Surface modification of pre-sintered BaTiO$_3$ particles

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Abstract

Generally, the surface properties of powder particles strongly influence the sintering behavior of the resulting compacts. This paper describes the surface modification of pre-sintered BaTiO$_3$ particles (5–10 μm in size) by leaching under different hydrothermal conditions (leaching medium, time and temperature). These modifications enable to control the thickness and the degree of crystallinity of the resulting TiO$_2$-rich surface layer on the BaTiO$_3$ particles. A hydrothermal treatment for 1 h at 100°C in 0.1 M acetic acid results in the formation of an amorphous, TiO$_2$-rich, and 5 nm thick surface layer as revealed by high-resolution electron microscopy and electron energy loss spectroscopy. Microwave radiation was found to have no significant influence on the leaching processes under the conditions used here. Modified surface layers improve the densification behavior of the BaTiO$_3$ particles, but are insufficient to promote the evolution of a completely dense microstructure of the ceramics. A further improvement in densification and the formation of grain boundaries free of pores and with a high electrical conductivity can be achieved by hot isostatic pressing. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Barium titanate; Surface modification; Leaching; Microwave; Hydrothermal; High-resolution electron microscopy

1. Introduction

The sintering behavior of a powder compact can be adjusted by the surface properties of the powder particles [1,2]. Recently, we described the surface modification of BaTiO$_3$ powders prepared via the classical mixed-oxide method by milling in distilled water [2,3] or in a Ca(NO$_3$)$_2$ solution [4,5], and the influence of this modification on the properties of the final ceramics.

In case of milling in water the modification of the starting powder generated core-shell structures consisting of a BaTiO$_3$ core (about 500 nm in diameter) covered with a 3–5 nm thick amorphous TiO$_2$-rich layer, and an intermediate layer of about 10 nm in dimension with a molar Ba/Ti-gradient from 0 to 1. The formed amorphous TiO$_2$ surface layer favored the densification process by accelerating the sliding of the modified individual BaTiO$_3$ powder particles. Additionally, the homogeneous distribution of the excess of TiO$_2$ on the surface of the BaTiO$_3$ particles enabled proper conditions for the formation of the TiO$_2$-rich secondary phase Ba$_6$Ti$_{17}$O$_{40}$, and in this way it promoted the homogeneous recrystallization of the powder mediated via the liquid phase of the eutectic BaTiO$_3$–Ba$_6$Ti$_{17}$O$_{40}$ mixture at 1332°C [6].

The hydrothermal modification in Ca(NO$_3$)$_2$ solution yielded BaTiO$_3$ particles surrounded by small CaTiO$_3$ crystallites of 20–100 nm in diameter which act as seeds in the recrystallization process of the matrix material [5], thus improving the sintering process and favoring the evolution of a homogeneous microstructure of the resulting ceramic. Therefore, the sintering of these modified BaTiO$_3$ powders which are used to produce ceramic devices, having a positive temperature coefficient of resistivity (PTCR), can be regarded as a densification process followed by the recrystallization and growth of the sub-micrometer starting material to form grains of at least 5 μm in diameter [7].

The properties of the final ceramics are not determined by the original modified starting BaTiO$_3$ particles, but by the recrystallized grains.

