esteem3

Enabling Science through European Electron Microscopy

Report on protocols for sample preparation techniques of materials for energy

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Revision history log

Version number	Date of release	Author	Summary of changes
V0.1	01/03/2023	A. Kruk	Task 8.4
V0.1	05/03/2023	G. Nicotra	Task 8.4
V0.1	07/03/2023	S. Boninelli	Draft version of the deliverable
V1.0	13/04/2023	Peter A. van Aken	Minor amendments and approval
V1.1	13/04/2023	Aude Garsès	General review and minor changes

Context of the present report

Quoted from the proposal:

Task 8.4: Sample Preparation of Materials for Energy (KRA, LJU, CAD, CAT, TOU)

This task will optimize TEM sample preparation of materials/devices for energy applications. For materials for energy applications, it is generally important that a very specific region of interest (ROI) must be extracted prior to TEM investigations.
Therefore, the ultimate goal of this task is to define the most appropriate and optimized sample preparation techniques for high quality specimen preparation with high site specificity and with no (or at least minimum) preparation-induced artefacts.

Deliverable D8.4 belongs to WP8 Materials for Energy. In this work package, Task 8.4 is reported.

Task 8.4: Sample Preparation for Materials for Energy

The following study presents the most optimal sample preparation methods for TEM analysis from materials used in the power industry. This task will describe optimal techniques for preparing thin artefact-free TEM samples (FIB-SEM lamella) for various "difficult" materials used in conventional energy systems, e.g., martensitic 9-12% Cr steels, advanced austenitic steels (e.g. Sanicro 25, HR6W) and Ni-based superalloys. The nickel-based superalloys' heat and oxidation resistance results from forming a protective oxide scale on their surface, usually Cr_2O_3 or Al_2O_3. However, the extensive chemical composition of nickel-based superalloys (about ten alloying elements added) leads to the formation of much more complex, multi-layered systems, where chromia and alumina are accompanied by other products' oxidation.

Due to the specific nature of materials used in energy systems, we are usually subject to microscopic analysis:

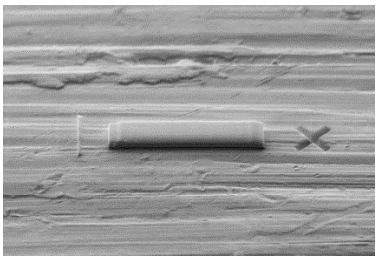
- a layer of scale formed on the surface of the element during its operation in challenging environmental conditions,
- the subsurface layer, where internal oxidation processes take place and new phases appear,
- a layer of the base material, where the structure degradation processes occur, causing a decrease in the strength properties of materials, so we are dealing with their degradation.

From our experience, we can say that the basic methods of preparing samples for TEM testing from the materials mentioned above are:

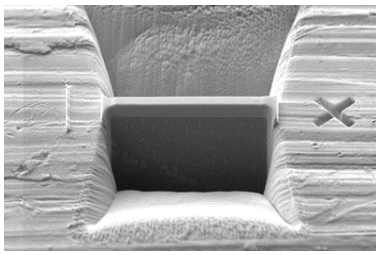
- FIB lift-out technique.
- FIB-SEM 3D tomography with the preparation of cross-section lamellae using the FIB lift-out technique.

1. TEM Sample Preparation using FIB, the FIB lift-out technique

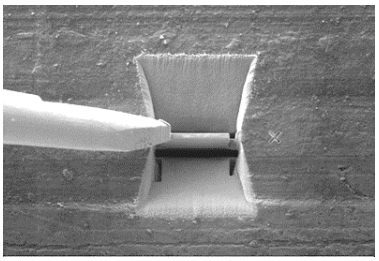
The sample surface is imaged with a FIB before cutting to determine the region of interest (ROI). Then, the sample is milled and polished with predefined milling patterns. Variables that should be considered during sample preparation using a FIB and affecting the final thickness of the lamella preparation process are: ion energy, angle of incidence, vacuum, initial surface topology, initial chemistry, initial orientation, initial crystallography of the surface, beam energy, and beam profile. During TEM sample preparation using a focused ion beam, the real-time SEM imaging allows for very tight control of the sample thickness/transparency and the danger of destroying the fine lamella is reduced to a minimum. Ion milling involves bombarding delicate thin TEM specimens with highly energetic (30 keV) Ga^+ ions or neutral Ga atoms and sputtering material from the surface of the specimen, until the sample will be thin enough and transparent for electrons, thus suitable for a TEM study. In the final step, the sample can be cut out of the substrate and transferred to a TEM grid. The final prepared TEM specimen must be electron-transparent and representative of the material to study. In most cases, we need specimens to be uniformly thin, which is essential in the case of high-resolution studies (HRTEM, HRSTEM), chemical composition analysis using EDX or EELS, stable under the electron beam and in the laboratory environment, conducting, and non-magnetic. The successive stages of lamella preparation for TEM testing using the FIB lift-out technique are shown in **Figure 1**.



