables on the deposit composition, leading to correlations which are coherent with the results of electrochemical essays.

References

1. C. R. Tomachuk, C. R. et al. Características morfológicas, estruturais de resistência à corrosão da liga ZnCo obtida por corrente pulsada. Revista Matéria, vol. 7, n. 1, 2002

2. J. M. Falcón Roque. Estudo da eletrodeposição da liga Zn/Co sobre aço carbono e sua resistência à corrosão. MSc dissertation, Escola Politécnica da USP, 2010.

3. V.A. Solé, E. Papillon, M. Cotte, Ph. Walter, J. Susini, A multiplatform code for the analysis of energy-dispersive X-ray fluorescence spectra, Spectrochim. Acta Part B 62 (2007) 63-68.
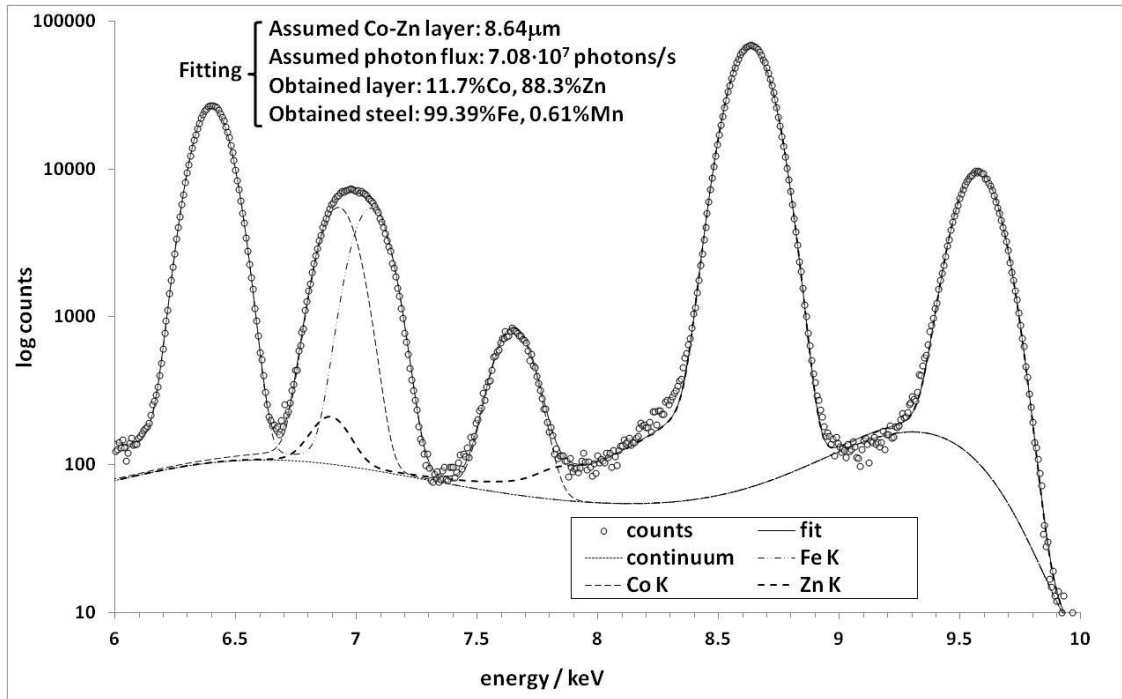
Figure 1 - EDXRF spectrum of sample deposited at -1450mV from solution A, with the fitted Fe-K, Co-K and Zn-K curves for layer thickness of 8.64μm
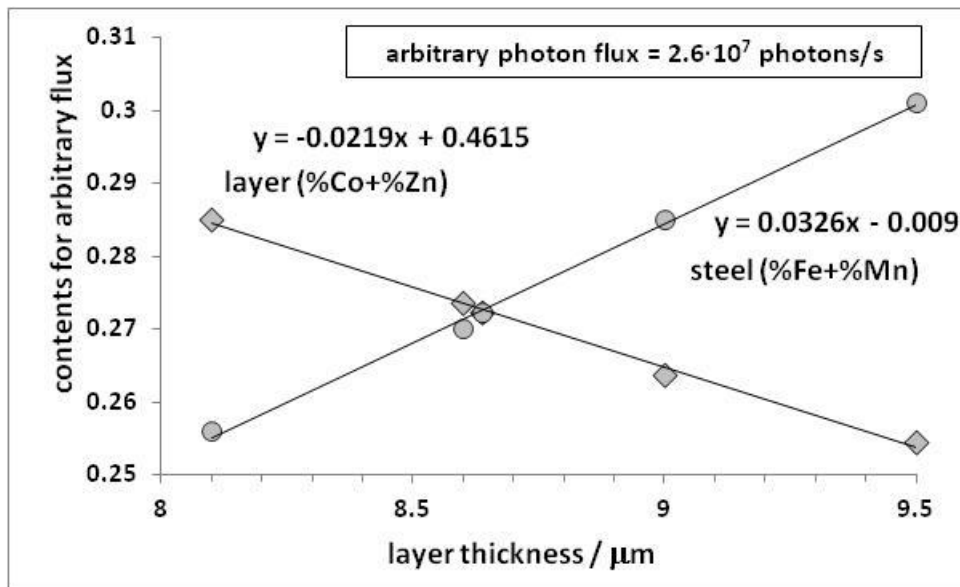

