

DualBeam™ and FIB capability applied to metals research

The values of DualBeam™ for metals research

The availability of Focused Ion Beam (FIB) capacity on a DualBeam™ has allowed many researchers to open up their sample and locally study the internal structure. In addition, a locally prepared TEM sample can be made easily and quickly with high reliability. This application note provides methods and results for important examples in the field of metals research. It clearly shows the high value that a DualBeam™ offers when applied properly, to important issues for metals research, such as for coatings and stress analysis studied with indentations. It also shows the useful combination with ultimate TEM sample analysis on FIB prepared samples. This document has been written by Dr. Valerie Sivel of Netherlands Institute of Metals Research (NIMR), Rotterdamseweg 137, 2628 AL Delft, The Netherlands. Sample courtesy Jeroen van den Brand and Nuno Carvalho, NIMR.

DualBeam used for creation of delicate TEM sample of aluminum/epoxy coating

Metals researchers are often interested in mechanical properties of metal/coating systems for automotive, airplane, or food industry applications. Today these characteristics are routinely measured, but further information about interface structure is crucial in order to understand, for example, adhesion performance and to improve it. TEM observation of a cross-section of a substrate/coating interface provides the necessary information such as presence and shape of oxide, hydroxide,

interface layer or voids. Conventional preparation methods, however, are time consuming and sometimes unsuccessful in making electron transparent cross-sections from delicate materials, most often because these methods deform the materials or mix the different components. The DualBeam offers a solution to this problem and has already proven its efficiency in many cases as shown in the following example.

The materials system of interest is composed of an 80 μm thick epoxy coating applied via a solvent onto a 1 mm thick AA1050 aluminum alloy substrate. The properties of such a material strongly depend on the way in which it is created and on the environment to which it is exposed. When exposed to an aqueous environment, water penetrates into the epoxy and a hydroxide layer grows at the metal/coating interface. This modifies the adhesion of the coating to the substrate, compared to a non-exposed sample. Furthermore, if during the creation of the material the substrate is first placed in boiling water for a few seconds prior to applying the epoxy coating, a pseudoboehmite layer grows at the aluminum surface. The thickness of this layer, as measured by spectroscopic ellipsometry, is about 100 nm. The strong adhesion of this second sample makes it interesting to investigate and compare with the first sample. TEM characterization of both interfaces is an efficient way to do this; information about the thickness and the roughness of this layer is essential to link the microscopic structure of the interface to macroscopic properties of the material.

For this case study, three sample types were used:

- Type 1: Al plus deposition of 80 μm epoxy
- Type 2: Al plus 80 μm epoxy exposed to aqueous environment
- Type 3: Al exposed to boiling water followed by deposition of 80 μm epoxy layer

Sample preparation

- a) Conventional sample preparation: the preparation of a cross-section with the conventional method was unsuccessful. In this process, a slice is cut from the sample and glued to a piece of glass for mechanical polishing. The glue is then removed with acetone and the specimen is put on a copper TEM grid for low energy ion milling down to electron transparency. Unfortunately the epoxy coating, smoothed by acetone, did not resist the low energy ion milling and the interface was therefore destroyed.
- b) Creating a thin sample using FIB: the FIB was found to be the only suitable technique for this material. Two issues had to be addressed prior to cutting with the FIB. Firstly, the epoxy coating of the initial sample was too thick for practical FIB preparation (80 μm), so the surface was mechanically polished with a slight slope. As a result, increasing coating thicknesses were available from 0 μm at one side of the sample, to 80

μm at the other side. As a result, few micrometer thick areas were available close to the bare substrate. Secondly, a charging effect due to the non-conductivity of the coating was eliminated by spraying a thin layer of platinum, inside the DualBeam, to cover the area of interest. A 15 μm wide and 10 μm deep cross-section made as close as possible to the bare substrate confirmed the presence of the interface a few microns below the surface, a depth reachable by the ion beam (figure 1). The sample was then ready to be cut with the FIB. The sample generation was realized by using FEI’s “runscript” software on the DualBeam. In this process the chosen position is marked by milling two crosses alongside the area of interest which is then protected by a platinum layer.