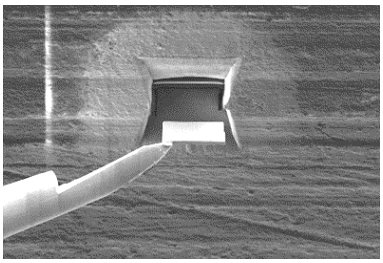
Stage 1: Selection of the area to cut out the lamellae (ROI) and place for deposition of the Pt layer.



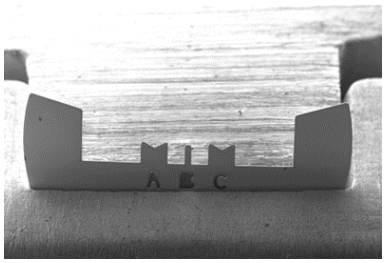
Stage 2: Pre-cutting of the lamellae.



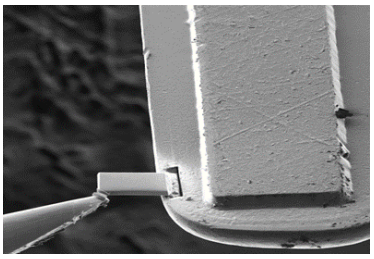
Stage 3: Welding the needle to the pre-cut lamella for pulling it out.



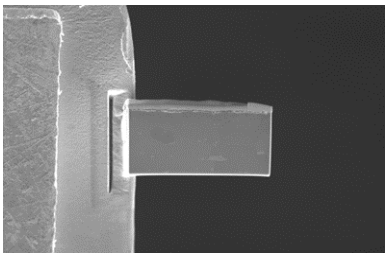
Stage 4: Pull out the pre-prepared lamella.



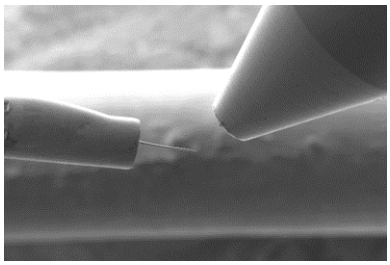
Stage 5: Scheme of the front side of a standard TEM grid.



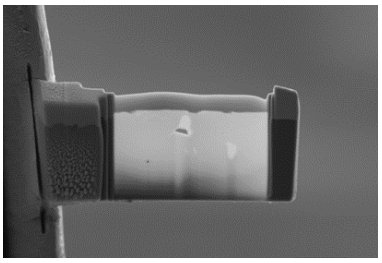
Stage 6: The stage of fixing the lamellae on the grid.



Stage 7: View of the mesh with the lamella attached.



Stage 8: The stage of final thinning of the lamellae.



Stage 9: Finished thin lamella.

Figure 1. Successive stages of FIB lamella preparation for TEM investigation. FIB ZEISS NEON 1540EsB CrossBeam.

2. Correlative multiscale electron microscopy, 3D FIB-SEM tomography with detailed TEM investigation - Targeted Sample Preparation Stage

An excellent example of applying TEM preparation to materials for the power industry can be investigating the oxide scale formed on nickel-based superalloy, ATI 718Plus, during oxidation at 850 °C up to 4000 hours. The targeted sample preparation method was used to analyze oxidation products of nickel superalloy ATI 718Plus. Because the analysis concerned the scale layer, it was essential to use a preparation method that would not lead to a chipping of the scale layer from the sample surface. In this case, we used an original approach, combining analytical electron microscopy with FIB-SEM tomography to identify phases and show a 3D distribution of phases formed in the near-surface area during oxidation.

A novel methodology for combining FIB-SEM 3D tomography with the preparation of cross-section lamellae using the FIB lift-out technique has been developed (**Fig. 2**). FIB-SEM tomography is an imaging technique that combines a focused ion beam (FIB) with a scanning electron microscope (SEM) to obtain information on the internal structure of specimens. It allows for visualizing the particles' shape and spatial distribution, enabling us to carry out a qualitative and quantitative analysis of the microstructural element. In a typical FIB-SEM tomography experiment, the specimen is situated at the coincident point of the ion (FIB) and electron (SEM) beams (54° to the electron optic-axes). After finding an area of interest (AOI) on the sample surface and depositing the platinum protective layer (IBID - ion-beam induced deposition), a trench is first carved on the upper surface of the sample with the FIB. The trench helps prevent the adverse effects of material re-deposition during the imaging process of a newly exposed material surface. Line marks are made for a further stack alignment and slice thickness calibration. The successive stages of the FIB-SEM tomography technique application for microstructural characterization materials for energy are presented below:

