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EELS Analysis of Nano-Sized Particles in a Matrix

AJ Craven[1], B Sala[1] and I MacLaren[1].

[1.] School of Physics and Astronomy, University of Glasgow, Glasgow, G12 8QQ, Scotland, UK.

Using spectrum imaging (SI) in STEM-EELS provides a wealth of information down to the atomic scale. Extracting interpretable information provides many challenges, however. This paper is concerned with the analysis of small precipitates within a steel matrix. The approach offers a number of advantages over the traditional extraction replica method and can be adapted for a wide range of systems where small particles require analysis in the presence of a more extensive material.

Previously, the approach has been successfully applied to nano-sized (Ti,V)(C,N) precipitates in an austenitic Fe-20%Mn-1.5%Al-0.6%C-0.2%V steel [1, 2]. The precipitate signal was separated from the matrix, whose thickness was also determined. The thickness, volume and composition of the precipitates can be determined with good sensitivity and accuracy. As part of this work, a method of determining accurate inelastic mean free paths and experimental EELS cross-sections was developed [3]. The electron optical coupling of the spectrometer to the specimen was also optimised [4].

Extending the approach to Nb-containing precipitates in a bainitic Fe-1.8%Mn-0.06%C steel containing microalloying additions of Ti, V and Nb requires cross-sections for NbC and NbN. This has highlighted the effect of the residual non-linearity in the dispersion of the spectrometer noted in [1] and this non-linearity is shown in Fig. 1a. Correcting this non-linearity brings the splice ratio between the low- and high-loss datasets into good agreement with the ratio of the exposure times. It also improves the energy calibration, the background shape before the $M_{4,5}$-edge, and the accuracy of the low-loss cross-section. Fig. 1b shows the experimental cross-section from $NbC_{0.95}$ after linearization.

One of the practical issues in this type of analysis is finding precipitates since their contrast in the HAADF image is very low. In the low-loss region, the thresholds of the $M_{2,3}$-edges of Fe and Mn are significantly different to those of the Ti and V $M_{2,3}$-edges and the $N_{2,3}$-edges of Nb. Thus, high contrast maps of precipitates can be obtained from a rapid low-loss SI. These maps can be used for selection of precipitates for detailed analysis. Such low-loss SIs also allow direct determination of precipitate thickness and size using experimental low-loss standards. Fig. 1c is the profile of two precipitates along the line marked on the inset map, showing low background level and high sensitivity. Thus size distributions and volume fractions can be measured from larger volumes of material using low-loss SIs.

In the earlier work, all the small precipitates were (Ti,V)(C,N) and so the experimental cross-sections allowed the signal contributions from precipitates to be extracted and quantified in one step [3]. In the current work, the intended small precipitates were (Nb,Ti,V)(C,N) with low or zero N. However, a much more diverse range of precipitates was found. Thus the approach was modified to optimise the removal of the matrix contribution. As well as using components from the standards (TiC_x, VC_x, NbC_x, C, N) and the matrix in the MLLS fit, components for Fe, Mn, S and P edges were also included, giving a good fit over the 150eV to 750eV range. While S and P are present at trace levels in the steel, their use to improve the MLLS fit does not prove their presence in the precipitates. Thus it is essential to subtract the matrix from the SI and examine the spectra from the precipitates themselves over the full energy range. Fig. 2a is an energy slice of an SI from a specimen with t/λ of 0.97 using a loss of 635eV i.e. before the Mn $L_{2,3}$-edge. It shows a large $(Fe,Mn)_3C$ (cementite) precipitate and an array of smaller precipitates, some of which appear to have nucleated on it. The spectrum from the cementite was extracted, included in the MLLS fit and its contribution then subtracted, giving the energy slice in Fig. 2b and revealing these precipitates more clearly. Figs. 2c-j show background subtracted maps for the Si $L_{2,3}$-, S K-, Nb $M_{4,5}$-, C K-, Ti $L_{2,3}$-, V $L_{2,3}$-, Mn $L_{2,3}$- and Fe $L_{2,3}$-edges respectively. Figs. 2i and j show that the Fe:Mn ratio in the cementite varies. It also shows precipitates based on Mn(S), (Ti,V)(C), (Ti,V)(S), and (Ti,V)(Si) with some core-shell structures but no clear Nb-containing precipitates.