Figure 2 - Values of %Co + %Zn and %Fe + %Mn obtained from fittings with five different layer thicknesses of the spectrum of Figure 1
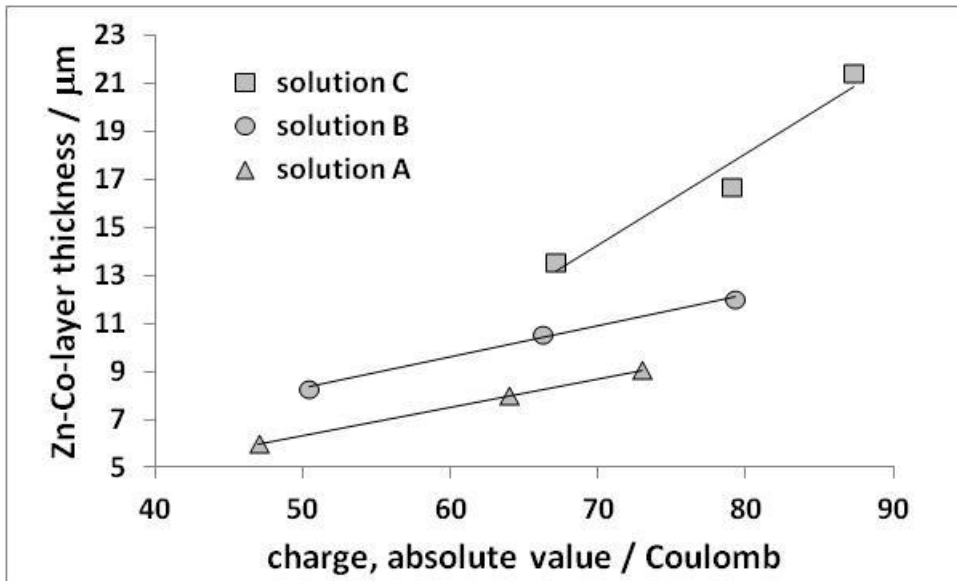
Figure 3 - Layer thickness obtained in the fitting as function of the charge used in deposition
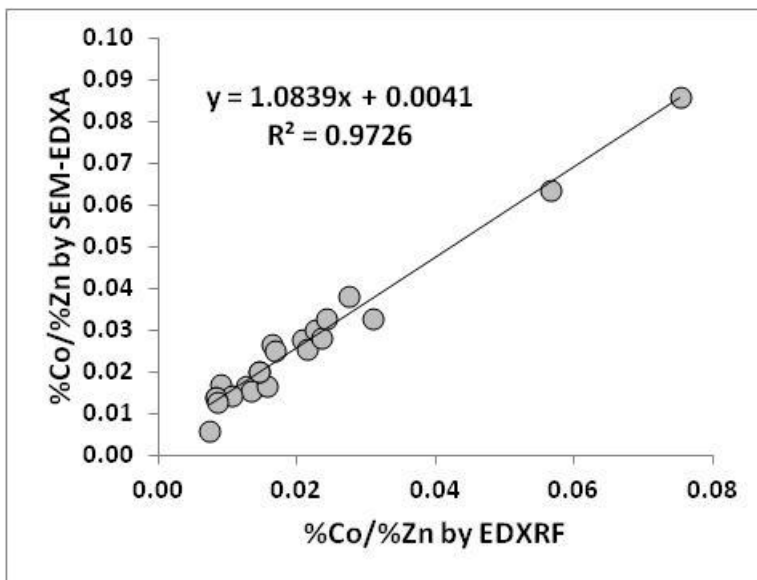

