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Surface Science 433–435 (1999) 136–141

surface science

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# Application of parallel factor analysis and X-ray photoelectron spectroscopy to the initial stages in oxidation of aluminium

T. Do [a,b,*], N.S. McIntyre [b,c]

[a] *Department of Materials & Mechanical Engineering, The University of Western Ontario, London, Ont. N6A 5B7, Canada*
[b] *Surface Science Western, The University of Western Ontario, London, Ont. N6A 5B7, Canada*
[c] *Department of Chemistry, The University of Western Ontario, London, Ont. N6A 5B7, Canada*

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## Abstract

The three-way parallel factor analysis (PARAFAC) has been used to decompose a set of XPS (X-ray photoelectron spectroscopy) spectra which result during the oxidation of aluminium surfaces by water vapour. Al(2p) and O(1s) core-level photoelectron lines have been used to follow oxide film growth on clean aluminium surfaces as a function of exposure time and pressure of water vapour. The PARAFAC solution provides new information on elemental processes in the very initial stages of oxidation kinetics, showing new components in the XPS spectrum, as well as their evolution through the range of time and pressure variables. Reaction of $H_2O$ vapour with aluminium results in attenuation of the metallic peak, binding energy (BE) at $72.87 \pm 0.05$ eV, and increase of the oxidic peak, BE at $75.80 \pm 0.05$ eV. An additional factor is identified, which suggests the formation of an interface metal hydride, with BE at 72.4(4) eV, as well as a concomitant oxide peak at 75.4(3) eV. At pressures above $1.3 \times 10^{-5}$ Pa this factor is diminished; this is presumably due to the increase in recombination of atomic hydrogen. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Aluminium hydride; Aluminium oxide; Oxidation; Surface chemical reaction; XPS

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## 1. Introduction

In general, the formalism of the quantitative XPS involves two distinguishable procedures: the identification of recorded signals or peaks in a spectrum, and measurement of the photoelectron intensity [1]. In practice, there is no problem in quantitative analysis using XPS for well-defined systems, i.e. a traditional curve fitting technique can be used to identify all signals. However, in more complicated cases, where several peaks representing different chemical environments of an element closely overlap, or where more than one variable changes simultaneously, the curve fitting technique cannot provide an answer without some measure of ambiguity. This paper reports the first use of the more advanced parallel factor analysis (PARAFAC) to the effective decomposition of XPS spectra. This method has successfully been used to analyse several series of XPS spectra from a study of the oxidation processes of aluminium surfaces.

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* Corresponding author. Fax: +1-519-661-3709.
*E-mail address:* thando@surf.ssw.uwo.ca (T. Do)

PII: S0039-6028(99)00064-3

## 2. Application of parallel factor analysis to XPS data

PARAFAC is a three-way decomposition method developed as an improvement of a traditional two-way factor analysis method by analysing three-way data. While the data matrix in the standard factor analysis is two-dimensional, the data matrix for PARAFAC is three-dimensional; this results in a much higher degree of confidence of the analysis. Founded independently by Harshman [2] and by Carroll and Chang [3], and used initially in psychometrics, the PARAFAC method has recently attracted more interest from other areas of science, particularly chemometrics.

The *n*-factor PARAFAC model is mathematically expressed as [2]:

$$y_{ijk} = \sum_{f=1}^{n} a_{if} b_{jf} c_{kf} + e_{ijk} \qquad (1)$$

where the quantity $y_{ijk}$ measured at level $i$ of variable A, level $j$ of B and level $k$ of C is a linear combination of $n$ factors; each is determined by three factor loadings or weights $a_{if}$, $b_{jf}$ and $c_{kf}$ for the $i$th level of variable A, the $j$th level of B and the $k$th level of C, respectively; $e_{ijk}$ is the residual or error term. The factor loadings $a_{if}$, $b_{jf}$ and $c_{kf}$ are elements of three factor loading matrices, often referred to as 'Mode A', 'Mode B' and 'Mode C'; the variables A, B and C are independent.

The estimation of the PARAFAC model simply requires best fit of the model to the data, i.e. minimization of the error function, which is the sum of error squares $e^2_{ijk}$. This can be achieved by using several regression algorithms, which make the PARAFAC technique totally different from the traditional factor analysis. It has been mathematically proved [4–6] that if the factors show distinct independent patterns of variation across all three modes, the PARAFAC solution is unique. In the case where the expected standard deviation of the measurement error changes from element to element in the data matrix, the weighted least squares algorithm [7] offers a better fitted solution. The error function is now a sum of weighted error squares $w_{ijk}e^2_{ijk}$ where $w_{ijk}$ is the weight given to $y_{ijk}$; it is usually equal or close to $1/s^2_{ijk}$ where $s_{ijk}$ is the estimated standard deviation of $y_{ijk}$.

