Abnormal grain growth in DC flash sintered 3 mol% yttria-stabilized zirconia ceramics

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Abstract

The origin of non-uniform microstructure and abnormal grain growth was investigated in flash sintered 3YSZ ceramics. The microstructural homogeneity decreased with increasing direct current (DC) density and with dwell time in a flash state, eventually resulting in abnormal grain growth (AGG) in the specimen core, the first observation of AGG in 3YSZ. Abnormal grains up to 100 μm in size emerged when the DC density was ≥ 160 mA/mm^2 and the specimen's density exceeded 99 % of theoretical, starting from the cathode and propagating towards the anode. The results are discussed by comparison with established mechanisms and previous experimental evidence concerning AGG in oxides, focusing on the possible effects of the electrochemical reduction at the cathode end of the specimen.

Key words

zirconia: yttria stabilized, Field Assisted Sintering Technology (FAST), grain growth, abnormal grain growth

1. Introduction

The flash sintering (FS) of 3 mol% yttria-stabilized zirconia (3YSZ) ceramics was attempted by several research groups in the past decade with the aim of preparing dense and fine-grained specimens with uniform microstructures.[1,2] The FS process often resulted in almost fully dense specimens after a few seconds or minutes in the flash state, depending on the electric field and current density. The common agreement is that the ultra-fast densification is mainly initiated by rapid Joule heating, similar to the rapid densification caused by a high heating rate during fast firing.[3] However, while the fast firing can produce a uniform microstructure without grain size gradients even in relatively large 3YSZ samples[4,5], the direct electric current (DC) utilized by the FS is responsible for additional effects that have a considerable impact on the grain growth kinetics.

With short flash sintering times, Ji et al.[6] were able to obtain finer grain sizes in dense specimens compared to the fast firing and conventional sintering. This was attributed to the effect of the electric field in slowing grain growth reported by Ghosh et al.[7] which the authors tentatively associated with the interaction between the electric field and the grain boundary space charge.

Further effects on grain growth have been reported in 3YSZ subjected to longer times under a high DC. A high current density initiates the so-called electrochemical blackening of the base 3YSZ material.[8–11] The stoichiometric ZrO_2 is reduced to $ZrO_{2-\delta}$ starting from the cathode side and eventually affecting the entire section between the electrodes.[9] As shown in recent studies involving the application of DC to 3YSZ ceramics, the oxygen reduction influences the grain growth kinetics dramatically, with very large grains, unusual in 3YSZ, being observed in the section of the specimen nearest the cathode.[10,11] Both these very large grains and the much smaller grains on the anode side of the specimen had normal grain size distributions but the grain growth kinetics were enhanced remarkably in the oxygen reduced region on the cathode side.

In this study, we sintered relatively large 3YSZ samples by utilizing the stepwise FS approach under a broad range of current densities. The application of a high DC and long time spent in flash state resulted in hitherto unseen microstructures in the flash sintered 3YSZ bearing distinctive marks of abnormal grain growth (AGG).

2. Materials and Methods

Green bodies were prepared from commercially available 3 mol% yttria-stabilized zirconia powder (TZ-3YB, Tosoh Corp., Japan) with an average particle size of around 60 nm. As received powder was consolidated by uniaxial pressing at low pressure in a steel die followed by cold isostatic pressing at 250 MPa. The green bodies had a length of ~ 31 mm and a cross-section of around 5.8 × 3.5 mm. The two holes for the platinum wires were drilled at the ends with a gap of 25 mm between them. The green bodies were then either annealed at 600 °C for 2 h or pre-sintered at 1000 °C for 10 h in a conventional furnace before the FS process. Ends of the green body, including the inner surfaces of drilled holes, were painted with Pt paste (refer to Fig. S1a).

The FS was carried out in a modified box furnace in an air atmosphere. The original door was replaced with an insulating refractory wall equipped with a quartz window. The DC power supply (360 V, 15 A, 1500 W, Elektro-Automatik, Viersen, Germany) was connected to the specimen using Pt wires that were looped over an electrically non-conductive alumina scaffold inside the furnace (Fig. S1b). The furnace was conventionally pre-heated up to 900 °C. The DC power supply was turned on under voltage control using a voltage of 125 V (electric field of 50 V/cm) in all FS experiments and then switched to the current control regime after reaching an electric current of 0.4 A. The electric current was subsequently increased by steps of 0.4 A with 30 s dwell time at each step until the final current of 1.2, 1.6, 2.0, or 2.4 A was achieved (refer to Fig. S2). The final current was maintained for 30 or 60 s and then the DC power supply was switched off. The FS experiments were recorded on the video camera through the quartz window of the furnace. The camera images served for the measurement of instantaneous sample dimensions during sintering.

