Indentation size effect in barium titanate with spherical tipped nanoindenters

T. Scholz
Advanced Ceramics Group, Hamburg University of Technology, Germany

J. Muñoz-Saldaña
Centro de Investigación y de Estudios Avanzados del IPN, Unidad Querétaro, Querétaro, México

M. V. Swain
Dept. of Biomaterials, Faculty of Dentistry, University of Sydney, Australia

G. A. Schneidera)
Advanced Ceramics Group, Hamburg University of Technology, Germany

(Received 15 August 2005; accepted 24 January 2006; published online 1 March 2006)

Nanoindentation tests in an 90°-ac-domain area of an {001} oriented barium titanate single crystal were performed using four different indenters (two with cube corner and two with spherical shape) with tip radii from 61 nm to 1.9 μm. Extensive calibrations of the tips on fused quartz and sapphire defined the penetration depth range for approximately spherical contact prior to indentation of barium titanate (BaTiO3). The measured elastic modulus is independent of the different indenters. The measurements showed plastic deformation after “pop-in”. The calculated mean pressure remained constant for each indenter, but clearly depends upon the indenter radius. The indenter radius dependence of the hardness support the concept of “geometrically necessary dislocations”, proposed by W. D. Nix and H. Gao [J. Mech. Phys. Sol., 46, 411 (1998)] and its extension to spherical tipped indenters [J. G. Swadener, E. P. George, G. M. Pharr, J. Mech. Phys. Solids, 50, 681 (2002)]. The results show this concept fits the data generated with indenter radii which are at least an order of magnitude lower than investigated by Swadener. Furthermore, the results agree with estimates of the statistically stored dislocation density determined for BaTiO3. © 2006 American Institute of Physics. [DOI: 10.1063/1.2177364]

Nanoindentation is widely used for measuring the elastic modulus, $E$, and the hardness, $H$, of small volumes of material and thin films. A more critical appraisal of the force-displacement response of the samples during nanoindentation experiments can however provide far more significant insights into the mode and onset of plastic deformation or fracture of a material.

Recently, it is has become possible to perform indentation tests at dimensions of tens to hundreds of nanometers using nano- and microindentation methods. At these small indentation depths classic plasticity theory predicts constant hardness using a geometrically self-similar indenter on a homogenous material. Nevertheless a strong size dependent indentation hardness result is well known for metallic materials. This so-called “indentation size effect” (ISE) characterized by an increasing hardness (up to a multiple of the macroscopic hardness) as the indentation depth is reduced to the order of microns or submicrons. This phenomenon was interpreted by Nix and Gao, based on the works of Fleck et al., and Ma and Clarke. Nix and Gao showed that the ISE for crystalline materials can be explained using the concept of “geometrically necessary dislocations”, which leads to a strain gradient plasticity law. Swadener et al. extended this model for the case of spherical indenters. Recently Feng and Nix showed for small indentations that the ISE model overestimates the hardness of MgO single crystals.

The present work focuses on the nanoindentation behavior of a {001} oriented BaTiO3 giant grain using four different indenters with tip radii from 61 nm up to 1.9 μm. This material displays classic dislocation associated with plastic deformation. For loads up to and exceeding that to initiate pop-in at the beginning of the elastic/plastic part of the loading curve all indents can be described by an approximately spherical contact. They were analyzed using the approach of Swadener et al., which proposes that spherical indenters show a dependence of hardness on the indenter radius rather than on the depth of the penetration.

In this work, we report on nanoindentation tests with two spheroconical (CON1, CON2) and two nominally cube corner (CC1, CC2) shaped indenters with different effective tip radii. The full loading range of our testing device (TriboScope, Hysitron, Minneapolis, USA), from 0.25 mN to 10 mN was used.

More than 80 unloading curves on a fused quartz sample (Hysitron, Minneapolis, USA) were fitted to calibrate every indenter tip area function using the method of Oliver and Pharr. Furthermore, the calibration of the sharpest cube corner (CC1) was improved by additional indentations on sapphire, especially for small penetration depths.

For the investigation, {001} oriented BaTiO3 giant grains with typical dimensions of ~500 μm were prepared in house, described elsewhere.

A series of indents were carried out in a 90°-ac-domain area for which the force-displacement curves were acquired. The slopes of the unloading curves lead to a measured stiffness $S$ versus indentation depth $h$ function.

---

a)Author to whom correspondence should be addressed; electronic mail: g.schneider@tuhh.de
Every indenter was calibrated using a fused quartz or sapphire sample, respectively, which leads to a set of measured contact areas over the indentation contact depth $h_C$. Assuming a spherical tip contact for small indentation depths, the contact area $A$ was fitted by geometrical considerations [equation in Fig. 1(a)] where $a$ is the contact radius and $R$ is the indenter radius.

