Hybrid processing and anisotropic sintering shrinkage in textured ZnO ceramics

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Abstract
We have studied the combined effects of the templated grain growth and magnetic alignment processes on sintering, anisotropic sintering shrinkage, microstructure development and texture in ZnO ceramics. Suspensions of 0-10 vol % ZnO template particles were slip cast in a 12 T rotating magnetic field. Sintering and texture characteristics were investigated via thermomechanical analysis and electron backscatter diffraction, respectively. Sintering as well as texture characteristics depend on template concentration. For the studied ZnO system, there is a critical template concentration (2 vol % in this study) above which densification is limited by the templates owing to constrained sintering. Below this limit, the densification is enhanced and the anisotropic shrinkage is reduced, which is attributed to densifying characteristics of the templates.

Keywords: sintering, anisotropy, texture, magnetic field, ZnO

1. Introduction

Many physical properties of ceramics depend on their microstructure. Therefore, microstructural design is very important in the search for better materials. One of the ways to control microstructure, and thus material properties, is by manipulating the orientation of the constituent crystallites, which is texture engineering. In the context of materials science, texture is defined as the orientation distribution of crystallites in a polycrystalline material [1]. There are several methods of controlling the texture, all relying on the anisotropic behavior of the grains under external perturbations. These perturbations may include mechanical, thermal or electromagnetic gradients [2].

Thermal gradients can induce pronounced texture in melt-cast materials, especially in metals. Application of thermal gradients during solidification is known to result in rapid growth of cubic crystals parallel to the direction of heat flow [3], causing (100) fiber texture in cubic crystals of some metals and alloys [4, 5]. Texture degree in thermally oriented microstructures can be controlled by such parameters as undercooling level, heat flow direction and composition. Unlike metals, ceramics are difficult to texture via thermal gradients and there are only few reports on this subject. Textured Al₂O₃ was produced via non-equilibrium solidification evoked by combination of a combustion synthesis and ultrahigh centrifugal force [6]. Although this texture was attributed to the ultrahigh gravity field by the authors, it might as well be classified as a hybrid method since non-equilibrium solidification also played a role in the formation of non-conventional, arrayed grain microstructure. Melt texturing is also applied to the high-temperature superconductors for increasing the critical current density via engineering a textured microstructure [7]. Nevertheless, melt casting of ceramics is inconvenient for large-scale production of textured ceramics because of the high-temperature requirements.
In texture engineering of ceramic materials, mechanical methods include tape casting, extrusion, uniaxial pressing and similar forming techniques. They can be used in conjunction with texture-developing heat treatment processes such as oriented consolidation of anisometric particles (OCAP) [8–10], templated grain growth (TGG) [2, 11–13], reactive templated grain growth (RTGG) [14] and hetero-templated grain growth (HTGG) [15]. Applications of OCAP, TGG, RTGG and HTGG to the production of textured piezoelectric materials have been recently reviewed by Kimura [16]. In these methods, a shear force is applied to powders composed of either anisometric particles (templates), to induce preferred orientation as in OCAP, or small numbers of large template particles mixed with smaller matrix powder, as in TGG, RTGG or HTGG. The former process is different from the last three methods in that although highly textured materials can be produced with it, a large number of anisometric particles are required, which can be rare or unavailable. Another problem is the low sinterability of large and anisometric particles due to the low radius of curvature of their well-faceted surfaces. The TGG, RTGG and HTGG methods require fewer anisometric particles. They can result in high degrees of texture upon sintering and grain growth, but the result still depends on the morphology of the raw material (particle anisotropy). These methods use mechanical force to align particles. Although they all employ standard industrial shaping techniques, the need for considerable amount of anisometric particles hinders their large-scale application. Limited availability of templates affects even laboratory scale production of textured ceramics. Another limitation of such techniques is their requirement of liquid phase formers to enhance densification and reduce the constrained sintering effect due to template particles. Therefore, obtaining single-phase materials is difficult with such methods and sometimes requires pressure-assisted sintering techniques.

