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A global investigation into *in situ* nanoindentation experiments on zirconia: from the sample geometry optimization to the stress nanolocalization using Convergent Beam Electron Diffraction

E. Calvié, L. Joly-Pottuz, C. Esnouf, T. Douillard, L. Gremillard, A. Malchère, K. Masenelli-Varlot

INSA-Lyon, MATEIS UMR5510, 7 avenue J. Capelle, F-69621 Villeurbanne Cedex

Summary

Nanoindentation experiments inside a transmission electron microscope (TEM) are of much interest to characterize specific phenomena occuring in materials, like for instance dislocation movements or phase transformations. The key points of these experiments are i) the sample preparation and the optimization of its geometry to obtain reliable results and ii) the choice of the TEM observation mode, which will condition the type of information which can be deduced from the experiment. In this paper, we will focus on these two key points in the case of nanoindentation of zirconia, which is a ceramic material well known to be sensitive to stress since it can undergo a phase transformation. In this case, the information sought is the stress localization at the nanometer scale and in real time. As far as the sample preparation is concerned, one major drawback of nanoindentation inside a TEM is indeed a possible bending of the sample occurring during compression, which is detrimental to the experiment interpretation (the stress is not uniaxial anymore). In this paper, several sample preparation techniques have been used and compared to optimize the geometry of the sample to avoid bending. The results obtained on sample preparation can be useful for the preparation of ceramics samples but can also give interesting clues and experimental approaches to optimize the preparation of other kinds of materials.

The second part of this paper is devoted to the second key point, which is the determination of the stress localization associated to the deformation phenomena observed by nanoindentation experiments. In this paper, the use of Convergent Beam Electron Diffraction (CBED) has been investigated and this technique could have been successfully coupled to nanoindentation experiments. Coupled nanoindentation experiments and CBED analyses have finally been applied to characterize the phase transformation of zirconia.

Keywords: Transmission Electron Microscopy; In situ; CBED; zirconia

* Corresponding author: Lucile Joly-Pottuz
Lucile.Joly-Pottuz@insa-lyon.fr
Tel: +33-4-72-437102; fax: +33-4-72-437930

1- Introduction

In situ mechanical testing inside a transmission electron microscope is a quite new technique available by the development of new TEM sample holders. It has already been used to study several phenomena in materials: plasticity in aluminum grains (Minor, 2006)-(Soer, 2004)-(De Hosson, 2006) or in iron single crystal (Zhang 2011), failure of single nanoparticles (Shan, 2008)-(Beaber, 2010) or interaction between grains in aggregates (Lockwood, 2009). Ceramics materials were also recently studied (Lee, 2010). Grain boundary activities and grain rotations were followed inside a ceramic nanocomposite thin foil. From all these results, it seems that the great advantage of this technique is the availability to study and to follow in real time structural changes occurring inside materials during stress. Thus this technique seems to be also well adapted to follow and understand stress-induced transformations.

Ceramic materials are used in a large range of applications but one of their main problems is their propensity to brittle failure. Zirconia (ZrO_2 as TZP - Tetragonal Zirconia Polycrystal) was found to be very interesting because of a toughening mechanism reducing propagation of cracks (Chevalier, 2009). This mechanism is based on a phase transformation from tetragonal to monoclinic phase at the tip of cracks which stops or slows down cracks propagation. But this phase transformation can also occur at the surface of zirconia components (head of HIP prothesis for instance) in presence of water or moisture. In this case, it is particularly detrimental because it leads to a roughness increase and in some cases to failure. This phase transformation has been widely characterized (Deville, 2003) and studied (Chevalier, 2009). Nevertheless, it has never been observed in real time. Furthermore, to better understand the tetragonal/monoclinic transformation mechanisms, the critical stress value above which transformation occurs has to be determined. One innovative tool to

visualize the phase transformation and to measure this stress value is *in situ* nanoindentation inside TEM.

In this paper, we consider the *in situ* nanoindentation experiment in its whole, that is to say from the sample preparation to the data analysis. The materials studied will be zirconia but the procedure described here could be applied to different materials, from polymers to metals, by taking into account their specificities. In this investigation, two key steps will be considered, namely the choice of the sample preparation (which may be specific for the *in situ* tests) and the choice of the TEM observation mode, which conditions the type of information that can be deduced from the nanoindentation test.