In the XPS analysis, the peak intensity at binding energy $E$ measured by the photoelectron current can be represented by the following expression:

$$I_{Z,ij}(E) = \sum_{f=1}^{n} I_{Z,f}(E) a_{if} b_{jf} + e_{ij}(E) \qquad (2)$$

where $n$ is the number of peaks present in a given XPS spectrum; $I_{Z,f}(E)$ is a concentration dependent factor; indexes $i$ and $j$ indicate the $i$th and the $j$th level of two other physical parameters $a$ and $b$, respectively, e.g. impurity concentration and pressure, which simultaneously affect the XPS intensity; $e_{ijk}(E)$ is an error term. By defining the number of peaks as the factor number, the similarity of Eq. (2) to the trilinear model described by Eq. (1) ensures the applicability of the PARAFAC technique to analysing the XPS data. However, our motivation to apply the PARAFAC technique is to make use of the solution uniqueness, which is its main advantage over the curve fitting technique and the traditional factor analysis [8].

In this work, a PARAFAC program called 'PMF3' (positive matrix factorization, three-way [9]), written in Fortran by Pentti Paatero, University of Hensinki, Finland, has been used to analyse the XPS data. This program is based on a curve-fitting type optimization method which implemented both a weighted least squares regression and a non-negativity constraint.

## 3. Experimental

Polycrystalline aluminium (99.999% purity) was supplied by Alcan aluminium Ltd., Kingston, Ontario. Specimens were polished to a 0.05 μm $Al_2O_3$ finish, degreased ultrasonically, annealed in vacuum (573 K, 30 min) and cleaned by $Ar^+$ ion bombardment (3 keV, 10 min). Clean surfaces were then exposed to water vapour in a separate custom-designed preparation chamber attached to the XPS spectrometer at six pressures levels ranging from $2.0 \times 10^{-6}$ to $6.5 \times 10^{-4}$ Pa and exposure times from 1 to 60 min at 15 separate time levels for every minute from 1 up to 10 min, and after that for 15, 20, 30, 45 and 60 min. After exposure to water vapour the sample was transferred back into the XPS analytical chamber and an XPS spectrum was measured at an operating base pressure of $4.0 \times 10^{-7}$ Pa. All XPS spectra were obtained using a Surface Science Laboratories SSX-100 spectrometer equipped with monochromatic Al Kα (1486.6 eV) X-ray source; the BE scale was calibrated to give an Au($4f_{7/2}$) line position at 83.98 eV. The uptake of oxygen on aluminium surfaces, at room temperature, was monitored by following the changes in the intensity of XPS Al(2p), and O(1s) photoelectron lines. A Shirley background subtraction was performed for all spectra as the data preprocessing.

The real XPS data matrix (dimensions $90 \times 15 \times 6$) for the three-way analysis is built up from all Al(2p) spectra taken through the ranges of exposure time and pressure studied. It consisted of six slices and on each slice there are 15 columns representing XPS spectra for 15 time levels at one pressure level. In three-dimensional space, the data matrix containing the XPS intensities is represented by three variables: the BE channel number (90 levels), the exposure time (15 levels) and the pressure (six levels), all in increasing order. In the solution, factor loadings are extracted into three matrices: BE mode, time mode and pressure mode, corresponding respectively to three factor loading matrices in Eq. (1).

## 4. Results and discussion

Increasing exposure time causes a growth of oxide layers resulting in an attenuation of the intensity of the Al(2p) metallic component with BE at $72.87 \pm 0.05$ eV, and an increase of the Al(2p) oxidic component with BE at $75.80 \pm 0.05$ eV [8]. Such evolutions of these components were observed for all other pressure levels and have been used as main features to verify the physical meaningfulness of the factor loadings in the time mode. The peak positions, in turn, were used to identify peaks in the BE mode. In the pressure mode, to verify the physical meaningfulness of the factor loadings, one can use the fact that the Al(2p) metallic component should not be affected by pressures of water vapour.

Our previous work [8] showed that the PARAFAC three-factor model is the only one suitable to characterize our XPS Al(2p) data matrix. Fig. 1 shows the three modes in the three-factor solution using the 'PMF3' program. Three factors represented in this solution can be identified as the following.