In order to get a more direct correlation between the surface modification of BaTiO$_3$ powders and the properties of the final ceramics, we investigated the hydrothermal modification of already pre-sintered and classified BaTiO$_3$ particles with a grain size in the range of 5–10 μm [8]. These BaTiO$_3$ seeds were leached in a 0.1 M acetic acid solution at 180°C for 24 h. Analytical electron microscopic investigations revealed the formation of crystallites of anatase on the surface of the BaTiO$_3$ particles. This can be explained by the dissolution of the surface layers of the original BaTiO$_3$ particles and the following recrystallization of the dissolved TiO$_2$ on the surface of the BaTiO$_3$ particles with the Ba ions retaining...
BaTiO$_3$ powder (grain size fraction 5–10 μm) was pre-sintered as a loose fill, followed by classification in an Alpine zig-zag laboratory stirrer. The pre-sintered powders were used as precursor for microwave radiation experiments. The starting materials for the La$_{0.002}$Ba$_{0.998}$TiO$_3$ powder, prepared by conventional mixed-oxide method, were BaCO$_3$ (Solvay Sabed VL 600, Lot 325510), TiO$_2$ (Merck 808) and La$_2$(C$_2$O$_4$)$_3$·9 H$_2$O (SKW Piesteritz). The La$_{0.002}$Ba$_{0.998}$TiO$_3$ powder was pre-sintered as a loose filling on a platinum plate at 1350°C for 1 h, then milled in a planetary mill (Fritsch pulverisette 5, 50 g powder, 100 ml propan-2-ol, ZrO$_2$-balls and -pot and -lid, 1 h milling time) followed by classification in an Alpine zig-zag laboratory classifier (the La doping is necessary to make the ceramics semiconducting).

For the leaching experiments, 10 g of the classified BaTiO$_3$ powder (grain size fraction 5–10 μm; labeled in the following as BaTiO$_3$ seeds) were suspended in 40 ml of the leaching medium in a teflon container. The leaching was performed in these containers either under conventional hydrothermal conditions (laboratory autoclave Berghoff HR 200) or under the influence of microwave radiation (microwave accelerated reaction system MARS 5 (CEM Corporation)) with stirring of the suspension by a magnetic stirrer. For the leaching experiments, 10 g of the classified BaTiO$_3$ powder (grain size fraction 5–10 μm; labeled in the following as BaTiO$_3$ seeds) were suspended in 40 ml of the leaching medium in a teflon container. The leaching was performed in these containers either under conventional hydrothermal conditions (laboratory autoclave Berghoff HR 200) or under the influence of microwave radiation (microwave accelerated reaction system MARS 5 (CEM Corporation)) with stirring of the suspension by a magnetic stirrer.

We determined the effect of leaching primarily by the analysis of the Ba content in the leaching medium using atomic absorption spectroscopy (Varian SpectrAA 20). After adding a press aid solution (polynvinylalcohol), the leached powders were uniaxially pressed to tablets (density close to 3.4 g cm$^{-3}$). These greigs were dilatometrically investigated (Setaram TMA92, air, 1 g load, heating rate 10 K min$^{-1}$, temperature range 20–1500°C), and sintered (T$_s$ = 1300, 1350, 1400°C, dwelling time: 1 h). Selected powder compacts were hot isostatically pressed (Fa. ABRA (Switzerland)) at 1350°C with an Ar pressure of 150 MPa for 15 min. These final tablets were ground and polished, and characterized regarding their microstructure and electrical properties (resistivity at room temperature $\rho_{20}$).

The microstructure and composition of the as-modified powders and the sintered tablets were examined by high-resolution and high-voltage transmission electron microscopy in a Philips CM 20 FEG-TEM/STEM and a JEOL 1000-06, respectively. Electron energy loss spectroscopy (EELS) was performed with an energy resolution of 0.8–1 eV using the Gatan image filter (GIF 200) attached to the CM 20 FEG microscope. For transmission electron microscopy (TEM) investigations, powders were prepared by dispersing a small amount in pure alcohol, mixing it in an ultrasonic generator, and pipetting a drop of this dispersion on a copper mesh covered with a holy Formvar film. The preparation of the sintered and hip material was performed by standard grinding, dimpling and ion-milling techniques.

