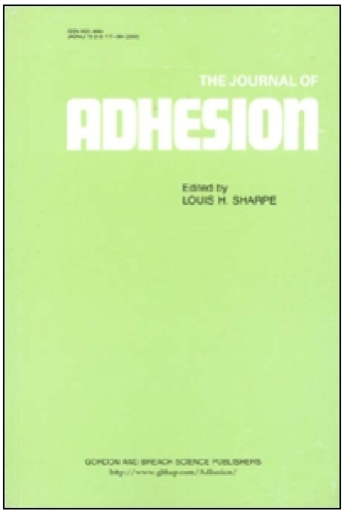

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Recent Developments in the Spectroscopic Characterization of Modified Surfaces for Adhesive Bonding or Painting

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Recent Developments in the Spectroscopic Characterization of Modified Surfaces for Adhesive Bonding or Painting†

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Low-Energy Electron-Induced X-ray Spectroscopy (LEEIXS) and X-Ray Fluorescence Spectroscopy (XRFS) have been used to study the near-surface chemistry of metallic substrates submitted to various pre-bonding or pre-painting chemical or electrochemical treatments. Applications given in this paper concern firstly stainless-steel and Ti-6Al-4V adherends and secondly steel and galvanized steel sheets. Experiments provide the information necessary to understand how treatments such as anodization, chemical conversion, rinsing . . . affect the chemistry and properties of surfaces. So, specific examples are shown, outlining how the chemistry of the adherend surface may be correlated with its bondability, the strength of bonded joints being determined using a three-point flexure test. In addition, it is discussed why the information available through the spectroscopic techniques used are quite complementary to the ones provided by more sophisticated surface analysis instrumentations.

KEY WORDS Adhesion; Low-Energy Electron-Induced X-ray Spectroscopy (LEEIXS); near-surface chemistry; prebonding treatments; steels; Ti-6Al-4V adherends.

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1 INTRODUCTION

During the past two decades many new spectroscopic techniques have been developed and refined further to provide information on the chemical composition of solid surfaces and interfaces. This effort is fully justified by the increasing recognition of the decisive role played by the surface of a material in determining its properties on a macroscopic scale. So, surface-sensitive techniques such as X-ray photo-electron spectroscopy (XPS), Auger electron spectroscopy (AES), secondary ion mass spectroscopy (SIMS) and ion scattering spectroscopy (ISS) have been largely employed and their usefulness has been amply demonstrated in many areas.

In the particular field of adhesion these methods have been essentially applied to the study of either the surface properties of the metallic adherend materials or the interfacial interactions between organic polymer (adhesive or paint) systems and various metals or alloys (see, for instance, References 1–8). In these studies, it is shown that numerous parameters may play a major role in the formation of a metal–polymer bond, in the initial strength of the bond and in its durability in various agressive environments. One of these parameters, the chemistry of the metallic substrate, is particularly important. Indeed, the overall performances of adhesive or paint/metallic substrate systems have been shown to be clearly dependent, among other factors, on the nature and manufacturing process of the substrate and on the nature of the pretreatments and treatments used to modify its surface before it is bonded or painted. In these studies, it has been also shown that these techniques, which offer different sensitivities, information depths, lateral resolutions, etc . . . provide complementary data and that a more or less complete understanding of a problem involves at least, the use of a multi-method approach. In these conditions, and account being taken of their specificities and their potential uses, these techniques undoubtedly will be, in the future, more and more employed in the study of the effects of surface chemistry on the bond characteristics of adhesives or paint coatings on various substrates. However, it is also clear that a definite need exists for techniques able to provide surface information not only from the outermost atomic layers but equally from thicker zones (*e.g.* of several tens of nanometers or more), the chemical properties of which may change considerably when substrates are submitted to pre-bonding or pre-painting treatments. In this context, the main objective of the present paper is to describe results of surface characterization experiments using non destructive (*i.e.* without sputtering) and largely unexploited X-ray emission techniques (XRFS, LEEIXS) and to demonstrate their large interest for obtaining the information necessary to develop a better adhesion on metallic substrates and a better durability of the relevant systems.

2 EXPERIMENTAL

X-ray fluorescence spectrometry (XRFS) is an emission technique based on excitation of the atoms constitutive of the sample to be analysed. In general, excitation is produced by a primary X-ray beam emitted by a Coolidge tube. The wavelength (wavelength dispersive spectrometry/WDS) or energy (energy dispersive spectrometry/EDS) of the emitted photons (secondary X-rays) is measured to determine what elements are present in the specimen (qualitative analysis) and the intensity of the corresponding characteristic X-rays is a direct or non-direct measure of the amount of each element in the specimen (quantitative analysis). Despite largely spread ideas to the contrary, XRFS must be considered as a surface technique[9–11] when the X-rays being measured only originate from ultra-thin or even thin films, *i.e.* when the surface layer of interest contains elements not present in the substrate. In these conditions, the intensity of a relevant X-ray signal is generally a direct function of the surface concentration of the element being investigated. Obviously such a statement is essentially valuable for elements which can be detected with a sufficient sensitivity (*i.e.*, in routine, for elements of $Z \geqslant 11$).