*Factor 1*. Based on the peak position (BE at 72.9 eV) and peak shape in the BE mode in Fig. 1a, this factor can be identified as the pure metallic Al(2p) peak. Verification that factor 1 represents an XPS Al(2p) spectrum of aluminium with a clean surface can be provided by comparing its factor loadings in the BE mode with photoelectron intensities in the real spectrum. As shown in Fig. 1a, the peak represented by the factor 1 loadings (solid line) exactly reproduces the XPS Al(2p) spectrum (filled circles) obtained for aluminium after surface cleaning by $Ar^+$ ion bombardment. Fig. 1b shows the evolution of loadings of factor 1 through the time levels, which reflects the attenuation of the metallic peak due to a growth of thin oxide films with increasing exposure time. In the pressure mode (Fig. 1c), as expected, the factor 1 loadings remain practically unchanged across all pressure levels, indicating independence of the metallic peak on the water vapour pressure.

*Factor 2*. From Fig. 1a, factor 2 is shown as a single peak located at BE of 75.8 eV, which can be assigned to the oxidic component in the XPS Al(2p) spectrum. Again, the evolution of this peak in the time mode (Fig. 1b) confirms its identification in the BE mode, showing an increase in factor loading with increasing exposure time, which corresponds to the growth of oxide layers on aluminium surfaces. In the pressure mode (Fig. 1c), the factor 2 loadings show a slight increase with increasing pressure.

*Factor 3*. Fig. 1a shows factor 3 as a double peak with maxima at 72.4(4) and 75.4(3) eV. In the time mode (Fig. 1b) the factor 3 loadings increase as the exposure time increases, and then slightly decrease after 5 min exposure. In the pressure mode (Fig. 1c) it has a maximum at pressure level 3 ($1.3 \times 10^{-5}$ Pa). The full identification of this factor is discussed further below.

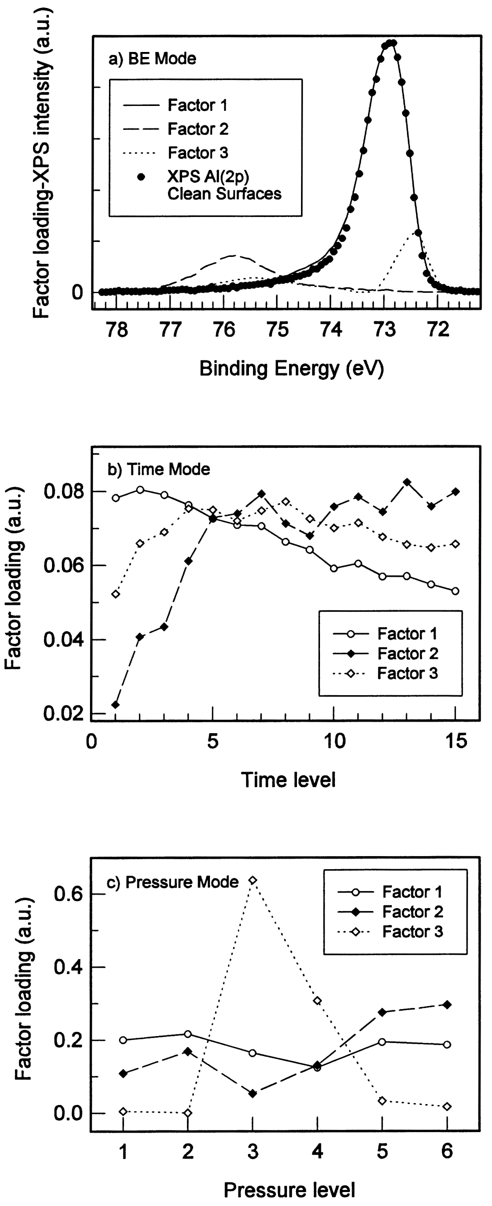

Fig. 1. Factor loadings for the solution using the 'PMF3' program for the three-factor model with weighted regression and constraint on non-negativity: (a) BE mode; (b) time mode; and (c) pressure mode. In BE mode, the filled circles represent the experimental XPS Al(2p) spectrum obtained for clean aluminium surfaces. For comparison the peak height is normalized to the maximum of factor 1 loading.

It is known that at room temperature the adsorption of water molecules on clean aluminium surfaces is completely dissociative [10], giving three possible elementary adsorbed species on surfaces: OH groups, hydrogen and oxygen atoms. Further reaction leads to formation of different chemical bonds with aluminium atoms, such as Al—O in oxides and hydroxides, and Al—H in hydrides, which will be reflected in the number of peaks present in the XPS spectrum of aluminium and the peak positions in BE. The chemical shift of aluminium in thin oxide films is well-documented in the paper of Olefjord et al. [11], in which the BE of the metallic state Al$^0$ and the chemical shift of Al$^{3+}$ are $73.0\pm0.1$ and $2.8\pm0.1$ eV (i.e. the oxide state Al$^{3+}$ is at BE $75.8\pm0.1$ eV), respectively. Our experimentally observed values of binding energies for metallic and oxidic peaks, and those extracted by PARAFAC, are in good agreement with the above values.

