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Mechanical behavior law of ceramic nanoparticles from transmission electron microscopy *in situ* nano-compression tests

E. Calvié [a], J. Réthoré [b], L. Joly-Pottuz [a], S. Meille [a], J. Chevalier [a,*,1], V. Garnier [a], Y. Jorand [a], C. Esnouf [a], T. Epicier [a], J.B. Quirk [a,2], K. Masenelli-Varlot [a,1]

[a] INSA-Lyon, MATEIS UMR5510, 7 Avenue J. Capelle, 69621 Villeurbanne Cedex, France
[b] INSA-Lyon, LaMCoS UMR5259, 7 Avenue J. Capelle, 69621 Villeurbanne Cedex, France

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ABSTRACT

A methodology has been developed to determine constitutive laws of nanoparticles from *in situ* nano-compression experiments in a transmission electron microscope. It is based on image analysis to obtain relevant load–displacement curves, followed by finite element analysis associated to an inverse method. A transition alumina, stable only at the nanometer size, has been characterized as an example. The Young modulus and yield strength of this transition alumina, not available for such crystallographic structure, have been obtained.

1. Introduction

In materials science, a constitutive law describes the response of a material to an external solicitation. With the growing importance of nanotechnology in materials design and fabrication, access to constitutive laws at the nanoscale is a topical issue [1]. Several studies have dealt with the determination of the Young's modulus of nano-objects with high aspect ratios [2–5], eventually incorporating the yield or failure stress [6]. For example, plasticity could be observed in silicon, which is known to exhibit brittle behavior at the macroscopic scale [7]. In parallel, the development of *in situ* nano-indentation in TEM has been a major breakthrough, since it allows both local determination and the observation in real time of the nanoparticles' mechanical behavior [6–10]. However, no attempt was made to obtain their mechanical behavior constitutive law.

The plastic deformation of small commercial alumina nanoparticles has recently been reported [13]. Based on these observations, the objective of the present work was therefore to obtain constitutive laws from *in situ* nano-compression experiments in the transmission electron microscope (TEM) from image processing and load–displacement curves. The transition alumina nanoparticles are currently used for the fabrication of ceramic bulk materials. However, their mechanical properties remain unknown since the transition phases are not present in the sintered state and cannot be experimentally tested with conventional mechanical techniques.

2. Materials and methods

The commercial transition alumina powder (NanoTek®, Nanophase Technologies Corporation, Romeoville, IL, USA) is produced by Physical Vapor Synthesis (PVS). It was dispersed in acidified water at pH 4 using a 100 W ultrasound probe for 2 min, in order to test particles individually [14,15].

In situ nano-indentation tests were carried out using a dedicated straining sample holder from Nanofactory Instruments, fitted in a JEOL 2010F microscope operating at 200 kV accelerating voltage. The sample holder was equipped with a truncated diamond tip with a flattened area of about 500 nm^2 and a load cell (maximum load of 3 mN). Particles were positioned on a sapphire substrate of 0.75 μm thick, moving towards the tip during compression at a controlled displacement rate (0.5 nm/s). Images of the experiment were directly recorded using a Gatan Orius 200 camera and video sequences acquired by the freeware CamStudio (v2.0, http://www.rendersoftware.com/products/camstudio).

The real displacement applied to the nanoparticle was determined by using Digital Image Correlation (DIC) from the experimental micrographs. By comparing two successive images, the displacement of the grey level transition at the boundary of the support and at the boundary of the tip was estimated. DIC usually allows arbitrary displacement fields to be estimated with a sub-pixel resolution (about 1/100 pixel), but in the present work only

* Corresponding author.
E-mail address: Jerome.chevalier@insa-lyon.fr (J. Chevalier).
[1] Member, Institut Universitaire de France.
[2] Now at Imperial College, London.