Large holes are milled by a 5 nA ion beam from both sides in such a way that just a 1 μm thick foil remains (figure 2a). At this step, as shown in figure 2a, one side of the specimen can be cut free in order to release the stress and to lower any bending effect during the final thinning.

The foil is finally thinned and cleaned line by line at lower ion currents (down to 100 pA). The final thinning until electron transparency is done manually on a selected area of the produced specimen, just before cutting it

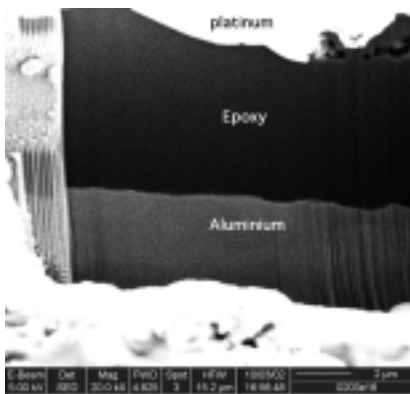


Figure 1: Example of specimen creation of sample type 2. Electron beam image of the FIB cross-section milled in the thin part of the polished coating. The surface is protected by a platinum layer and a strong contrast clearly shows the interface. The expected 30 nm thick interface layer is too small to be resolved by the electron beam on this 45° inclined cross-section.

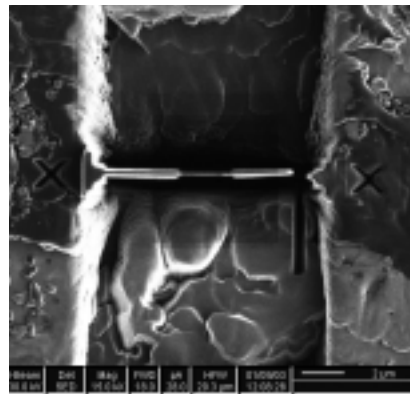


Figure 2a: Top view SEM image of a lift-out specimen at the final step of preparation. The two crosses alongside the foil are used by the software as a reference for the chosen position. The specimen has been thinned down to about 300 nm. The thinnest area has been reduced further until optimal electron transparency (less than 100 nm).

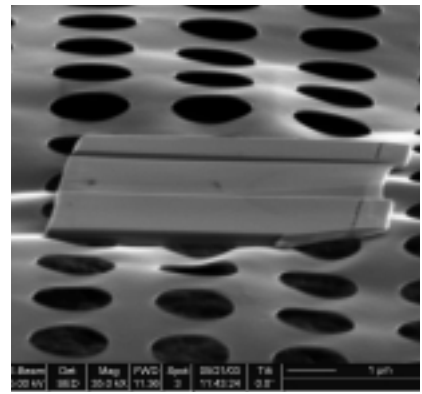


Figure 2b: TEM specimen has been lifted ex-situ the DualBeam and deposited on the carbon foil of a copper grid.

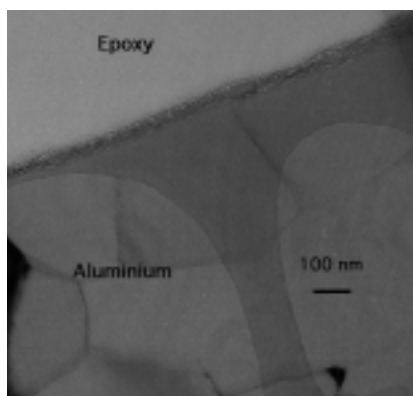


Figure 3a: TEM pictures of the interface Aluminum (lower part of the picture) /Epoxy coating (upper part). In the sample exposed to aqueous environment (sample type 2), a 30 nm thick hydroxide layer is visible. The round features are due to the holes of the holey carbon film below the specimen.

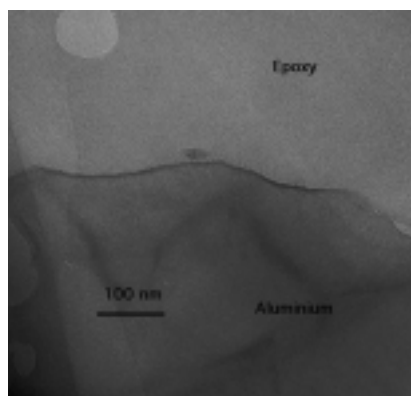


Figure 3b: In the non-exposed sample (sample type 1) no layer is visible.