The third factor extracted by PARAFAC, shown in Fig. 1a, has a shape with distinct defined positions of maxima and their discrepancies, which clearly indicate a two-peak structure. These two peaks might represent the contributions from two other distinguished chemical bonds with aluminium to the XPS Al(2p) spectrum. It must be emphasized here that the peak structure (Fig. 1a) has been derived as the only solution, whose uniqueness is guaranteed by the principle of PARAFAC analysis [4–6], and which cannot be provided by any other technique. These two peaks in the third factor cannot result from a broadening effect, i.e. from charging problem, as follows. First, no charging effect was observed; the adventitious reference C(1s) peaks were obtained in all experiments at BE of $286.20\pm0.05$ eV. Second, the broadening of a peak would result in an additional peak, single or in linear combination with another, at the same peak position (the BE of peak maximum) in the PARAFAC solution. Finally, the appearance of two peaks in one factor indicates that these two components, or formations of two chemical species, are associated in a chemical process. A consistent physical explanation for that and consequences from other factors will undoubtedly also confirm the uniqueness of solution.

For the third factor, while the peak at BE 75.4 eV, located between oxidic (75.8 eV) and metallic (72.9 eV) states, can intuitively be identified as a contribution from other oxidized species, the assignment of the associated peak at BE 72.4 eV needs additional discussion. It is likely that the negative shift in BE of the XPS Al(2p) line may result from an increase of electron density due to the presence of a hydride of aluminium. Such a change in valence band has been shown in a theoretical work by Gupta and Burger [12], where the density of state calculated at the Fermi level in both AlH and $AlH_2$ is about 25% higher than in pure metal. Other workers have reported the presence of an $AlH_x$ species located at the metal–oxide interfaces based on studies using electron energy loss spectroscopy (EELS) and thermal desorption spectroscopy (TDS) [13]. In our PARAFAC solution, the variation of factor 3 loading in time mode (Fig. 1b) also suggests that the Al—H bonds would be found at the metal–oxide interface; the aluminium hydride could be formed on clean surfaces at the very initial stages, competitively with other species such as the oxide and the hydroxide. After surface coalescence, these hydride species may be covered by oxide overlayer, which will cause an attenuation of photoelectrons produced from aluminium hydride. This would explain the decreasing behaviour in loadings of the third factor in the time mode, parallel to that of factor 1, the metallic component.

As shown in the PARAFAC solution, the peak at 75.4 eV in the third factor is closely connected to the formation of the hydride. The association of these two peaks can be explained using the following reaction:

$$2(a+b)\mathrm{Al}^0+2\mathrm{H_2O}\rightarrow 2\mathrm{Al}_a\mathrm{OH}_y+2\mathrm{Al}_b\mathrm{H}_x+[2-(x+y)]\mathrm{H_2}\uparrow. \quad (3)$$

In reaction (3), the other oxidized species represented as $Al_aOH_y$ can be one of the intermediate aluminium–oxygen structures such as Al—O—H, Al=O or Al—O—Al. The ratio between the numbers of hydride and the other oxidized species is $b$:$a$, which is the ratio of peak areas in the third factor (estimated as 1.6). From Eq. (3), in order to keep the ratio $b$:$a$ constant, the rate of hydrogen release from the surface in a recombination reaction must increase at higher pressure of water vapour. That requires a change in mechanism of hydrogen absorption on aluminium surfaces, which is simply proportional to the pressure at lower range. Such an effect can be postulated from the work of Winkler et al. [14] on hydrogen desorption from clean and partially oxidized aluminium surfaces using the TDS technique. This, in turn, will result in a decrease in hydride amount, in the same degree as the increase of hydrogen recombination, and will benefit in oxide growth as the water vapour pressure increases. The behaviour of factor 2 and 3 loading in pressure mode (Fig. 1c) fully supports the above considerations.

## 5. Conclusions

PARAFAC is shown to be a useful tool in XPS analysis with its capacity to dissect a complex system into a set of independent components which are interpretable using basic physical parameters. A unique three-factor model has been extracted from the XPS Al(2p) data. These three factors represent three components in an XPS Al(2p) spectrum as follows: the metallic peak with binding energy at 72.9 eV, the oxidic peak at 75.8 eV and a new third component with two peaks at 72.4 and 75.4 eV, respectively. The third component in the XPS Al(2p) spectrum has been identified with the peak at a binding energy of 72.4 eV for an aluminium hydride and the associated peak for another aluminium oxidized state at binding energy of 75.4 eV. The evolution of the third peak across the entire time range suggests that the aluminium hydride was formed at the metal–oxide interface.

## Acknowledgements

The authors wish to thank Dr. P. Paatero for kind permission to use the 'PMF3' program and helpful discussions, and Alcan for supplying the aluminium samples used in this study.

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