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Improving EFTEM data using multivariate statistical analysis

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Abstract. In this paper, the benefits of processing Energy-Filtered TEM (EFTEM) datasets with Multivariate Statistical Analysis will be described. These include: Isolation of the main sources of information, identification of features masked by noise and/or background and, more importantly, almost “noise-free” data reconstruction.

1. Introduction

Multivariate statistical analysis (MSA) can be considered a group of processing techniques designed to analyze the information contained in large multidimensional datasets. In the last two decades it has been successfully applied to the area of analytical electron microscopy, in particular to electron energy loss [1,2] and energy dispersive X-ray spectra [3,4] both in scanning and transmission electron microscopy (SEM and TEM). Recent advances in hardware and software are allowing the automatic acquisition of EELS or EDX datasets typically containing more than 20 million data points. Traditional methods for the extraction of chemical information rely on background subtraction and edge or peak signal integration. However, only a relatively small fraction of the available information is used. MSA, on the contrary, analyses the whole dataset in a purely mathematical and unbiased way.

Although MSA has been proven a very useful technique for processing microanalysis data, it has not been fully implemented by the electron microscopy community and, unfortunately, only a limited number of groups use it regularly. For this work, the “R-factor” method has been used, which combines “Principal Component Analysis” (PCA) and “Factorial Analysis of Correspondence” (FAC) [1,2].

2. Methodology

Energy-Filtered (EF) series of images were acquired using a Jeol 2200FS equipped with an Ω -filter and two Cs-correctors, operated at 200kV. The images were hardware binned by 4 to a total of 512x512 pixels. Cs correction allowed the use of a bigger condenser aperture, increasing the signal.

A TEM sample from a piece of Inconel 600 was prepared by electropolishing. The region chosen for analysis contains two chromium carbides and one titanium carbo-nitride, all embedded in the nickel-rich matrix.

The MSA software was written in C++ as a plug-in for Gatan’s Digital Micrograph. For a full description of the mathematical procedure, see [1].

The EFTEM acquisition was performed using a self-written script for Digital Micrograph. Prior to MSA processing, spurious pixels caused by X-rays as well as some damaged pixels were removed from each image and the drift measured and corrected [5]. Two energy filtered series of images were acquired. The first series ranged from 2.5 to 102.5eV energy losses, in steps of 5eV and using a 5eV

energy slit (21 images). The second series ranged from 390 to 920eV energy losses, in steps of 10eV and using a 10eV energy slit (53 images). A 12.2 mrad half-angle objective aperture was used for both acquisitions.

The current version of the MSA software needed less than 1 minute to process the biggest dataset (512x512x53 pixels) using a Pentium D 3GHz with 4Gb RAM under Windows x64.

3. Results

MSA of both datasets revealed that most of the information was contained in the first 5 eigenvalues: 98% in the first dataset and 97% in the second one. The most significant eigenvalue accounted for the fact that the Cr carbides are significantly enriched in Cr and depleted in Ti, Ni and Fe (see Fig. 1). The second eigenvalue accounted for the extra Ti in the Ti nitride and the third one for a slight change in thickness across the field of view. The fourth and fifth eigenvalues jointly accounted for a subtle oxidation around the carbides (see Fig. 2) which had passed unnoticed since the O signal is very weak in the second dataset.

