

Practical applications of electron microscopy II

Experiment 4: Electron energy loss spectroscopy (EELS) and electron spectroscopic imaging (ESI)

The objective of the experiment is to determine the local composition of nanoscale precipitates along a grain boundary in a nickel-based superalloy using electron energy loss spectroscopy (EELS: Electron Energy Loss Spectroscopy) and to determine the spatial distribution of various alloying elements using electron spectroscopic or energy filtered imaging (ESI: Electron Spectroscopic Imaging) in a transmission electron microscope (TEM) with an imaging energy filter (Gatan imaging filter, GIF).

Electron energy loss spectroscopy and energy-filtered TEM (EFTEM), in addition to conventional TEM, are used:

- for qualitative and quantitative elemental analysis (especially light elements are easily
- for determining the local sample thickness based on the low-loss spectrum,
- for filtering out the inelastically scattered electrons, to increase the information content of diffraction images and improve image quality when imaging thick samples,
- to detect two-dimensional elemental distributions in a short time with high spatial resolution (about 5 nm and better) both qualitatively and semi-quantitatively,
- to obtain information about binding ratios of an element.

Sample

Ceramic thermal barrier coating systems based on ZrO_2 are used in many areas of modern gas turbines. The use of thermal barrier coatings allows the operating temperature of the metallic substrate materials (here a nickel-based superalloy) to be lowered while maintaining the same combustion temperatures, thus extending the service life of the gas turbine. This also improves the efficiency of the turbine and thus reduces CO_2 emissions.

Under the influence of heat, fine-grained carbides (< 100 nm) form by diffusion of carbon along the grain boundaries, which can lead to embrittlement of the substrate and premature failure of the component.

Investigations of microstructural changes in the substrate material are necessary in order to be able to make statements about the efficiency of ceramic coatings. Due to the limited lateral resolving power of analytical techniques such as WDXS or EDXS, the characterization of the occurring chemical phases in the scanning electron microscope is only possible to a limited extent or not at all.

The sample to be examined is a thinly polished TEM foil of a heat-treated Inconel 617 Ni-based alloy [9] (Al: 0.8 - 1.5%, C: 0.05 - 0.15%, Cr: 20 - 24%, Co: 10 - 15%, Cu: 0.5%, Fe: 3% (maximum), Mg: 1% (maximum), Mo: 8 - 10%, Si: 1% (maximum), S: 0.0015%, Ti: 0.2 - 0.5%, remainder is Ni). All values in wt.%.

Microscope

TEM/STEM FEI Titan³ 80-300 with 300 kV accelerating voltage and an imaging energy filter type GIF Tridiem 865 ER. The main components of the microscope and the adjustment are demonstrated.

Preparation

Keywords: elastically and inelastically scattered electrons, electron energy loss or electron energy loss spectroscopy (EELS), ionization edges, valence electron and plasmon excitation, near edge fine structure (ELNES) of an ionization edge, electron spectroscopic or energy filtered imaging and diffraction (ESI/EFTEM)

Preparatory questions for the experiment

- 1) How should a sample be optimally prepared for the EELS experiment at the transmission electron microscope?
- 2) How does an electron energy loss spectrometer or imaging energy filter work in principle? (a good overview is provided e.g. <https://eels.info/products/gatan-imaging-filter-gif>)
- 3) What prominent energy losses occur in the low-energy (< 50 eV) and high-energy regions of the EEL spectrum?
- 4) How can sample thickness be determined using EELS? (see e.g. <https://eels.info/how/quantification/plural-scattering-and-sample-thickness>)
- 5) What is the cause of the appearance of edge fine structures (ELNES)?
- 6) How are elemental distribution images registered using electron spectroscopic imaging (ESI or EFTEM)? What is the difference between the 2-window (jump ratio) and 3-window method?
- 7) What are the advantages/disadvantages of EELS compared to WDXS and EDXS analyses?