Image Acquisition

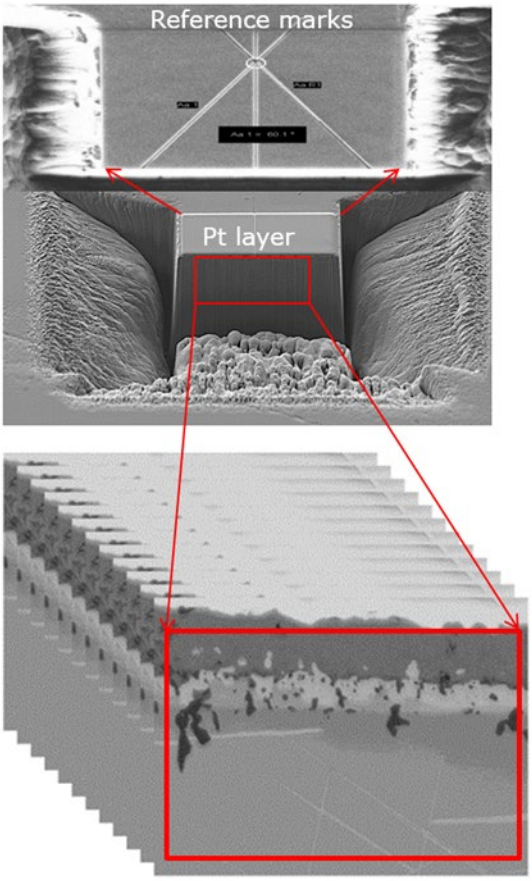
- Deposition of a Pt layer
- Application of reference marks
- Preparation of a cube of suitable size
- Calibration of the ion-beam shift for automated drift correction
- Choice of imaging methods (BSE or/and SE detectors)
- Choice of the voxel size depending on the size of the analyzed object
- Serial sectioning and acquisition of a data stack, including drift correction after each cycle of imaging and erosion

Off-line data processing

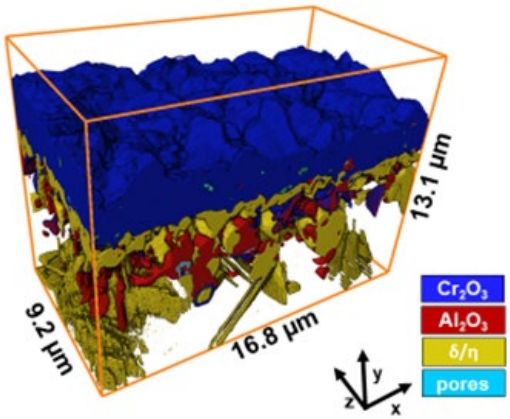
- Raw data stack - shift correction
- Reconstruction filtering and binarization
- Segmentation
- Quantification (measurements and analysis)

TEM Sample Preparation using FIB, the FIB lift-out technique

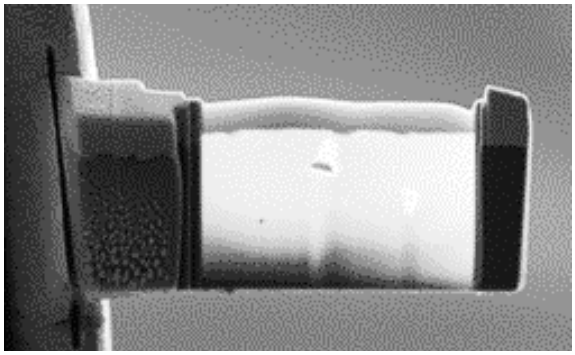
Lamella prepared following the steps of the FIB lift-out technique as the next stage after the tomographic acquisition of a series of images.



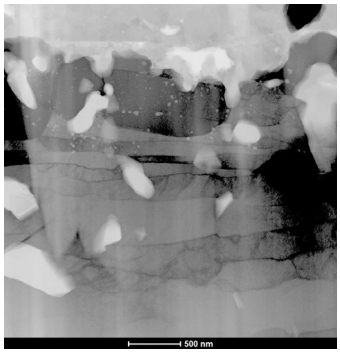
Tomographic series of SEM-BSE images from the area of the substrate material and the scale layer of the oxidized nickel superalloy sample.



