Control of Texture in ZnO by Slip Casting in a Strong Magnetic Field and Heating

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Anisotropic susceptibilities of feeble magnetic ceramics such as zinc oxide are quite small; therefore, it had been difficult to control the textured microstructures of these ceramics using a magnetic field. However, fabrication of the textured ZnO is achieved by slip casting in a strong magnetic field followed by heating. After the stable suspension of ZnO fine particles was compacted by slip casting in a strong magnetic field, a green body with a slight degree of crystalline texture was obtained. Densification and the grain growth enhanced the degree of texture during the sintering.

Zinc oxide is an important electronic ceramic for use in diverse applications, for example, in semiconductor pyro-, piezo-, gas sensors. Zinc oxide with a predominantly *c* axis orientation is useful for acoustic and piezoelectric devices as a result of the large coupling coefficients for these effects. The controlled development of the crystal orientation in zinc oxide is one of the ways for effectively improving these properties.

A crystal with an anisotropic magnetic susceptibility will rotate to an angle minimizing the system energy when placed in a magnetic field. The reduction of the magnetic energy on the rotation is $\Delta E = -(\Delta\chi VB^2)/2\mu_0$, where $\Delta\chi = \chi_{a,b} - \chi_c$ is the anisotropy of the magnetic susceptibility, V is the volume of each particle, μ_0 is the permeability in a vacuum and B is the applied magnetic field. This is the driving force for magnetic alignment.

It is generally difficult to utilize a magnetic field for controlling the texture in diamagnetic ceramics such as Al_2O_3 and ZnO because these ceramics exhibit only a small anisotropic susceptibility. Recently, the development of superconducting magnets has been extending the potential applications of strong magnetic fields. Interesting phenomena associated with strong magnetic fields have been reported[1,2] and magnetic fields have been used to produce a textured microstructure.[3–6] The texture in zinc oxide is believed to be controlled by a strong magnetic field.

The dispersion of powders in a suspension is necessary for the effective utilization of the magnetic field, because a strong interaction between the agglomerated particles in a suspension prevents the particles from rotating by applying a magnetic field. Colloidal processing is very effective in developing consolidated fine particles to avoid heterogeneous agglomerates by using repulsive surface forces.[7]

We first demonstrated in this study that a stable suspension containing ZnO fine particles could be prepared by colloidal processing and that the textured microstructure in ZnO can be controlled by a strong magnetic field applied to these powders in a suspension during slip casting followed by heating.

The starting material was fine ZnO powder (Sakai Chemical Industry Co., Ltd., Japan). This powder's purity was 99.6%. The particles were spheroid; the length and width were 50 nm and 25 nm, respectively. This powder was dispersed in distilled water with an added polyelectrolyte (poly(ammonium acrylate) A-6114, Toaghosei Co., Japan) to ensure dispersion by electrosteric repulsion between the particles.[8] The amount of the polyelectrolyte for maximum dispersion for each powder was determined from previous viscosity experiments. The suspensions were prepared with 20 vol% solids. The suspensions were mixed with a magnetic stirrer, and an ultrasonic horn (UPS-600, Shimazu Inc., Japan) was operated for 10 min to disperse the powder.[9,10] The suspensions were degassed in a vacuum, then poured into a gypsum mold, and left to consolidate. A strong magnetic field of 10 T was applied to the suspensions during the slip casting at room temperature. The green compacts were further densified by cold isostatic pressing (CIP) at 392 MPa for 10 min. The samples were isothermally heated in the temperature range of 773–1673 K for 2–5 h in air without exposure to a magnetic field. The samples were polished and then thermally etched for the microstructure analysis using a scanning electron microscope (SEM). Grain size measurements were made on the surface parallel to the magnetic field using the linear intercept method.

Figure 1 illustrates the XRD profiles of the specimen which was compacted by slip casting in 10 T, followed by heating at 1673 K for 5 h in air. The direction of the magnetic field was parallel to the casting direction. In the surface perpendicular to the magnetic field (VT in Figure 1), the intensities of the 100 and 110

