In situ testing of ceramic materials inside transmission electron microscope

1. Scientific context

Nanotechnology has invaded our everyday life, not only in cosmetics, food or medicine, but also within materials. For instance, crystalline ceramic materials are elaborated using a "bottom-up" process, from individual nanoparticles, i.e. particles with diameters below 100 nm. The major advantage of nanoscale materials lies in their large surface areas, which can greatly affect their macroscopic properties. This is also true in bulk nanostructured materials, which contain a large fraction of interfaces. However, the crucial influence of interfaces - such as surfaces, grain boundaries or twins – on the deformation is still a pending issue[1,2]. Plasticity is especially badly understood in the case of ceramics. Indeed, ceramics are known to be "hard and brittle", although large plastic behaviours have been observed either at high temperatures[3] or at the nanoscale[4]. Interestingly, a recent study showed that ceramic nanolattices can exhibit ductile-like deformation and recoverability, with an appropriate choice of the structure dimensions[5].

Scanning Electron Microscopy (SEM) as well as Transmission Electron Microscopy (TEM) have become major characterisation techniques in the development and optimisation of materials and several developments have increased the technique capabilities. *In situ* mechanical testing inside microscopes has been further developed since the 1990s thanks to the development of miniaturised sensors and actuators. Solicitation in TEM or SEM is probably the most powerful way to investigate the mechanical behaviour at the nanoscale, as it can provide simultaneously quantitative mechanical data (force-displacement curves) and images

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[1] Meyers, M.A., Mishra, A., Benson, D.J., "Mechanical properties of nanocrystalline materials", *Progress in Materials Science* **2006**, 51, 427-556.
[2] Mishin, Y., Asta, M., Li, J., "Atomistic modelling of interfaces and their impact on microstructure and properties", *Acta Materialia* **2010**, 58, 1117-1151.
[3] Maehara, Y., Langdon, T.G., "Superplasticity in ceramics", *Journal of Materials Science* **1990**, 25, 2275-2286.
[4] Han, X.D., Zhang, Y.F., Zheng, K., Zhang, X.N., Zhang, Z., Hao, Y.J., Guo, X.Y., Yuan, J., Wang, Z.L., "Low-temperature *in situ* large strain plasticity of ceramic SiC nanowires and its atomic-scale mechanism", *Nanoletters* **2007**, 7, 452-457.
[5] Meza, L.R., Das, S., Greer, J.R., "Strong, lightweight, and recoverable three-dimensional ceramic nanolattices", *Science* **2014**, 345, 1322-1326.

of the sample during deformation[6]. Such experiments permit not only to go beyond the numerous works on plasticity mechanisms in bulk materials, with characterisations before/after conventional mechanical tests, but also to analyse the mechanical behaviour of individual nano-objects.

In situ mechanical tests in TEM on ceramics have been developed at INSA since 2009 mainly in the framework of two PhD theses: E. Calvié's PhD focused on individual alumina nanoparticles[7], whereas I. Issa's PhD focused on MgO nanocubes[8]. Experiments on alumina showed that nanoparticles of crystalline alumina could undergo large plastic deformation[9] (see Figure 2a). The parameters of a constitutive law for alumina at the nanoscale could be identified by Digital Image Correlation and Finite Elements Simulations[10]. Studies performed within I. Issa's PhD have focused on the deformation mechanisms in MgO, by comparing experimental data with Molecular Dynamics (MD) simulation results[11]. Large plastic deformation was also observed (see figure 2b). These studies clearly showed that plastic deformation can occur for materials known to be fragile. This plasticity at nanometer scale can have several impacts on the processing or the use of these materials. To go further, it is now necessary to perform these experiments under environment since environment might have an influence on the mechanical behavior of ceramic materials. PhD work of Rongrong Zhang, former CSC PhD student, show the interest of developing TEM in situ mechanical testing to compare the behavior of CeOx nanocubes depending on their composition

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[6] Minor, A.M., Moris Jr, J.W., Stach, E.A., "Quantitative *in situ* nanoindentation in an electron microscope", *Applied Physics Letters* **2001**, *79*, 1625-1627.

[7] Calvié E. Contribution de la nanoindentation *in situ* en Microscopie Electronique en Transmission à l'étude des céramiques, PhD thesis, 2012, **prize of the best PhD thesis of the GFC** (French group of laboratories developing ceramic materials) in 2013

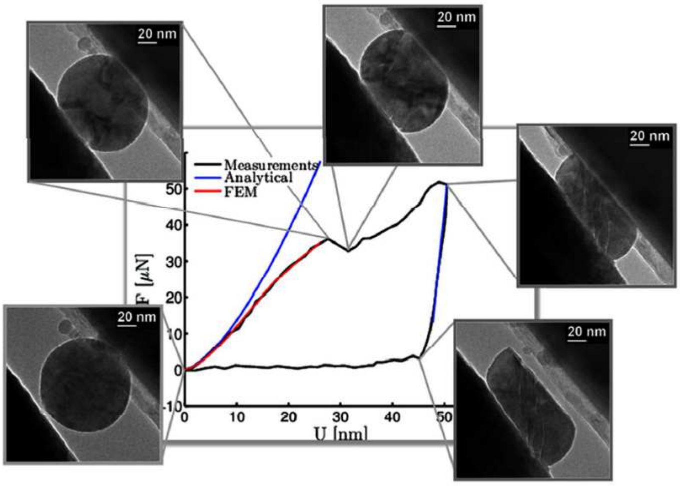
[8] Issa I. In situ TEM Nanocompression & Mechanical Analysis of Ceramic Nanoparticles, PhD thesis, 2016, **2[nd] price of the Speaker Contest of CIEC14**

[99] Calvié E., Joly-Pottuz L., Esnouf C., Clément P., Garnier V., Chevalier J., Jorand Y., Malchère A., Epicier T., Masenelli-Varlot K., "Real-time TEM observation of room temperature plasticity in nano-crystalline alumina ceramic particles", *Journal of the European Ceramic Society* **2012**, *32*, 2067-2071.