Indeed, the first key point of nanoindentation tests inside a TEM is the sample preparation. The success of the whole experiment depends on this step as well as the reliability of the quantitative data which can be measured. The sample must be thin enough for TEM observations and must have a suitable geometry (to be deformed by the tip in the expected way). In this paper, several preparation techniques are compared, namely ultramicrotomy, tripod and ion milling or Focused Ion Beam (FIB). All these preparation techniques have been used on zirconia and their advantages and drawbacks are discussed below. The second key point corresponds to the choice of the TEM observation mode which will be suited for a quantitative analysis of the *in situ* experiment. In the specific case of zirconia, which can undergo a phase transformation due to stress, the information needed is the localization of stress at the nanometer scale and in real time. Among the different modes available in a TEM, the use of Convergent Beam Electron Diffraction (CBED) is evaluated.

2- Experimental

The stable zirconia phase at room temperature is monoclinic. Thanks to the addition of Yttrium or Cerium, it can be stabilized into the tetragonal phase. In order to delay the phase transformation from tetragonal into monoclinic, two stabilized zirconia phases were prepared: 3Y-TZP and 12Ce-TZP. 3Y-TZP is stabilized in the tetragonal phase with the introduction of 3%mol of Y_2O_3. The powder (TZ3YS made by Tosoh Company) is dispersed in water and, after homogenization, slip casted in a plaster mould. Finally, debinding and sintering processes were performed respectively at 600 and 1400°C for 5h. 12Ce-TZP (CEZ-12 powder made by Daiichi Company), which tetragonal phase is stabilized with 12%mol of CeO_2 was processed by uniaxial pressing at 200MPa and sintering at 1400°C for 2h. The average grain sizes are 0.3 and 1 µm for 3Y-TZP and 12Ce-TZP, respectively.

In situ experiments were conducted using an *in situ* nanoindentation sample holder manufactured by Nanofactory Company. The sample movement is controlled in three dimensions by a piezoelectric tube in a precision movement as fine as 0.1 nm per step. The tip is fixed on the sensor at the back of the sample holder and remains fixed. Two kinds of tips can be used on the sample holder: a wedge shaped diamond tip (tip length of 1µm and diameter of 40 nm) and a pyramidal shaped diamond tip with a flat top geometry (500nm²). Both can reach a maximum load of 3000µN. For this study, the wedge shaped diamond tip was used since its geometry is more adapted for thin foils compression by avoiding slipping between the tip and the sample.

Conventional, high resolution and *in situ* TEM analyses were conducted within a JEOL 2010F transmission electron microscope operating at 200 kV. Images were captured with a GATAN CCD Orius camera and analysed by Digital Micrograph. Movies were captured with Camstudio free software (24 frames per seconds without any compression). The images and CBED patterns related to *in situ* nanoindentation tests were directly extracted

from the movies. In CBED mode, the beam was focused on the thin foil in an area of about 2 nm in diameter and the convergence angle (angular opening) was about 10mrad. Due to a broadening effect through the sample thickness, the illuminated area increased up to 10 nm at the bottom of the thin foil. Such a value has been calculated from Doig's formula (Esnouf, 2011). The sample was first oriented in a low index zone axis and then slightly tilted to obtain the sharpest Bragg lines. Using this new zone axis, a selected-area electron diffraction pattern (SAED) was first acquired and indexed. Then the beam was focused and the convergence angle gradually increased to get a whole CBED pattern with Bragg lines easily indexed from the SAED pattern. The acquisition and indexation procedure is described elsewhere (Calvié, 2012).

SAED patterns were also acquired on a JEOL 200CX transmission electron microscope, operating at 200 kV. The objective aperture diameter was 50 µm so that a large number of grains could be simultaneously analysed, and the camera length was set to 137 cm.

Several thin foil preparations were used and compared to obtain the most appropriate sample for TEM observations and nanoindentation inside the TEM. The techniques are tripod polishing followed by ion milling, ultramicrotomy and FIB.