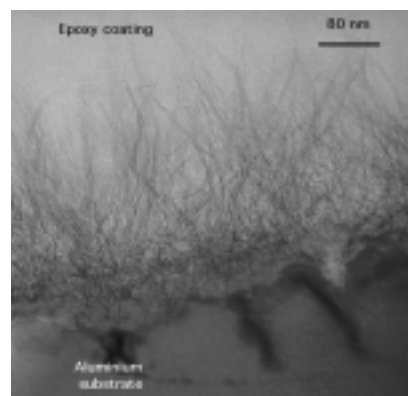


Figure 4: TEM picture of a FIB cross-section of a pseudoboehmite interface layer (sample type 3).

free. The use of the electron beam during this process is very convenient to check the quality of the specimen and the thickness of the remaining protective layer. It provides non-destructive 52° side views of the specimen without undesired milling, and helps to control the thickness of the specimen. The transfer of the foil from the sample (the lift-out) to a TEM grid covered with a carbon foil is made outside the DualBeam. It is realized by the electrostatic force of a glass needle attached to an optical microscope. The specimen lying on the grid is thus ready for TEM observation (figure 2b).

A lift-out specimen was cut from a first aluminum/epoxy sample exposed to aqueous environment (sample type 2). As a reference, a second specimen was cut from a non-exposed sample (sample type 1). Finally, a third specimen was cut from the sample with a pseudo-boehmite layer (sample type 3). Each specimen was prepared within less than 3 hours, with about $4 \times 6 \mu\text{m}^2$ electron transparent areas around the interface.

TEM observation

The TEM bright field picture of the sample type 2 clearly shows a 30 nm thick layer at the interface between the epoxy coating and aluminum substrate (figure 3a). This layer is highly regular in thickness along the whole interface. In contrast to sample type 2, no layer is visible in the non-water-exposed material (sample type 1, figure 3b).

The third sample (sample type 3) was investigated. The bright field TEM picture, made with a CM30T, shows a well-resolved needle shape layer, 150 nm in thickness (figure 4). This non-homogeneous layer is completely embedded into the electron transparent coating, creating a large contact area, which can explain the high measured adhesion. Please note that the FIB preparation creates no de-lamination at the interface and does not damage the very fine needle structure either. In other words, the interface is well preserved.

Conclusion

The DualBeam is a powerful instrument for TEM specimen preparation, especially in the field of metals research. Specimens are easily cut within a few hours, without damaging the area of interest. The metal deposition option protects fragile top layers and solves the charging problem in situ within a few minutes. Furthermore, the associated electron beam which is not always essential in the process, is a welcome help to control the quality of the final specimen and to make high resolution images without any damage. Finally, the FIB (and especially the DualBeam) often provides a solution where conventional TEM preparation methods fail, as in the example presented above. It is especially useful when several phases are present like in metal/ coating systems. That is why the FIB is increasingly used in materials and metals research.

DualBeam: a highly efficient technique for nano-indentation cross sectioning (part 1)

Metals research has a high interest in metal/coating systems. One of the goals is to improve their mechanical properties and as a first step to independently study the coating's properties. Nano-indentations are a good way to measure the hardness of a thin layer (up to a few microns), without any influence of the substrate. In this technique a load is applied through a triangular or spherical indenter to the surface. The measurement of the penetration and final depths of the deformation give access to the hardness of the film and is calculated during the process. It is also useful to study the damages made by this deformation in the film; this can only be done by cross-sectioning an indentation. In this case the FIB beam has a powerful capability due to its ability to cut a sample at the exact chosen position. Furthermore, the DualBeam system offers some more possibilities thanks to its associated electron beam. The application of the DualBeam to the characterization of nano-indentation impact in a multi-layer coating is presented below.