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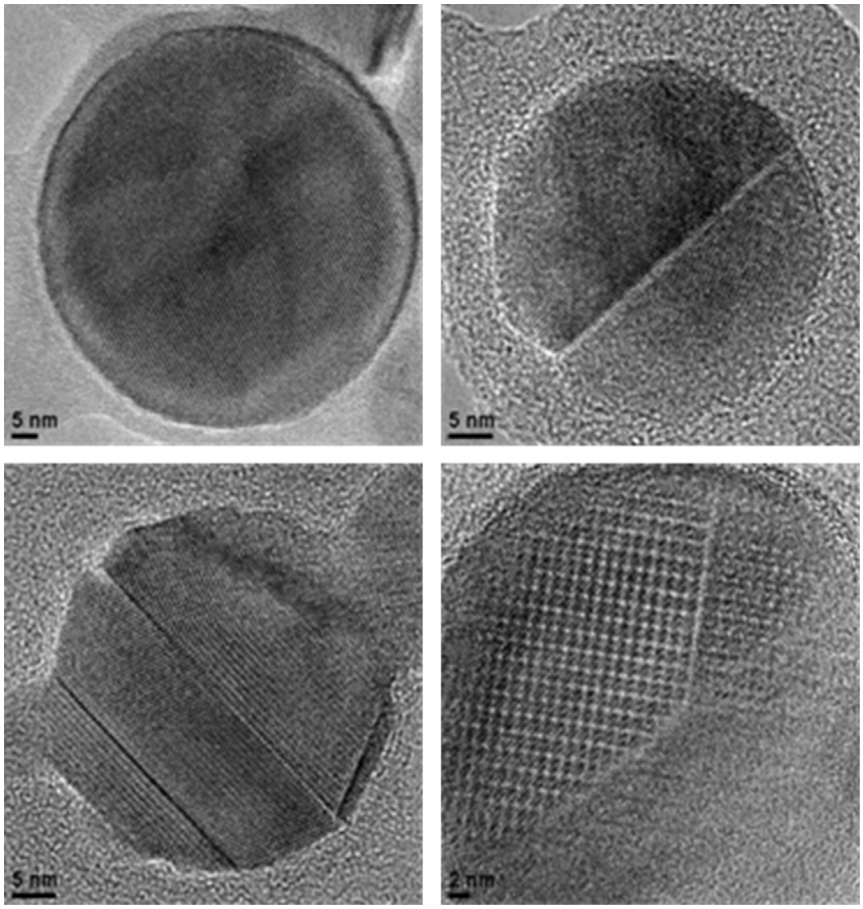

Fig. 1. High resolution TEM micrographs of several alumina nanoparticles, showing the crystallinity quality and the presence of twin boundaries (in very few particles).

a rigid translation was searched for the measurement of this displacement; the actual displacement applied to the particle was obtained. Initially measured in pixels, this was further converted into nanometers by using the TEM scale bar.

Finite element (FE) simulations were performed using ABAQUS® software. The initial particle was modelled as a sphere, its radius being estimated from the first image of the sequence. An axisymmetric model was built and the analysis accounted for geometrical non-linearities and contact with the tip and the support. Among the data available from the analysis, the reaction force for applying the displacement was extracted. Then, based on an inverse method, the parameters of the material constitutive model were adapted so that the reaction force matches the force measured during the experiment.

3. Results and discussion

Fig. 1 displays high resolution transmission electron micrographs of several nanoparticles. They are well crystallized, with eventually twin boundaries in very few of them. The indexation of the electron diffraction patterns revealed the presence of transition phases of Al_2O_3, namely δ (ICCD no. 16-0394) and γ (ICCD no. 29-1486), with proportions of about 30 and 70 wt%, respectively, in agreement with X-ray diffraction [11]. In order to preserve the integrity of the particles during exposure to the electron beam, no extensive electron diffraction work was performed before testing to identify their precise crystallographic nature, and characterize the twins possibly present. However, as twins are mostly observed in the biggest nanoparticles, and because we tested only perfect spheres, it is thought that the *in situ* nanoindentation experiments were carried out on nanoparticles without twins.

An experimental force–real displacement curve, recorded for a nanoparticle of 96 nm in diameter with compression of 50 nm, is displayed in Fig. 2 (see Video 1, as Supporting information). We confirm the existence of plasticity at the nanoscale, even on a material exhibiting fragile behavior at the macro-scale. The parameters of a constitutive law have been extracted from the force–displacement curve using two different methods, namely an analytical one – using either the theory of a Hertz contact in a sphere-plane geometry for the load curve or the elastic response of a cylinder for the unload curve – and the inverse method described above.

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In the case of DIC–FE analysis, the force–displacement curve was fitted up to the onset of strain localization. To obtain a satisfying fit between the computed and the measured forces, a Von Mises elastic–plastic model with linear isotropic hardening is used. The yield limit is thus a linear function (initial value σ_y, slope H) of the accumulated plastic strain. The constitutive model used herein thus involves four parameters: the Poisson ratio ν which has been fixed to 0.3, the Young′s modulus E, the initial yield stress σ_y and strain hardening coefficient H. The Poisson′s ratio was fixed to 0.3, since this is a conventional value generally observed on crystalline solids. This is also roughly the value for bulk alumina. Moreover, its value had a negligible influence on the other, the most important parameters. E, H and σ_y are adjusted until a satisfying agreement between the experimental and the computed response is obtained, as illustrated in Fig. 2 and summarized in