Experiment

1. Imaging in scanning transmission electron microscopy mode (STEM):
 - a) Adjustment of the STEM mode and search for a suitable sample site (precipitates at a grain boundary at a thin sample site)
 - b) Acquisition of STEM-images for overview
2. STEM-EELS point analysis at selected sample locations:
 - a) Demonstration: Adjustment of the beam in the GIF entrance aperture and recording of the aperture edge with the zero beam slice to determine α and β (Fig. 1 in [1]).
 - b) Demonstration of the different setting options of the EELS spectrometer (energy dispersion, drift tube energy offset).
 - c) Recording of *core-loss spectra* on any precipitates and the matrix (3-4 sample sites)
 - d) Acquire *low-loss spectra* near the sample edge adding a thicker region of the matrix to estimate the local sample thickness (adjust $\beta \geq 20$ mrad)
3. ESI/EFTEM imaging:
 - a) Acquisition of unfiltered and *zero-loss/elastically* filtered CBED diffraction images with *convergent beam electron diffraction* (CBED) illumination in STEM mode
 - b) Switch to TEM mode with parallel illumination of the specimen
 - c) Optional: acquisition of unfiltered and *zero-loss/elastically* filtered bright-field TEM images
 - d) Acquisition of *core-loss* ESI/EFTEM elemental distribution images of Cr, Ni, and C using the two- (*jump ratio*) and three-window methods

Test evaluation

A1

Qualitatively describe the captured STEM images in terms of the resulting contrasts and visible specimen details (precipitates/matrix area/grain boundary).

A2

- 1) **Qualitative elemental analysis:** check with tabular data (e.g., EELS atlas, <https://eels.info/atlas>) which elements are measured in the core-loss point spectra and whether the energetic location of the core-loss ionization edges match literature values.
- 2) **Quantitative elemental analysis: Quantify 2 selected core-loss spectra (e.g. one from the matrix, one from a precipitate) to obtain an estimate of the percentages of the respective elements.** After reading an EELS spectrum into a suitable software (Python or HyperSpy [7], Fiji, Origin, Excel, ...), the background in front of the element edge to be analyzed must be subtracted, usually in the form of a power law $A \cdot E^r$ (Fig. 39.10 in [2], Fig. 3 in [3]). Then the net intensity in an energy interval ΔE is summed up (Fig. 39.9 in [2]). The net intensity I is then scaled with the partial effective cross section $\sigma(\alpha, \beta, \Delta E)$ of the element in the same energy interval ΔE . The required effective cross sections $\sigma(\alpha, \beta, E)$ will be calculated by the supervisor. For the concentration ratio (in at.%) of two elements A and B then applies:

$$\frac{C_A}{C_B} = \frac{\sigma_B(\alpha, \beta, \Delta E)}{\sigma_A(\alpha, \beta, \Delta E)} \cdot \frac{I_A(\beta, \Delta E)}{I_B(\beta, \Delta E)}$$

If more than 2 elements occur, the percentages are normalized to 100%, i.e. $\sum C_i = 1$. Compare the found Ni/Cr ratio with the nominal values for Inconel 617.

- 3) **Estimate the relative (t/λ_{imfp}) and absolute (t) local sample thickness from the low-loss spectra.** First calculate the ratio t/λ_{imfp} , with the mean free path length for inelastic scattering λ_{imfp} :

$$\frac{t}{\lambda_{\text{imfp}}} = \ln\left(\frac{I_t}{I_0}\right)$$

The latter can be used to calculate the absolute specimen thickness with known specimen density ρ ($=8,36 \text{ g/cm}^3$ for Inconel 617 [9]), α and β can be estimated using the formula of Iakoubovskii et al. [8]:

$$\frac{1}{\lambda_{\text{imfp}}} = \frac{11\rho^{0.3}}{200FE_0} \ln\left(\frac{\alpha^2 + \beta^2 + 2\theta_E^2 + |\alpha^2 - \beta^2|}{\alpha^2 + \beta^2 + 2\theta_C^2 + |\alpha^2 - \beta^2|} \cdot \frac{\theta_C^2}{\theta_E^2}\right)$$
$$F = \frac{(1+E_0/1022)}{(1+E_0/511)^2}, \quad \theta_E = \frac{5.5\rho^{0.3}}{FE_0}, \quad \theta_C = 20 \text{ mrad}$$

With the units of primary voltage E_0 (kV), angle α and β in (mrad) and the sample density in (g/cm^3) results in λ_{imfp} in (nm).

- 4) If the quality of the C-K ELNES obtained from precipitates allows, compare them with reference spectra of carbides, graphite, and diamond (Fig. 24 in [1], [6]).

A3

- 1) Describe qualitatively the contrast changes in the CBED and TEM bright-field images, respectively, obtained using zero-loss energy filtering.
- 2) Interpret the Cr, Ni, and C distribution at the grain boundaries using the two-window elemental distribution images.

3) Compare the element distribution images of the two/three window method. What are advantages/disadvantages of each method (see, e.g., 39.9.A/B in [2], [4])?

Literature

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