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Study of chromate coatings obtained on phosphatized steels: a characterization by AES and XPS techniques

L. FEDRIZZI
Engineering Department, University of Trento, 38050 Mesiano di Povo, Italy
F. MARCHETTI
Material Science Division, I.R.S.T., Trento, Italy

Electrogalvanized and phosphatized steel sheets were passivated in chromate baths, and both the composition and temperature of these were varied in order to study the effects of such parameters on the chromate film formation. Scanning electron microscopy (SEM) together with microanalytical electronic spectroscopy techniques such as Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were chosen as the most useful methods for a suitable and careful study of the chromate presence, distribution and thickness. The chromium presence on the treated surfaces is easily detectable by XPS. Moreover it is possible to compare the surface chromium content of differently produced specimens. The detection of chromium is more difficult using AES, due to charging problems. Nevertheless, by this technique we found that the passive film is not homogeneously distributed on the whole phosphatized surface, but it is localized on randomly distributed areas, the chromate passive layer being very thin (about 4 nm). With respect to corrosion resistance of electrogalvanized steel, it seems that passivation in baths containing only Cr^{3+} is more effective than passivation in baths containing Cr^{6+}.

1. Introduction

Protection of metal surfaces is a critical factor in determining the extended service life of a structure in polluted and hostile environments. There is currently a rapid growth in the technology of the protective coating of cold rolled steel and, in this field, outstanding Japanese achievements are being followed by developments in the U.S.A. [1].

As is well known, chromates are successfully employed as corrosion inhibitors of various metals if added in sufficient quantity to aggressive aqueous solutions. Moreover, a noticeable improvement in the ability of a metal surface to resist atmospheric corrosion is achieved by superimposing a thin chromate conversion coating obtained by dipping the metal into a chromic acid bath. "Chromatizing" is widely used directly on metals (aluminium alloys) or as a final treatment on electrogalvanized steels in order to reduce the formation of white rust [2].

A typical procedure consists of dipping the items for some minutes in an acid bath containing Cr^{6+} and Cr^{3+}, so obtaining a very thin film of a hydrated chromium–chromate ($Cr_2O_3 \cdot CrO_3 \cdot nH_2O$) [3].

More recently chromate treatments were performed also on phosphatized steel and this process appears to be of special interest [4]. The coating quality and effectiveness are strongly dependent on the bath composition and on the process parameters. Many investigations are under way seeking a better knowledge and an improvement of this treatment. In particular the use of newly formulated baths containing Zn^{3+} or only Cr^{3+} salts, resulted in an improved resistance of electrogalvanized steel samples in the salt spray chamber test [5].

The aim of this work is the study of the chromate passivation film obtained on electrogalvanized and phosphatized steels from baths of different formulations. Particular attention was paid to the surface distribution and thickness of the passive layer as well as to its chemical composition. Because of the non-homogeneous distribution and the extreme thinness of the chromate film, X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) techniques were chosen as the most useful for a suitable and careful study of our materials [6].

2. Experimental details

The substrates chosen for our investigation were usually electrogalvanized steel sheets coated with a 2 μm thick phosphatized layer. The phosphatizing bath was composed of nickel, manganese and zinc salts with nitrites and chlorates as etching agents. As is well known, the presence of Mn in the phosphatizing bath favours the formation of "pseudophosphophyllite" crystals also on the zinc substrates and the presence of such crystals was shown to favour paint adhesion and consequently corrosion resistance [7, 8].

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TABLE I

Bath	Composition	Concentration (g/l)	pH
1	Cr^{6+}, Cr^{3+}	0.5	3.7
2	Cr^{3+}	1	3.7

The samples were then passivated by immersion in two different chromate baths as shown in Table I. The immersion time was 60 seconds and two different bath temperatures were chosen: 20 °C and 50 °C.

The morphological and chemical characterization was performed by scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDXS). All electron spectroscopy measurements were performed in the same ultra-high vacuum system (base pressure at 10^{-10} torr). The Auger depth profiles were obtained using a Perkin Elmer PHI 590 scanning Auger spectrometer along with argon ion etching. The electron beam energy was 3 keV and the beam current was about 200 nA. The argon ion beam, with an energy of 2 keV, was rastered over a 2 mm^2 area. The X-ray photoelectron spectroscopy (XPS) data were acquired using a Perkin Elmer PHI 545 double pass analyser with a bandpass energy of 100 eV. An Mg K_α non-monochromatized X-ray source operating at 400 W was used to generate XPS data

Finally the specimens were painted with a usual car cycle and subjected to the salt spray chamber test for 700 hours.