Owing to their versatility, magnetic field based methods of texturing polycrystalline ceramics have gained much interest in the last decade. The diamagnetic susceptibility of virtually all non-cubic ceramic crystals is anisotropic, that can be used to align their particles with a magnetic field. However, this anisotropy is very small [17], and therefore magnetic fields are required for the alignment [18]. This requirement is facilitated by the availability of commercial superconducting magnets generating magnetic fields higher than 10 T. Magnetic field is usually applied while green parts are shaped via wet forming methods such as slip casting [19, 20], gel casting [21] or even electrophoretic deposition [22]. The main advantage of this method is the elimination of the template particles. Rather than morphological non-isometry, a strong magnetic field exploits the anisotropic diamagnetic susceptibility to orient the particles. When the magnetic field is applied to particles suspended in a liquid, the particles reduce their energy by aligning to the field, and this energy reduction \( \Delta E \) is given as [23]

\[
\Delta E = -\frac{\Delta \chi VB^2}{2\mu_0},
\]  

\(\Delta \chi = \chi_a - \chi_c.\)  

Here \( V \) is the particle volume, \( B \) is the applied magnetic field, \( \mu_0 \) is the permeability of vacuum, \( \chi_a \) and \( \chi_c \) are diamagnetic susceptibilities along the \( a \) and \( c \) crystal axes, respectively, and \( \Delta \chi \) is the anisotropic diamagnetic susceptibility. From equation (1) diamagnetic orientation can be achieved if the particles are either large or have strongly anisotropic diamagnetic susceptibility, so that their alignment overcomes the thermal motion. This is expressed by the condition \( \Delta E > k_B T \), where \( k_B \) is Boltzmann constant and \( T \) is temperature. Equation (2) predicts how individual particles of a particular material will orient themselves with respect to the magnetic field. For example, ZnO particles have \( \chi_c < \chi_a < 0 \) and therefore will align their \( c \)-axis perpendicular to the direction of applied rotating magnetic field [20]. Particles aligned in magnetic field retain their orientation after sintering. The disadvantages of this method are high cost of the setup and difficulties in scaling up the production. Magnetic field texturing of weak diamagnetic materials has been recently reviewed by Sakka and Suzuki [23].

Despite the promises of texture engineering, there are serious difficulties with its wide implementation to the industry. In addition to problems related to templates (in TGG-type processes), such as scaling up of processes and high costs, the sintering suffers from loss of dimensional control and residual stresses caused by anisotropic sintering shrinkage of textured ceramics. Anisotropic sintering shrinkage has been investigated in several systems but this phenomenon is not yet understood. The reported causes of anisotropic sintering shrinkage include (i) green compacts being composed of oriented anisometric particles [24], (ii) large, oriented, non-densifying, anisometric inclusions in randomly oriented matrices [25, 26], (iii) anisotropic surface or grain boundary energy in largely oriented green compacts [27, 28], and (iv) anisotropic pore morphology and contact anisotropy [29, 30]. These causes are interrelated; they might co-exist and one of them can be dominant. For example, in an OCAP process anisotropic surface energy and contact anisotropy would be equally important; whereas, if spherical particles are slip cast in magnetic field, anisotropic surface energy would dominate over other causes, if packing is assumed to be homogeneous and isotropic (i.e. no anisotropic pore morphology).

By combining different texture-inducing methods such as TGG and magnetic alignment one can overcome some of the difficulties associated with the individual production methods. For example, by hybridization of TGG and magnetic field alignment techniques, it might be possible to decrease the required template amount and/or avoid using a liquid phase which is required in most TGG family methods. Elimination of the liquid phase can result in single-phase textured materials. By combining magnetic field method with TGG, one can hope to achieve good alignment of grains, as templates are big particles which can be aligned at much lower magnetic field strengths [17]. In some recent studies anisometric, large inclusions were utilized in order to take advantage of their different properties [31, 32] from those...
of the matrix. In conventional TGG process, matrix particles around templates are usually randomly oriented whereas the matrix particles would be oriented in the same manner as the templates when using a hybrid process. In summary, process hybridization may overcome some of the difficulties related with individual processes and improve the texture engineering technology.

In this study, we investigated the effect of hybridization of TGG and magnetic alignment processes on sintering, microstructure development and texture of a model material system, ZnO. Zinc oxide is an important multifunctional oxide, which exhibit highly anisotropic properties owing to its hexagonal wurtzite structure ($P6_3\overline{mc}, a = b = \sim 0.3249$ nm, $c = \sim 0.5206$ nm). A wide band gap ($\sim 3.3$ eV at room temperature) [33] compound semiconductor, ZnO demonstrates such properties as piezoelectricity, luminescence [33, 34] and thermoelectricity [21]. Although ZnO is available as single crystals [35–37], polycrystalline ZnO is also important for practical applications.