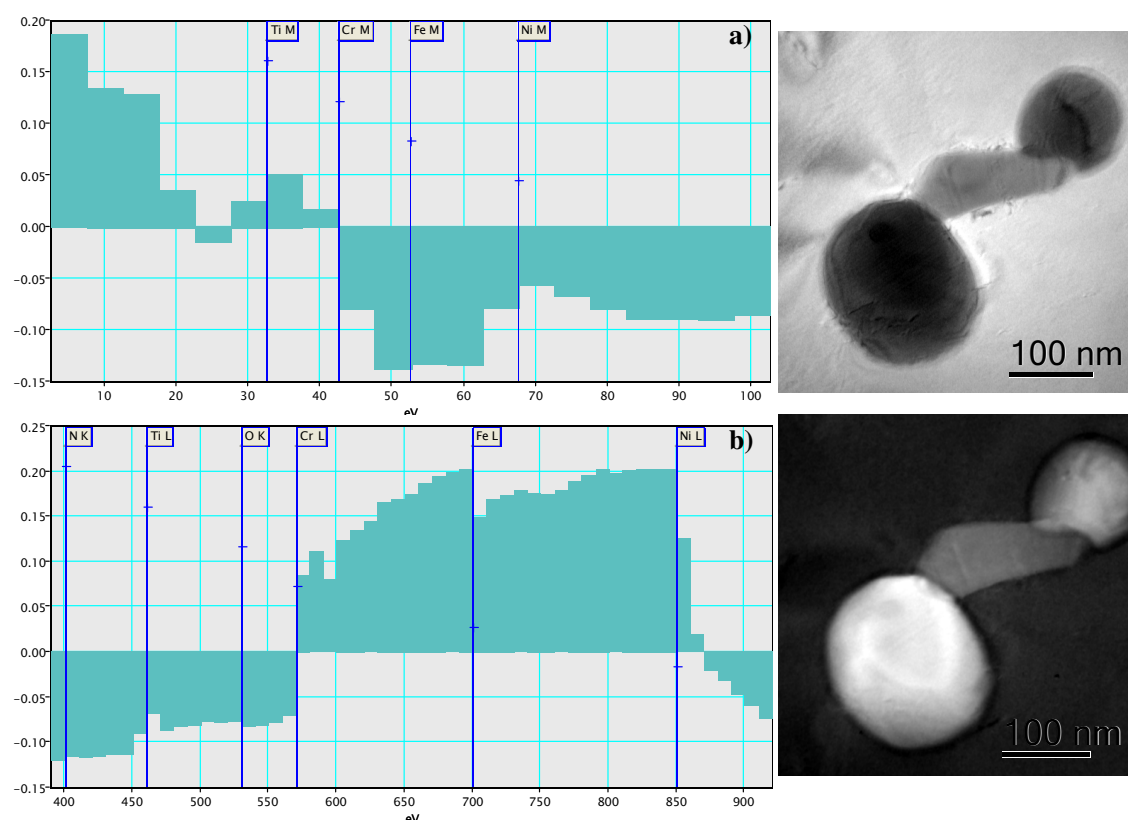


Figure 1. Most significant eigenvalue and associated eigenimage (a) [2.5-102.5eV], 63% of information, showing anticorrelation of Cr and Ni-Ti signals; (b) [390-920eV], 60% information, showing anticorrelation of Ti-Cr with Fe-Ni signals.

3. Discussion and conclusions

It has been shown how MSA can easily process big EFTEM datasets and isolate the different sources of information. More importantly, it can achieve similar results when processing low-loss M edges and core-loss L edges, as in the case of the chromium carbides and titanium nitrides embedded in a nickel matrix. It can also help revealing “hidden” sources of information, such as the oxide shell around the Cr carbides. However, one of the strongest reasons for using MSA is its ability to separate true

information from noise. The [390-920eV] dataset was reconstructed using the first 5 eigenvalues, which contained 97% of the information. The remaining 47 eigenvalues can be safely neglected, since they only account for the noise in the data. The improvements in the quality of the reconstructed maps are obvious, as can be seen in Fig. 3. The three elements with the lowest signal have been chosen to better illustrate the results. Oxygen, iron and titanium maps were drastically improved after reconstructing the original data with MSA. As an example, the O signal at the oxide shell had a SNR of 4.3 in the raw data map and 16.6 in the reconstructed map.