3. Results and discussion

3.1. Variation of the leaching conditions

As to indicate the effect of the leaching process we estimated the dissolved Ba$^{2+}$ content in the liquid phase after separation from the solid. The results of the analysis of these liquids for the various leaching conditions are summarized in Tables 1–3 (the amount of dissolved Ba was correlated to the Ba in the starting BaTiO$_3$ powder). At first, the amount of dissolved Ba ions can directly be influenced by the variation of the leaching time. The results regarding the time dependence of the leaching of BaTiO$_3$ seeds at 100°C in 0.1 M acetic acid are shown in Table 1: the dissolved Ba amount doubles from 0.74 to 1.54 mol% by prolonging the leaching time from 1 to 4 h. With increasing Ba dissolution

<table>
<thead>
<tr>
<th>Leaching time (h)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved Ba amount</td>
<td>0.74</td>
<td>1.12</td>
<td>1.28</td>
<td>1.54</td>
</tr>
</tbody>
</table>

Table 1 Ba$^{2+}$ amount (in mol%) dissolved from BaTiO$_3$ seeds after different leaching times at 100°C in 0.1 M acetic acid.

<table>
<thead>
<tr>
<th>Leaching conditions (°C)</th>
<th>40</th>
<th>100</th>
<th>180</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved Ba amount</td>
<td>0.41</td>
<td>0.74</td>
<td>1.33</td>
</tr>
</tbody>
</table>

Table 2 Ba$^{2+}$ amount (in mol%) dissolved from BaTiO$_3$ seeds at different temperatures after 1 h leaching time in 0.1 M acetic acid.
the Ba-depleted layer acts as a buffer. Thus, after leaching for 24 h a dissolution of only 2.0 mol% Ba$^+$ was found. Assuming the leaching kinetics of the dissolution of the Ba ions from the BaTiO$_3$ seeds follows Eq. (1), according to the solution of Fick’s diffusion laws:

$$\Delta n_{Ba} = k t^x$$

where $\Delta n_{Ba}$ is the dissolved Ba-amount, $t$ the leaching constant, $t$ the leaching time, $x$ the leaching exponent. The experimental data result in a leaching exponent $x$ of 0.5, i.e., the leaching process is mainly determined by diffusion.

The dissolution of Ba ions from the BaTiO$_3$ seeds was also analyzed at varying temperatures. The experimental results for the leaching at 80, 100 and 180$^\circ$C are shown in Table 3. Varying the leaching temperature, the power was reduced to only 10–20% of the maximum in order to maintain the temperature level. To avoid this disadvantage further experiments using a microwave system with a batch reactor under reflux are in progress.

### Table 3

<table>
<thead>
<tr>
<th>Leaching condition</th>
<th>Dissolved Ba amount (mol%)</th>
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<tr>
<td>H$_2$O</td>
<td>0.09</td>
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<tr>
<td>0.1 M CH$_3$COOH</td>
<td></td>
</tr>
<tr>
<td>10.0 M CH$_3$COOH</td>
<td></td>
</tr>
</tbody>
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### Table 4

<table>
<thead>
<tr>
<th>Leaching condition</th>
<th>Dissolved Ba amount (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>With microwave radiation</td>
<td>Without microwave radiation</td>
</tr>
<tr>
<td>$1^a$</td>
<td>0.14</td>
</tr>
<tr>
<td>$2^b$</td>
<td>1.40</td>
</tr>
<tr>
<td>$3^c$</td>
<td>0.736</td>
</tr>
</tbody>
</table>

#### Notes:

- $^a$ Medium: H$_2$O; temperature: 100$^\circ$C; time: 5 min heating-up time + 60 min dwelling time.
- $^b$ Medium: H$_2$O; temperature: 100$^\circ$C; time: 1 h in 0.1 M acetic acid.
- $^c$ Medium: 0.1 mol/l acetic acid; temperature: 180$^\circ$C; time: 60 min dwelling time.

#### 3.2. Characterization of the modified particle surfaces

As described in the previous section, more or less Ba is dissolved from the BaTiO$_3$ particles during the leaching procedure. Qualitatively, however, the modification of the structure and composition of the particle surface should remain almost similar and will be described in the following for leaching at 100$^\circ$C, 1 h in 0.1 M acetic acid exemplarily.