Indentation profile in cross-section

Using different loads, a triangular indenter was applied to the surface of a (TiN)/(Ti,Al)N multi-layer coated steel substrate. The created nano-indentations were scanned both with the electron and ion beam, allowing to measure the feature sizes at the surface of the coating (figure

5a). After ion beam assisted in-situ deposition of a 1 μm thick protective platinum layer onto the interesting part of the indent (figure 5b), the specimen was ready for cutting. A large hole was first milled close to the indentation, using an ion current of 3 nA, in order to create a free path for electron beam side view imaging. The cross section was then cleaned at lower currents (figure 5c). During all the milling steps the sample was inclined at 52° in order to align the normal of the sample surface with the ion beam. The indentation was then cut, slice by slice, using a 300 pA ion beam current. After each cut, the sample was tilted back to 45° for cross section imaging with the electron beam. This tilted sample position avoids wrong measurements on cross sections. Figures 6a and 6b show 2 different slices of a nano-indentation. Thanks to the high SE signal of the platinum layer, the shape of the deformed surface is clearly visible. Electron beam single scans, grabbed after cutting each slice, provide a 3D profile of the indentation. The same result can be obtained using "Auto slice", FEI software, which automatically cuts slices at equal distance and grabs single scans in between. These recorded images are then presented as a movie.

Apart from the indentation profile, additional information is available in cross-section images, and the successive layers of the coating are visible (figure 6b). Through the deformation of these layers, it is easy to measure the impact depth of the indentation and to check whether the substrate has been reached. However, the resolution of the electron beam is not good enough to study details

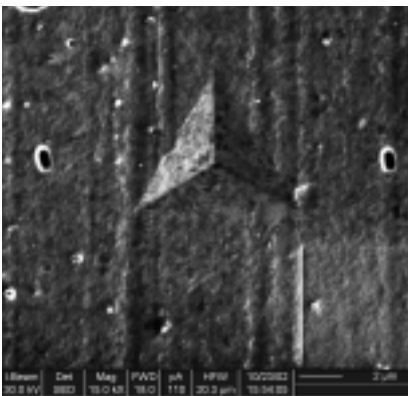


Figure 5a: Electron beam top view of an indentation.

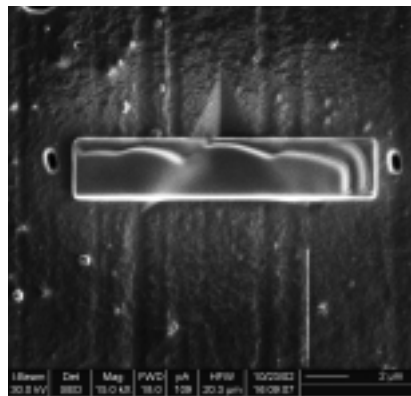


Figure 5b: Indentation covered by a layer of platinum.

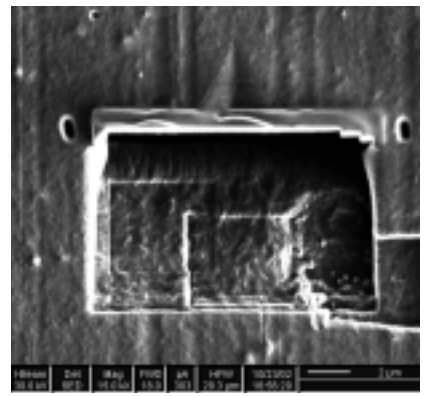


Figure 5c: Cross-section milled in the indentation.

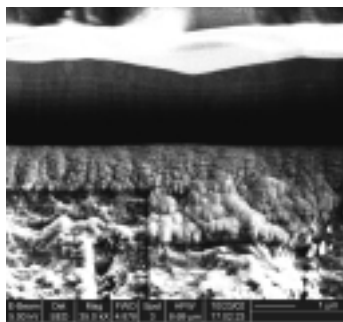


Figure 6a: 45° SEM scan of the cross section showing the profile in the middle of the indentation.

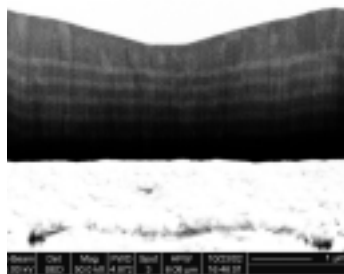


Figure 6b: Further cross-section. Distinct layers are visible, showing some deformations below the indentation.