Tripod was used to prepare a thin foil by gentle mechanical polishing. When the 3Y-TZP sample was reduced to the required dimensions (1mm height, 2 mm long and 100µm thickness) with a Buehler diamond saw (0.3mm thickness), it was mounted on a home-made tripod to plane polish the first side of the sample with Buehler plastic disks embedded with diamond grains with sizes 30, 15, 9, 6, 3, 1, 0.5 and finally 0.1 µm. The second side was slightly angled (0.7°) thanks to micrometer screws and was then polished as previously. Finally, electron transparency was achieved with an ion miller PIPS (Gatan – beam characteristics: 4.5 kV and an angle of 6° above and below the sample).

Ultramicrotomy is usually used for soft materials such as polymers but has also been carried out on the 3Y-TZP sample by Diatome Company. The sample size was reduced to 1 mm high, 2 mm long by sawing with a diamond blade and polished to a thickness of 60µm. It was then fixed to an AFM holder and the pyramid was carved with an abrasive stone. Sections were cut with a 45° diamond knife at a speed ranging between 1mm/sec and 100 mm / sec. The sections were 20-70nm thick and were deposited on a copper grid covered by a thin holey carbon film.

Two Focused Ion Beam (FIB)-TEM sample preparations were envisaged and performed: "lift out" and "H-bar" techniques (Li, 2006). The thin foil of 12Ce-TZP was prepared by the "lift out" method using a ZEISS Nvision 40 Focused ion Beam microscope. First a foil of the 12Ce-TZP was prepared by using the "lift-out" technique (Giannuzzi, 1999). For that purpose, milling was performed at 55° with an accelerating voltage of 30kV; weak currents (3 nA) were used in order to avoid phase transformation of zirconia by ion milling. The 400 nm-thick foil was then glued on a gold wire previously prepared by FIB to have a well-suited shape (Figure 1a). Then a final thinning of the zirconia foil was performed with the ion beam to obtain a final thickness of 120 nm (calculated by JEMS simulations (Stadelman, 1987) of CBED patterns obtained on the sample). Weaker currents and voltages (150-80-40 pA at 30kV then 50pA at 2kV) were used to have a precise thinning without any phase transformation. The thin foil of 3Y-TZP was prepared by "H-Bar" method by SERMA Technologies Company. The sample was cut with a wire saw, polished to a thickness of 30µm and then pasted in both sides on a copper half grid. Finally, an electron transparent window was thinned using a FEI STRATA Dual Beam FIB (Figure 1b). An electron energy-loss spectroscopy (EELS) spectrum was acquired on the plasmon low loss regions. By using a mean free path of electrons (λ_p) equal to 150 nm in zirconia (determined by using the formula

proposed by Egerton (Egerton, 1986)) and a ratio t/λ_p measured close to 1, the thickness of the thin foil could be estimated to 150 nm.

Finally, Electron Backscattered Diffraction (EBSD) was performed directly on the 12Ce-TZP thin foil with a Scanning Electron Microscope Supra55VP from Zeiss, equipped with an EBSD Nordlys S camera (Oxford Instruments/HKL). Orientation maps were obtained with an accelerating voltage between 12 and 15 kV, a step between 30 and 50 nm and a partial pressure of nitrogen equal to 15 Pa. The patterns were acquired with the acquisition software Aztec and orientation maps calculated with the software Tango (channel 5).

3- Results and discussion

3-1. Optimization of the thin foil preparation for *in situ* nanoindentation tests

a) Tripod polishing

Figure 2a displays a 3Y-TZP sample prepared by tripod polishing and broad ion beam milling. The thin foil border is obviously amorphized. It is difficult to distinguish the grains which size should be about 0.3µm and the contrast can hardly be interpreted. In addition, the sample is cracked and therefore very fragile. This is expected to lead to significant problems during indentation experiment. Indeed, Figure 2b and Figure 2c show that the sample is not really compressed but complies under the indenter and when the experiment is completed, the sample does not recover its initial shape. We can deduce that this preparation method induces a significant modification of the sample and therefore is not suited to the study of zirconia. Indeed curling of the thin foil avoids achieving a proper compression of the sample, and in the event that phase transformation occurs, it is not possible to measure the stress at which transformation is initiated. To summarize, although this preparation method is time consuming, it has the advantage of being suitable for hard materials. Unfortunately, in the case of our study it causes excessive modifications of the zirconia microstructure, which is

particularly sensitive to mechanical stress. However, for the study of ductile materials like metals (to see dislocations under strain for example), tripod polishing might be better suited.