2. Experimental details

Since high-quality rod-like ZnO particles are not commercially available, we have synthesized them for our experiments, via hydrothermal method as described by Lu and Yeh [38]. Initially, 0.5 M clear zinc solution was prepared by dissolving zinc nitrate hexahydrate (Merck GmbH, Darmstadt, Germany) in distilled water. Zinc hydroxide was precipitated by mixing the zinc solution with 0.1 M aqueous ammonia ($\text{NH}_4\text{OH}$) solution. After precipitation, the product was washed rigorously with distilled water and fed into a hydrothermal reactor. Hydrothermal reaction was carried out in a Teflon-lined stainless steel autoclave at 100 °C for 3 h under autogenous pressure. During the synthesis, the reactor was mixed at a stirring rate of 50 rpm. The synthesized powder was washed with distilled water by centrifugation and subjected to freeze drying.

ZnO samples containing 0 to 10 vol % of template particles, were prepared by slip casting with and without applying a 12 T rotating magnetic field. Schematic of the experimental setup and model structure are shown in figure 1(a). Suspensions of 20 vol % solid loading were prepared from ZnO powder (JIS1, HakusuiTech Co. Ltd, Osaka, Japan) and 5 vol % (based on liquid volume) glycerol-containing aqueous medium. The commercial ZnO powder was composed of particles with a variety of morphologies (figure 2), and 0.5 wt% poly(ammonium acrylate) (A6114, Toagosei Co. Ltd), based on solid loading, was used as a dispersant. Suspensions were homogenized by ultrasonication for 10 min. The sample cast without magnetic field and containing no templates is labeled as 100c0 T, while 100c12 T refers to the sample that was slip cast with no templates in 12 T rotating magnetic field; 98c2r12 T, 95c5r12 T and 90c10r12 T samples contain 2, 5 and 10 vol % templates (solid content), respectively. These samples were slip cast in 12 T rotating magnetic field. After compaction in magnetic field, all samples were isostatically cold-pressed at 392 MPa for 10 min.

Green densities of the samples were calculated from shrinkage values by assuming that the shrinkage is symmetric.
in the transverse direction. To study the sintering behavior of green samples by thermomechanical analysis (TMA), specimens were cut as rectangular prisms with the longer axis normal to either the basal or prismatic plane oriented faces. For the randomly oriented sample 100c0T, TMA specimens were cut so that the measurement direction was parallel either to the c-axis or the radial direction (figure 1(b)). In TMA, organic components of slip compositions were burned out at 400 °C for 2 h. Then, specimens were heated at 5 °C min⁻¹ to 1200 °C and sintered at this temperature for 2 h. Their densities were measured after sintering by the Archimedes’ method. Top surfaces of c-axis oriented samples, which were sintered at TMA, were polished to the roughness of 0.26 µm for electron backscatter diffraction (EBSD) study; (0001) pole figures obtained from the EBSD data were averaged over entire azimuthal angle range yielding the pole figure profiles. These orientation distribution profiles were fit to the March–Dollase equation [11, 39]

\[ P(r, \omega) = (r^2 \cos^2(\omega) + r^{-1} \sin^2(\omega))^{(-3/2)}. \]  

In equation (3), \( \omega \) is the angle between sample normal and the normal of the basal plane of ZnO crystal (c-axis). Parameter \( r \) can take a value between 0 and 1; it defines the texture quality, i.e., the width of the orientation distribution function—smaller \( r \) means finer quality.

