

Decomposing Electron Diffraction Signals in Multi-Component Microstructures

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The question of overlapping signals in measurements recorded in the transmission electron microscope is not a new one. The very name, transmission indicates that the recorded image will be a projection through a given thickness of the sample. In this process the ability to distinguish detail along the beam direction is usually lost. One common approach to separating the combined signals in TEM is through tomography, where multiple projections of the sample from different angles (typically through a systematic tilt-series) are combined to create a volume representation of the sample [1]. In this way some unique signal can be localized within the volume.

In this work an alternative approach is used, namely the use of statistical decomposition of the recorded data in order to identify the character and extent of the unique signals existing within the TEM data. Such techniques are known as multivariate statistical analyses (MSA), among which principal component analysis (PCA) [2] and non-negative matrix factorization (NMF) [3] are two widely known and commonly employed methods. The technique takes a set of measurements and determines the subset of signals that can be combined in differing proportions (potentially both positive and negative) to accurately describe the whole.

One of the earliest examples of this approach in TEM was to study STEM-EELS data [4]. In this situation a sample of titanium dioxide and tin oxide was scanned with the electron beam and an EELS spectrum recorded at each point. Given the close proximity in energy between the major edges for the two metals it was extremely difficult to separate their contributions quantitatively using conventional analytical approaches. However through MSA both the physical localization of each component, and their relative contribution to each EELS spectrum could be determined and so the microstructural within the scanned area analyzed.

While MSA has been shown to be extremely powerful for such spectroscopic analyses, there is no fundamental difference between spectral data and the structural information contained in a diffraction pattern. Using the scanning diffraction analysis developed by Nanomegas and Grenoble University (a technique referred to as ASTAR or ACOM) [5] it is possible to record spatially resolved diffraction data by scanning an electron beam across the sample and recording a whole diffraction pattern at each point. Like the EELS example shown previously, the presence of multiple different crystals within a sample (which can encompass differently oriented grains, bent or otherwise strained regions as well as different phases) all can give rise to complex diffraction patterns containing multiple different signals, and which can be decomposed to determine the individual diffraction signals.

An initial proof of principal study for this technique was performed on a nickel superalloy sample. Here a carbide precipitate was found embedded within the nickel matrix. This particular system showed a strong crystallographic registry between the matrix and precipitate, making simple separation of the multiple diffraction patterns impossible. Instead through MSA the unique diffraction signal from all of

the phases in the structure could be identified and localized. In this study the process was taken further by recording a tilt-series of such data, in this way the diffraction signal from each phase allowed a volume reconstruction of each of the major components under scrutiny in the microstructure (shown in Figure 1a). Furthermore the inter-related information about the morphology of the microstructure and the crystalline orientation of the components allowed interface relationships within the structure to be unambiguously determined (Figures 1b and 1c), leading to the identification of a hitherto unreported crystallographic registry between the carbide and matrix phases [6].

Further studies have been undertaken looking into a variety of different materials systems; from interfaces in twinned gold nanoparticles and semiconductor nanowires; through to the distribution of oxide phases in zirconium layers. In this latter case the separation of the principal diffraction signals from different regions confirmed the existence of a proposed sub-oxide phase [7] and by identifying the overlapping grains with different oxygen content further insight into the nature of the EELS signal recorded from such samples is expected.

[1] P. A. Midgley and R. E. Dunin-Borkowski, *Nature Materials* **8** (2009), p. 271-280

[2] H. Abdi and L.J. Williams, *Wiley interdisciplinary reviews: computational statistics* **2** (2010), p. 433-459

[3] D. D. Lee and H. S. Seung, *Nature* **401** (1999), p. 788-791.

[4] F. de la Peña. *et al.* *Ultramicroscopy* **111** (2011), p. 169-176

[5] E. F. Rauch *et al.*, *Microsc. Anal.* **22** (2008), p. S5-S8

[6] A. S. Eggeman, R. Krakow and P. A. Midgley, *Nature Communications in press.*

[7] J Hu *et al.*, *Micron* **69** (2015), p. 35-42

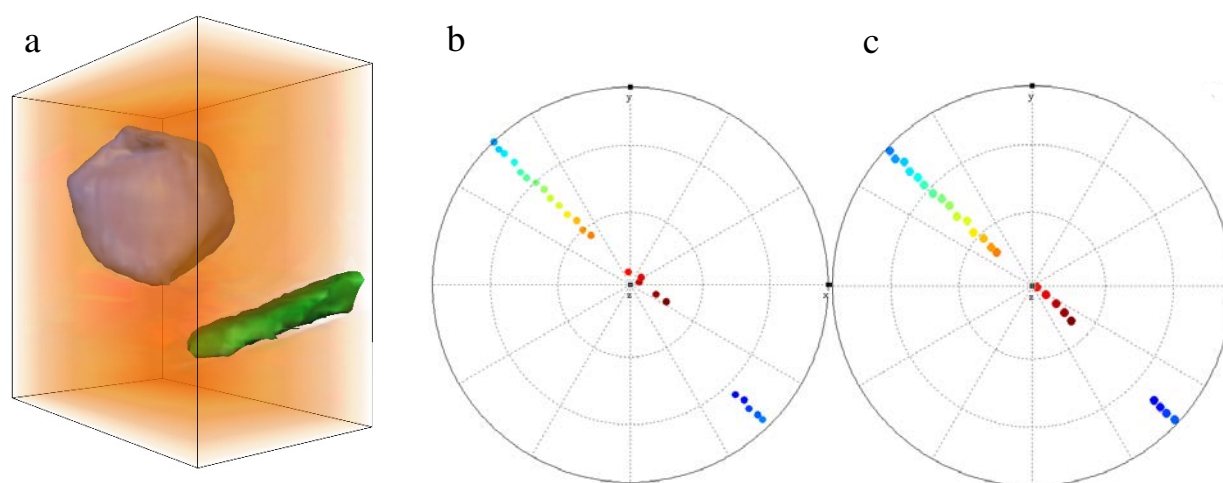


Figure 1. a) Reconstructed volume of superalloy sample showing carbide (blue) and η -phase (green) precipitates within a nickel matrix (orange). The localization of unique diffraction signals was used as input for the reconstruction. The cube side is approximately 200nm. b) and c) pole-figures for the (220) planes in the carbide and the (026) planes in the nickel matrix respectively across the tilt-series (each tilt is indicated by a different colour). The correspondence highlights the crystallographic registry between the two structures.