b) Ultramicrotomy

Ultramicrotomy is extensively used for the preparation of thin sections of soft materials. However, sections of hard materials have successfully been prepared by ultramicrotomy like, for instance, chondrites meteoritic materials (Bradley, 1986). In the case of 3Y-TZP, ultramicrotomy reveals to be complicated because most of the cuts naturally tend to crumple or to curl, as observed in Figure 3a by Optical Microscopy, even without any mechanical solicitation. TEM observations of the crumpled sections reveal a lot of cracks (Figure 3b). Figure 3c clearly exhibits small crystals of a few nanometers which are in diffraction conditions (they appear in bright in the dark field TEM image). Their mean diameter is far smaller than the initial average grain size, which is 0.3µm in this sample. It is concluded that the grains may have been broken during cutting.

Figure 4a and 4b display a HRTEM image and the Fourier Transform (FFT) of a selected region of the zirconia ultramicrotomic section. The good quality of the image can be attributed to the fact that the amorphization of the sample is minimized, which is known to be one of the main advantages of ultramicrotomy. However, the zirconia crystallographic structure has been greatly altered. Indeed, indexation of the FFT of the HRTEM image (fig 4c) shows the monoclinic form of the zirconia (JCPDS sheet number 00-037-1484). Thus the 3Y-TZP tetragonal phase has been transformed into the monoclinic phase. This transformation most probably occurred because of the severe mechanical stress imposed by the sample preparation. Initial pyramid prepared by sawing and polishing previously to ultramicrotomy has been investigated by XRD experiments and it turns out that it was still in the tetragonal phase (JCPDS sheet number 00-050-1089) (Figure 5). So the cutting step with

the diamond knife has caused phase transformation in zirconia by imposing high shear stresses. It is noteworthy that this phase transformation also accounts for the reduced grain size and can explain the thin sections rollup during cutting.

Figure 3d displays a diffraction pattern acquired on a section. It provides an evidence of the reduced grain size. Indeed it can be considered as a Debye-Scherrer pattern whereas a diffraction pattern with localized spots was expected from the grain initial size. A quantification of the monoclinic/tetragonal ratio has been determined from the intensities between rings at 1.80 Å and 3.70 Å after correction by the Lorentz factor. This ratio has been found to be equal to 88 vol.% of monoclinic grains, when assuming that the monoclinic and the tetragonal grains have the same average diameter and that the polaroid has a linear response. In practice, the polaroid film does not have a linear response but exhibit a saturation for high intensities. This implies that the fraction of monoclinic grains may have been overestimated. To our opinion, a realistic order of magnitude would be close to 75 vol% of monoclinic grains in the ultramicrotomic section.

To study zirconia by *in situ* nanoindentation, it can be concluded that preparation by ultramicrotomy is not suitable. However it is one of the best techniques to prepare soft materials such as polymers and could be successfully used on harder materials which are not sensitive to the high mechanical stress induced by the diamond knife. A suitable geometry for performing nanoindentation experiments could be to deposit an ultramicrotomic section onto the border of a half microscopy grid. Then, nanoindentation experiments can be carried out by compressing the section between two grid rods. This geometry is potentially well adapted because the cut is held on its sides by the grid rods (by Van der Waals forces) avoiding any cut slipping or curling under the nanoindentation tip.

c) Focused Ion Beam

Focused Ion Beam microscopy is nowadays widely used for TEM sample preparation. It seems particularly well suited for brittle materials because they suffer no mechanical stress. Two kinds of preparation by FIB were investigated: the “lift-out” and the “H-bar” method (Figure 1). Figure 6 shows two regions of the 12Ce-TZP thin foil prepared with the “lift-out” method, which is not cracked nor damaged: one highly stressed region, just below the indentor tip (Figure 6a) and another area, away from the tip (Figure 6b). Figure 6a is a bright field image but contrast has been optimized in order to clearly distinguish the grains. Grains which average size is 1μm are not broken, unlike what was observed by ultramicrotomy. Nevertheless, two major drawbacks can be expected with this sample preparation: (i) Ga ions contamination of the sample, (ii) induced amorphization or phase transformation. EDX analysis was performed on the thin foil and confirms that gallium traces have been implanted into the material during preparation (Fig 6b). Nevertheless it does not affect the sample composition since all the grains, including those in the implanted zone, exhibit similar ratios between Zirconium (85 at.%) and Cerium (15 at.%). Moreover, no amorphization could be observed. Concerning implantation, for instance, the depth was estimated to be equal to 50 nm in the case of copper material with a perpendicular Ga^+ bombardment at 30 keV (Kiener, 2007). A recent study on yttrium-stabilized zirconia showed through Monte Carlo simulations that Ga ions penetration was 54 Å at 30 kV when the FIB probe was at 1° from the sample surface (Saowadee, 2012). In our case, the bombardment angle is equal to 55°, and the Ga penetration depth is probably equal to a few tens of nanometers, that is to say between those values taken from the literature. In the following, all the grains studied always lie outside this “critical” layer, where Ga implantation could have modified zirconia.

