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Short communication

Real time TEM observation of alumina ceramic nano-particles during compression

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Abstract

The behavior of alumina nano-particles taken from a commercial powder is investigated during *in situ* compression experiments in a transmission electron microscope (TEM). Small particles of 40 nm in diameter can undergo severe plastic deformation without failure, whereas brittle fracture is observed for 120 nm sized nano-particles. This is evidence of a critical size under which alumina, at least in the form of nano-particles, cannot be considered as brittle materials even at room temperature and a direct observation of the grinding limit generally observed during ball milling.

Keywords: Nano-particles; Ceramics; Compression; Transmission electron microscopy; *In situ*

1. Introduction

Nanometer-size polycrystalline ceramics are currently attracting attention, due to specific mechanical properties, such as high hardness, crack propagation resistance, or optical properties such as transparency. Many research projects are currently in progress to optimize the properties of nanometer-size grain ceramics since they are expected to present great potentials.[1] It has been reported[2] for example that bulk ceramics composed of nano-grains could undergo ductile deformation under pressure at very low temperature (180 °C).

An important point to improve the processing of nano-ceramics is the better understanding of how single particles behave under pressure or applied external stresses even before sintering. Propensity to plastic deformation during compaction may for example open a new route to deformable ceramics, even at room temperature. Ball milling is often used to decrease particle sizes toward the nano-scale. Particles are submitted to very large mechanical solicitations and broken to reduce their sizes. However, there is a critical size, the grinding (or comminution) limit, below which the particles cannot be broken further.[3] It is therefore of great interest to follow and understand the behavior of ceramic nano-powders under load. *In situ* testing of ceramic nano-particles, coming from commercial source, and with sizes of less than hundred nanometers has never been conducted, despite its potential impact for the processing (*i.e.* compaction, ball milling) or the design (*i.e.* mechanical properties) of nano-structured bulk ceramics.

In situ mechanical testing inside a TEM is probably the best-suited strategy to investigate the mechanical behavior of materials at the nano-scale or more precisely the mechanical behavior of nanometric particles. Impressive nano-compression experiments were, for example, carried out recently on CdS hollow spheres, with diameters ranging from 200 to 400 nm,[4] or on silicon nano-particles of roughly 100 nm.[5] Failure was observed at a very high stress, after considerable deformation. Recent investigations showed that Si nanopillars could exhibit a brittle–ductile transition during compression tests: pillars having a diameter larger than 400 nm developed cracks as expected for brittle materials, whereas smaller pillars could present a ductility comparable to metals.[6]

However, these results cannot be extrapolated to alumina in the form of spherical nano-particles, since the hollow sphere or pillar geometry undoubtedly plays a major role on the mechanical properties of the particles and plasticity in alumina may occur for different sizes than that of CdS or Si.

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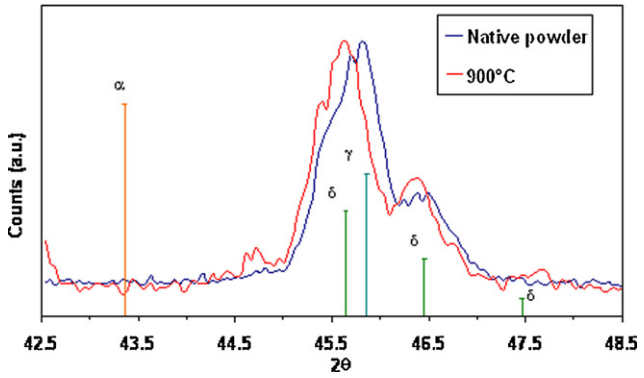

Fig. 1. XRD diffractograms of the native powder and powder treated at 900 °C.

This is therefore the aim of this paper to investigate the mechanical behavior of a commercial alumina during compression tests in a TEM, in order to investigate such a plasticity limit in a real powder and check its relevance in ceramic processing.

2. Experimental

In situ nano-compression tests were carried out using a dedicated 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 (flattened area of about 1 μm^2) and a load cell (maximum load of 3 mN). Particles were positioned on a substrate, moving toward the tip during compression tests at a controlled displacement rate (2.5 nm/s). This setup configuration does not allow HRTEM observations because too much vibrations are present, furthermore diffraction patterns are not able to be obtained because the beam focalization is too intense for the particle to resist, and the particle is ejected from the substrate. Images of the experiment were directly recorded using a Gatan Orius 200 camera installed on the microscope. The nature, thickness and alignment of the substrate must be optimized to obtain reliable measurements of the normal force applied during compression. Indeed, substrates that are too thin, as those commercially available, present two major drawbacks: a deformation of the substrate which can be observed during the nano-compression test and/or the nanoparticle can slip from the edge of the support. On the contrary, a substrate that is too thick often induces a shadowing effect on the region of interest, hindering a precise positioning of the particle–substrate contact area. The best configuration was found to be nano-particles deposited onto a 1 μm thick silicon wafer.