Low-energy electron-induced X-ray spectrometry (LEEIXS) is a new soft and ultra-solft X-ray emission spectroscopy.[10–14] The device used is a wavelength-disperive (WDS) X-ray spectrometer, equipped with a gas discharge tube (or cold cathode tube) operating in the primary vacuum of the spectrometer. This source is used to bombard the sample surface with a quasi-monoenergetic electron beam, the energy of which is selectable over the range 0.5 to 5 keV. The probed depth, depending among other parameters upon the incident electron beam energy and upon the sample nature, typically ranges from 5 to 100 nm, the probed area being about 1 cm^2. This technique allows both atomic (qualitative and quantitative) and molecular (qualitative) analysis. It is suited very well to the analysis of light elements (B, C, O, N, F . . .) and so, to the measure of oxide layer thicknesses by using either an external standard or an auto-standardization method.

The three-point flexure test[15–18] used in this work is a useful mechanical method developed in order to determine the practical adhesion[19] (*i.e.* the forces or the work required for the disbondment either at the interface or in the interfacial region) of adhesive or paint/metallic substrate systems. This test has already shown its potential not only in evaluating the effects of various adherend treatments but in optimizing, for a given treatment, the experimental conditions to be chosen in order to produce better adhesion. Flat adherend sheets, about 1 mm in thickness, are prepared by die-cutting to provide identically-sized strips (50 × 10 mm) and then are submitted, prior to bonding, to different surface treatments. The single adherend/adhesive specimen geometry and the specimen preparation fixture have been previously described.[15–17] A three-point flexure tester (FLEX 3 from IRSAP, France) is used and fitted to an APPLE IIe microcomputer in order to monitor the cross-head displacement, to record the load/displacement curve and to calculate the parameters of interest {slope of the load-displacement (P *vs.* d) curve in the linear zone, ultimate load (P_{max}) and displacement (d_{max}) before sample failure}.

3 RESULTS AND DISCUSSION

3.1 Prebonding treatments of metallic adherends

Many chemical etchings and oxidising treatments are commonly used on metals and alloys in order to produce a strong and durable surface layer which enables good long-term properties of the adhesive-substrate interfacial zone even in agressive environments. Anodization is one of these treatments. It has been largely used for aluminum, titanium and their respective alloys (see, for instance, References 20–22 and cited literature). Recent investigations concerning stainless steels[23–25] show that the formation of "thick" films by such a process can also produce steel/adhesive bonds which are stronger than those obtained using other, more widespread, prebond treatments[26–29] such as acid etchings or mechanical roughenings.

The first examples described here are relative to stainless steel adherends. The specimens used are industrial quality AISI 304 L sheets, acetone degreased, acid pickled and then galvanostatically anodized in a hot sulfuric acid-potassium dichromate bath. The effect of anodization of steel surfaces can be followed using LEEIXS. Spectra (a) and (b) in Figure 1 are typical of such substrates which are subjected (a) to chemical pickling (in 15% HNO_3, 5% HF at 22°C for 5 min) and to rinsing in deionized water and (b) to anodization ($j = 1$ mA cm^{-2}) in a hot (70°C) concentrated (400 g l^{-1} $K_2Cr_2O_7$ – 475 g l^{-1} H_2SO_4) electrolyte for 15 min. These spectra are obtained using an electron beam of 3 keV at a current density of 0.3 mA cm^{-2} and using a TlAP dispersing crystal ($2d =$ 2.571 nm). Under the energy conditions used in these experiments,

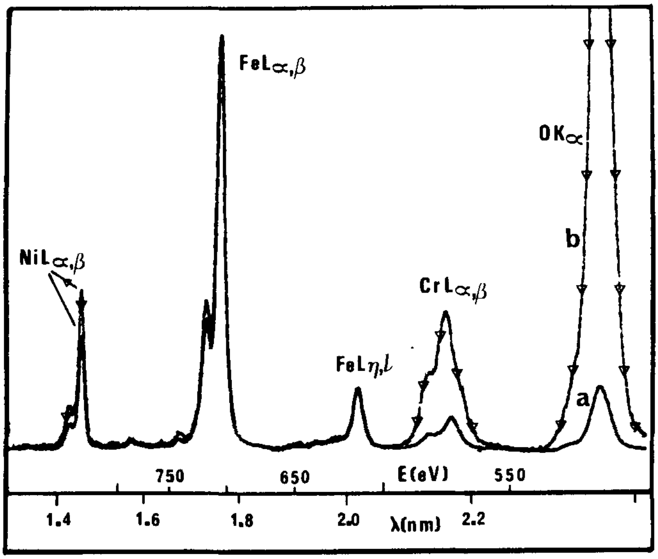


FIGURE 1 LEEIXS spectra of a stainless steel surface (a) before and (b) after anodization in a hot H_2SO_4–$K_2Cr_2O_7$ bath.

the maximal depth of analysis is about 50 nm in the metallic matrix (case a) and 90 nm in the Cr_2O_3/Fe_2O_3 oxide matrix (case b). More particularly, the comparison of these spectra shows evidence of the formation of a "thick" oxide film on the sample surface (a large increasing of the OK_α emission band intensity can be observed). It is also to be noticed that the intensity of the OK_α signal from spectrum (a) is associated with a residual oxide, the thickness of which is about 6 nm. In addition, it can be seen that the surface treatment used modifies the superficial concentrations of the alloying elements (significant changes in the relative intensities of Ni, Fe and Cr $L_{\alpha,\beta}$ emission bands can be reported). Figure 2 graphs the results of a quantitative analysis. It shows, as a function of