As for ultramicrotomy, SAED diffraction patterns (not shown) have been acquired on the thin foil to estimate the ratio between monoclinic and tetragonal phases. In this case,

where no grain breakage has been observed, the diffraction pattern is composed of spots and not rings. Due to the presence of spots and the overlap of both monoclinic and tetragonal contributions, such quantification is not reliable. The manual indexation of diffraction patterns on different grains confirms that most of the grains remain under the tetragonal phase. Rare grains were found to be in the monoclinic form. Quantitative results van be deduced from EBSD performed directly on the thin foil. Indeed, Figure 7 displays a map associated with Euler angles and band contrasts (in half transparency). The large field of view (8.5 x 5.5 µm) permits to analyze a lot of grains. On the orientation map, the white points correspond to those with no indexation. They correspond to only 4% of the orientation map pixels. A detailed observation of the orientation map compared with the backscattered electron image indicates that all the not indexed points are located at the grain boundaries or in holes. All the indexed picels have been assied to the tetragonal phase, without any texture. Thus, no monoclinic phase has been detected, even at higher spatial resolution (lower accelerating voltage and smaller steps). From a statistical point of view, no monoclinic phase over 76 analyzed grains corresponds to a fraction of monoclinic phase in the whole sample lower than 5% (bilateral interval with a level of confidence of 95%). This result indicates that the microstructure has not been strongly modified by FIB ion machining since most of the material remains in tetragonal form (Figure 8), despite the fact that the 12Ce-TZP is highly transformable (Rauchs, 2001).

Nanoindentation experiment was performed on this thin foil. Figure 9 presents the evolution of a same region during solicitation. During loading, bend contours appear and move perpendicularly to the load direction (fig. 9b). During unloading, bend contours have a reverse movement (fig. 9c) until a complete recovery of the sample initial structure (fig. 9d). Undoubtedly, such observation indicates a thin foil bending during nanoindentation test, rendering the experiment quite difficult.

The “H-bar” preparation technique was performed on the 3Y-TZP. An overview of the sample in Figure 10a presents the structure of the sample. The advantage of this preparation technique is the presence of only one small part of the thin foil which is thin enough to be electron transparent. Thus it can be expected that the sample will be less inclined to bend during solicitation. Direct observation of grains and selected–area electron diffraction reveal the presence of both monoclinic and tetragonal phases (Figure 10b to d). The proportion of monoclinic phase has not been quantified but it seems that this sample presents a higher fraction of monoclinic phase than the 12Ce-TZP sample. This result is quite surprising since 3Y-TZP zirconia is less easily transformable than 12Ce-TZP but it can be explained by the sample preparation. 3Y-TZP was polished before ion beam milling. This preliminary polishing may have induced a phase transformation or stresses that have induced a more important phase transformation during ion milling. In the case of 12Ce-TZP the thin foil was cut directly from the bulk zirconia without polishing.

During solicitation of this thin foil, phase transformation from tetragonal to monoclinic phase was observed. The direct observation of this phase transformation is not obvious because it is a first order displacive transformation occurring very quickly (Kelly, 2002). Figure 11 presents bright field images of the sample during solicitation (contrast has been optimized after acquisition in order to clearly distinguish the grains). The contrast of the grain in the center of the image significantly changes during solicitation and sudden changes occur as fast as the expected tetragonal / monoclinic phase transformation (Kelly, 2002). Indeed, features such as parallel lines appear in this grain. (Figure 11d). The phase transformation occurs at around 300 nm from the top surface of the thin foil. It is quite surprising since it may be expected that the maximal stress is applied at the surface of the thin foil just below the tip. However, on amorphous glassy polymers, the localisation of the zone

