Low-temperature Sintering Behavior of TiO_2 Activated with CuO

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ABSTRACT

In TiO_2 -CuO systems, low-temperature sinterability was investigated by a conventional sintering method. Sintering temperatures were set at under 950°C , at which the volume diffusion is inactive. The temperatures are less than the melting point of Ag (961°C), which is often used as an internal conductor in low-temperature co-fired ceramic technology. To optimize the amount of CuO dopant, various dopant contents were added. The optimum level for enhanced densification was 2 wt% CuO. Excess dopants were segregated to the grain boundaries. The segregated dopants supplied a high diffusion path, by which grain boundary diffusion improved. At lower temperatures in the solid state region, grain boundary diffusion was the principal mass transport mechanism for densification. The enhanced grain boundary diffusion, therefore, improved densification. In this regard, the results of this study prove that the sintering mechanism was the same as that of activated sintering.

Key words : TiO_2 , Dielectric ceramics, Activated sintering, Low-temperature sintering, Grain boundary diffusion

1. Introduction

TiO_2 is a strong candidate material for microelectronic devices and microwave communication systems owing to its characteristics of high relative dielectric constant and low dielectric loss.¹⁾ In microwave communication and microelectronic systems, the integration of devices is necessary. To simultaneously integrate circuits and modules of devices, low-temperature co-fired ceramic (LTCC) technology is imperative as well. Sintering temperatures of dielectric ceramics for such devices, thus, should be below the melting points of Ag (T_m : 961°C) and Cu (T_m : 1083°C), which are used as internal conductors. For this purpose, TiO_2 -CuO systems have been investigated, instead of using pure TiO_2 with a high sintering temperature.

In our previous study,²⁾ we demonstrated that sintering for a short time at a low temperature was effective for TiO_2 -CuO systems, because high temperature or extended time induced rapid grain growth. The mechanism of low temperature sintering for TiO_2 -CuO systems, however, has not been systematically investigated. For now, a reduction of sintering temperature with additives is usually attributed to the formation of a liquid phase. As the eutectic temperature is uncertain in the TiO_2 -CuO system, however, systematic observation is needed regarding the sintering mechanism.

Recently, Harmer *et al.*³⁾ showed a structural disordering of grain boundary caused by the excess CuO for a CuO-doped TiO_2 bicrystal. The disordering enhances the grain boundary diffusion along and across the grain boundary. The enhanced grain boundary diffusion was thus proposed as a main cause for the improved densification at a low temperature of 850°C . The improved densification by enhanced grain boundary diffusion at the low temperature, at which volume diffusion is inactive, is called activated sintering or activated solid-state sintering.⁴⁾ In activated sintering systems, the solubility limit of the matrix material in the dopant or activator must be large, while that of the activator in the matrix material should be low. Matrix materials have higher melting points than those of activators. The content of the dopant must exceed its solubility in the matrix at the sintering temperature. Another characteristic of activated sintering is to be an effective limit (optimum level) of dopant for densification. Namely, there is no further densification above the optimum level of dopant. In addition, rapid grain growth is concomitant with enhanced densification. Activated sintering behavior was typically observed in W metal^{5,6)} and ZnO ceramic systems.⁷⁾

In this context, for the present system, the characteristics of activated sintering were investigated using the conventional sintering method. Densification, grain growth, solubility limit of dopant, optimum level of dopant, and grain boundary phase were discussed for this purpose. From the results of this study, the current system showed good activated sintering behavior.

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2. Experimental Procedure

Pure TiO₂ (Kojundo Chemical Co., Japan; purity: 99.9%) and TiO₂ mixed with CuO (Kojundo chemical Co., Japan; purity: 99.9%) were used as the starting materials. For the pure powders, two types, anatase and rutile phases, were used. Mixed powders were prepared by wet-milling pure TiO₂ powders adding CuO (~0.1 - 8 wt%) for 24 h in a polyethylene bottle. Zirconia balls and ethyl alcohol were used as the milling media and the solvent, respectively. After the ball milling, the powders were dried at 100°C for 24 h. Then, the dried powders were crushed and sieved (500 mesh). 2 g samples of each powder were uniaxially pressed into pellets at under 0.5 MPa; then, the pellets were cold isostatically pressed at a pressure under 100 MPa for 3 min. The green pellets were ~13 mm in diameter and 7 mm high. The green compact pellets were sintered at a temperature between 800 and 950°C at an interval of 50°C for various times under air in an MoSi₂ resistance box furnace. The heating and cooling rates were both ~5°C/min.