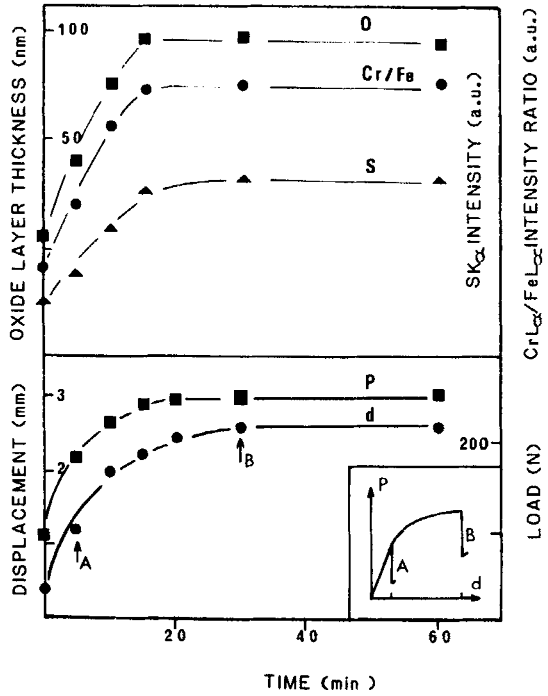


FIGURE 2 Anodization of stainless steels in a hot H_2SO_4–$K_2Cr_2O_7$ bath. Effects of anodization duration firstly on oxide film thickness, sulfur impurity incorporation (SK_α variations), Cr/Fe superficial concentration changes (CrL_α/FeL_α variations) and secondly on ultimate load (P_{max}) and ultimate displacement (d_{max}) of bonded specimens.

treatment duration, firstly the variation in thickness of the oxide films formed during the electrochemical process ($K_2Cr_2O_7$ concentration: 400 g l^{-1}; bath temperature: 70°C; current density: 1 mA cm^{-2}) and secondly the corresponding SK_α intensity and the CrL_α/FeL_α intensity ratio variations. It is noteworthy that the oxide thickness determination requires the measurement of the OK_α signal intensity and a standardization using either a self-calibration method or a specimen, the oxide thickness of which is known (*e.g.* measured by another technique).[30] Also to be noted is that those results concerning OK_α intensity measurements are obtained using an electron beam energy (4.5 keV) such that the thickness of the probed material is always greater than those of the oxide films. This condition is absolutely necessary for obtaining a direct relation between OK_α intensity and oxide layer thickness all along the investigated thickness range.

It is quite clear from the data presented in Figure 2 that: (i) the larger oxide thicknesses (90 nm or so) are obtained for treatment durations equal to or greater than 15–20 minutes, (ii) sulfur impurities are incorporated (probably in the anionic form SO_4^{2-}) into the anodic oxides and that to an amount roughly proportional to the film thickness, (iii) the sample surfaces become markedly more and more chromium-enriched (as Cr^{3+}) when the oxide film thickness increases. This enrichment seems to be consistent with a relative insolubility of this element compared to that of iron and nickel in the sulfo-chromic medium. It should be noted here that FeL_α and CrL_α intensity measurements are performed using a 3 keV primary electron beam and that, in these conditions, the maximal analysed thickness (*i.e.* 90 nm in the case of the fully oxided matrix and less when a part of the metallic substrate is analysed) is roughly the one of the thickest oxide layer. This fact explains why the Cr/Fe ratio remains constant for treatment durations greater than 15–20 minutes.

Figure 2 also represents (in the inset) typical load-dispacement curves (*P vs d*) obtained, using the three-point flexure test, from two anodized stainless steel/epoxy systems (treatment duration of the adherend being respectively 5 and 60 minutes). The adhesive used is a two-component epoxy resin (Araldite AY 103 with hardener HY 991). The bonded specimens are submitted to curing for 2 hours at 80°C, stored for 24 hours in a dessicator and then exposed to a humid environment for 72 hours at 70°C, 95% R.H. before testing. This procedure is used here because non-aged specimens exhibit such good interfacial properties that they undergo failure within the adhesive. Lastly, Figure 2 shows the variations, *versus* anodization duration, of both ultimate load (P_{max}) and displacement (d_{max}). It should be noted that P_{max} and d_{max} show quite similar evolutions. It is now of particular interest to point out, by comparing all the results presented in Figure 2, that there exists a remarkable correlation between the increasing of the oxide layer thickness and of the Cr/Fe ratio and the increasing of d_{max} or P_{max}. In other words, the strength of the joint varies with the two former parameters.