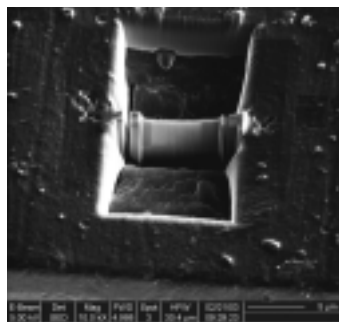


Figure 7: SEM image of a lift-out specimen just before the transfer to the TEM grid-

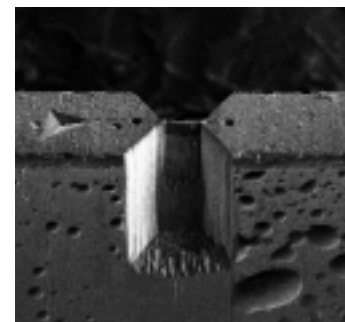


Figure 8: Side view of a pre-thinned sample made with the FIB.

of the cracks and dislocations below the indentation. This can only be done by TEM and therefore TEM specimens had to be prepared from this exact location.

TEM specimen preparation

TEM specimens were prepared in nano-indentations made with various loads in the previous steel (TiN/(Ti,Al)N) material, using conventional and FIB methods of preparation.

Conventional method

TEM cross-sections of nano-indentations were prepared by low energy ion milling of a 50 μm thick sample. However, producing a final specimen exactly at the center of the indentation requires frequent checks in the SEM. Consequently, the preparation of a sample takes several days.

FIB lift-out method

The FIB offered a good solution: TEM specimens were prepared exactly at the area of interest in 2 or 3 hours depending on the specimen size, using “runscript”, FEI software dedicated to TEM specimen preparation. After in-situ protective platinum deposition, material is removed automatically from both sides of the chosen area using an ion beam current of 5 nA. The remaining material is then automatically thinned using low currents (from 3 nA to 300 pA) down to a thickness of about 300 nm. For the last milling step, the operator cleans and thins a selected area down to TEM electron

transparency, which is less than 100 nm (figure 7). The following step is that the sample is placed at 45° viewing angle and cut free by the ion beam. The produced lamella is finally lifted out of the sample ex-situ and deposited on the carbon foil of a copper grid, ready for TEM observation.

In the TEM, cracks and dislocations created below the indentations were studied to determine the relation between the applied load and the damage done in the coating.

FIB Pre-thinned process

Another process, called “pre-thinned samples preparation” is available with “runscript”. A 50 μm thick slice of the sample, containing the area of interest, is first cut and fixed vertically. It is automatically thinned from both sides of the chosen feature and manually cleaned until electron transparency (figure 8). As in this process the specimen is not cut free, the sample is not tilted for a side view scan with the ion beam. As a result, the electron beam side view (at 52° with respect to the specimen cross-section) is very helpful to select the final area to be thinned to electron transparency (figure 8).

This process is also used to control the milling depth and the specimen quality. The whole sample is finally stuck on a grid in such a way that the TEM electron beam can pass through the thinnest area.

Advantages of the FIB techniques

The advantages of the pre-thinned technique are that there is no need to lift out the specimen and that it can be brought back into the system if a further milling turns out to be necessary. On the other hand, lift-out specimens require no previous sample preparation and a very small amount of material is used.

Compared to the conventional methods, the main advantage of both FIB techniques in TEM cross-section preparation is their ability to cut a specimen at the precise selected position in a short time frame. Another common advantage of the application presented here, is that TEM specimens can be prepared from several nano-indentations made in the same sample and fixed onto the same TEM grid. In this way the number of manipulations to insert the specimens in the TEM is reduced to a single one. Consequently, the manipulation time in the TEM is significantly reduced.

Conclusion

The ability of the FIB to provide cross-sections and TEM specimens at the exact position of interest in a short time makes it especially powerful in case of nano-indentation; the area below the center of the indentation; can be investigated with a high precision. "Lift-out" and "pre-thinned" processes are two different methods of TEM specimen preparation with the FIB which both have specific advantages. Each can be used with a single beam, but the electron beam of the DualBeam system improves the control of the specimen quality at each step of the fabrication by providing a non-damaging side view of the specimen.