3. Results

Figure 3 shows hydrothermally synthesized ZnO particles which were used as templates in this study. The templates are 7 µm long and 1.5 µm wide, on average. Comparison of the x-ray diffraction (XRD) patterns of rod-like particles and commercial powder revealed a preferential orientation in (1010) plane (figure 4). Minor impurities such as Si and Fe in the templates were revealed by x-ray fluorescence analysis (not shown). However, the 0.42° shift in the XRD peak positions was attributed not to impurities, but to a measurement artifact, as the same shift was observed in all peaks. The preferential orientation is caused by the shear due to smear during the preparation of the XRD sample; it can also be observed in the elongated morphology of the templates (figure 3). This result confirms that long axes of the templates coincide with the crystal c-axis direction, and the short axes are parallel to the prismatic plane normals. As stated above, anisotropic diamagnetic susceptibility of ZnO forces the c-axis to align perpendicular to the applied rotating magnetic field, meaning that rods must align their long axes perpendicular to the rotating magnetic field. Accordingly, figure 5 shows that the model of figure 1 is realized after slip casting in rotating magnetic field. Several template particles can be seen aligned perpendicular to the magnetic field direction, as well as a few slightly misaligned templates.

Figure 6 shows sintering characteristics of the systems that were studied in this work. The 100c0T sample that was slip cast without magnetic field and template particles exhibit anisotropic shrinkage; they shrink about 14% in the z-direction and a little less in the radial direction (~13%, figures 6(a) and (f)). The shrinkage in the z-direction starts at a higher temperature of about 815 °C than shrinkage in the radial direction, which starts at 735 °C (figure 7). Sample 100c12T exhibits less shrinkage along the c-axis
Figure 6. TMA shrinkage curves of (a) 100c0 T, (b) 100c12 T, (c) 98c2r12 T, (d) 95c5r12 T and (e) 90c10r12 T samples and (f) variation of the total shrinkage with the template contents and magnetic field.

(11.4%) and the radial direction (11.7%, figures 6(b) and (f)), as compared to a sample with the randomly oriented grains. Shrinkage begins at around 850 °C along the c-axis and at 740 °C in the radial direction (figure 7). Since the sintering curve in the c(z)-direction did not reach a plateau during the test (figure 6(b)), from the sintering curve of this highly c-axis oriented specimen, it can be concluded that the shrinkage did not complete by the end of sintering. Interestingly, the sample with 2 vol % template addition (98c2r12 T) demonstrates almost isotropic sintering shrinkage which amounts to ∼12.9% and ∼12.8% for the radial and c-axis directions, respectively (figures 6(c) and (f)). Shrinkage in the 95c5r12 T sample is anisotropic; it starts at 757 °C for the c-axis and at 840 °C along the radial direction (figures 6(d) and (f)). The anisotropic shrinkage is most pronounced in the 90c10r12 T sample (figures 6(e) and (f)), with the values of 11.8 and 8.8% in the radial and c-axis directions, respectively. Figure 6(f) shows shrinkage at the 450th minute of the TMA analysis as a function of template content, magnetic field and its direction. The randomly oriented sample exhibits anisotropic sintering shrinkage and the maximum total shrinkage among all samples. The final shrinkage values for both directions of the 100c12 T and 98c2r12 T samples are almost isotropic, although in the 100c12 T sample the onset sintering temperatures are different for the two directions. As the template content increases above 2 vol %, the shrinkage becomes more and more anisotropic owing to constrained sintering. Green densities of the samples tend to increase slightly as the templates are incorporated into the system (figure 8). This can be attributed to high density of the templates in comparison to the green compact.
Figure 7. Dependences of the onset temperature of sintering and shrinkage rate on template content and magnetic field conditions.

Figure 8. Relative green and sintered density of samples as a function of template content and magnetic field condition.

Figure 9 shows the backscattered electron diffraction orientation maps, which reveal individual orientations of each grain. The 100c0 T sample has almost randomly oriented microstructure after sintering (figure 9(a)), as expected, since no magnetic field was applied during forming of the compact. On the other hand, the 100c12 T sample exhibits strong texture (figure 9(b)). Samples containing 2, 5 and 10 vol% templates demonstrate maximum MRD (multiples of a random distribution) values of 11.3, 9.1 and 11.7, respectively, which are much smaller than that of the 100c12 T sample (18.45, figures 9(c)–(e)). The higher maximum MRD value means that more grains are oriented along the c-axis, assuming the same measurement area. Figure 10 shows distribution of MRD values of (0001) pole figure profiles and March–Dollase fits for all samples. For a random sample (100c0 T) the MRD value fluctuates by about 1. For a highly textured material, such as 100c12 T, the distribution becomes narrower and reaches higher values at lower angles meaning that more grains are oriented at that particular angle and its vicinity. The addition of templates results in a shallower orientation distribution (figure 10). Figure 9(f) shows a typical microstructure of the 98c2r12 T specimen which is taken from the radial direction.