In the same manner, Figure 3 shows, as a function of anodization current density, respectively the variation in thickness of the oxide films formed during the electrochemical process ($K_2Cr_2O_7$ concentration: 400 g l^{-1}; bath temperature: 70°C; treatment duration: 15 min), the variation of SK_α intensity and CrL_α/FeL_α intensity ratio and the variation of P_{max} and d_{max} for the corresponding anodized stainless steel/epoxy systems. From these curves several conclusions are evident. Firstly, the thickest layers (90 nm or so) are associated with current densities about 1 mA cm^{-2}. Secondly, sulfur impurity incorporation and chromium enrichment (compared to that of iron) are, as in the previous experiments, directly dependent upon the oxide film thickness. Both these observations are consistent with the formation of an ever thicker oxide layer when current density increases in the range 0–1 mA cm^{-2}. Similarly, it can be noted that there is a drastic improvement in the mechanical properties of the bonded specimens (as shown by d_{max} increasing). In addition, for current densities above 1 mA cm^{-2}, the oxide film dissolution becomes the predominant phenomenon. The slight decrease of d_{max} is associated with thinner oxide layers when current density increases. However, the relevant mechanical properties remain strong. This fact can be explained by the presence at the adherend outermost surface layers of a very chromium-enriched zone as that has been observed by Auger electron spectroscopy.[31] Obviously, in this particular case, LEEIXS is not the more appropriate investigation method, on account of its relatively large analysis depth compared to the very low thickness of the modified zone remaining at the sample surface. Lastly, it should be noted, in contrast with the previous case (Figure 2), that P_{max} and d_{max} exhibit here quite different evolutions. The inset of Figure 3 emphasizes, in the present case, that d_{max} is the more significant parameter.[18] Indeed, the failure occurs in a *P vs d* curve zone for which, roughly, P_{max} does not vary while d_{max} goes on increasing.

These studies concerning anodizations *versus* process duration or current density highlight the major role played in the overall performances of the stainless steel/epoxy bonded joints by oxide thickness and surface chromium enrichment. However, this last parameter, as shown in Figure 3, seems to be the predominant factor. Some complementary studies (performed either by varying

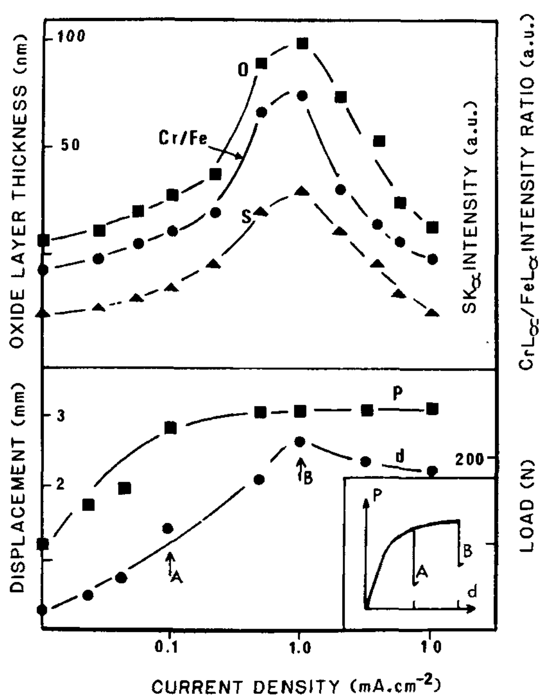


FIGURE 3 Anodization of a stainless steels in a hot H_2SO_4–$K_2Cr_2O_7$ bath. Effects of anodization current density firstly on oxide film thickness, sulfur impurity incorporation (SK_α variations), Cr/Fe superficial concentration changes (CrL_α/FeL_α variations) and secondly on ultimate load (P_{max}) and ultimate displacement (d_{max}) of bonded specimens.

other parameters such as electrolyte concentration and bath temperature or by using other oxidizing acid media such as nitric acid solutions) confirm this fact.[24,25]

The second example described here is relative to Ti–6Al–4V alloy adherends treated with a conventional phosphate-fluoride process (*i.e.* an aqueous solution containing 5% trisodium phosphate, 0.9% sodium fluoride and 2.6% hydrofluoric acid; treatment duration: 2 min at room temperature). This industrial surface preparation process, often described as a conversion treatment, is known to produce relatively thick "oxide" layers. However, con-

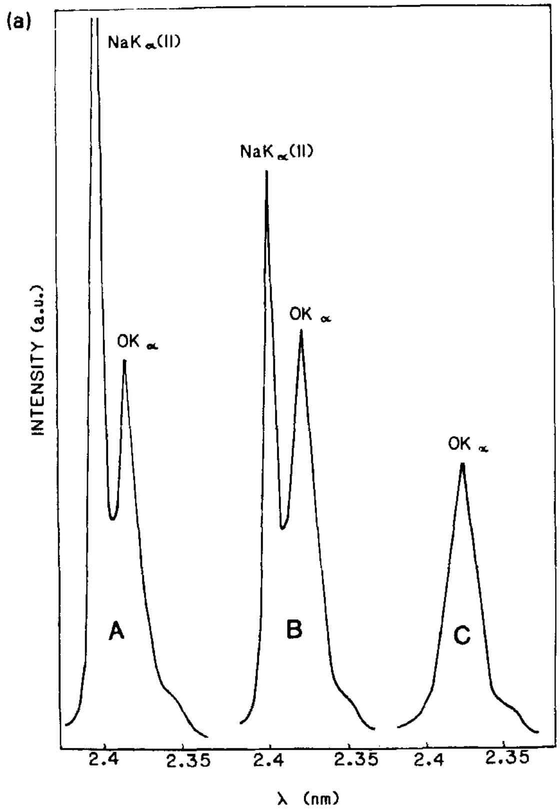


FIGURE 4 NaK_α(II), OK_α and FK_α LEEIXS spectra from the surface of a Ti–6Al–4V substrate submitted to a phosphate–fluoride process and rinsed for 10 (A), 30 (B) and 60 (C) seconds.