Specific alumina nano-particles with a spherical shape were chosen. This is simply because, plastic deformation of a sphere is easier to observe, quantify and model. A transition alumina powder produced by physical vapor synthesis (PVS) (NanoTek®, Nanophase Technologies Corporation, Romeoville IL, USA) was used in this study. XRD revealed that the powder consisted of a mixture of $\delta \approx 70$ wt.% and $\gamma \approx 30$ wt.% alumina phases (see Fig. 1). The as-received powder was dispersed in acidified water at pH = 4[7,8] using a 100 W ultrasound probe for 2 min. In order to start with particles of a given well known crystallography (δ phase), some batches of the alumina nanoparticles underwent a heat treatment at 5 °C/min up to 900 °C followed by natural cooling. XRD shows that the heat treatment affects the nano-particles crystallinity: they are almost exclusively in the δ phase, with only 1% and 4% of θ and γ phases, respectively. HRTEM images obtained from several nanoparticles deposited on copper grid (covered by a holey carbon film) have confirmed the crystallinity and the nature of delta alumina crystallographic phase whatever their size (40 nm or 120 nm). During these observations no phase transformation were observed even after long time of electron beam irradiation. A slight surface degradation can occur but it only concerns the first atomic layers and not the whole particle, and it leads to a characteristic faceting of the surface of the particles, easily observable on TEM images. Native and heat treated nanoparticles were deposited onto the silicon substrate and tested by *in situ* compression. For each kind of particle tested, experiments were performed on at least 10 isolated nano-particles to insure a good reproducibility of the behavior observed.

3. Results and discussion

A full compression experiment of two alumina nanoparticles of 40 nm diameter with a final applied force of 40 μN is presented in Fig. 2. Strong, irreversible, deformation of the particles is observed, which is typical of plastic deformation, and no crack is visible even at high strains. The particles have therefore plastically deformed without failure for such small sizes. Note that these observations shown on the two particles as in Fig. 2 were obtained for all small size particles of around 40 nm. Some tests were also performed on native powders (without any thermal treatment) that also exhibited the same behavior. Therefore, even if not statistically significant, it appears that transition alumina nano-particles of around 40 nm can plastically deform, whatever the crystallography may be. The loading–unloading curves were technically not able to obtain for small nanoparticles because such small particles always slide and deformed in the same time during compression test, therefore the real loading curve measured does not reflect what really happened. An improvement of the loading procedure of small particles is under progress to obtain reliable loading–unloading curves.

To investigate the effect of the nanoparticle size, experiments were performed on both types of nano-particles (before and after heat treatment) in the 120 nm diameter range. All tested nano-particles exhibited an elastic behavior up to the maximum load reachable with the nano-compression device or up to failure in a few cases. Fig. 3 shows the TEM pictures and the load–displacement curve recorded during the compression of a 125 nm diameter nano-particle. Failure occurred at an applied displacement of 30 nm with a corresponding load of 50 μN.

Finite elements simulations were performed to estimate the maximum tensile stress that the 120 nm particle could sustain for a load of 50 μN. A purely elastic model was used, with elastic constants taken from literature for bulk alpha alumina because data on bulk transition alumina is not available. Given the limits of such model, especially where elastic constants are concerned (bulk alumina being in the α phase), the calculated maximum