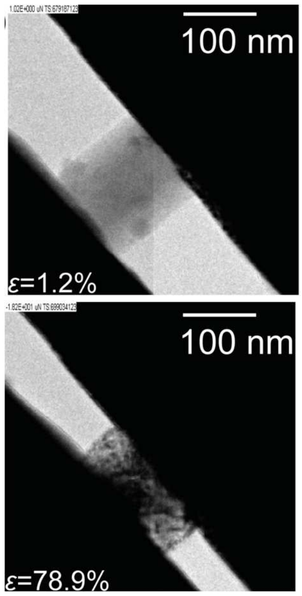
[10] Calvié E., Réthoré J., Joly-Pottuz L., Meille S., Chevalier J., Garnier V., Jorand Y., Esnouf C., Epicier T., Masenelli-Varlot K., "Mechanical behaviour law of ceramic nanoparticles from Transmission Electron Microscopy *in situ* nano-compression tests", *Materials Letters*, **2014**, *119*, 107-110.

[11] I. Issa, J. Amodéo, J. Réthoré, L. Joly-Pottuz, C. Esnouf, J. Morthomas, M. Perez, J. Chevalier, K. Masenelli-Varlot, "*In situ* investigation of MgO nanocube deformation at room temperature", *Acta Materialia*, 2015, 86, 295-304.

(1.5<x<2)[12], thus showing the importance of nanoparticles environment since the presence of oxygen hinders the reduction of CeO2 nanocubes.



a)



b)

Figure 2: a) in situ mechanical test in a TEM on a single alumina nanoparticle. The experimental curve was fitted with an elasto-plastic law (E = 115 GPa; σ_y = 10 GPa). b) MgO nanocube compressed in situ in TEM after a deformation of ε = 1.2% and ε = 78.9% respectively

2. Aim of the PhD thesis

Environmental analyses, *i.e.* in a controlled atmosphere (not under vacuum), are possible by using a dedicated environmental TEM. The environmental transmission electron microscope (ETEM) allows a partial pressure of gases around the sample holder. The team has recently bought a sample holder to perform *in situ* mechanical tests under environment and has started collaboration with the world leading manufacturer, Hysitron. Such in situ tests has been presented in a world premiere in the 16th European Microscopy Congress.

Analyzing the mechanical behavior at the nanoscale and under a gaseous environment will be the core of this PhD thesis. The experiments will be carried out on several types of

[12] L. Joly-Pottuz, R. Zhang , T. Albaret, T. Epicier, I. Jenei, M. Cobian, D. Stauffer, K. Masenelli-Varlot, CeOx elastic properties: an in situ ETEM nanocompression study, JOM, 2024, 76: 2326-2335

ceramics, among which ceria. Ceria is a crucial component of automotive catalysts and is developed for Solid Oxide Fuel Cell applications. Aside these applications, ceria is an interesting material to develop in situ experiments in the presence of environment. Indeed, ceria is reduced under the electron beam when observed under vacuum, and this reduction can be avoided by introducing oxygen inside the microscope. Thus during the PhD, it will be possible to continue the works done by R. Zhang on Ceria (effect of the electron beam (under vacuum) and the environment (under oxygen)) and develop these observations to other ceramic materials subject to reduction. Alumina nanoparticles will also be considered since they are sensitive to water Alumina nanoparticles have a spherical shape and a more complicated structure but are used to process alumina bulk materials used in various applications. Their sensitivity to water (during storage for instance) is important to be studied to enhance their processing method.

All the data processing tools developed during the previous PhD theses. For instance, Digital Image Correlation will be used to compute the stress-strain curves. The movies acquired during the experiments will be analyzed to identify the type of defects created under solicitation. To do so, different kinds of imaging have to be considered and optimized: high resolution imaging, dark field imaging in two waves mode. The deformation mechanism will be compared with the results of simulations carried out through collaboration with other scientists specialized in simulation works.

3- Description of the laboratory and the research team:

This PhD thesis will be held at MATEIS Laboratory. MATEIS is a laboratory of Materials Science at the intersection between chemistry, physics and mechanics. Its studies are focused on the three classes of materials (metals, ceramics, polymers) and composites by considering the characteristics in volume, surface and interfaces.

The main objective of the researches conducted at MATEIS is to find a relationship between process / microstructure / properties of materials, with an experimental approach and / or modeling. Thus researches are developed in the framework of advanced development processes, microstructural characterization, often performed in situ and / or 3D modeling at different scales; and characterization of functional properties. Multifunctional materials for health, energy, transport or building are part of the materials developed.

The PhD thesis will be supervised by Lucile Joly-Pottuz, Associate Professor, and Karine Masenelli-Varlot, Professor. Lucile Joly-Pottuz develops *in situ* testing inside electron microscopes (scanning electron microscope (SEM) and Transmission Electron Microscope (TEM)) since 2008 to characterize ceramics materials (microstructure and behaviour under solicitation). The main researches activities of Karine Masenelli Varlot concern the in situ testing in TEM, 3D characterization of materials by tomography and environmental SEM. The PhD student will be part of the Microscopy Group at MATEIS. This group is composed of 3 professors and 6 associate professors, 4 engineers, 6 PhD students and 3 postdoctorate students.