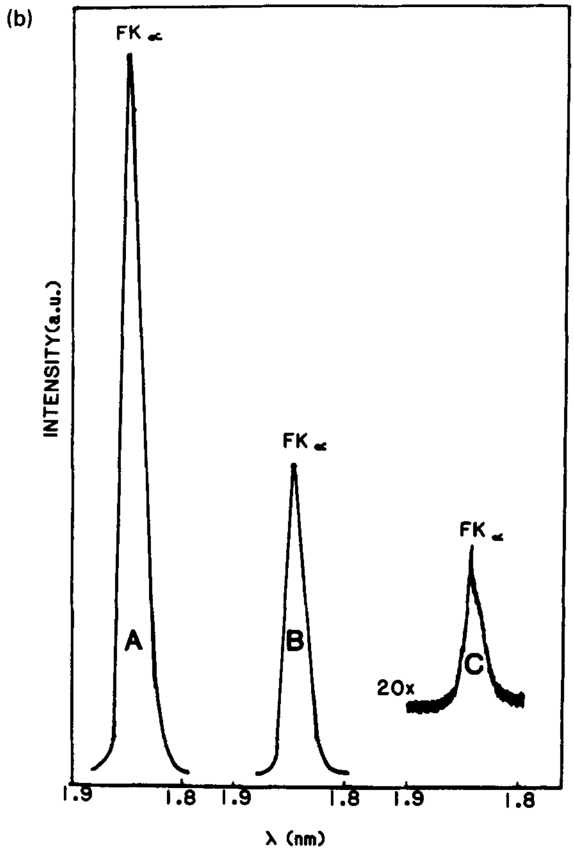
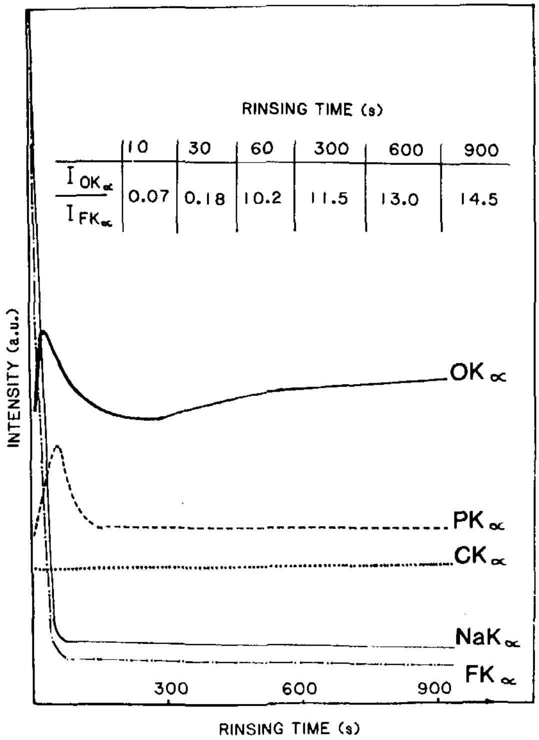


FIGURE 4 (*continued*)

troversial data have been reported concerning their thickness and composition as well as their crystallographic structure.[32–38] So, Hamilton *et al.*[32–34] show, using XPS, that the conversion coating is basically a titanium oxide TiO_2 which contains "impurities" such as F, P, Na, Al and C while Roche *et al.* infer, from AES, SIMS, ISS and LEEIXS studies, that the main surface compounds are titanium and sodium fluorides (TiF_4 and NaF).[13,39,40] As a matter of fact, the composition of the conversion coating is strongly influenced by the action of the rising procedure subsequent to the conversion stage. Figures 4a and b contain NaK_α (II), OK_α and FK_α LEEIXS spectra from Ti–6 Al–4 V panels treated as described above and rinsed in running tap water for 10 (A), 30 (B) and 60 (C) seconds, respectively. In addition, Figure 5 summarizes the effects of this treatment by following, as a function of rinsing time, the variations in intensity of CK_α, OK_α, FK_α, NaK_α and PK_α. It should be noted here that intensities of these signals cannot be directly compared, practical emission yields being very dependent upon the wavelength of the corresponding radiations. However, interesting observations can be made firstly about the largely decreasing amounts of fluorine and sodium with rinsing time and secondly about the presence (as impurities) of phosphates {quite similar PK_α and OK_α intensity variations can be seen during the first 100–150 s, the sharp increase during the very first seconds being associated with the removal of



RINSING TIME (s)	10	30	60	300	600	900
$\frac{I_{OK_\alpha}}{I_{FK_\alpha}}$	0.07	0.18	10.2	11.5	13.0	14.5

FIGURE 5 Effects of rinsing time of a Ti–6Al–4V substrate submitted to a phosphate–fluoride process on CK_α, OK_α, FK_α, NaK_α and PK_α intensity variations.

the outermost layers which are constituted of highly solubles compounds (TiF_4 and NaF)}. In addition, Figure 6 represents the X-ray emission bands $TiL_{\alpha,\beta}$ characteristic of the conversion coating after 10 s (A) and 600 s (B) rinsing time, a degreased titanium alloy substrate (C) covered only by its residual oxide layer, the thickness of which is about 5 nm and a TiF_4 standard (D). Let us point out here that an X-ray emission band is associated with electronic transitions between valence levels and a core level of a given atom. The chemical bonding influencing the electronic distribution in the valence levels, the structure of the X-ray emission band may also suffer this influence. The spectral modifications (named chemical effects) can, therefore, be used with the intent of characterizing the