4. Discussion

Even though it was manufactured without magnetic field, and no preferred orientation can be observed from the top surface (figures 9(a) and 10), the 100c0 T sample shows some anisotropy in the final shrinkage and large difference in the onset temperature values for the radial and z directions (figure 6(a)). This sintering anisotropy may be process related and material related. The former causes can originate from a non-uniform distribution of polymeric additives, non-uniform packing and/or slight orientation due to the processing conditions, whereas the latter causes include anisotropy in the particle morphology and surface energy which is also related to the curvature. Non-uniform distribution of glycerol is unlikely since glycerol has high solubility in water and the amount of dispersant was negligible. Non-uniform orientation may arise from the effect of suction force on anisometric particles during the slip casting (figure 2). Although not directly observed in our case, anisometric particles are known to align in the presence of suction forces as explained previously by Tanaka [40] and Chen et al [41]. The effect of suction on anisometrically shaped particles is demonstrated in figure 11(a). However, it should be noted that the orientation mentioned is rather small and further decreases as the distance from the mould surface increases, which is probably the reason why the EBSD analysis shows random distribution for the top surface. Even such heterogeneity at the bottom surface can cause some anisotropy in the sintering shrinkage as shown in figure 6(a). The largest shrinkage in this sample (figure 6(f)) might be attributed to relatively low initial packing density due to the overall random distribution of particles, in spite of the possible small particle alignment at the bottom part. Overall random distribution is also confirmed with the almost identical shrinkage rate along the radial and z directions (figure 7).

In the highly textured 100c12 T sample, the predominant mechanism resulting in the anisotropic shrinkage is the anisotropic surface energy due to strong fiber texture. Implications of this strong fiber texture are as follows: in the c-axis direction which is parallel to the sample z-axis, basal planes confront each other in the green compact resulting in a low lattice mismatch (i.e. low-energy grain boundaries), whereas in the radial direction different crystal planes come across each other since rotations of crystals about c-axis are random, as shown in figure 11(b). Therefore, the grain boundary energy is higher in the radial direction in comparison to that in c-axis oriented direction as a result of higher lattice mismatch. According to Zavaliangos et al [27], this creates anisotropy in the grain boundary diffusivity rate, which in turn results in sintering anisotropy. Furthermore, Shui et al concluded that the anisotropic mass transfer rate causes sintering anisotropy in highly textured materials [28]. Consequently, the sintering rates are different in the c-axis and radial directions. Anisotropic surface energy distribution
Figure 9. EBSD maps for the c-axis oriented faces of TMA specimens: (a) 100c0 T, (b) 100c12 T, (c) 98c2r12 T, (d) 95c5r12 T, (e) 90c10r12 T and (f) a typical microstructure of 98c2r12 T viewed from the radial direction.

Figure 10. (0001) EBSD pole figure profiles of sintered samples. Curves present the March fit to the MRD data and the inset shows dependence of the orientation parameter \( r \) on the template content and magnetic field. Also manifests itself in the difference in onset temperatures, as sintering starts at almost 110 °C lower temperature in the radial direction than that in the c-axis direction. Shrinkage rates show the same trend, namely a slower shrinkage rate is observed in the c-direction (0.21% min\(^{-1}\)) than in the radial direction (0.29% min\(^{-1}\), figure 7). These results agree well with above-mentioned literature reports.

The sintering curves, sintering rates and onset temperatures of the 98c2r12 T sample are almost the same for both directions as shown in figure 7, and the sintered density was the highest for this sample. This is an interesting result since templates, generally, retard sintering and worsen the densification. This is widely documented in the literature which concludes that rigid, non-densifying templates cause constrained sintering. When introduced in large amounts they also tend to form a rigid skeleton via percolation thereby reducing the sintering ability [25]. However, Bocaccini and Olevsky proposed that, for a hypothetical case, inclusions can enhance densification as they would contribute to the overall energy of the system [26] if these particles have a surface.
Figure 11. Schematic drawings of (a) influence of fluid suction on anisometric particles at the bottom of slip casting slurry without applied magnetic field and (b) high- and low-angle grain boundaries in a textured material.