Analyses of the solubility of CuO in TiO₂ and of the developed phases of the sintered body were performed using standard X-ray diffraction with a diffractometer (D/Max 2000, Rigaku Co., Japan). For the test, the sample surfaces were polished with diamond paste down to 1 μm. In particular, peak intensities were obtained after removing the background intensities to determine the solubility limit of CuO in TiO₂. Sintered densities were obtained using the Archimedes method with distilled water as the immersion medium. Every density datum was determined using an average of three similar specimens. Micrographs of the sintered samples were obtained for the fractured surfaces by scanning electron microscopy (SEM) (Jeol-6200, Japan). Average grain sizes were determined from the SEM micrographs using the linear intercept method⁸⁾ with at least 300 grains counted for each sample. To observe the grain boundary structures of the CuO-doped TiO₂, HRTEM and energy-dispersive spectroscopy (EDS) were performed using a 200 kV JEOL TEM (JEM-2010).

3. Results and Discussion

3.1. Solubility of CuO in TiO₂ matrix

Figure 1 shows the X-ray diffraction patterns with the additive amounts of CuO-doped TiO₂ (rutile) sintered at 950°C for 1 h in the air. For simplicity, only one peak of rutile (101) and one peak of CuO(111) were considered for the estimation of the CuO solubility in TiO₂. The CuO(111) peak was observed only in the TiO₂ doped with CuO at an amount > 0.5 wt%, as can be more clearly seen in Fig. 2, which shows the intensity ratio of the peaks of rutile (101) and CuO (111). No second phase due to the reaction between TiO₂ and CuO was observed. The results are supported by the previous results,⁹⁻¹¹⁾ suggesting that the extent of solid solution of CuO (0.35 mol% ≈ 0.35 wt%) is not sufficient for the formation of a second phase, and by other

Fig. 1. XRD results of TiO₂ (rutile) with CuO content: (a) 0 wt%, (b) 0.2 wt%, (c) 0.5 wt%, (d) 1.0 wt%, (e) 2.0 wt%, (f) 4.0 wt%, and (g) 8.0 wt%, sintered at 950°C for 1 h.

Fig. 2. $I_{\text{CuO}(111)} / (I_{\text{rutile}(101)} + I_{\text{CuO}(111)})$ of TiO₂(rutile) with CuO content, sintered at 950°C for 1 h.

works in the literature that show a CuO-TiO₂ phase diagram without a terminal solid solution.¹²⁾ As a result, it is believed that the solubility limit of CuO in the TiO₂ matrix is very low, and that the sintered TiO₂ samples with CuO content over the solubility limit consist of a mixture of TiO₂ and CuO without any second phase.

3.2. Densification

For a simple calculation of the relative density, the theoretical density of each sample was obtained using the rule of mixtures and based on the X-ray result showing that there was no second phase (Fig. 1). The theoretical densities of pure TiO₂ (rutile) and CuO are 4.249 g/cm³ and 6.505 g/cm³, respectively.¹¹⁾ The calculated theoretical densities of the TiO₂-CuO samples are shown in Table 1. With the increase in the CuO content, the calculated theoretical density of the TiO₂-CuO sample increases because the density of CuO is higher than that of TiO₂. In the case of an anatase starting

Table 1. Calculated Theoretical Density of CuO-doped TiO₂ (rutile) with CuO Content

Amount of CuO (wt%)	0.1	0.2	0.5	1.0	2.0	4.0	8.0
Theoretical density (g/cm ³)	4.252	4.254	4.261	4.272	4.294	4.339	4.429

*In this system, the weights and mole percentages of TiO₂ and CuO are nearly equal, because of the nearly identical molecular weights of TiO₂ and CuO.

powder, the pure rutile density was used, considering that the phase transformation of anatase- to- rutile is over 800°C.¹³⁾

Figure 3 shows the densification behaviors of the CuO-doped TiO₂ (anatase) samples sintered at various temperatures. The densification behaviors were identical at each sintering temperature. Namely, up to an amount of 2 wt% CuO, the sintered densities increased, whereas the sintered densities decreased slightly at amounts of >2 wt% CuO. In the case of CuO-doped TiO₂ (rutile) samples, the densification behaviors were the same as those of the anatase samples, as shown in Fig. 4. The obtained density was, however, higher in the rutile samples than in the anatase samples.