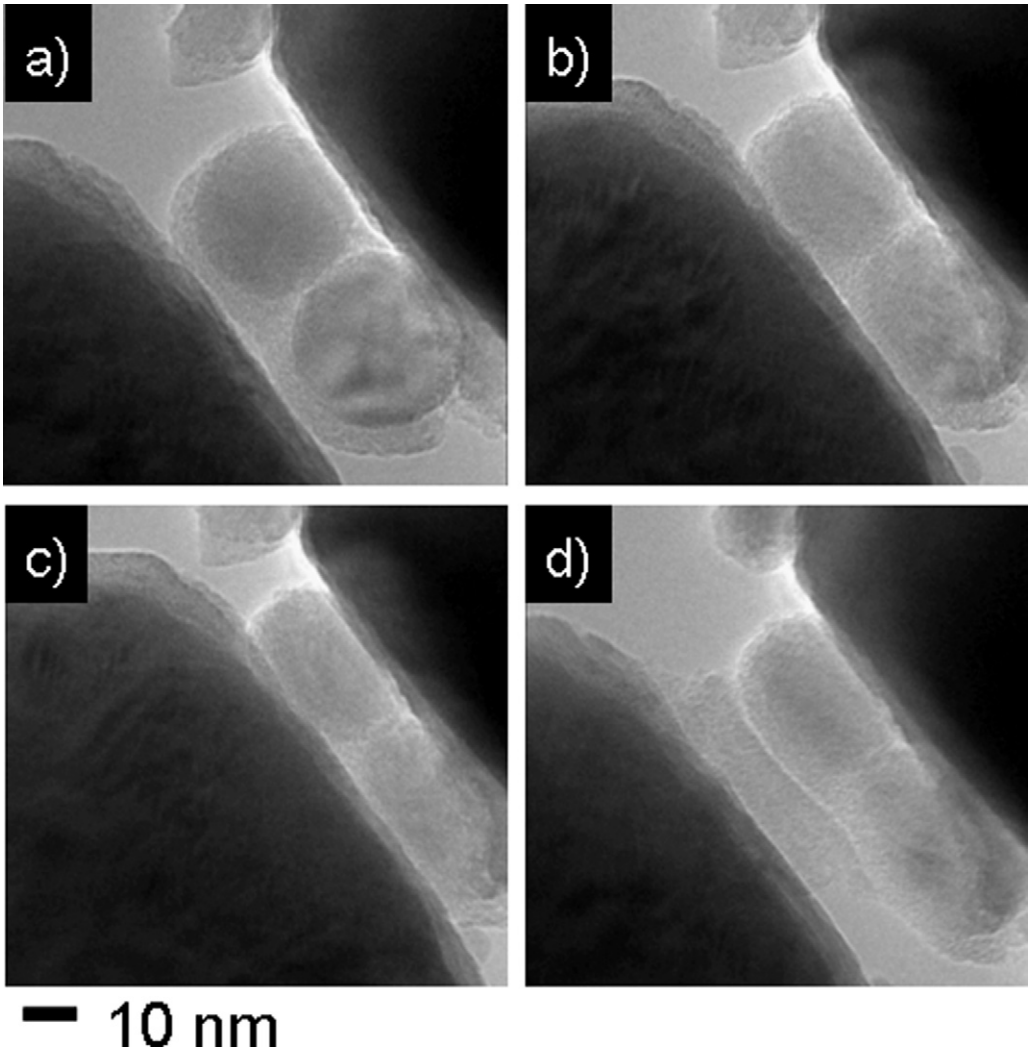

Fig. 2. Full compression of two alumina nano-particles: (a) initial state, (b) and (c) images during compression process, and (d) after unloading. No crack is observed during compression.

tensile stress of 3.4 GPa, is more of a rough estimation rather than a precise value. It can however, be noticed that this value is much higher than the ultimate tensile stress observed for sintered alumina (generally between 400 and 600 MPa).[9] It can also be noticed that the calculated maximum stress is significantly lower than the theoretical value necessary to cleave alumina (around 10 GPa, value depending on crystallographic planes involved[10]), which may be explained by the presence of a surface defect that is big enough to initiate the crack. In order to further explain why failure was not observed for all 125-nm particles, it is proposed that this defect must probably be in a particular position inside the particle (relative to the substrate and indenter positions) and the non-ideal surfaces of the indenter/substrate must probably allow to locally reach the maximum stress on the defect. For all the other particles, an elastic behavior has been observed without any failure. It can be proposed that either the defect was absent or the stress localization (due to the non perfect indenter/substrate surfaces) did not appear on the defect. For the unbroken particles, this means that tensile stresses higher than several GPa could be sustained without failure.

Even if the number of compressive tests performed in the present study is limited, it seems that small particles (*i.e.* 40 nm) show plastic deformation (at high stresses) without failure, while big particles (larger than 100 nm) show elastic behavior until failure. This is in agreement with the recent findings of Gerberich et al. for other inorganic materials.[6,11,12] The brittle-to-ductile transition in these alumina nano-particles is lower than for Si nanopillars (below 100 nm as compared to 400 nm). This is due to the different crystallography and shape of the nano-objects tested in this work. The brittle–ductile transition at 40 nm for an alumina powder means that breakage of particles below this critical size is not possible, and is a direct observation of the grinding limit (sometimes called the comminution limit) observed for ceramic materials (between 5 nm for zirconia and 50 nm for $CaCO_3$).[3] The fact that the brittle–ductile transition for this transition alumina is higher than the comminution limit observed for alpha alumina (around 20 nm) is due to the different type of loading and the different crystallography. However, the results are consistent. The grinding limit can therefore be viewed as the size of particles for which the elastic energy stored in the particle is