Figure 12. Rod-like ZnO templates after annealing at 1100 °C for 2 h.

energy that exceeds that of the matrix powder. Therefore, rigidity of the templates was investigated at the sintering temperatures (Note that here rigidity refers to the stability of the templates at high temperatures, i.e. ability to retain their shape during the sintering. It does not refer to any particular mechanical property). When the templates were annealed at 1100 °C for 2 h they could not retain their initial anisometric shape and tended to reduce their surface energy by losing their well-faceted morphology (figure 12). This result suggests that the initial shape of the templates is not thermally stable at the sintering temperature used in this study, that is 1200 °C, and that template particles can sinter with the surrounding matrix powders and enhance densification. The decrease in the final texture (inset in figure 10) can be attributed to the suction force on templates during slip casting. This suction force tends to align templates perpendicular to the gravity opposing the rotating magnetic field, which tries to align templates parallel to the direction of gravitational pull. The negative effect of gravity on alignment of rod-like or whisker-shaped particles was reported previously [23]. Apparently in the reported here template + matrix system, gravitational force could not disturb the alignment of templates in magnetic field significantly as described in [23], which may be due to surrounding powder. On the other hand, the scanning electron microscopy (SEM) image of raw 95c5r12 T (figure 5), which is typical of all systems, reveals occasional misaligned templates. Therefore, when compared to 100c12 T, the 98c2r12 T sample shows slightly lower texture quality (inset of figure 10). Here it should be noted that the strong alignment of the matrix particles might play an important role in the reduction of the anisotropic sintering shrinkage. A further study was carried out to test this hypothesis, as discussed below in this article. This high degree of matrix particles alignment along with the templates cannot be achieved in any other process than magnetic alignment. Matrix particles alignment combined with densifying behavior of the templates with volumes less than a critical value resulted in a material with less anisotropic shrinkage, less constrained sintering and enhanced densification, which is comparable to that of the random sample.

As the template content was increased from 2 to 5 vol %, the sintering anisotropy reappeared and the relative sintered
density decreased. This result suggests that there may be a critical amount of densifying inclusions (templates in this case) which may enhance the densification behavior as suggested by Boccacini and Oleisky [26]. Although the shrinkage rates increase slightly, the increase of template content from 2 to 5 vol% raises the onset temperatures (figure 7). In a previous study, Suvaci and Messing [12] showed that when the critical amount of templates is exceeded, individual template particles can come into close proximity and start interacting. This may result in misoriented template particles. Similarly, as the volume of templates increases from 2 to 5 vol%, the effect of interaction may become more significant. This will decrease the distance between two templates, that, combined with the increase in the number of misoriented templates, can reduce the density, as in the case of 95c5r12 T sample. The lower texture quality (i.e. larger r value), can also be attributed to larger number of misaligned templates, as the number of template particles increases.

As the template content is further increased to 10 vol%, anisotropic shrinkage and constrained sintering become more dominant. For the 90c10r12 T sample, the difference in total shrinkage is the largest (figure 6(f)) and the onset temperatures for sintering are very high; 865 °C and 848 °C for the radial and c-axis directions, respectively. The corresponding shrinkage rates, 0.23 and 0.16% min⁻¹, are the lowest among all samples (figure 7). These results indicate that the constraining effect of template particles becomes important when their amount in the system exceeds the critical value. This results in a reduced relative sintered density (figure 8). Besides the constraining effect of the templates, the addition of such an amount of template into the suspension affects rheological characteristics of the suspension and may cause non-uniform packing. While the bottom part of the 90c10r12 T sample has a very low density, the top part was much denser (not shown). Reduced density in the bottom part might be caused by sedimentation of templates as the dispersion of templates into the matrix becomes more and more difficult with increasing template concentration.

Because of sedimentation, the amount of template particles might become very high in the bottom part, resulting in a low density in the 90c10r12 T sample. Sedimentation of templates also explains the higher orientation quality for this specimen. Since the template amount decreases in the top part, the lower r value compared to that of the 95c5r12 T sample (inset of figure 10) can be attributed to the reduction of template amount in the top part due to sedimentation.