3. Results

The morphological characterization (Fig. 1) shows the typical crystal microstructure of the phosphate coating grown on zinc substrates, the average grain size being slightly higher with respect to data in the literature [9]. No evidence of morphological differences was revealed by the observation of the specimens passivated at different temperatures in the two baths. The "chromatizing" treatment in fact is very short and only relevant to the superficial layers so that it cannot produce noticeable modifications of the phosphate crystal morphology and microstructure. Moreover we found, randomly distributed on all the analysed samples, a very fine microstructure, easily discriminated and localized between the phosphate crystal grains. Nevertheless by EDXS analyses performed on microareas with an extremely reduced electron beam size, we did not detect the presence of chromium anywhere on the whole sample surface, for any bath composition or temperature. The thickness of the chromate film or some effects due to electron beam interaction with this material (surface diffusion) can explain the inability of this technique to detect chromium.

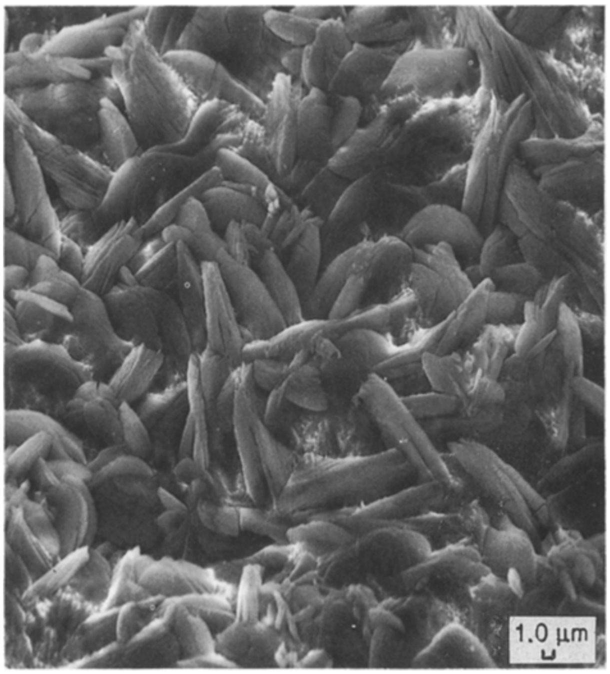

Figure 1 Typical SEM micrograph of passivated specimens.

To accurately characterize this system we used specific analytical techniques very sensitive to the surface (few monolayers) like electronic spectroscopies (AES, XPS). In particular the scanning AES was chosen to combine chemical information with lateral resolution, whereas the XPS was used to try to identify the chemical valency of the film components and to avoid electron beam radiation damage. As shown in Fig. 2 the XPS spectrum points out the peaks relevant to the coating component elements together with some surface pollutants, like carbon. (We did not perform cleaning procedures before the analysis.) The chromium presence on the surface of the samples obtained in bath 2, both at 20 °C and 50 °C, is well detectable by the presence of two peaks at the binding energy of 574.1 and 583.4 eV (Fig. 3). These peaks are weak and less defined on the samples treated in bath 1; nevertheless chromium traces may be identified.

As proposed by Biestek *et al.* [10], the formation of a chromate coating on zinc substrates involves the dissolution of the zinc and the evolution of hydrogen which is able to reduce the hexavalent chromium to the trivalent state. The Cr^{3+} precipitates as a gelatinous chromium hydroxide on the zinc substrate including a certain quantity of Cr^{6+}. Supposing a similar deposition mechanism also on phosphatized surfaces to justify the differences observed between the two "chromatizing" baths, we might assume that the reduction of the hexavalent chromium is hindered on such surfaces.

With respect to the treatment temperature, it appears that a temperature increase leads to an improved chromium deposition. In fact, semiquantitative data, obtained by the calculation of the chromium peaks area, gives a higher value for the samples obtained in bath 2 at 50 °C. On the other hand, owing to the small intensity of the chromium peaks, it is very difficult to gather information on the amount of chromium in the samples obtained in the bath containing Cr^{6+}.