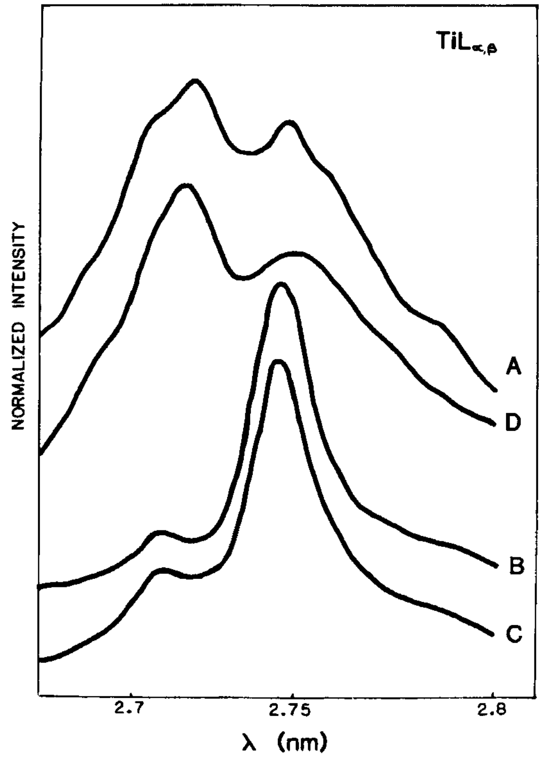


FIGURE 6 $TiL_{\alpha,\beta}$ LEEIXS emission bands from a Ti-6Al-4V substrate submitted to a phosphate-fluoride process after 10 (A) and 600 (B) seconds rinsing time, from a degreased Ti-6Al-4V substrate (C) and from a TiF_4 standard (D).

chemical state of some elements incorporated in a solid surface layer.[14] In the case studied here, comparison of the $TiL_{\alpha,\beta}$ spectra from Figure 6 and from other standards such as TiF_3, TiO and TiO_2[13,40] confirms that titanium fluorides are largely present in the conversion film (spectrum A is typically characteristic of the TiF_4 species) and that these titanium fluorides also undergo dissolution during the rinsing states. In addition, both the comparison of (B) and (C) emission bands (Figure 6) and the marked increase of the OK_α/FK_α intensity ratio (see Figure 5 inset and note that emission yield for FK_α is greater than for OK_α) clearly indicate that rinsing for a sufficiently long time leaves the surface mainly covered by a titanium oxide which is about 10 nm in thickness and which still contains "impurities" such as P and F. Lastly, it should be noted that (i) the thickness of the remaining oxide is directly determined by comparing OK_α intensities of the sample under investigation and of a standard obtained by anodization of a Ti–6Al–4V substrate,[40] (ii) another recommended rinsing procedure (15 min soak in deionized water at 90°C) leaves a slightly thicker oxide layer (15–20 nm) and (iii) these last thickness values are quite small in comparison with those relative to conversion coatings claimed by different authors (for example, from 150 to 300 nm[33,41]) but are in good agreement with those reported by Wegman *et al.*[35]

3.2 Pre-painting treatments of metallic substrates

Many chemical or electrochemical treatments of metallic substrates have also been commonly used both to promote adhesion of thin polymeric coatings such as paint or varnish films and to protect them against corrosion. Indeed, as noted by Dwight and Wightman "corrosion is closely related to adhesion; the appearance of corrosion is indicative of loss of adhesion between the paint and the underlying substrate."[42] Generally, the substrate can be any metal but it is usually aluminum, zinc, steel, tin-plated, galvanized or electro-galvanized steels, and among the treatments extensively employed we may especially note phosphatizing and chromatizing.

The example described here is relative to steel and galvanized steel sheets for automotive applications. It concerns the deposit of phospate conversion layers, such substrate/coating systems being usually post-passivated by chromatizing. This rinse in a Cr^{3+} or

Cr^{3+}/Cr^{6+} solution is known to provide an additional corrosion resistance probably owing to the incorporation of chromium ions mainly between the phosphate crystals but equally at the surface of these crystals.[8] In Figure 7 the effect of an alkaline solution at pH = 12 on unchromated and chromated specimens is demonstrated. The interest of such studies has recently increased considerably because (i) during wet corrosion, hydroxyl ions may be formed beneath the paint films, (ii) during cataphoretic paint deposition, the pH at the electrode surface may locally increase up to 12. In such conditions an attack of the phosphate crystals occurs and changes in the surface composition may be responsible for adhesion loss. These experimental results obtained by XRFS give, as a function of immersion duration in the alkaline solution, the intensity variations of the PK_α radiations emitted by the phosphate crystals remaining after each leaching step. In each case, the decrease of the analysed signal represents the dephosphating of the surface layer and consequently should the solubility of the phosphate crystals at high pH. In addition it can be seen that: (i) the dissolution rate varies largely with the type of substrate, (ii) chromatizing does not necessarily improve the behaviour of the galvanized substrates in the alkaline solutions, (iii) chromatizing alone ($t = 0$) is responsible for a partial dissolution of the phosphate layer. The two former observations are not quite wholly explained