undergoing the maximum hydrostatic stress has been shown to be either ahead of the crack tip if deformation occurs with plasticity or at the crack tip in the case of elastic deformation (Hill, 1998)-(Estevez, 2000). The comparison between zirconia and amorphous glassy polymers is not obvious and it can be noticed that in our case, the localisation of the transformed zone may also be explained by stresses present in the thin foil and induced by the sample preparation; or by surface relaxations due to the low thickness of the sample. Simulations by finite elements of the behaviour of the thin foil during solicitation may give important clues to better understand the behaviour of the foil during the experiments and the repartition of stresses. Furthermore, during solicitation, a small bending of the thin foil is observed, although less pronounced that in the case of the thin foil prepared by the "lift-out" technique. This bending also leads to non homogeneous triaxial stresses inside the thin foil, which may partially account for the localisation of the transformed zone.

At this stage, it can be recalled that two points are very important concerning the preparation of thin foils for the observation of phase transformation in zirconia: (i) no phase transformation of zirconia during sample preparation, (ii) a sample with a low propensity to bend during solicitation. Bending needs to be minimized since it complicates the solicitation process and thus the experiment interpretation. An ideal solicitation would be pure compression in order to easily correlate observations to solicitation process. Using both FIB-based preparations techniques, phase transformation could be observed. In terms of geometry, the "H-bar" sample is better suited for nanoindentation experiments because it presents a lower propensity to bending. This is due to the fact that only one part of the sample is very thin. This gives a higher stiffness to the whole sample.

3.3- Stress nanolocalization by Convergent Beam Electron Diffraction

The complete study of the phase transformation in zirconia requires the measurement of the local stresses inside the sample to better understand the mechanisms which trigger the transformation. Several analytical techniques available in TEM theoretically permit the measurement of local stresses. For example, Joly-Pottuz et al. studied by Electron Energy Loss Spectroscopy the difference observed on the volume plasmon energy on a DLC coating after friction experiments (Joly-Pottuz, 2007). According to Oleshko's theory (Oleshko, 2002), a shift of the volume plasmon peak could be attributed to a change of hardness inside the coating, which could be related to residual stresses. Correlation between volume plasmon and hardness is not obvious but is most easily applicable in the case to amorphous materials like DLC coatings. For an application to zirconia polycrystalline materials, the correlation between the plasmon energy the hardness and the residual stresses becomes more complicated than in the case of DLC coatings. NanoBeam Electron Diffraction (NBED) may also be a well suited technique to measure local stresses. This method has been successfully applied on semiconducting structures (Béché, 2009). As far as zirconia is concerned, the use of NBED might be difficult, mainly because the strain is measured by comparing the NBED patterns of the area of interest and of an unstressed area (either in the same sample or in a reference sample). The existence of such an unstressed area in a sintered material under the form of a thin film might indeed be discussed. In the context of nanoindentation experiment, HRTEM technique is not available due to non adapted specimen holder in regard of vibration effects. Finally, Large Angle Convergent Beam Electron diffraction (LACBED) and Convergent Beam Electron Diffraction (CBED) are also a interesting tools to measure local stresses and could be performed on both FIB samples. To our knowledge, CBED experiments have never been performed during solicitation and two major issues can be pointed out: (i) the analysis must be performed on the same grain during the experiment but grains tend to move under the beam because of the solicitation, (ii) the foil bends during solicitation, which induces at the

same time a shift of the grain and a focus change (in addition to the fact that the stress is not uniaxial, as expected for a compression experiment). As a consequence it can be difficult to have clear information on the diffraction patterns obtained during solicitation. Nevertheless a simple comparison of the diffraction patterns before and after solicitation can give some valuable pieces of information.