In the case of pure anatase, the anatase-to-rutile phase transformation occurs at between ~400 and 1000°C.¹⁴⁾ In the current sample, the phase transformation occurred at 800°C.¹³⁾ Because of the phase transformation, vermicular microstructures are produced owing to volume contraction (~8.6%) during the transformation. Additional pore channels are thus left in the sintered body,²⁾ decreasing the density of the anatase samples rather than that of the rutile samples. In consideration of the applicable sintered body, the optimal sintering temperature seems to be between 900 and 950°C. Actually, stable dielectric properties were obtained at a sintering temperature of 930°C in our previous study,²⁾ where CuO doping was shown to be more effective at lower temperatures than at temperatures >1000°C for TiO₂ sintering. Concerning the sintering temperature, temperatures >1200°C (0.66 T_m) are needed to sinter pure TiO₂.¹⁵⁾ Based on sintering theory, volume (lattice) diffusion

as a mass transport mechanism is active during the densification at the temperature >1200°C. In the current research, however, ~96% of the maximum sintered density was obtained despite a low temperature of 950°C for the CuO-doped rutile (Fig. 4). Because the sintering temperature of 950°C relative to the melting temperature (T_m) of TiO₂ corresponds to merely 0.52T_m, volume diffusion can hardly be expected during densification. Therefore, other mass transport mechanisms might be contributing to the densification at low temperatures. There are two considerations here, the grain boundary diffusion and the eutectic liquid contributing to the densification. Both grain boundaries and eutectic liquids can supply high diffusion paths of mass transport for densification at low-temperature sintering.

The phase diagram of the TiO₂-CuO system has not been well explained. The eutectic temperature in the binary phase diagram was not clearly determined. In air, the eutectic temperature was 900°C, as determined from the calculated data,¹²⁾ or 1000°C, as determined from the experimental data.¹⁶⁾ Assuming that the eutectic temperature is between 900 and 1000°C, a eutectic liquid may possibly exist at temperatures between 900 and 950°C, whereas the possibility of the existence of a eutectic liquid will be rare between 800 and 850°C. Figs. 3 and 4 show that the densification behavior is hardly affected by increases in temperature, suggesting that the formation of a liquid can be ruled out during the elevation of temperature. That is, sintered density increased to a maximum and then slightly decreased with increasing CuO content; this is typical behavior in activated sintering.⁴⁾ The densification mechanism of the current

Fig. 3. Relative density with CuO content for CuO-doped TiO₂ (anatase) sintered at various temperatures: (a) 800°C, (b) 850°C, (c) 900°C, and (d) 950°C for 1 h.

Fig. 4. Relative density with CuO content for CuO-doped TiO₂ (rutile) sintered at various temperatures: (a) 800°C, (b) 850°C, (c) 900°C, and (d) 950°C for 1 h.

samples is thus thought to be the same as that in the solid state before the formation of a eutectic liquid, even though a eutectic liquid phase did exist.

Based on the phase diagram for solid-state activated sintering, a eutectic liquid can form at temperatures slightly above the activated sintering range. In the presence of a eutectic liquid, thus, it is difficult to differentiate activated sintering from liquid phase sintering.⁴⁾ It should be noted, however, that activated sintering starts at temperatures well below the eutectic temperature. For example, in the case of a W-Ni-Fe system, which is a representative activated sintering system with a clear eutectic liquid during heating to eutectic temperature, relative density (%) increased from 57 for the green compact sample to 95 at the end of the heating stage before the formation of a eutectic liquid. The eutectic liquid made very little contribution to the densification.^{17,18)}

In our systems, similar densification behaviors are shown in Figs. 3 and 4 as well. It is therefore thought that enhanced grain boundary diffusion played a main role in the densification at low sintering temperatures before the formation of eutectic liquid. CuO as an activator in grain boundaries thus supplied a high diffusion path for mass transfer, requiring low activation energy, such as is imparted by the activator in the W-Ni^{5,6)} and ZnO-Bi₂O₃⁷⁾ systems. The optimal level of activator in the present systems is likely to be 2 wt% CuO, considering that the maximum densities were obtained at 2 wt% CuO. The activator in activated sintering must fulfill the requirement of low solubility in a matrix for the mass flow to follow unipolar diffusion through the activator.⁴⁻⁶⁾ From the XRD data (Figs. 1 and 2), the solubility of CuO in the TiO_2 matrix can be seen to be very low (< 0.5 wt%). Consequently, the CuO-doped TiO_2 systems, irrespective of the type of starting powders, satisfied the requirements for activated sintering well, as is shown in Figs. 2-4.