Although not very dominant, a morphological texture was present in the samples when viewed from the radial direction in a scanning electron microscope. This morphological texture can be quantified by measuring the grain sizes along the c-axis and radial direction with the Lince software, TU Darmstadt, Germany. Figure 13 shows that the largest difference in grain sizes along the radial and c-axis directions is in the 100c12 T sample, which is highly textured. Grain size decreases with the template content, and the randomly oriented sample 100c0 T has an almost isometric grain shape.

To test the effect of matrix orientation on texture development, we tape cast 0 and 2 vol% template systems and studied their shrinkage and orientation characteristics after densification. The 2 vol% system showed less densification and slightly more anisotropic shrinkage, it shrank less in the casting direction that is atypical for slip casting in magnetic field. Even though templates were very well aligned in the green compact, neither samples had a good orientation (texture) after sintering which is probably a consequence of negligible matrix alignment in the green compacts. Lotgering factors [42] of two systems were similar, and a very small degree of texture was present (not shown). These results demonstrate the crucial role of matrix alignment for texture development in ZnO material without liquid phase via TGG-type processes.

The above discussion suggests that sintering can be enhanced by introducing small amount (below some critical value) of densifying template particles into a textured matrix. By combining the present and previous results, one can derive a hypothetical map for describing densification behavior in a system which is sintered without addition of the liquid
phase. Oriented matrix, low amount of oriented templates and densifying matrix behavior are desired for a good densification. In figure 14, there is a critical volume ratio of densifying and/or unstable template particles (i.e. Vc) above which densification is inhibited, whereas below this critical value densifying templates enhance densification behavior by regulating the matrix powder. This volume ratio was found to be 2 vol% in this work. The densifying behavior of the inclusions is also critical, as a recent study by Zhu et al [32] demonstrated that as low as 5 wt% of rigid β-Si3N4 caused an anisotropic shrinkage, almost three times different parallel and perpendicular to the whisker alignment direction. As discussed above, for a good densification and less anisotropic shrinkage, matrix orientation and template orientation should have a similar degree, the template content must be below the critical value, and templates should be thermally unstable. Here we assume that the template particles have the same orientation characteristics as matrix powder, and there is no liquid phase, since situation can be quite different if the matrix powder is randomly oriented and/or there exists a liquid grain boundary phase. There might be a critical value for the rigid template volume at which constrained sintering is negligible, but such critical volume should be very small.

An interesting outcome of the hybridization of TGG with magnetic alignment method is the fact that template particles in this process could have been merely equiaxed particles of larger size than matrix powder, since morphological anisotropy is not necessary, as in conventional TGG process. This has obvious advantages such as the elimination of dependency on the anisometric templates. As a consequence of using bigger particles, it might be possible to decrease the strength of magnetic field, since aligning micron-sized particles is much easier to achieve. This will have positive effects on the initial cost of the magnetic alignment setup. Yet another possibility is selecting the template size distribution instead of using templates with narrow size distribution. This will reduce the effects of anisotropic shrinkage by regulating the particle size distribution for better initial packing that should result in enhanced sintering. These template size related topics need a further investigation.

5. Conclusions

Hybridization of the TGG and magnetic alignment processes was successfully realized for the model ZnO system. Densification behavior could be controlled by introducing aligned, non-rigid, densifying, template particles into a textured matrix below a critical amount. In this way, effects of anisotropic shrinkage can be reduced, if not eliminated completely. Such hybrid processing can overcome the problems associated with the texture engineering by reducing costs and/or refining the raw materials. Further studies are needed to clarify the effects of coarse densifying inclusions on sintering characteristics and sintering mechanisms.