The relative densities of the FS specimens were measured based on the Archimedes principle (EN 623-2). A theoretical density (TD) of 6.08 g/cm^3 was used.[12] The relative density of FS specimens was measured on the dense central part excluding the poorly densified areas around the electrodes. The microstructure was investigated by scanning electron microscopy (SEM, Verios 460L, Thermo Fisher, Czech Republic). The specimens were polished and thermally etched at 1200 °C for 10 min. The grain size was investigated at 0.1, 0.5, and 0.9 of normalized distance from the anode. For each distance, the SEM images were taken from the core area and surface area (around 100 µm from the edge). The grain size of fine-grained areas only, abnormal grains were not included in these values, was calculated by the linear intercept method (EN 623-3) and then multiplied by a factor of 1.56.[13] The size of abnormal grains was calculated according to Equation 1 and then multiplied by a factor of 1.2:[14]

$$d = \left(\frac{4S}{\pi}\right)^{1/2} \tag{1}$$

where d is the grain size and S is the grain area obtained from the SEM image. The crystallographic orientation of the grains was evaluated by electron backscatter diffraction (EBSD). The SEM equipped with the EBSD camera (EDAX DigiView IV, EDAX, Germany) was used and the raw datasets were analysed using data analysis software (OIM Analysis^{TM} v8, EDAX, Germany). Grain orientation was analysed with respect to the direction normal to the sample surface.

3. Results and discussion

During the stepwise FS experiments, we observed the characteristic FS phenomena such as an abrupt increase of specimen conductivity, bright light emission, and rapid densification. All flash sintered 3YSZ specimens were partially reduced which was evidenced by their darker colour (Fig. 1). Based on the observations carried out at room temperature, the oxygen reduction was more severe in the core of the specimens compared to the surface and at the cathode side compared to the anode side.

The final densities and grain sizes of the FS samples are given in Table 1. The grain size was generally smaller at the surface compared to the core, even for low current densities, and the difference increased with an increasing current density. This was explained by concentration of the current density along the central line of the specimen resulting in the “inside out” heating[15] and thus significantly lower temperature at the surface compared to the specimen’s core.[16–18] A second, less significant grain size gradient was found at the surface in the direction from the cathode to the anode, with slightly smaller grains being observed at the cathode. This is consistent with a slightly lower temperature at the cathode side due to electrochemical reduction of the 3YSZ which reduces its resistivity.[9,16]

The temperature distribution alone would lead to the same grain size gradient in the core as well, however, the strong oxygen reduction observed in the core (see Fig. 1) became a major factor governing grain growth kinetics here. While the microstructure in the core was found to be uniform in sample #1 (Fig. 2a), it is important to notice that some core areas possessed accelerated grain growth kinetics over the others as the current density increased (Fig. 2b,c). This could be connected to the localization of the current density along the central line of the specimen.[15] Based on several SEM images from different core locations within sample #4, some locations exhibited overall a smaller grain size (Fig. 2b), similar to the surface, but others exhibited much coarser grains (Fig. 2c), eventually leading to the AGG (sample #6, Fig. 2d). The abnormal grains emerged at the cathode side if the current density was ≥ 160 mA/mm^2 and the final density was > 99.0 %TD. Their spread continued towards the anode and was more pronounced with increasing current density as well as the relative density of the FS samples (see Table 1). The abnormal grains rapidly grew to an average size of about 50 µm in samples #7 and #8 (Fig. 2e), some of them approaching 100 µm in size (Fig. 3). Such microstructural inhomogeneities are not acceptable for structural applications and must be avoided to maintain high mechanical strength. The fine, "normal" grains surrounding the abnormal grains continued to grow slowly (Fig. 2f).

The abnormal grains had random crystallographic orientations in the perpendicular and parallel directions with respect to the electric current (Fig. 3). Therefore, we can rule out the potential field-induced grain rotation and/or enhanced grain growth in favourably oriented grains or grain boundaries. The same conclusions were, for example, presented by the work of Rufner et al. on magnesium aluminate spinel.[19]

Grain growth in conventional sintering of 3YSZ is always slow and AGG such as that shown here has not been reported previously as far as the authors are aware. However, rapid, apparently normal grain growth on the cathode side of the specimen has been described in several previous works involving the passage of a DC electric current through specimens of YSZ.[10,11,20] There is general agreement in these works that the increase in grain growth rate near the cathode is related to the electrochemical reduction that occurs there.[11,21] Additional support for this idea comes from the absence of rapid grain growth when using AC[20] and the observation of grain growth acceleration using chemical reduction.[10] The AGG in this work also occurred in the blackened, electrochemically reduced regions at the cathode side of the specimens (Fig. 4).