A typical example of the outermost region of a BaTiO$_3$ seed is shown on the HREM image of Fig. 1. An amorphous layer with a typical thickness of 5 nm has formed, the composition of which could be deduced from the series of EEL spectra (cf. Fig. 2) recorded along the line shown in Fig. 1. The result of the quantification of these spectra is graphically outlined in Fig. 3 as a function of the distance of the measuring points from the surface. This figure clearly shows the depletion of Ba and the corresponding enrichment of Ti in the thin surface region. The two maxima of the electron loss near edge structure (ELNES) of the Ti-L$_{23}$ edge of the outermost layer on the leached BaTiO$_3$ seeds indicate a shift of 1–1.5 eV to lower energy values compared to the bulk spectra (cf. Fig. 4). This shift is a characteristic of Ti(OH)$_4$ clusters compared to the TiO$_2$ units in the perovskitic bulk BaTiO$_3$ [3].

Thus, the leaching processes under these relatively mild reaction conditions can be described as the favored dissolution of Ba ions out of the perovskitic structure of the thermodynamically unstable BaTiO$_3$ with $V_{Ti}^{0}$ defects remaining. The $V_{Ba}^{0}$ defects are compensated by in-diffusion of protons from the leaching medium [3,11], which are located at O sites because of their size and charge density, thus forming...
Fig. 1. HREM micrograph of a BaTiO$_3$ seed hydrothermally leached; leaching conditions: 100°C, 1 h leaching time in 0.1 mol l$^{-1}$ CH$_3$COOH.

Fig. 2. EEL spectra recorded along the line shown in Fig. 1.
OH₀⁺ defects [Eq. (2)].

\[
(Ba₂Ba + Ti₃Ti + 3O₂)_{\text{solid}} + 2H₂O⁺
\leftrightarrow \left[V_{Ba} + Ti₃ + O₂ + 2OH₀⁺\right]_{\text{solid}} + Ba²⁺ + 2H₂O
\]  

(2)

The remaining TiOₓ is deposited as an amorphous layer on the surface due to the low solubility of Ti species [11]. We found this amorphous surface layer on the seeds after leaching at 80 and 100 °C. In case of leaching at 180 °C, the TiO₂ has formed nanocrystals of anatase on the BaTiO₃ grains [8]. This different behavior is attributed to a change in the leaching mechanism: at the temperature of 180 °C the leaching of BaTiO₃ can be described as dissolution–precipitation process. The solubility of Ti ions increases [12], and the soluble Ti species (e.g. Ti(OH)₄ or Ti(OH)₃(CH₃COO)) polycondensate and nucleate finally on the surface of the BaTiO₃ seeds.

3.3. Properties of the final ceramics

The dilatometric analyses revealed that the BaTiO₃ powders investigated can be divided into two groups regarding their shrinkage behavior during sintering. These groups are defined by the critical value of 0.09 mol% dissolved Ba (cf. Fig. 5). The first group with a dissolved Ba content of <0.09 mol% is characterized by a total relative shrinkage \(\Delta L/L₀\) of about 10% (\(L₀\)—initial length). There are shrinkage rate maxima at 1216, 1280 and 1332 °C. The maxima at 1216 and 1280 °C are attributed to sliding processes of the grains, and the maximum at 1332 °C corresponds to the appearance of a eutectic melt [6].

The second group of powders with a dissolved Ba content of \(\geq 0.09\) mol% exhibits a total relative shrinkage \(\Delta L/L₀\) of about 14%, and the shrinkage rate maxima at 1280 and 1332 °C are larger than in the first group. This is a consequence of the higher TiO₂ excess located at the surface of the grains which favors the sliding processes and increases the amount of melting phase. In case of powders with a dissolved Ba content of \(\geq 1.5\) mol% the peritectic temperatures in the system BaTiO₃–TiO₂ at 1350 and 1365 °C [6] are unambiguously detectable as further local shrinkage rate maxima.