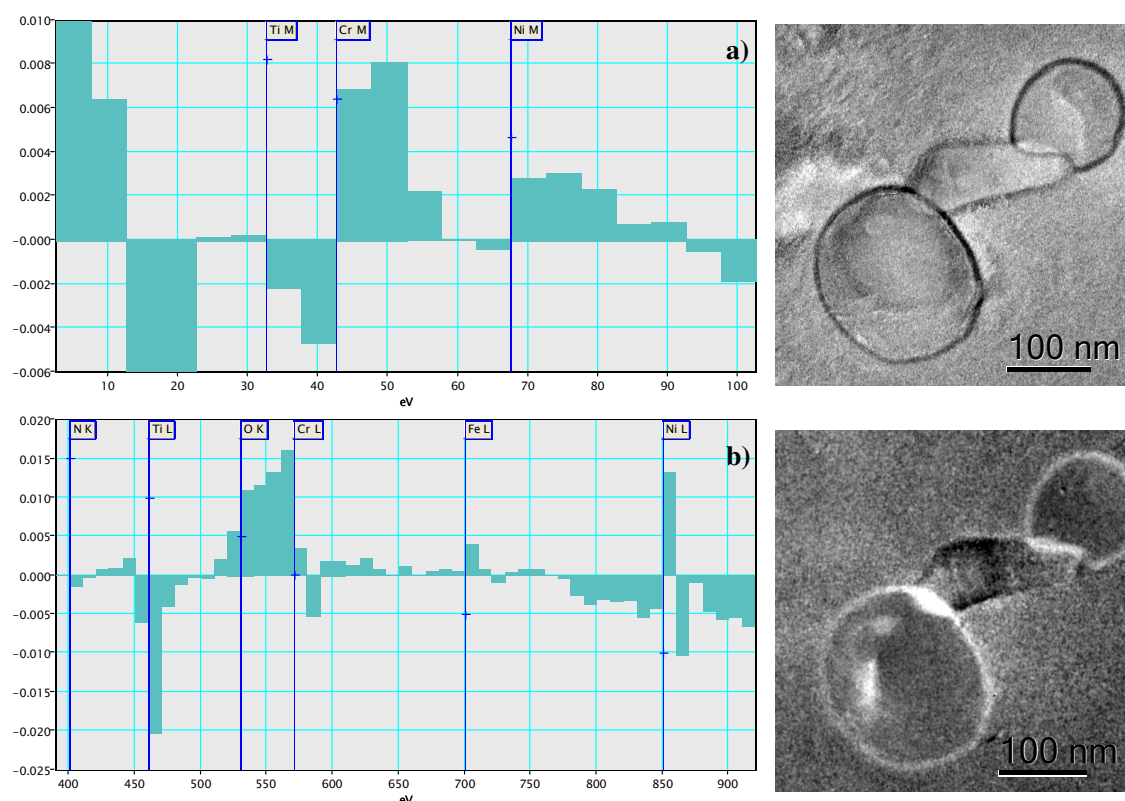


Figure 2. Fifth most significant eigenvalue and associated eigenimage (a) [2.5-102.5eV], 0.45% of information, showing a Cr-Ni-depleted region; (b) [390-920eV], 0.13% information, showing anticorrelation of O-Ni-Fe with Ti signals. A change in Ni edge fine structure is also revealed.

However, MSA of EFTEM data can produce misleading results if the necessary care is not taken. Particular attention should be paid to:

- Image cross correlation: For every image that is not aligned properly, a new source of information is introduced in the data, which will appear isolated as a new eigenvector or combined with a real source.
- Data-cubes splicing. This is the equivalent to splice two or more EEL spectra which have been acquired separately, typically with different acquisition times and noise levels, but with an overlapping range of energy channels. If the differences in noise levels are too pronounced, the Scree test will fail and the relevant eigenvectors will appear in two regions.
- Diffraction contrast. Diffraction contrast can change from energy-filtered image to image, acting as an un-desired source of information and interfering with real eigenvectors.
- X-rays in the image. Pixels with abnormally high counts, such as those produced by an X-ray hitting the CCD will appear as big sources of information. Fortunately, several X-ray removal routines can be found in the software and/or literature and “clean” the images before processing.

- The low-loss part of the spectrum is dominated by the plasmon peak, which can change its amplitude and position with chemical composition, thickness, etc. Therefore, if present in the EF series, its changes will be always associated with at least one eigenvalue.

It has been shown how MSA can extract the same information from low-loss and core-loss edges. The eigenvalues also shared the same amount of information, proving the consistency of the method. It should be noticed that low-loss edges are more difficult to analyse with traditional methods, since their background is not so easily removed. MSA can prove a very effective way of dealing with this type of data. It has also been demonstrated how effectively this method can be when separating the true sources of information from the noise. The reconstructed datasets can be processed in the usual way for extracting elemental maps with improved noise levels.

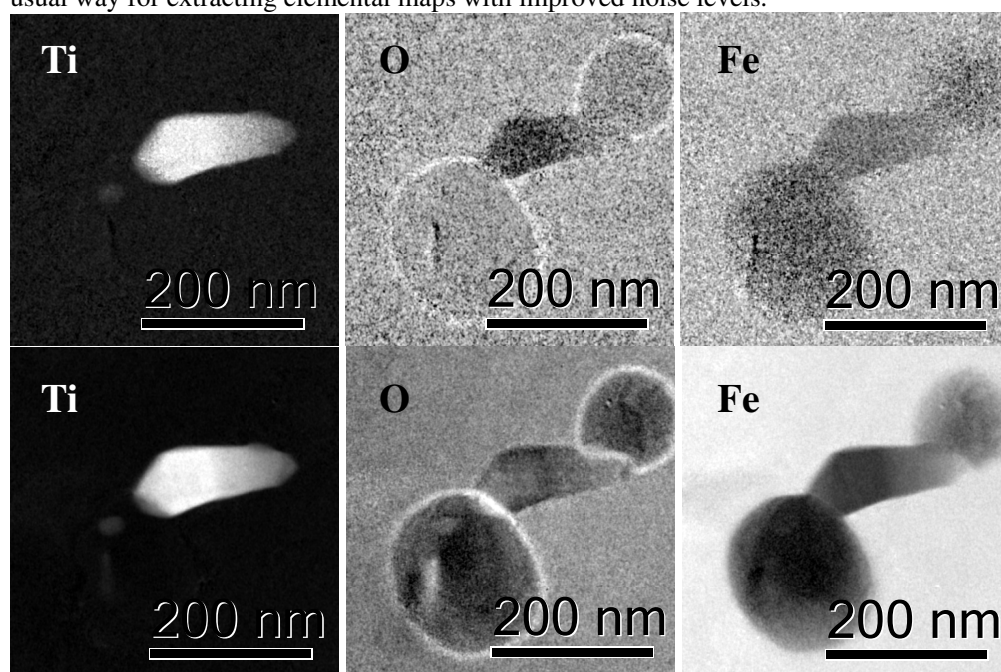


Figure 3. Top row: Ti, O and Fe maps from [390-920eV] dataset using raw data; Bottom row: Ti, O and Fe maps from [390-920eV] dataset using reconstructed data.

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