In conclusion, a combination of removing instrumental artefacts, correcting remaining artefacts, using experimental cross-sections and using MLLS fitting allows number densities, volume fractions, size distributions, compositions and amounts of elements precipitated to be estimated.

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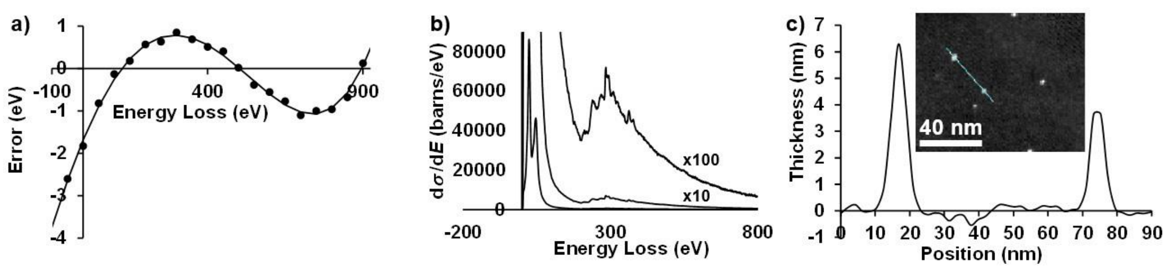

Figure 1. a) The error in the energy scale due to dispersion non-linearity; b) The experimental cross-section for $NbC_{0.95}$; c) Thickness profile of two precipitates in a Nb,Ti containing Fe-20%Mn steel taken from a map (inset) obtained from a low-loss SI. The specimen has t/λ from 0.22 to 0.53.

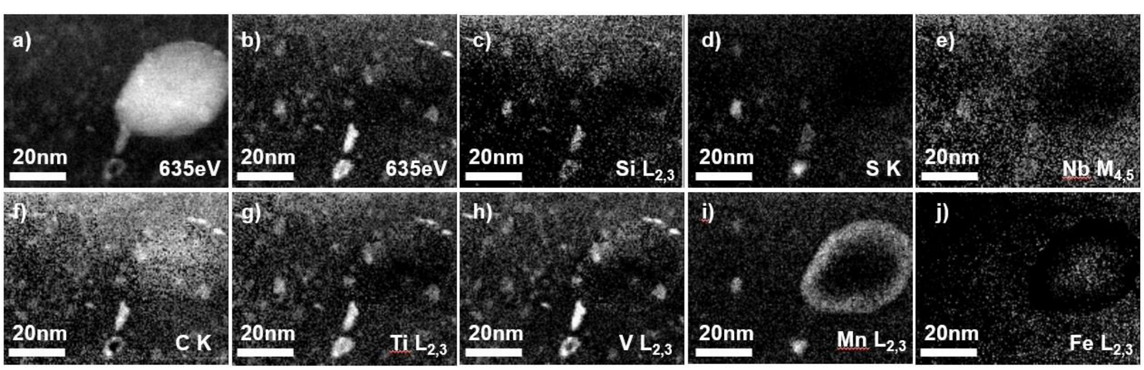

Figure 2. a) 635eV energy slice (immediately before the Mn $L_{2,3}$-edge) from an SI of precipitates in an Nb,Ti,V-containing Fe-1.8%Mn steel after removal of the matrix contribution; b) The same slice after further removal of the $(Fe,Mn)_3C$ precipitate contribution; c-j) Background subtracted maps for a range of edges taken from the SI used for b). The specimen has a t/λ of 0.97.

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