Plots of the radius of each of the indenters, as a function of contact depth, are shown in Fig. 1(a). The mean radii $R$ are listed in Table I.

Force-displacement curves in brittle materials indented with cube corner indenters typically display two pop-in events. This is clearly evident in barium titanate. The pop-in forces depend very strongly on the tip radius of the indenter used. The first pop-in event is related to the transition from elastic to elastic/plastic regime associated with the nucleation of plastic deformation due to dislocations which are well known in barium titanate. The second transition is related to the initiation of brittle fracture. It is possible to confirm these effects because unloading prior to the second pop-in leads to a residual impression but no cracks.

The mean contact pressures $P_m$ is determined from the applied load $P$ over the contact areas $A$. The contact areas were determined using the equation in Fig. 1(a). The required contact depth was calculated by two different approaches. Before the elastic-plastic pop-in and therefore in the elastic range it was possible to use an approach of Sneddon which proposes that the elastic displacement above and below the circle of contact are equal: $h_C = h/2$. In the elastic/plastic range after pop-in the contact depth was determined by Oliver and Pharr using the previous described linear fit of the unloading stiffness at maximum indentation depth.

The contact pressure results with the different indenters may be superimposed using the indentation stress/strain concept proposed by Tabor (see also Field and Swain, and Bushby and Dunstan) [Fig. 2(a)]. That is the contact pressure $P_m$ [given by the equation in Fig. 2(a)], where $E^*$ is the composite modulus, $a$ the contact radius and $R$ is the indenter radius. Figure 2(a) shows only one measurement for every tip whereas four measurements using CC2 are shown in Fig. 2(b). The mean values and the standard deviation were calculated using a number of measurements given in Table I.

Therefore, the elastic modulus does not change for the different indenters in Fig. 2(a), whereas the hardness does. Finally, $E^*$ was calculated to 234 GPa. This leads to an elastic modulus of 257 GPa of barium titanate using a Poisson’s ratio $\nu = 0.35$ and the properties of the indenter ($E_i = 1140$ GPa, $\nu_i = 0.07$).

After the pop-in the elastic/plastic contact pressure $P_m$ response remains almost constant with increasing indenter penetration. The maximum acceptable penetration depends on the consistency of the spherical approximation and therefore on the tip geometry. The measured mean values of the hardness as a function of the indenter tip radius are shown in Table I. But probing of different volumes of material could lead to different hardness values as well, if the $a$ and $c$ domains would have different hardness values. For the CC1 and CC2 indenters the maximum penetration depths were 15 nm and 70 nm, respectively. This corresponds to maximum contact radii of 40 nm and 173 nm. The indented $a$ and $c$ domains were 1.1 $\mu$m and 0.8 $\mu$m wide. Therefore it was possible to position the CC1 and CC2 indenters always in the middle of the domains. Nevertheless no differences in hardness were detected for the different domain orientations within the scope of the accuracy of the measurement: For the CC1 indenter the $a$ domains showed a hardness of 19.4±0.4 GPa and the $c$ domains showed 19.7±0.3 GPa. Using the CC2 gives 18.0±0.1 GPa, for both domain orientations. For the bigger indenters CON1 and CON2 it was not possible to position them precisely into one domain. Nevertheless, the hardness results of these indenters were reproducible and did not show any sign of a hardness difference between $a$ and $c$ domains. Therefore, the measured size effect cannot be attributed to different hardness values of the $a$ and $c$ domains.

The question arises whether domain nucleation or domain wall motion processes contribute to the plastic response. First of all the pop-in stresses are approximately 1000 times higher than typical coercive stresses for the ferroelastic response. Therefore, domain-wall motion should occur at loads well before the elastic/plastic pop-in event. Loading/unloading curves below the elastic/plastic pop-in.

---

**TABLE I. Indenter radii and measured hardness.**

<table>
<thead>
<tr>
<th>Indenter</th>
<th>CC1</th>
<th>CC2</th>
<th>CON1</th>
<th>CON2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$ [nm]</td>
<td>61±17</td>
<td>249±26</td>
<td>952±93</td>
<td>1897±207</td>
</tr>
<tr>
<td>$h_C$ [nm]</td>
<td>88±17</td>
<td>307±28</td>
<td>1758±11</td>
<td>3641±122</td>
</tr>
<tr>
<td>$H$ [GPa]</td>
<td>19.3±1.2</td>
<td>18.0±0.3</td>
<td>12.3±0.3</td>
<td>9.3±0.2</td>
</tr>
<tr>
<td>No. measurements</td>
<td>5</td>
<td>12</td>
<td>5</td>
<td>2</td>
</tr>
</tbody>
</table>
event sometimes show an extremely small hysteresis (1–2 nm) which might be a result of the motion or bending of existing domain walls. One can think about nucleation of new domains during the pop-in due to the energy which is stored in the ceramic during the pop-in. For example approximately \( W = 10^{-11} \) J are stored in the case of the CC2 during the pop-in. Assuming this energy is concentrated in a cube (underneath the indenter) with a width of two times the contact radius, we can calculate the possible number of small domains by the following simple model. We assume that the domains are equally sized small cubes of edge length \( l \) inside this strained volume of edge length \( L \). The domain-wall area is approximately \( 3L^2/l \). With the specific domain-wall energy \( \gamma = 7 \text{ mJ/m}^2 \), it follows

\[
I = \frac{3L^3 \gamma}{W} = 5 \cdot 10^{-12} m.
\] (1)