DualBeam: a highly efficient technique for nano-indentation cross sectioning (part 2)

The application of an indenter creates a deformation which depends on the indenter shape, the applied load and the mechanical properties of the material. Dislocations and cracks might therefore be created below the indentation.

TEM is the only way to investigate the area of interest with sufficient resolution. That is the reason why electron transparent specimen preparation, at the precise indentation center, is a big issue. The conventional method by low energy ion milling may take up several days for a single sample.

Thanks to its ability to cut at the exact chosen position, the FIB is the ideal tool for creation of cross-sections exactly through the nano-indentation, and specimens can easily be prepared within a few hours. However, if the sample contains too many cracks combined with stress, the lamella breaks before the end of the thinning process. A specific process, presented below, must then be applied.

What happens if no care is taken for a sample containing cracks ?

A three-sided pyramidal indenter was applied by using different loads to the surface of a (TiN/(Ti,Al)N) multi-layer coated steel substrate. The measured size of the created indentations (see figure 9) at the surface varied from about 5 microns for a load of 50 mN to 15 microns for a load of 1N.

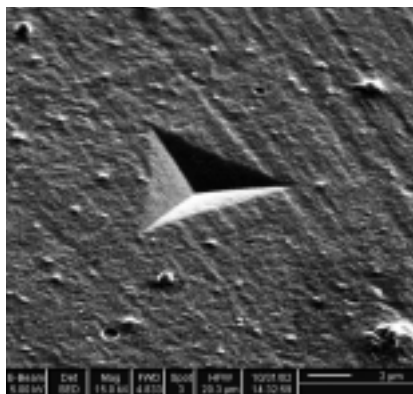


Figure 9: Indentation created by a three-sided pyramidal indenter on a multi-layer (TiN/(Ti,Al)N) coating.

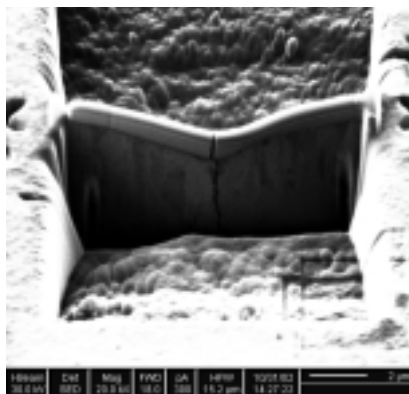


Figure 10a: SEM side view of TEM specimen broken during preparation and using the lift-out process.

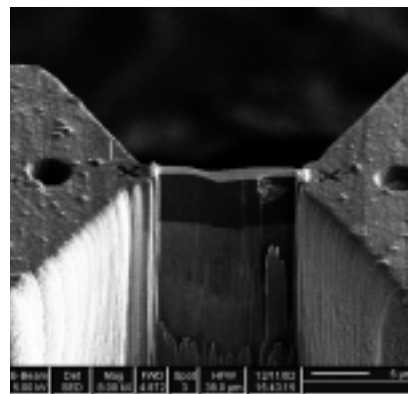


Figure 10b: TEM specimen broken during preparation, using the pre-thinned process.

Damage was created and cracks were expected in the 6 μm thick coating, especially below large indentations. In order to prepare the required TEM specimens, the lift-out process was first applied using “runscript” software. Following this process, a cross section lamella was cut from the sample surface, lifted outside the FIB and deposited onto a carbon covered TEM grid. In order to release the stress in this multi-layer material, one side of the lamella was cut free at the same time as the bottom, prior to final thinning. Specimens nevertheless broke before the end of the process, along vertical cracks (figure 10a). The second automatic process of preparation, called “pre-thinned specimen preparation” was then tried. This process requires previous preparation of a 50 μm thick sample. Indentations are applied onto the top of it. Material is then removed from both sides of the indentation, in order to create a free path for the TEM electron beam, and the remaining part is thinned until electron transparency. The whole sample is subsequently stuck onto a TEM grid, in such a way that the TEM electron beam can go through the thin area. In this case too, the specimen broke (figure 10b) before the end of the thinning process. This breaking of the specimen during the creation of the thin TEM lamella happens very easily and so we had to find a more robust way to prepare TEM specimens from this delicate material.

