TEXTURE IN ALUMINUM TITANATE CERAMIC MATERIALS

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Dry pressing and filtration of a mixture of platelike corundum and rutile powders shows a slight to sharp texture of the corundum particles. The reaction sintering forming aluminum titanate destroys the texture of the green compact. When starting with a rutile texture in the green compact there exists a texture of tietilite in the reaction product. Furthermore we developed a process for production of platelike tietilite monocrystalline particles which should be very suited for texturing of the ceramic material.

KEY WORDS: tietilite, texture, pressure filtration

I INTRODUCTION

Aluminum titanate, also named tietilite (Jamaguchi), is isomorphous with pseudobrookite Fe₂TiO₅. They both belong to a class of materials called anosovites, named after the mineral anosovite (Ti₃O₅), crystallizing in the orthorhombic space group Cmcm. The polycrystalline materials are characterised by a microstructure consisting of many microcracks due to a large thermal expansion anisotropy resulting from the very special atomic arrangement (Hamelin). It has been proved that the amount of microcracks is strongly grain size dependent (Cleveland). The critical grain size for aluminum titanate is about 1 μm (Cleveland). This grain size is too small for the conventional processing route so there is no control over the amount of microcracking.

Tietilite has a perfect thermal shock resistance due to a very low macroscopic thermal expansion coefficient but a very low strength due to microfracture. Due to the microcracks the thermal expansion shows a hysteresis which can be explained as follows. When cooling the microcrack-free material from the sintering temperature to room temperature the thermal expansion mismatch between neighboring grains results in thermal stresses which reach the strength of the material when cooling below 600°C. Thus the material expands due to the sudden development of microcracks. When heating the material it expands into the microcrack volume showing almost no macroscopic expansion until the microcracks begin to heal at higher temperatures. This is shown schematically in Figure 1.

There have been a lot of efforts to raise the strength by introducing a second phase. Pohlmann reached 100 MPa by using SiO₂, in comparison with 10–30 MPa for undoped material. Nevertheless, these efforts couldn’t satisfy the hope for broader application.

Another possibility is a control over microfracture by texturing the material. This has been shown for pseudobrookite by Paulík, who introduced a sharp fibre texture by pressure filtration assisted by a magnetic field which aligned the particles due to the anisotropy of the paramagnetic susceptibility.
Another problem arising with the use of tielite is its metastability below 1300°C. This could be improved by incorporation of foreign cations into the lattice or by a grain boundary phase, the best results were reached by the use of MgO and SiO$_2$ (Ishitsuka).

A good literature review is given in the articles from Hahn and Thomas, which both deal with all aspects concerning tielite.

**EXPERIMENTAL AND DISCUSSION**

It is often quite problematic instead of trivial to measure the texture of ceramic materials, especially those which show low symmetry and exhibit multiphase systems. We deal here with low intensities and overlapping of peaks. Thus it is convenient to show first of all the x-ray 2θ scans of the phases under consideration.

The starting materials for the reaction of tielite were corundum ($\alpha$-Al$_2$O$_3$) and rutile (TiO$_2$). Corundum crystallizes in the hexagonal system in the space group R32/c, rutile in the tetragonal system in the space group P 4/mmm. Their calculated x-ray intensities (Cu K$_\alpha$) are shown in the Figures 2 and 3 (Powder Cell Version 1.5). For the evaluation of the texture of aluminum oxide we used the pole Figures of the reflexes (012), (104), (110), (024), and (116). The texture of rutile was calculated with the data of the reflexes (110), (101), (111), (211), (100) and (310).

The 2θ scan of tielite is shown in Figure 4. We used the pole Figures of (020), (023), (025), (110), (111), (130), (024), (043), (200), (006), (060) and (135) for the calculation of the ODF.

For our purpose of texturing of tielite we investigated the reaction of the starting oxides by reaction sintering of two different starting powders, showing a texture of corundum or rutile.
Figure 2 Calculated x-ray intensities of corundum (Cu $K_{\alpha}$).

Figure 3 Calculated x-ray intensities of rutile (Cu $K_{\alpha}$).