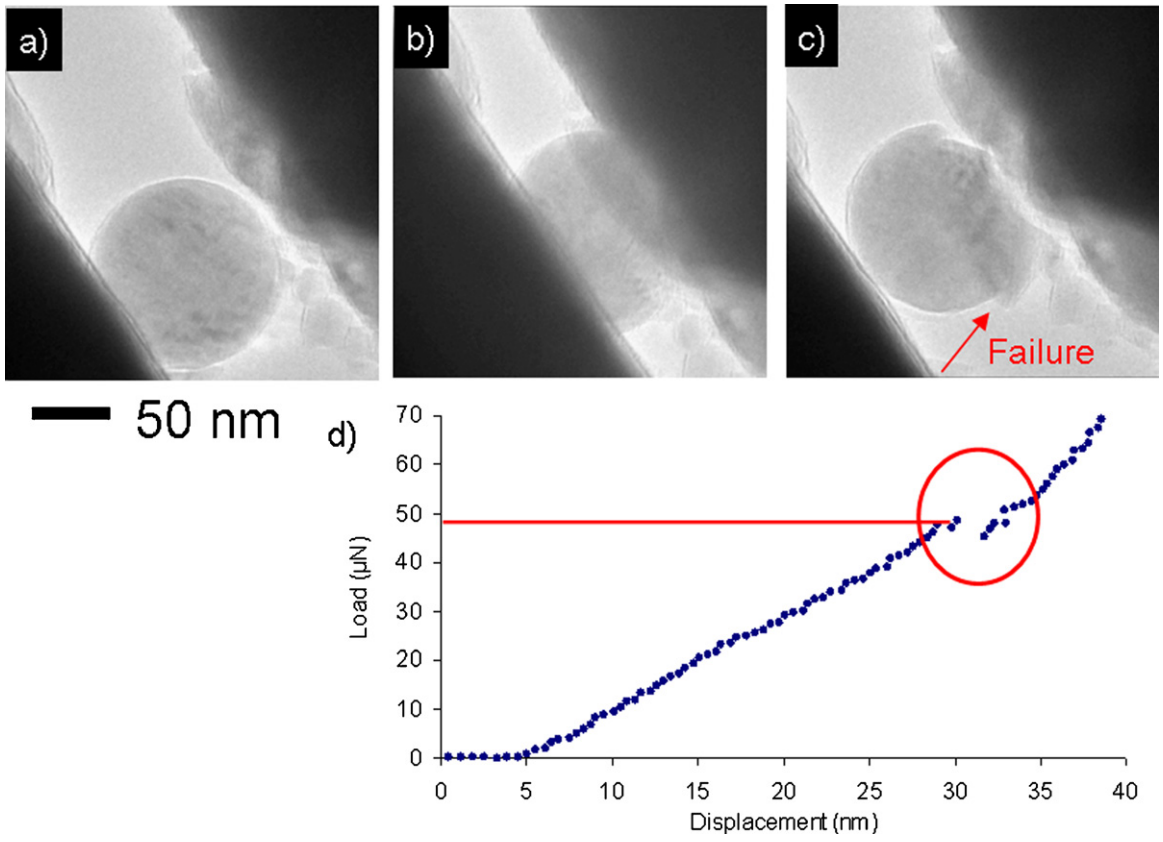

Fig. 3. Compression experiment of a 125 nm diameter δ-alumina nanoparticle. (a) initial state, (b) during compression, (c) after unloading, and (d) corresponding load–displacement curve, with emphasis on the detection of the fracture.

not enough to lead to breakage and for which yield occurs before cleavage.

Further works are in progress to accurately determine the critical size of this transition alumina and to study how this transition is modified with the crystallography of alumina. The atomic stacking of the transition alumina (γ, δ, η, θ phases) is quite similar: the oxygen atoms have almost a close-packed fcc arrangement while the aluminum atoms are distributed inside the octahedral sites (one site for one oxygen atom). Due to the stoichiometry of Al_2O_3, only 2/3 of octahedral sites are statistically occupied. So, the vacancies and aluminum atoms inside are more or less randomly distributed.[13] On the contrary, the crystallography of the stable alumina (α-phase), indicates that aluminum vacancies have well-determined positions. Their mobility is expected to be hindered leading to less plasticity and therefore still lower critical size for the ductile-to-fragile transition.

4. Conclusion

The compressibility of the nanocrystalline transition alumina was investigated by compression tests inside a TEM. These experiments revealed that particles in the 100 nm diameter range had an elastic behavior and the particles could be broken. On the contrary, nano-particles in the 40 nm diameter range exhibited a clear plastic behavior. Plastic behavior of ceramic nano-particles at ambient temperature is quite impressive and is of great interest in practice for ceramic processing. First, this is a direct evidence of the grinding limit for which particles cannot be broken any more. Second, it may apply to the compaction of nano-powders, for which some plastic deformation could be observed and used to obtain high green density.

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