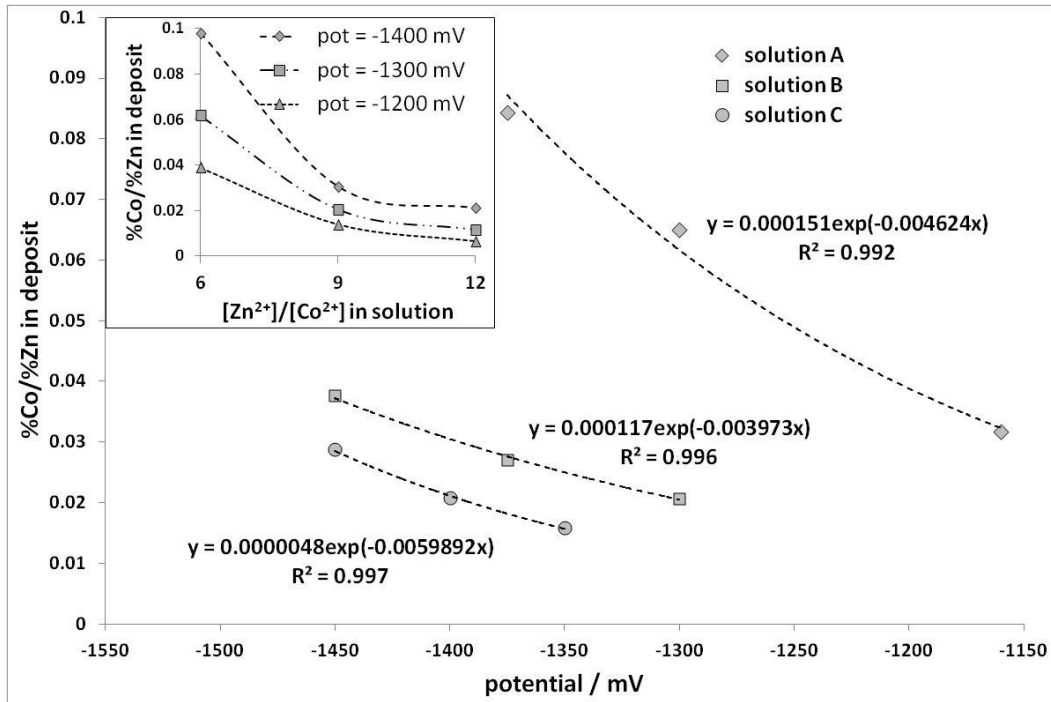Figure 4 - Comparison of %Co/%Zn obtained by EDXRF and SEM-EDXA

Figure 5 - %Co/%Zn ratio as function of deposition potential for solutions A, B and C (average values from three experiments for each point). In the inset, the effect of the solution composition on the deposit composition is described for three arbitrary potentials using the exponential correlations of the main graph for each solution (the lines in the inset graph are just illustrative).