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References

[1] Bunge H J 1995 Texture Stress Microstruct. 24 1
[2] Messing G L 2001 Encyclopedia of Materials Science and Technology (Amsterdam: Elsevier)
[3] Wassermann G 1962 Texturen Metallischer Werkstoffe (Springer: Berlin)
[4] Skrotzki W, Kegler K, Tamm R and Oertel C G 2005 Cryst. Res. Technol. 40 90
[5] Pötschke M, Gaitzsch U, Roth S, Rellinghaus B and Schultz L 2007 J. Magn. Magn. Mater. 316 383
[6] Pei J, Li J T, Liu G H and Chen K X 2005 J. Alloys Compd. 476 854
[7] Jin S, Tiefel T H, Sherwood R C, van Dover R B, Davis M E, Kamllott G W and Fastnacht R A 1988 Phys. Rev. B 37 7850
[8] Holmes M, Newnham R E and Cross L E 1979 Am. Ceram. Soc. Bull. 58 872
[9] Okazaki K, Igarashi H, Nagata K, Yamamoto T and Tashiro S 1986 6th IEEE Int. Symp. Applications of Ferroelectrics p 328
[10] Okazaki K 1996 Proc. Tenth IEEE Int. Symp. on Applications of Ferroelectrics vol. 2 p 779
[11] Seabaugh M M, Vaudin M D, Cline J P and Messing G L 2000 J. Am. Ceram. Soc. 83 2049
[12] Suvaci E and Messing G L 2000 J. Am. Ceram. Soc. 83 2041
[13] Suvaci E and Ozer I O 2005 J. Eur. Ceram. Soc. 25 1663
[14] Itahara H and Tani T 2004 R&D Review Toyota CRDL, 39 63
[15] Kimura T, Sakuma Y and Murata M 2005 J. Eur. Ceram. Soc. 25 2227
[16] Kimura T 2006 J. Ceram. Soc. Japan 114 15
[17] Ueda C, Takashima R and Tanaka K 2005 Appl. Phys. Lett. 86 094103
[18] Kimura T 2003 Polym. J. 35 823
[19] Suzuki T S and Sakkya Y 2002 Chem. Lett. 31 1204
[20] Tanaka S, Makiya A, Kato Z, Uchida N, Kimura T and Uematsu K 2006 J. Mater. Res. 21 703
[21] Kaga H, Kinemuchi Y, Tanaka S, Makiya A, Kato Z, Uematsu K and Watari K 2006 J. Ceram. Soc. Japan 114 1085
[22] Suzuki T S, Uchikoshi T, Okuyama H, Sakkya Y and Hiraga K 2006 J. Eur. Ceram. Soc. 26 661
[23] Sakkya Y and Suzuki T S 2005 J. Ceram. Soc. Japan. 113 26
[24] Raj P M, Odulena A and Cannon W R 2002 Acta Mater. 50 2559
[25] Ozer I O, Suvaci E, Karademir B, Missiaen J M, Carry C P and Bouvard D 2006 J. Am. Ceram. Soc. 89 1972
[26] Boccaccini A R and Olevsky E A 2000 J. Mater. Process. Technol. 96 92
[27] Zavalangos A, Missiaen J M, Bouvard D and Carry C P 2003 Sintering of Magnetic Materials, Sintering 03
[28] Shui A, Lingke Z, Liu P, Cheng X and Uematsu K 2006 J. Ceram. Soc. Japan. 114 290
[29] Wonisch A, Guillou O, Kraft T, Moseler M, Riedel H and Rodel J 2007 Acta Mater. 55 5187
[30] Ch‘ng H N and Pan J 2005 J. Comput. Phys. 204 430
[31] Tanaka S, Tomita Y, Furushima R, Shimizu H, Doshida Y and Uematsu K 2009 Sci. Technol. Adv. Mater. 10 04602
[32] Zhu X W, Sakkya Y, Suzuki T S, Uchikoshi T and Kikkawa S 2010 Acta Mater. 58 146
[33] Ozgur U, Alivov Y I, Liu C, Teke A, Reshchikov M A, Dogan S, Avrutin V, Cho S-J and Morkoc H 2005 J. Appl. Phys. 98 041301

[34] Klingshirn C 2007 Phys. Status Solidi b 244 3027

[35] Demianets L N, Kostomarov D V, Kuz’mina I P and Pushko S V 2002 Crystallogr. Rep. 47 86

[36] Maeda K, Sato M, Niikura I and Fukuda T 2005 Semicond. Sci. Technol. 20 49

[37] Reynolds D C, Litton C W, Look D C, Hoelscher J E, Claflin B, Collins T C, Nause J and Nemeth B 2004 J. Appl. Phys. 95 4802

[38] Lu CH and Yeh C 2000 Ceram. Int. 26 351

[39] Dollase WA 1986 J. Appl. Crystallogr. 19 267

[40] Tanaka S 2006 J. Ceram. Soc. Japan 114 141

[41] Chen W, Hotta Y, Tamura T, Miwa K and Watari K 2006 Scr. Mater. 54 2063

[42] Lotgering F K 1959 J. Inorg. Nucl. Chem. 9 113