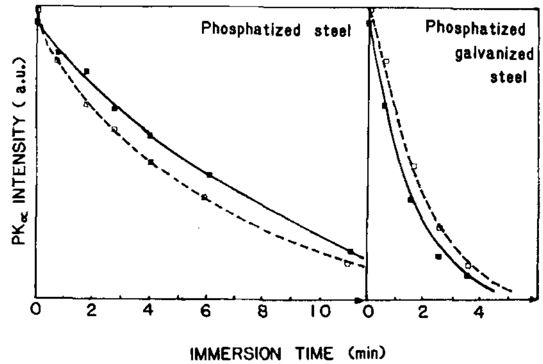


FIGURE 7 Behaviour of chromated (——) and unchromated (- - -) phosphated steel and galvanized steel in a alkaline solution at pH = 12. Effects of immersion duration on PK_α intensity (measured by XRFS).

at present but are probably associated with different phosphate compositions and morphologies since the corresponding crystals are grown on different substrates. In these preliminary experiments, XRFS is used to probe the entire thickness of the phosphate layers. In contrast, LEEIXS is able to provide information only from the surface of these layers. Figure 8 shows a partial LEEIXS spectrum from the surface of a galvanized steel sheet after a Zn–Ni phosphatizing. The main elements which are considered are oxygen, phosphorus, nickel and zinc. Figure 9 illustrates the applicability of LEEIXS to a Zn–Ni–Mn phosphatized steel surface analysis. It shows the comparison between the OK_α, PK_α, MnL_α, FeL_α, NiL_α and ZnL_α intensities before and after a sample immersion in an alkaline solution of pH = 12 during about 10 minutes. These results firstly confirm the dephosphating of the surface layers and secondly point out the corresponding increase of the (Fe + Mn + Ni)/Zn ratio. Furthermore, the slight decrease of the OK_α intensity would be in agreement with the transformation of phosphates into ferric zincates as that has been proposed by Van Ooij *et al.*[8] Although these studies are still under investigation (and then will largely be pursued in the future), it is evident that use of such spectroscopic methods will strongly help to understand the specimen behaviour in

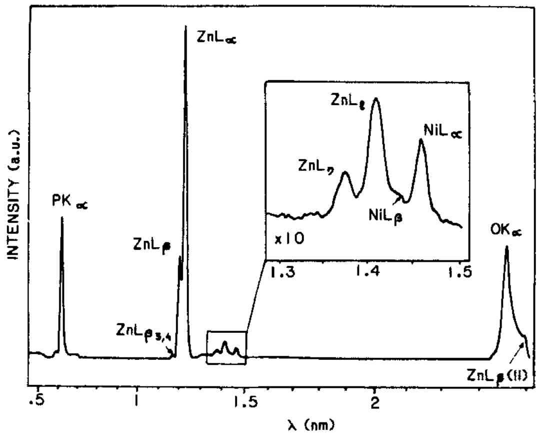


FIGURE 8 LEEIXS spectrum of a galvanized steel surface after a Zn–Ni phosphatizing.

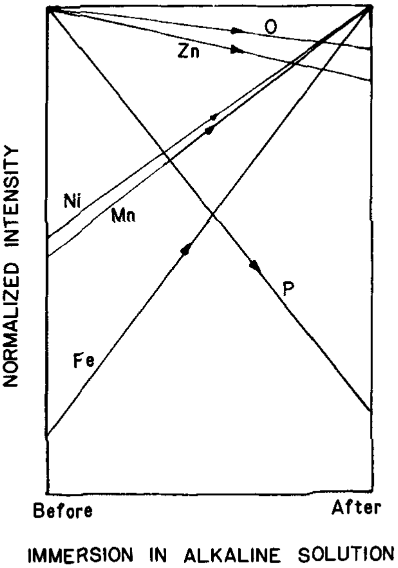


FIGURE 9 Behaviour of a Zn–Ni–Mn phosphatized steel in a alkaline solution at pH = 12. Normalized OK_α, PK_α, MnL_α, FeL_α, NiL_α and ZnL_α intensities before and after a 10 minute immersion.

service or test and then to formulate more corrosion-resistant and adherent new products.

4 CONCLUSIONS

In this paper, we have carried out a number of LEEIXS and XRFS studies emphasizing the potential of the relevant techniques to the characterization of metallic surfaces which have been chemically or electrochemically modified. A major conclusion from the applications described here is that significant progress in adhesion and paint sciences can be achieved by using suitable X-ray emission techniques and their specific advantages. More particularly, this statement is based on the fact that the techniques used are capable of giving both qualitative and quantitative chemical information about the composition of surface layers over a relatively larger range of thickness than real surface techniques like XPS, AES, SIMS or ISS. In other words, the methods of investigation used are able to provide extra information necessary to understand how chemical or electrochemical treatments affect the surface properties of adherends and various substrates and, therefore, are able to bring solutions as to the best processes and experimental conditions to be used in the preparation of surfaces.