In spite of the use of the XPS technique, from these experiments it is very difficult to obtain information about the chemical state of the detected chromium. This is due to our experimental conditions (high ana-

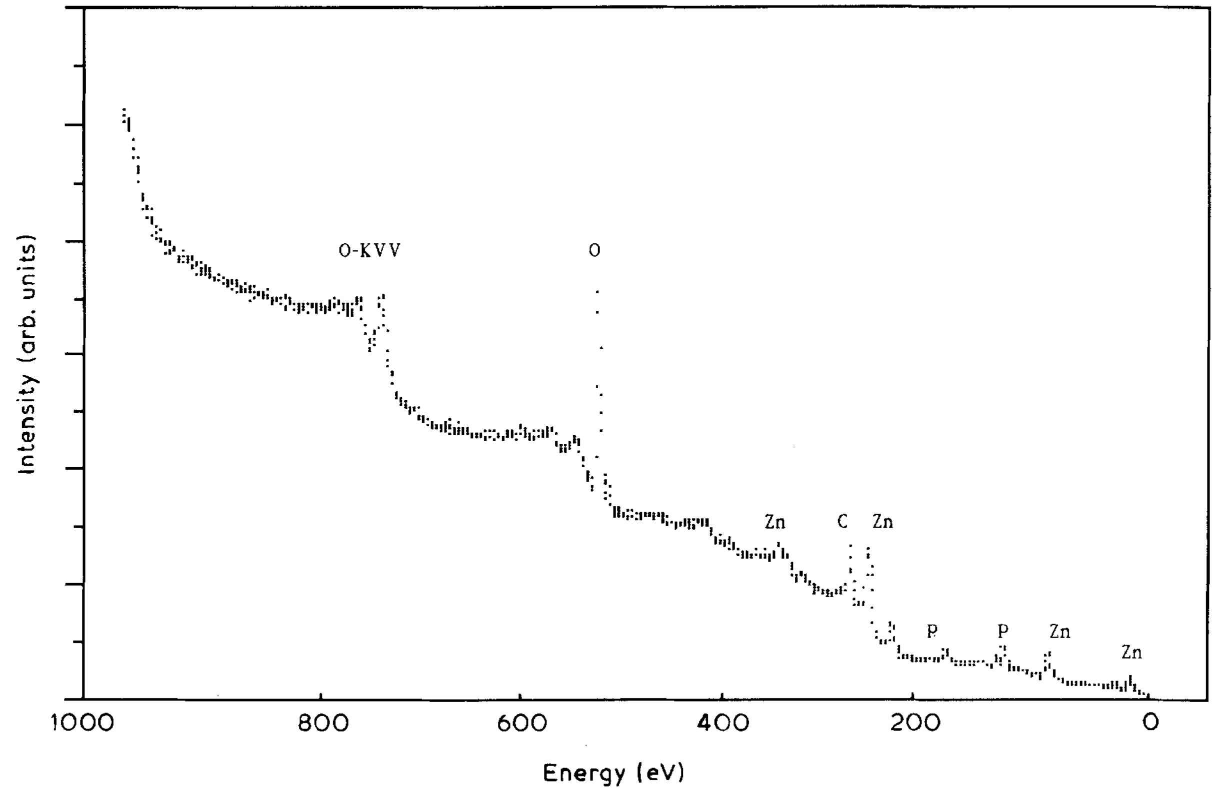

Figure 2 XPS spectrum before sputtering cleaning procedures.

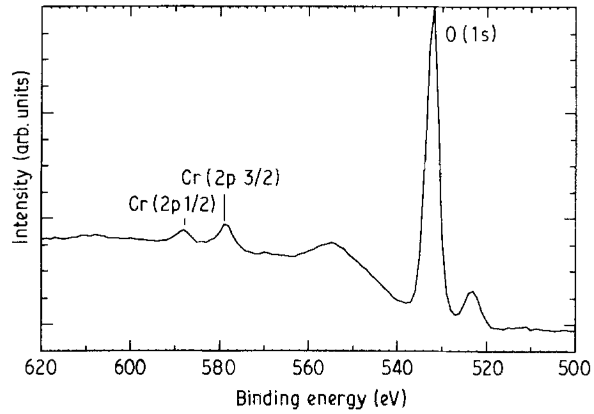

Figure 3 Detail of the XPS spectrum of Fig. 2.

lyser pass-energy) necessary to detect the chromium signal. As indicated in the recent literature [6] it is reasonable to attribute our signal to the presence of trivalent chromium on the samples' surfaces. The performed XPS analyses, involving a wide surface area, give interesting information about the average surface composition, but, because of the poor lateral resolution, no indication of the distribution and homogeneity of the passive layers was found. To obtain such information, we also used the scanning Auger technique, by which it is possible to carry out localized analysis on well identified points, up to a critical electron beam size of 300 nm in our instrumentation.