A solution to prepare a TEM specimen without breaking it

Using the lift-out process

This multi-layered coating breaks during TEM preparation due to stress release in cracked lamella. The usual way to avoid it is to cut free one side of the lamella while cutting free the bottom, before final thinning. As explained above, it was not enough in this particular case. Specimens were finally prepared successfully by thinning only a selected part of the lamella. The automatic process was used until the specimen reached a thickness of 1 μm . Then, the bottom and one edge were cut free, the sample being tilted at 7° (i.e., 45° with the ion beam). A selected area, about 8 μm in width, was thinned down to a thickness of 300 nm, using a current of 300 pA. During this process, the quality of both sides of the lamella was checked carefully with the side-view electron beam, thereby preventing cracked areas from further thinning. Finally, an area of a few microns was thinned to electron transparency using an ion current of 100 pA. Figures 11a and 11b show a specimen successfully prepared this way from a 500 mN indentation. This specimen was then investigated in TEM.

The same method was applied to the pre-thinned preparation process. Instead of using the automatic process, the first rough milling was done manually in order to control the depth of the specimen. A higher milling rate was achieved by starting to mill from the sample side-wall. Actually, milling an edge is faster than milling a flat surface. When the thickness of the remaining material was close to 15 μm , the automatic process was applied to thin the specimen down to a thickness of 1 μm . Then, in a similar way as previously described only a selected area was thinned further. During this process the lamella is not cut free, but when cracks appear cutting both edges helps to release the stress and

to avoid breaking the specimen. Figure 12 shows a pre-thinned specimen from a 50 mN indentation in the (TiN/(Ti,Al)N) multi-layer coating.

Conclusion

The DualBeam SEM/FIB is a very efficient tool for TEM specimen preparation, especially when a specific position is needed. However, the material's properties must be taken into account, and cutting a specimen from a sample containing cracks and stress is a challenge. The technique presented in this note saves substantial time compared to the conventional methods, without breaking the specimen during the thinning process.

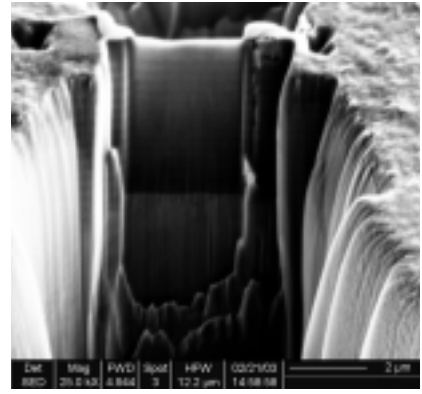
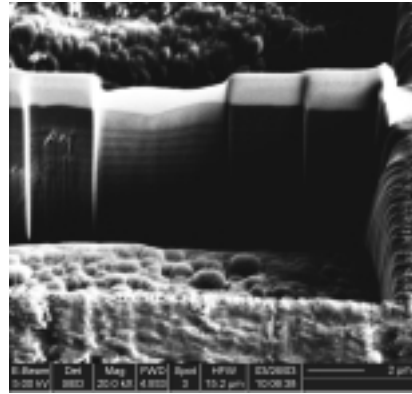
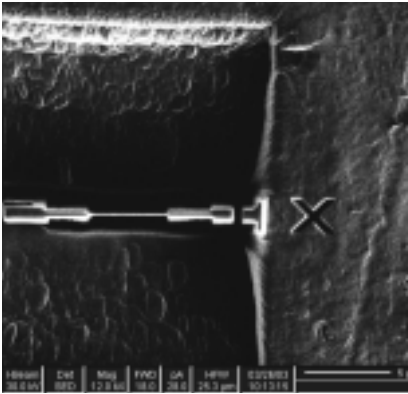


Figure 11a and b: Ion beam top view (left) and electron beam side view (right) of a lift-out TEM specimen prepared according to the process described in the text.

Figure 12: Pre-thinned TEM specimen prepared from a 50 mN indentation. Some material was left at the edges in order to avoid breaking the specimen.

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