Figure 4 Calculated x-ray intensities of tielite (Cu $K_{\alpha}$).
In the first process we produced hexagonal plates of corundum by annealing a mixture of \( \eta\)-\( \text{Al}_2\text{O}_3 \) and \( \text{AlF}_3 \) (25 wt %) for 1h at 1100°C. The \( \eta\)-\( \text{Al}_2\text{O}_3 \) was prepared by a 24 hour heat treatment of \( \text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O} \) (Fluka) at 300°C, followed by annealing at 900°C for 1h. This process was suggested by Kato et al (1986). The fluoride is strongly responsible for the crystal habit. It is thought to be adsorbed on certain crystal planes, thus enhancing the growth in special directions by an evaporation-condensation process. The resulting powder is shown in Figure 5. The corundum powder was wet milled with rutile powder (Riedel de Haen) and magnesium Nitrate (Riedel de Haen) in a ball mill in alcohol with alumina balls for 24h in the right proportions, taking into account the substitution of one Al by one Mg and Ti. The MgO compound of the nitrate serves as a stabilizer for tielite, which is metastable below 1300°C (Lang) as already discussed. The suspension was dried during simultaneous mixing to avoid sedimentation.

Figure 5 Corundum powder developed by heating a mixture of \( \eta\)-\( \text{Al}_2\text{O}_3 \) and \( \text{AlF}_3 \).
For the uniaxial dry pressing process we added 0.5 wt% PVA. The dimensions of the pressed specimen were 50×50×5mm. The pressure ranged from 100 to 175 MPa. The ODF’s for corundum in the green compact are shown in Figure 6. It can be seen from the inverse pole Figure (Figure 7) that there is a slight texture showing the basal plane in parallel with the pressing plane. A higher pressure is connected with a sharper texture (Figure 8). The rutile shows no texture at all (Figure 9).

Figure 6 ODF of corundum of the uniaxially pressed powder (100 MPa).
Figure 7 Inverse pole Figure of corundum of the uniaxial pressed powder (100MPa).

Figure 8 Inverse pole Figure of corundum of the uniaxially pressed powder (175MPa).
Figure 9 ODF of rutile of the uniaxially pressed powder (175MPa).
The pressed specimen were sintered for 4h at 1550°C. The inverse pole Figures in Figure 10 and 11 show that the texture was destroyed during reaction sintering. So there is no orientation relation of the reaction product to the corundum of the green compact.

Figure 10 Inverse pole Figure of tielite of the sintered specimen (100MPa).

Figure 11 Inverse pole Figure of tielite of the sintered specimen (175MPa).
We also prepared specimen by pressure filtration of the same powder used before. The corundum shows a sharper texture than before (Figure 12). Even the rutile shows some slight texture (Figure 13) which could have formed due to interfacial effects. The specimen were sintered at 1500°C for 4h. The reaction sintering had the same effect on the texture as discussed before that is it destroyed the texture completely (Figure 14).

**Figure 12** Inverse pole Figure of corundum in the green compact of the pressure filtrated specimen.

**Figure 13** ODF of rutile in the green compact of the pressure filtrated specimen.
More information about the experiments discussed before is given in the reference of J.-W. Kim.

It was convenient to use a powder which was suited to produce a texture of the rutile compound. For this purpose we annealed a tielite powder (Hüls ATG6) for 1h at 1000°C after adding 15wt% AlF₃. The resulting powder is shown in Figure 15. The uniaxial pressed (100 MPa) and sintered specimen (5h 1450°C) showed a slight texture (Figure 16), which is supposed to result from a texture of rutile in the green compact. There need to be further experiments to underline this result by producing a sharp texture of rutile in the green compact.

For further experiments we developed a powder consisting of platelike tielite particles. The process was first considered by Kato et al (1987). The sulphates of aluminum and titanium were dissolved in distilled water in a proportion to give an equimolar mixture of corundum and rutile. By adding diluted NH₃ we coprecipitated the hydroxides of both components. These were dried and calcined at 700°C for 1h to result in a mixture of anatase and γ-Al₂O₃. After addition of 3wt% MgO (Merck) and 15wt% AlF₃ the mixture was annealed at 1330°C for 90 minutes. The powder was dry milled in a ball mill for 1h. The resulting powder is shown in Figure 17. Our purpose is to produce specimens with a sharp texture by pressure filtration of the tielite powder to overcome the problem of uncontrolled microfracture.
Figure 15 Annealed tielite powder ATG 6 from Hüls.

Figure 16 (022) pole Figure of tielite of the reaction sintered specimen of the uniaxially pressed powder of Figure 15.
Figure 17 Tielite powder resulting from the reaction of $\gamma$-Al$_2$O$_3$, anatase and AlF$_3$.

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