Figure 12a presents a CBED pattern observed before solicitation of the 3Y-TZP sample (grain shown in Figure 10). In agreement to the indexation of the SAED pattern, the CBED pattern displayed in Figure 12a indicates the presence of both phases: the monoclinic phase (m) observed with a $[\overline{585},286,\overline{225}]$ zone axis, a tetragonal phase (t_1) observed with a [2779,60,63] zone axis and another tetragonal phase (t_2) observed with a $[\overline{2599},904,278]$ zone axis. Precise zone axes were obtained from cell parameter data given by Igawa (Igawa, 1993) available for pure zirconia and from a simulation work of CBED patterns using Electron Diffraction software (Morniroli, 1998). A simulation of yttrium-doped zirconia with 3% of yttrium has been performed. Unit cell parameters were determined by Rietveld refinement of a diffractogram obtained on 3% yttrium doped zirconia. The CBED pattern obtained from this simulation is closely the same than in the case of pure zirconia. Moreover, the intensities of the Bragg lines were calculated by using JEMS software. Calculations reveal that intensities on the experimental diffraction pattern do not correspond to the theoretical ones. In particular, the $(4\,3\,\overline{7})$ line of the monoclinic phase can be seen in the simulation but is absent in the experimental pattern. As it is a high order line, it is very sensitive to plane rotations. A small rotation perpendicular to the electron beam, possibly due to stress, can induce a large shift of this line, which experimentally would lie outside the fied of view. Another example concerns the $(0\,\overline{1}\,\overline{1})$ line in the tetragonal structure (Figure 12a). It is represented by a dotted line on the diffraction pattern because its intensity is very low, but from calculation this line should

be intense. This change in intensities might reflect the influence of the yttrium dopant on the zirconia structure or might be attributed to a modification of the cell because of an ongoing phase transformation. A comparison of the theoretical and experimental patterns clearly shows that the triangle shaped by three Bragg lines (dotted lines on Figure 12b) is distorted in comparison with the theoretical one. Here this reveals residual stresses inside the monoclinic cell. The local stress tensor is theoretically obtainable by a simulation approach based on the progressive evolution of the six parameters of the cell. Yet, such a complete determination requires the acquisition of several CBED patterns for different zone axes which is not possible during *in situ* experiments (Moraviec, 2007).

Sometimes, during solicitation, diffraction patterns exhibit a splitting of Bragg lines. For instance, Figure 13 shows a CBED pattern in $[30\bar{1}]$ zone axis of a tetragonal phase grain in the 12Ce-TZP sample. The maximum applied force is 100 µN, for a contact area of about 40*120 nm². Unfortunately from these experimental data, it is difficult to extract an order of magnitude of the applied stress because the thin foil bends during solicitation. Splitting can be induced by cell distortion under stress or as the result of a diffraction contrast in dynamic interaction conditions (Hirsch, 1969). A splitting was also observed on the 3Y-TZP before solicitation (splitting of the $(14\bar{3})$ line of the second tetragonal phase- not shown here). This splitting may be explained by the presence of nano-twinned zones premonitory at the zirconia structural transformation. A more specific study of the origin of this splitting is presented elsewhere (Calvié, 2012). Nevertheless, from these results, it can be stated that stresses are responsible for the splitting because they introduce a curvature or local modifications of lattice planes. From the splitting width, the angular spacing between the nano-twinned zones is very small and can be estimated to be equal to 4.10^{-2} degrees. It is difficult to determine a value of stresses from this result. Assuming that the cell remains monoclinic, with the β angle

unchanged, an acceptable fit of the $(\bar{2}\,\bar{4}\,0)$ and $(2\,1\,\bar{4})$ Bragg lines positions can be obtained with a = 5.752 Å, b = 4.782 Å and c = 5.876 Å. This would indicate a deformation of the unit cell of about +10% along the a and c axes, and -10% along the b axis.

Conclusions

Sample preparation is one key point to perform interpretable *in situ* nanoindentation experiments. An ideal sample should indeed be electron transparent, with the thin region accessible to the indentor tip. In the specific case of phase transformation studies, no phase transformation must obviously occur during sample preparation. Moreover, for a quantitative interpretation of the *in situ* experiment, with the determination of local stresses (in order to determine the stress necessary to trigger transformation), bending of the sample has to be avoided. Several preparation techniques have been investigated: tripod/ion milling, ultramicrotomy and FIB on zirconia. The first technique provides thin foils containing cracks, which are not suited for nanoindentation because they are too brittle. Ultramicrotomy permits to have clean (that is without any amorphization) and thin sections, even on zirconia, but the high mechanical shear induced by the diamond knife causes phase transformation. Finally, two different geometries ("lift-out" and "H-bar") obtained by FIB have been investigated. Both geometries are well suited for nanoindentation tests. As mentioned by Li *et al.* (Li, 2006), the major advantage of the "lift-out" technique lies in the fact that the TEM specimens are directly extracted from the bulk without any cutting or polishing step. On the other side, the "H-bar" geometry can be designed so that the electron transparent zone is held tight on its sides, which limits its bending during the nanoindentation experiment. The most suitable size of the electron transparent zone has to be defined to be wide enough to be correctly stressed by the tip - from a mechanical point of view, it is generally stated that the penetration depth