In this way we found two chemically completely different areas randomly distributed on the surface of all the analysed samples. Before sputtering cleaning, the spectrum more frequently found is shown in Fig. 4 and its main features are the following:

(a) the phosphorous signal is well defined with three sharp peaks;

(b) a carbon-related peak (pollutant) is present;

(c) there is a typical oxygen signal with three peaks, the right one being the most intense;

(d) the manganese, nickel and zinc peaks are well defined at the higher energies.

The second zone was significantly more difficult to find (Fig. 5). Moreover, in these zones we found charging problems during the analysis itself. When the analysis was finally completed the main characteristics

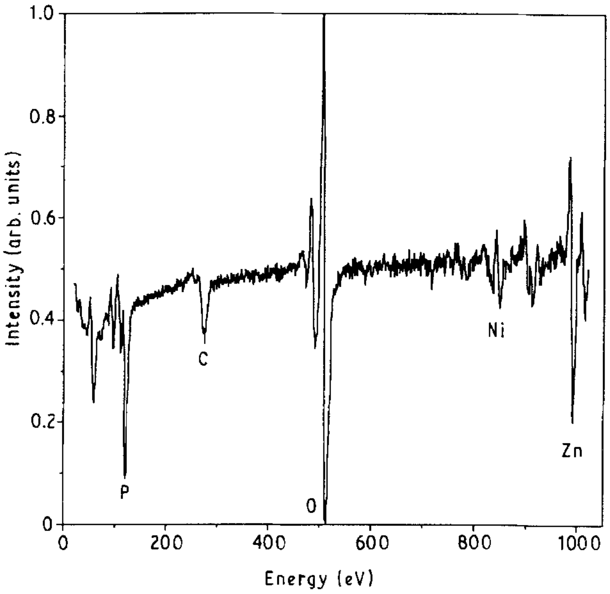

Figure 4 Typical AES spectrum of passivated specimens.

of the spectrum were:

(a) a peak related to phosphorus with a poor definition;

(b) absence of the carbon peak;

(c) a shift in the oxygen-related peaks towards higher energy values with the middle peak becoming the most intense;

(d) the manganese, nickel and zinc peaks are no longer clearly defined.

The charging problems mentioned above are clearly indicated by the presence at the lowest energy values of a strong peak [11]. This electrical behaviour could be attributed to the chromate coating presence.

To better understand the chemical meaning of the two detected areas we carried out a depth analysis. In Fig. 6 it is possible to observe the typical spectrum

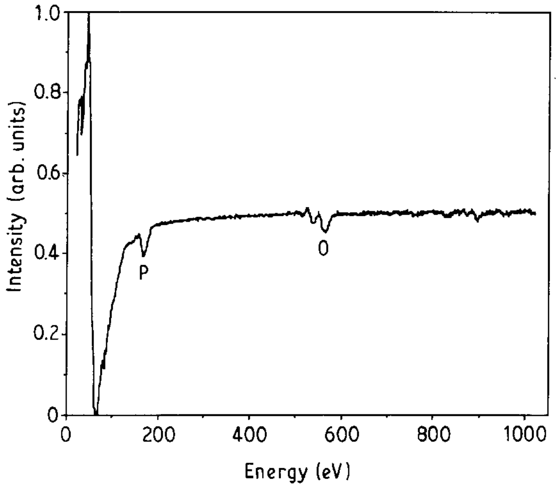

Figure 5 AES spectrum in the zones showing charging problems.

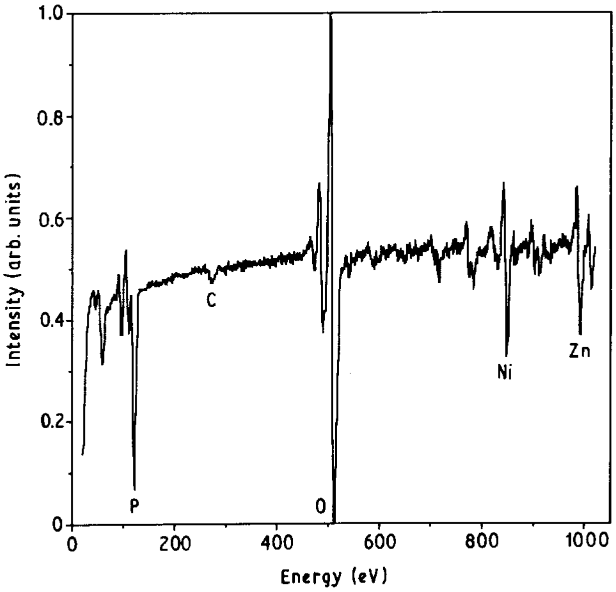

Figure 6 AES spectrum relevant to the zone analysed in Fig. 4, after 1 min. sputtering.