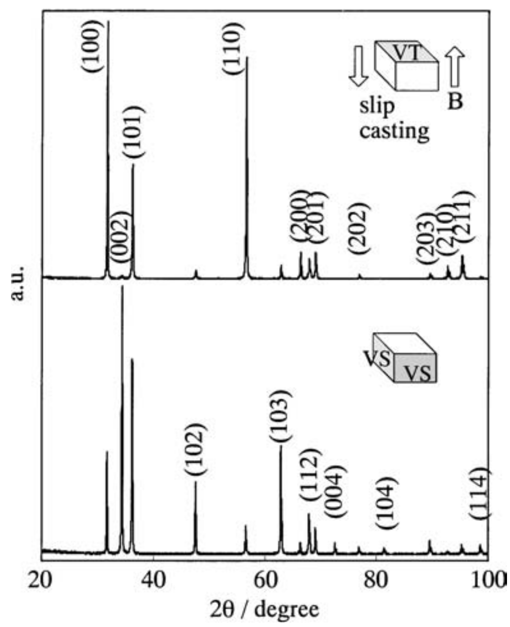

Figure 1. X-ray diffraction patterns of zinc oxide sintered at 1673 K in the planes perpendicular and parallel to the magnetic field, which is parallel to the casting direction.

reflections are very large. By contrast, in the surface parallel to the magnetic field (VS in Figure 1), the intensity of the 002 reflection is very large and the intensities of the (103) and (102) planes at the interplanar angle of 31.7° and 42.8° with the basal plane, respectively, are also large. Therefore, this demonstrates that a crystalline texture with the *c* axis perpendicular to the magnetic field had been developed by slip casting in a strong magnetic field followed by heating. The texture can be explained by the anisotropic susceptibility attributed to an asymmetric unit cell. It is probable that the energy of anisotropy, ΔE, is more than the energy of thermal motion (kT) at room temperature and that the magnetic torque originated from the $\Delta\chi$ rotated zinc oxide particles.

Figure 2 shows the degree of crystalline orientation together with the relative density and the grain size as a function of the heating temperature for the specimens prepared by slip casting in 10 T ($B \parallel$ the casting direction) and the specimens without applying a magnetic field. The degree of the crystalline orientation was estimated in terms of the Lotgering orientation factor f from the intensities of the X-ray diffraction measurement.[11] The orientation factor f is defined as $f = (P - P_0)/(1 - P_0)$ where P or $P_0 = \sum I(hk0)/\sum I(hkl)$. $\sum I(hkl)$ are the intensities from the *hkl* reflection over a certain range of 2θ values on the surface perpendicular to the direction of the magnetic field. The values of P were calculated from the ratio of the sum of the ($hk0$) intensities to that of all the (hkl) intensities for the zinc oxide prepared by this method, and the value of P_0 was calculated from the ICDD cards (#36-1451). For the random orientation sample, f is equal to zero, and increases with the increasing degree of orientation. The value of f approaches unity for an ideally textured material.

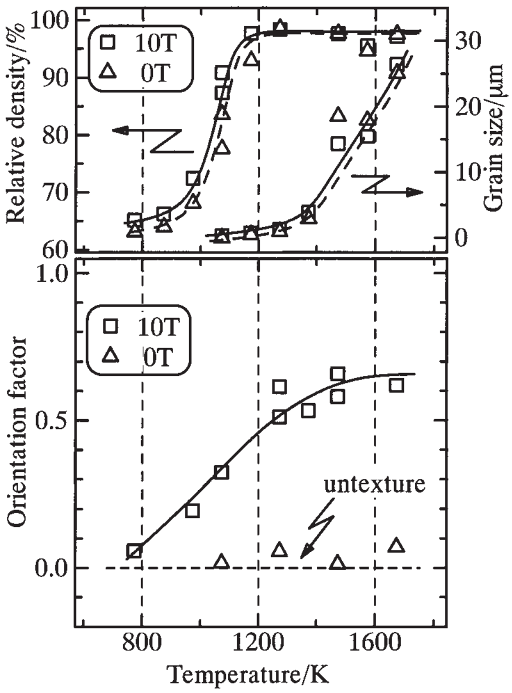

Figure 2. Effect of temperature on the degree of crystalline texture, density and the grain size.

For the specimens without applying a magnetic field, the degree of crystalline texture is in agreement with that calculated from the ICDD value. The specimen prepared without a magnetic field was confirmed to be a crystalline untextured material. The degree of crystalline texture up to 800 K was small in the specimens prepared using a strong magnetic field, but it should be noted that this value is larger than the zero of the untextured material. The degree of crystalline texture is small at 800 K, but it is larger than that of the untextured material. The degree of texture increases with the increasing temperature. The densities of the specimens were approximately 90% of the theoretical value at 1173 K with rapid grain growth occurring after 1273 K. From this comparison, it is clear that crystallographic texture development accompanies the densification and grain growth in the specimens.

By using colloidal processing, fine zinc oxide powder is well dispersed in the suspension. The suspension was consolidated by slip casting in a strong magnetic field (10 T) followed by heating. A green body with a slight degree of crystalline texture was obtained. Densification and the grain growth enhance the degree of texture with the *c* axis perpendicular to the magnetic field.

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