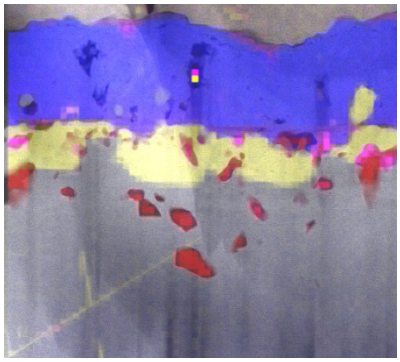
3D imaging of the microstructure elements of the base material and the scale on the surface of the 718Plus nickel superalloy sample.



Lamella prepared following the steps of the FIB lift-out technique as the next stage after the tomographic acquisition of a series of images.



TEM image of the fins in the area of scale and base material, nickel superalloy 718Plus.



Distribution map of selected elements (STEM-EDX) in the area of scale and base material, nickel superalloy 718Plus.

Figure 2. The results of using 3D FIB-SEM tomography in conjunction with the cutting of lamellas by the FIB method for the microstructural analysis of the scale formed on the surface sample of a nickel base superalloy 718Plus.

3. Exfoliation of 2D materials (CAT)

The preparation of a high-quality specimen for TEM analysis is the first prerequisite to obtain excellent images and to avoid preparation artifacts. The mechanical exfoliation of van der Waals materials is one of the most promising ways to achieve good quality TEM lamellae, but unfortunately, they are mostly affected by the presence contaminants such as solvents or glue residuals used for the exfoliation. The method we created is an improvement of the scotch tape method, where we replaced the common sticky tape with a special ultraclean icros UV tape, usually used as protective tape for the silicon-wafer back-grinding process in semiconductor manufacturing. In Figure 3, we show the classical method, step by step, based on commercial low adhesive power scotch tape. Here, multiple exfoliation steps are applied, each producing a slice with fewer layers, until only one remains. After exfoliation, the flakes are deposited on a silicon wafer. Crystallites larger than 1 mm and visible to the naked eye [Geim, A. K.; MacDonald, A. H. (2007). "*Graphene: Exploring carbon flatland*". Physics Today **60** (8): 35–41]. Layers deposited on a Si wafer are transferred to a holey carbon TEM grid by a bed-wetting of ethanol.

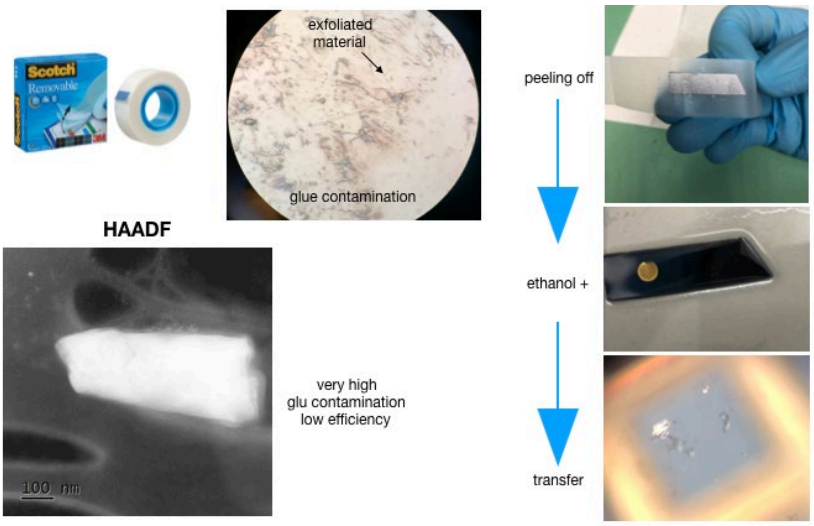


Figure 3. Classical mechanical exfoliation method for 2D materials shown step by step. Here, a commercial low-adhesive power scotch tape has been used. After multiple exfoliation steps, each step produces a slice with fewer layers, until only one remains. After exfoliation, the flakes are deposited on a silicon wafer. Layers are finally deposited on a Si wafer and transferred to a holey carbon TEM grid by a bed-wetting of ethanol. The HAADF image shows a very glue-contaminated specimen.

Our new method is shown systematically in Figure 4. Here, after peeling the layers off many times, until only one remains, we deposited it on a silicon wafer and then apply a UV flash to deactivate the glue. The surface of the wafer is now very clean end free of glue, thus implying a very clean transfer to the layer to the grid. After a final wash in an ethanol bath, KOH is applied in order to transfer the layer to the carbon holey carbon TEM grid.