has to be less than 10% of the sample dimension - but narrow enough to limit the bending. Furthermore it can be envisaged to couple the advantages of both FIB preparation techniques by performing a “H-bar” geometry on a thin section extracted by the “lift-out” technique. This method can be envisaged for the perparation of ceramics and metals sample.

Direct observation of phase transformation of zirconia is not obvious, even on well-defined samples geometries (such as those fabricated by FIB). Indeed, it is a fast transformation and its occurrence depends on the residual stresses, which have been created during the fabrication step (compaction, sintering) and the thin foil preparation and which most probably varies from one grain to the other. Thus, a localization of the stresses before and during the nanoindentation experiment will be required to fully understand phase transformation. The feasibility of such measurement by CBED has been investigated. First results indicate that CBED experiments can give valuable pieces of information. Indeed, the contributions of both tetragonal and monoclinic structures have been identified. In addition, a line splitting could be observed during solicitation, which may be attributed to curvature or local modifications of lattice planes due to local stresses.

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Figures captions

Figure 1: schematic representation of zirconia thin foils prepared by FIB: a) by “lift-out” method, b) in the “H-Bar” geometry.

Figure 2 : Sequence of images taken from the in situ TEM nanoindentation of 3Y-TZP thin foil : a) before indentation, b) during loading, c) after indentation.

Figure 3: Thin foil of 3Y-TZP prepared by ultramicrotomy : a) optical observation, b) bright field TEM observation, c) dark field TEM observation.

Figure 4: Thin foil of 3Y-TZP prepared by ultramicrotomy : a) HR observation, b) FFT of the boxed area, c) FFT indexing : monoclinic phase.

Figure 5: XRD diffractogram of 3Y-TZP sample after saw cutting and polishing. Positions of peaks of zirconia are represented by dotted line (tetragonal phase) and by solid line (monoclinic phase). The structure is clearly under the tetragonal phase.

Figure 6: TEM observations of 12Ce-TZP thin foil (120 nm thick) prepared by FIB “lift out” method : a) stressed area of the thin foil (just below the indentation tip), b) another area of the thin foil (away from the indentation tip).

Figure 7: Orientation map associated with Euler angles and ban contrasts (in half transparency) for the 12Ce-TZP thin foil prepared by FIB “lift out”. Field of view: 8.5x5.5µm. Step 50 nm. The white points are not indexed.

Figure 8: Diffraction pattern of two 12Ce-TZP grains which confirm the tetragonal structure (zone axis $[\bar{1}31]$).

Figure 9: Sequence of images taken from the in situ TEM nanoindentation of 12Ce-TZP : a) before indentation, b) during loading, c) during unloading, d) after indentation.

Figure 10: TEM observations of 3Y-TZP (150 nm thick) thin foil prepared by FIB “H-Bar” method before indentation : a) overview, b) magnification on the grain in the white circle on the figure a located at 0.7µm from the edge of the foil. Different phases are present in the same grain (shown in white dotted line): a monoclinic phase (shown in green dotted line) and two kinds of tetragonal phase (shown in blue and red dotted lines).

Figure 11: Sequence of images taken from the *in situ* TEM nanoindentation of 3Y-TZP thin foil.

Figure 12: CBED diffraction patterns on the 150 nm-thick 3Y-TZP H-bar sample prepared by FIB, before solicitation: a) Bragg lines indexing. Monoclinic structure in red, a first tetragonal structure in blue and a second tetragonal structure in green, b) simulated drawing diffraction pattern of the monoclinic structure observed with a $[\overline{585}, 286, \overline{225}]$ zone axis, obtained by using Electron Diffraction software (Morniroli, 1988) and JEMS (Stadelman, 1987) for intensity calculations. The triangle of experimental Bragg lines is represented in dotted lines.

Figure 13: CBED diffraction patterns on the 120 nm-thick 12Ce-TZP sample : a) before solicitation, b) during solicitation. A splitting of Bragg lines is observed.