The densities of the ceramics sintered for 1 h at 1350 and 1400 °C, respectively, are shown in Fig. 5 as a function of the dissolved Ba amount during leaching. Compared to the unmodified BaTiO₃ seeds, there are significant differences in the density of the final ceramics sintered at 1350 and 1400 °C. Already 0.09 mol% Ba dissolved is sufficient to increase the density of the ceramic sintered at 1350 °C from 4.85 to 5.3 g cm⁻³. But on the other hand, there are no significant differences in the final density of the ceramics with increasing Ba amount dissolved. Even the ceramic prepared from the seeds with 1.7 mol% Ba dissolved, and sintered at 1400 °C exhibits a density of about 5.4 g cm⁻³ only. This corresponds to 90% of theoretical density, i.e., there is still 10% of porosity.

A typical microstructure of the ceramics of the second group is shown in Fig. 6. As a consequence of the num-

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**Fig. 3.** Molar Ba/Ti ratio calculated from the EEL spectra shown in Fig. 2.

**Fig. 4.** Comparison of the Ti-L₂,₃-ELNES in the bulk and at the surface region of leached BaTiO₃ seeds.

**Fig. 5.** Densities of ceramics prepared from differently leached BaTiO₃ seeds, sintered at 1350 and 1400 °C for 1 h.
Fig. 6. Light micrograph of a ceramic prepared from BaTiO$_3$ seeds leached at 100$^\circ$C for 1 h in 0.1 M CH$_3$COOH, sintered at 1400$^\circ$C for 1 h.

Fig. 7. HVEM micrograph of a ceramic after hot isostatic pressing at 1350$^\circ$C for 15 min.

The modification of pre-sintered BaTiO$_3$ grains (5–10$\mu$m in size) by leaching under hydrothermal conditions was investigated using atomic absorption spectroscopy of the leaching solution and TEM methods including EELS for the modified particles. The results clearly indicate that it is possible to form leaching zones on the surface of BaTiO$_3$ grains in a defined way by exploiting the thermodynamic instability of BaTiO$_3$ in aqueous environment. The amount of Ba ions dissolved from the BaTiO$_3$ seeds (up to 2 mol%) and, therefore, the thickness of the depletion layer (up to 15 nm) can be adjusted by variation of the leaching temperature, leaching time and/or the leaching medium. Depending on the number of pores in this material and the resulting incomplete grain-to-grain contacts the electrical properties of the ceramics are poor. The electrical resistivity at room temperature is in the range of some k$\Omega$cm to M$\Omega$cm which is high compared to the few $\Omega$cm required for practical applications [13].

To overcome these disadvantages selected powder compacts were hip in addition. The microstructure of a hipped sample is shown in Fig. 7. It can be seen that the grain boundaries neither contain other phases nor pores although the sample is not fully dense yet. The electrical resistivity is now in the favorable range of about 10$\Omega$cm and is maintained in this range even after reoxidation at 1000$^\circ$C for 2 h in air.

4. Conclusions

The modification of pre-sintered BaTiO$_3$ grains (5–10$\mu$m in size) by leaching under hydrothermal conditions was investigated using atomic absorption spectroscopy of the leaching solution and TEM methods including EELS for the modified particles. The results clearly indicate that it is possible to form leaching zones on the surface of BaTiO$_3$ grains in a defined way by exploiting the thermodynamic instability of BaTiO$_3$ in aqueous environment. The amount of Ba ions dissolved from the BaTiO$_3$ seeds (up to 2 mol%) and, therefore, the thickness of the depletion layer (up to 15 nm) can be adjusted by variation of the leaching temperature, leaching time and/or the leaching medium. Depending
on the leaching temperature one can prepare a surface layer which consists of amorphous TiO$_2$ or anatase nanocrystals. The creation of such amorphous surface layers results in a higher densification compared to untreated seeds. Otherwise, a completely dense microstructure of the final ceramics cannot be achieved, as the TiO$_2$ layers are not thick enough to favor a sufficient sliding of the grains, and to accommodate the grain form to get close-packed ceramics. A further improvement in densification and formation of grain boundaries free of pores possessing a high electrical conductivity can be achieved by subsequent hot isostatic pressing.

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