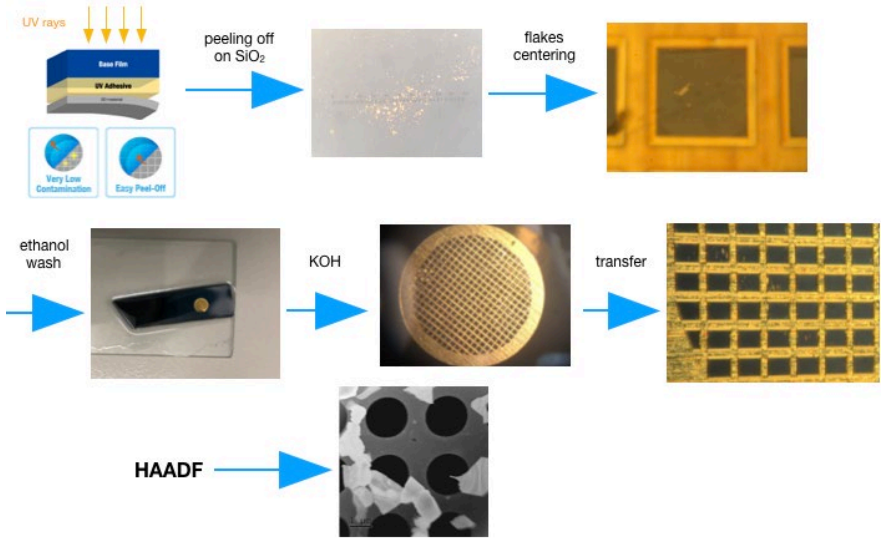


Figure 4. New exfoliation method based on ultraclean icros UV tape. After peeling the layer, we deposited it on a silicon wafer and then apply a UV flash to deactivate the glue. The surface of the wafer is now very clean end free of glue, thus implying a very clean transfer to the layer to the grid. After a final wash in an ethanol bath, KOH is applied to transfer the layer to the carbon holey carbon TEM grid. The HAADF image shows a very clean specimen.

In Figure 5 (a-d), we show the cleanliness of the wafer surface after the transfer of the layer onto the wafer using different tapes. Figure 5(a) is the one obtained using the ultra-clean icros UV tape; from Figure 5(b) to 5(c), other tapes were used as indicated in the figure. It seems obvious that the surface free of residual VAX is the one in (a). The HAADF reported in Figure 8 shows a very clean grating.

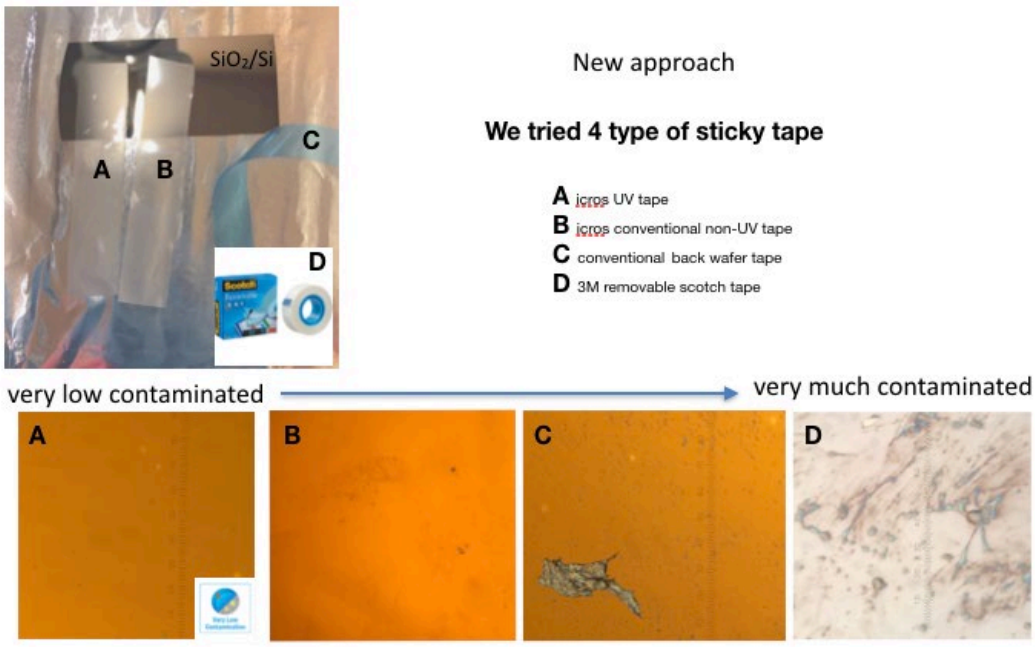


Figure 5. Comparison of Si wafer surface after layer transfer by different kind of sticky tape. From the comparison, it is apparent that the one transfered with the ultraclean icros UV tape is the cleanest.