The rapid grain growth at the cathode side in[10] was "normal", in the sense that the grain size distribution remained monomodal, but with a sharp transition to much finer, also normally distributed grains at the anode side. We presume that the reason these earlier works did not encounter AGG is that they used much more severe conditions, e.g. 250 mA/mm^2 for 20 h in[10], so there was time either for the abnormal grains to consume all the normal grains and join up with one another or for all the grain boundaries to attain the critical condition necessary for rapid grain growth. Kim et al.[22] and Dong et al.[10] suggest that rapid grain growth may occur if the cations, whose motion controls diffusion, are reduced at the cathode, thus lowering the migration barrier. This is an attractive idea but in its simplest form predicts a general increase in grain boundary migration rate. In contrast, the observation of a bimodal grain size distribution in the present work implies significant differences in migration rate between different grain boundaries.

In cases such as ours, where there is no evidence of second phases or pores to destabilise grain growth, the explanation must lie in the grain boundary structure. Two general models have been proposed, both relying on structural transitions in the grain boundaries when the relevant experimental conditions are applied. In the mixed control of boundary migration (MCBM) model,[23] AGG arises from the presence of faceted, atomically ordered grain boundaries, in which the migration rate can be limited by the interface, rather than being diffusion controlled. This leads to a highly non-linear grain boundary mobility that can lead to AGG. The other general model concerns the transition of grain boundaries from one structure, or "complexion" to another, also in response to the experimental conditions.[24] The different complexions have different mobilities and AGG is the result of the rapid migration of some boundaries with a highly mobile complexion.

The occurrence of AGG in the reduced regions of 3YSZ in this work superficially resembles the behaviour of several other ceramics to which the above models have been successfully applied, but differences in detail prevent direct transfer of the corresponding explanations. In 0.1 mol% TiO_2-excess $BaTiO_3$,[25] for instance, the grains were fine and monomodal when sintered in N_2-10%H_2 but AGG was observed in a more reducing N_2-15%H_2

atmosphere. On the basis of TEM observations, this was explained by an increase in disorder of the grain boundaries, lowering the interfacial barrier to migration. This allowed a few grains with highest driving force for growth to overcome the interfacial restriction and grow rapidly under diffusion control, yielding AGG. Our 3YSZ also exhibited AGG within a fine-grained microstructure when reduced, but it is accepted that the reason for the very fine grain size when sintering 3YSZ conventionally is strong boundary pinning by solute segregation and the associated space charge[26] rather than the ordered nature of the grain boundaries. It is not evident that lowering the ordering alone would alter this significantly.

In a different example, Nie et al.[24] found that the application of an electric current to Bi_2O_3-doped ZnO also induced AGG at the cathode end of the specimen. TEM and DFT modelling showed that the electrochemical reduction near the cathode led to a more ordered structure (complexion). The modelling indicated that reduction caused a lowering of the effective charge on the segregated Bi^{3+} ions, alleviating their pinning effect and increasing grain boundary mobility. In 3YSZ, however, the segregating dopant Y^{3+} cations have a lower valency than the host cations (Zr^{4+}), so again the details of the process must be different from the case of Bi_2O_3-doped ZnO, in which the dopant Bi^{3+} cations have a higher charge than those of the host (Zn^{2+}).

The above examples highlight not only the differences between 3YSZ and other ceramics exhibiting apparently similar effects, but also the more generally contrasting details of AGG in different systems: differences in applicable model, whether reduction leads to more or less ordering and whether an increase in ordering increases mobility (as in Bi_2O_3-doped ZnO) or diminishes it (as in TiO_2-excess $BaTiO_3$). In a further example of this wide range of possibilities, it is notable that when passing a current through undoped ZnO, AGG is found at the anode end rather than the cathode [27] as in Bi_2O_3-doped ZnO.

Although 3YSZ is evidently different in detail from the other ceramics described, the suggestion in[10,22] of a lowering of the host cation charge in response to the electrochemical reduction can be seen to have the potential to produce analogous effects: the host cation charge would be closer to that of the dopant cations and this would lessen the pinning of the grain boundaries and make them more mobile. The change in valency could also potentially change the boundary structure by analogy with the Bi_2O_3-doped ZnO system. However, the complexity of the sometimes contradictory effects in the examples discussed also makes clear that the correct explanation for this first observation of AGG in flash sintered 3YSZ can only be determined by further work. This is beyond the scope of this first report and should involve investigations of the grain boundary structure by electron microscopy and atomistic modelling.

4. Conclusions

The FS of relatively large 3YSZ samples resulted in a high relative density but non-uniform grain size distribution, especially after using higher current densities. The grain size near the specimen surfaces decreased in the direction from anode to cathode and the grains were significantly larger in the core compared to the surface of the specimen, which corresponded well to the temperature gradients reported in flash sintering. With increasing current density and dwell time under high current, the grain size distribution in the specimen core became wider and finally, AGG was found in specimens sintered to densities > 99 % with current densities ≥ 160 mA/mm^2. The AGG occurred first in the electrochemically reduced regions of the specimen at the cathode end and later spread towards the anode. The abnormal grains were equiaxed and had no preferred crystallographic orientation. This is the first observation of AGG in 3YSZ. The results are discussed in terms of the possible effect of the reduction on the cations with reference to previous results and models for AGG.

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