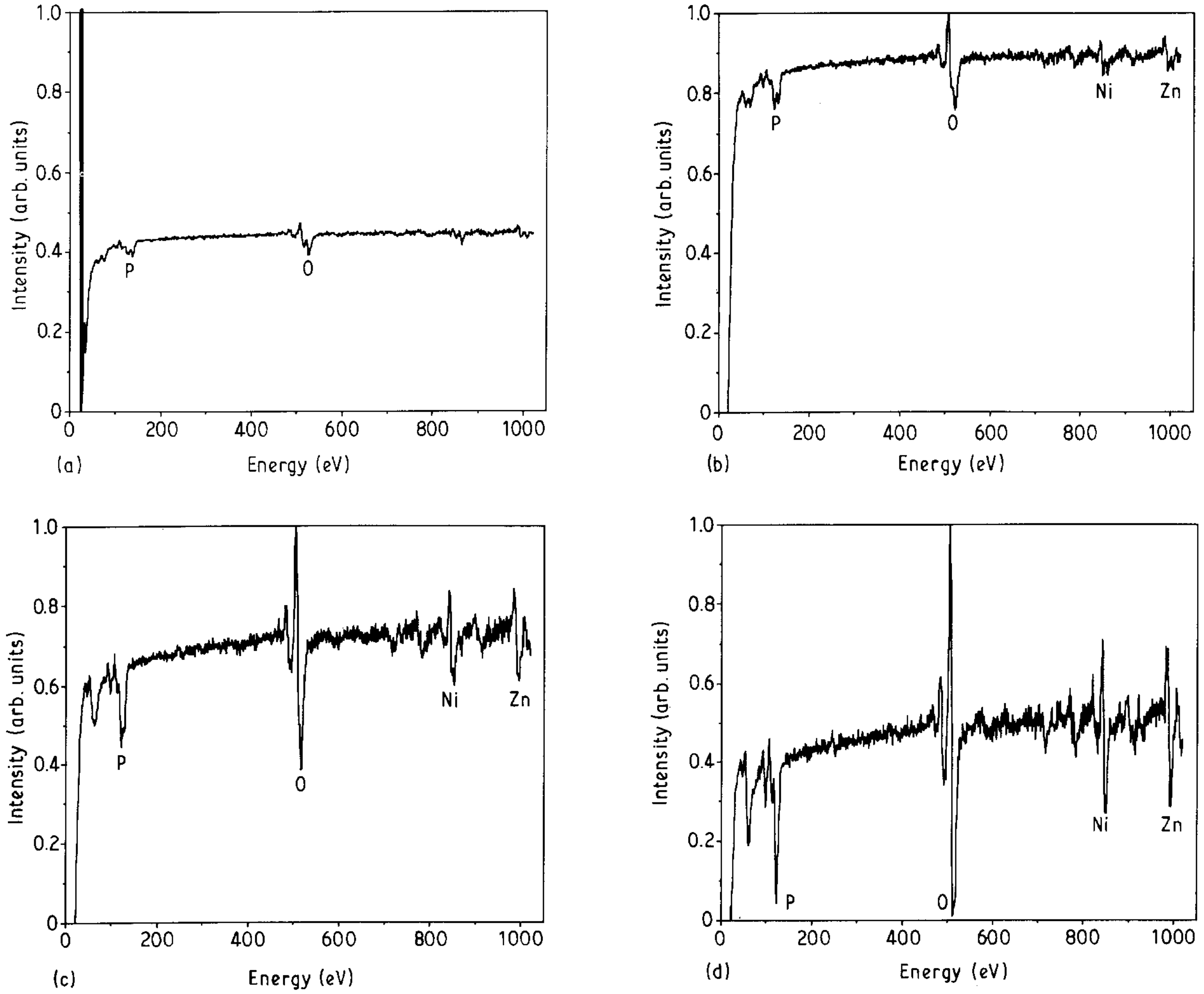

Figure 7 AES spectrum relevant to the zone analysed in Fig. 5 after (a) 0.5; (b) 1; (c) 1.5; (d) 2 minutes of sputtering.

obtained after sputtering of the area discussed in Fig. 4. The only difference between the spectra obtained before and after the sputtering treatment (of 1 min), is the noticeable decrease of the carbon related peak. This fact confirms that carbon is present in this zone as a contaminant which disappears during sputtering. This spectrum is representative of the phosphate crystals, mainly composed of phosphorous, oxygen, zinc and nickel.