References

1. W. L. Baun, in *Adhesion Measurement of Thin Films, Thick Films and Bulk Coatings* (ASTM-STP-640, Philadelphia, 1978), pp. 41–53.
2. J. S. Solomon and W. L. Baun, in *Surface Contamination—Its Genesis, Detection and Control,* Vol. 2 (Plenum Press, New York, 1979), pp. 609–634.
3. G. D. Davis and J. D. Venables, in *Durability of Structural Adhesives* (Appl. Science Publ., London, 1982), pp. 43–84.
4. J. M. Walls and A. B. Christie, in *Surface Analysis and Pretreatment of Plastics and Metal* (Appl. Science Publ., London, 1982), pp. 13–44.
5. W. L. Baun, *ibid,* pp. 45–72.
6. W. L. Baun, in *Adhesive Joints—Formation, Characterization and Testing* (Plenum Press, New York, 1984), pp. 3–17.
7. W. J. van Ooij, in *Physicochemical Aspects of Polymer Surfaces,* Vol. 2 (Plenum Press, New York, 1981), pp. 1035–1100.
8. W. J. van Ooij, T. H. Visser and M. E. F. Biemond, *Surf. Interface Anal.* **6,** 197 (1984).
9. J. V. Gilfrich, in *Characterization of Solid Surfaces* (Plenum Press, New York, 1974), pp. 275–306.
10. M. Charbonnier, M. Romand, A. Roche and F. Gaillard, *Int. J. Adhesion and Adhesives,* In press.
11. M. Romand, M. Charbonnier and E. Sahakian, *XVIII Fatipec Congress,* Venice, Italy, September 1986, Vol. 2/A, pp. 77–107.
12. R. Bador, M. Romand, M. Charbonnier and A. Roche, *Adv. X-Ray Anal.* **24,** 351 (1981).
13. A. Roche, *et al., Appl. Surf. Sci.* **9,** 227 (1981).
14. M. Romand, R. Bador, M. Charbonnier and F. Gaillard, *X-Ray Spectrometry,* In press.
15. A. A. Roche, J. S. Solomon and M. J. Romand, in *Microscopic Aspects of Adhesion and Lubrication* (Elsevier, Amsterdam, 1982), Tribology Series 7, pp. 333–342.
16. A. A. Roche, A. K. Behme and J. S. Solomon, *Int. J. Adhesion and Adhesives* **2,** 249 (1982).
17. A. A. Roche, M. J. Romand and F. Sidoroff, *Adhesive Joints—Formation, Characteristics and Testing* (Plenum Press, New York, 1984), pp. 19–30.
18. A. Roche, F. Gaillard, M. Romand and M. von Fahnestock, *J. Adhesion Science and Technology,* Submitted.
19. K. L. Mittal, in *Adhesion Measurements of Thin Films, Thick Films and Bulk Coating* (ASTM-STP-640, Philadelphia, 1978), pp. 5–17.
20. D. M. Brewis, in *Durability of Structural Adhesives* (Appl. Science Publ., London, 1982), pp. 215–254.

21. A. Mahoon, *ibid,* pp. 255–279.
22. A. C. Moloney, in *Surface Analysis and Pretreatment of Plastics and Metals* (Appl. Science Publ., London, 1982), pp. 175–197.
23. R. P. Haak and T. Smith, *Int. J. Adhesion and Adhesives* **3,** 15 (1983).
24. F. Gaillard, M. Romand, H. Hocquaux and J. S. Solomon, *Surf. Interface Anal.,* In press.
25. F. Gaillard and M. Romand, *Matériaux et Techniques,* In press.
26. M. Gettings and J. Kinloch, *Surf. Interface Anal.* **1,** 165 (1979).
27. T. L. Sterrett, *Int. J. Adhesion and Adhesives* **1,** 208 (1981).
28. W. L. Baun, Air Force Materials Laboratory, Technical Report TR-79-4138 (1979), Wright–Patterson AFB, Ohio.
29. W. Brockmann, in *Durability of Structural Adhesives* (Appl. Science Publ., London, 1982), pp. 281–316.
30. A. Roche *et al., J. Microsc. Spectrosc. Electron.* **4,** 351 (1979).
31. F. Gaillard *et al.,* Results to be published.
32. W. C. Hamilton, *Appl. Polym. Symp.* **19,** 105 (1972).
33. W. C. Hamilton and G. A. Lyerly, Picatinny Arsenal, Technical Report 4185 (1971).
34. W. C. Hamilton, G. A. Lyerly and G. Frohnsdorff, *ibid,* 4362 (1972).
35. R. Wegman, M. C. Ross, S. A. Slota and E. S. Duda, *ibid,* 4186 (1971).
36. F. Dalard, C. Montella and J. Gandon, *Surf. Technol.* **8,** 203 (1979).
37. T. Smith and D. H. Kaelble, Air Force Materials Laboratory, Technical Report TR-74-73 (1974), Wright–Patterson AFB, Ohio.
38. M. Natan, J. D. Venables and K. R. Breen, 27th National SAMPE Meeting, San Diego, CA (1982).
39. A. A. Roche, Air Force Materials Laboratory, Technical Report TR-80-4004 (1980), Wright–Patterson AFB, Ohio.
40. A. Roche, Thesis, Lyon (1983).
41. C. L. Hendricks and S. G. Hill, *Sampe Q.* **12,** 32 (1981).
42. D. W. Dwight and J. P. Wightman, *Surface Contamination—Its Genesis, Detection and Control, Vol.* 2 (Plenum Press, New York, 1979), pp. 569–586.