The value of \( I \) for the other indenters is in the same order of magnitude. Domains of these dimensions do not exist, and this is probably the reason why dislocations are created. We cannot exclude the idea that domain nucleation takes place to some extent; but the fact that the elastic modulus in Fig. 2(a) is identical within a certain experimental scatter strongly supports the argument that domain nucleation is not dominant in this region until the elastic/plastic pop-in event.

In the following paragraphs, the indentation size effect is analyzed by the concept of geometrically necessary dislocations. Swadener et al.\(^5\) applied the model of Nix and Gao\(^6\) to spherical indents and derived an expression relating the contact pressure \( H \) to the macroscopic hardness \( H_0 \), a material length scale \( R^* \), and the radius of the residual impression [equation in Fig. 1(b)]. \( R_c \) could be determined by geometrical considerations. The macroscopic hardness \( H_0 \) is correlated to a geometric constant \( \alpha \), which is in the order of 1.\(^6\) The shear modulus \( \mu \), the Burger’s vector \( b \), and the statistically stored dislocation density \( \rho_s \). Moreover \( R^* \) is dependent on the so called Nye factor \( \overline{r} \), which describes the ratio between the statistically stored dislocation density and the geometrically necessary dislocation density following Arsenlis and Parks.\(^7\)

Figure 1(b) shows the result of the data fit, with \( H_0 = 9.3 \) GPa and \( R^* = 847 \) nm. We excluded the sharp cube corner 1 indenter, because it obviously does not fit into the theoretical model. A similar effect was found by Swadener et al.\(^5\) in their investigation on copper but at much larger spherical impression radii of about 5 \( \mu m \). They argued that the most likely source of error in the model is the assumption that the dislocations are confined within a hemispherical volume that scales with the contact radius.

As a result of the now known fit parameter \( H_0 \) and \( R^* \), it is possible to calculate the statistically stored dislocation density using the equation in Fig. 1(b), which leads to \( \rho_s = 4.2 \times 10^3 \text{ ]/} \mu \text{m}^2 \) assuming a Burger’s vector of 0.56 nm in the (110) direction and a Nye factor of 2.\(^7\) Calculating the shear modulus \( \mu \) using an elastic modulus of 257 GPa and a Poisson’s ratio of 0.35 leads to the geometric constant \( \alpha \) of 0.5. This is in reasonable good agreement with the literature value, which is in the order of 1.\(^8\)

Nanoindentation experiments on single-crystalline barium titanate (BaTiO\(_3\)) with tip radii varying between 61 nm and 1.9 \( \mu m \) and forces in the range from 0.25 mN to 10 mN were performed and evaluated.

For all the indenters, during the initial elastic loading, the mean pressure \( \overline{P_m} \) plotted against \( a/R \) showed a monotonic increase prior to the first pop-in event independent of indenter tip radius and indicative of constant elastic modulus. Beyond pop-in, \( \overline{P_m} \) or the hardness, remains almost constant and clearly depends on the indenter radius in this case. A hardness increase form 9 GPa up to 19 GPa was measured. This observation supports the argument proposed by Swadener et al.\(^5\) following the Nix and Gao\(^6\) concept of geometrically necessary dislocations. In their work, this concept was validated for metals with a hardness of approximately 2 GPa using indenters with tip radii down to 14 \( \mu m \). In this work the approach was applied to a barium titanate ceramic with a ten times higher hardness using indenters with up to three orders of magnitude lower tip radii. The sharpest indenter does not fit into the theoretical model and may be a consequence of the high dislocation densities present in this case. Furthermore the statistically stored dislocation density for the barium titanate single crystal material investigated has been determined.

The authors gratefully acknowledge financial support by the German Research Foundation within the project “Strukturgradienten in Kristallen” (SCHN 372/7-3). One of the authors (M. V. S.) thanks the Alexander von Humboldt Stiftung for his stay at the Technical University of Hamburg-Harburg.

\(^7\) J. Muñoz-Saldaña, Fortschr.-Ber. VDI Reihe 5 Nr. 664 (2002).
\(^12\) D. Tabor, Philos. Mag. 74, 1207 (1996).