On the other hand, the areas represented by the spectrum of Fig. 5 undergo noticeable transformation during sputtering. As shown in Fig. 7, during sputtering we can observe a rapid evolution of the phosphorous and oxygen peaks towards the more usual shape, typical for the phosphate crystals. Moreover, at the lowest energy, the anomalous peak related to the conductivity properties of the analysed material disappears. In this way, after a short sputtering time, we obtain the same Auger spectrum as that shown in Fig. 6.

Though, as a consequence of the charging problems, the Auger chromium peak is not clearly detectable in our spectra, by the previously performed XPS analyses, showing the Cr presence, and by the different conductivity of the analysed zone, the very anomalous phosphorus and oxygen peaks' shape and the thinness of the analysed chemical compounds, we can deduce that these analysed areas are representative of the chromate coating.

Therefore the Auger analyses indicate that the chromate coating obtained on an electrogalvanized phosphatized steel is not uniformly distributed on the whole surface but appears randomly localized, probably as a function of the substrate morphology. In fact the very rough surface due to the presence of the phosphate crystals could produce microareas with a different chemical reactivity (various local pH values), or zones which can remain in contact with the bath solution for different times.

As mentioned above the passive layer thickness is very small (about 2–4 nm); consequently it is very difficult to ascertain, by sputtering, evident differences in thickness between the various tested samples, the film thickness not being homogeneous on the same analysed sample. Nevertheless the film obtained in bath 2 seems to be slightly thicker. On the contrary no differences in thickness are identifiable as a function of the treatment temperature.

To conclude our study we submitted all the samples to a salt spray chamber test after painting them with an epoxy type paint. The surfaces of the samples after 700 hours test are shown in Fig. 8. By comparing the scratches, it is clear that the behaviour of the samples passivated in the bath containing only Cr^{3+} ions is better because of the improved adhesion of the coating and the higher chromium content.

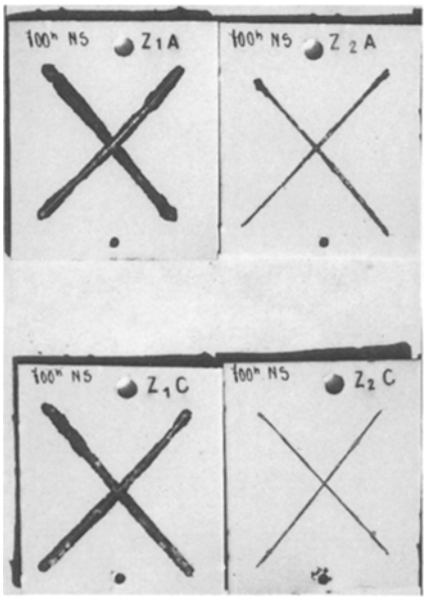

Figure 8 Surface morphology after 700 hours salt chamber test; at the left samples obtained in the bath 1.

4. Conclusions

Electrogalvanized and phosphatized steel sheets were passivated in baths containing Cr^{3+} and Cr^{6+} at two different treatment temperatures.

XPS and AES techniques were used to characterize the chromate coatings and were found to be quite useful in detecting the chromate presence, distribution and thickness. In particular, by XPS the chromium presence is easily detectable and it is possible to compare the chromium amount retained on the surface of differently produced specimens. Consequently we found that "chromatizing" in baths containing only Cr^{3+} is more effective than in baths containing Cr^{6+} and Cr^{3+}. Moreover, some small differences in the chromium content were also found comparing the specimens treated in bath 2 at different temperatures.

The detection of the chromium presence is more difficult using the Auger technique, due to charging problems. Nevertheless the passive layer presence is well detectable by the phosphorus peaks' convolution, the oxygen peaks' shift and by the changed conductivity of the chromium oxide layer. Due to these features we have found that the passive film is not homogeneously distributed on the whole phosphatized surface but is localized on randomly distributed areas, these areas being determined by the surface morphology. The Auger analyses combined with sputtering have also shown that the passive layer is very thin (about 2–4 nm).

To conclude, XPS and Auger analyses are both useful and necessary to clearly characterize "chromatizing" layers obtained on electrogalvanized and phosphatized steel sheets. Concerning corrosion resistance of electrogalvanized steel, it seems that passivation in baths containing only Cr^{3+} is more effective than that in Cr^{6+} baths.

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