3.3. Grain Growth

Activated sintering is accompanied by rapid grain growth as well as improved densification. Fig. 5 shows the microstructural variations of TiO_2 (anatase) with CuO content at a given sintering temperature. Overall, the grain size increased with the addition of CuO. Especially, the grain size increased drastically up to 0.5 wt% CuO, whereas it slightly decreased for CuO > 0.5 wt%. Fig. 6 also shows how the microstructure changes with CuO content for the rutile starting powder. As a whole, the dependence of the grain size on the addition of CuO was the same as that in the anatase samples. The tendency of the grain size variation was very similar to that in the anatase starting powder, as shown in Fig. 7.

As a result, the grain growth showed two distinct behaviors. The maximum grain sizes were obtained at 0.5 wt% CuO, which was coincident with the solubility limit calculated from the X-ray diffraction data (Fig. 2). The grain size increased with CuO addition up to the solubility limit and

Fig. 5. SEM microstructures showing the fracture surfaces of CuO-doped TiO_2 (anatase) with CuO content: (a) 0 wt% CuO, (b) 0.1 wt% CuO, (c) 0.2 wt% CuO, (d) 0.5 wt% CuO, (e) 1.0 wt% CuO, (f) 2.0 wt% CuO, (g) 4.0 wt% CuO, and (h) 8.0 wt% CuO, sintered at 950°C for 1 h.

then slightly decreased with further addition above the solubility limit, indicating that the grain growth has a certain relationship with the CuO solubility. As described by Yan *et al.*,¹⁹⁾ when sintering mixed powders under the solubility limit, the solid solution effect of a dopant can promote grain growth, whereas, above the solubility limit, a second phase effect can retard the grain growth. In the present system, however, no formation of any second phase was observed in the X-ray data. As shown in Fig. 8, excess CuO is located at the grain junctions or boundaries as isolated particles. In this case, therefore, it is reasonable that the hindrance of grain growth is caused by the solute-drag effect rather than by the second phase effect. Additionally, the grain growth was also obstructed by residual porosity.

This grain growth mode was also found in enhanced sintering systems such as Al_2O_3 -MgO,^{4,19)} which is not an activated sintering system. The rapid grain growth in the TiO_2 -CuO system, therefore, showed the characteristics of enhanced sintering as well. In addition, the largest grain size was obtained at a level near the solubility limit (0.5 wt% CuO). In contrast, the highest density was obtained at

Fig. 6. SEM microstructures showing the fracture surfaces of CuO-doped TiO₂ (rutile) with CuO content: (a) 0 wt% CuO, (b) 0.1 wt% CuO, (c) 0.2 wt% CuO, (d) 0.5 wt% CuO, (e) 1.0 wt% CuO, (f) 2.0 wt% CuO, (g) 4.0 wt% CuO, and (h) 8.0 wt% CuO, sintered at 950°C for 1 h.

the effective limit (2 wt% CuO).

3.4. Grain boundary phase

Figure 9 shows TEM micrographs for the 2 wt%-CuO doped TiO₂ (rutile) sintered at 850 and 950°C. For both samples, a grain boundary phase is observed, and its electron diffraction pattern shows a diffuse ring pattern, indicating that the grain boundary phase is amorphous. The phase is similar to those previously observed in both the ZnO-Bi₂O₃⁷⁾ and CaSrTiO₃-Li₂Si₂O₅ systems,²⁰⁾ which are also solid-state activated sintering systems. Fig. 10 shows the compositions of the grain boundary phase and the adjacent grain for the sample sintered at 950°C. The grain boundary phase was Cu-enriched compared to the adjacent grain. This means that, because of its low solubility in the TiO₂ matrix, CuO was segregated in the grain boundaries.

The grain boundary phase is called an intergranular film; it is a segregated layer of the activator.^{7,21)} An equilibrium thickness exists for the segregated layer for the W-Ni and ZnO₂-Bi₂O₃ systems and is equivalent to the optimum level

Fig. 7. Average grain size with CuO content for (a) CuO-doped TiO₂ (anatase), and (b) CuO-doped TiO₂ (rutile), sintered at 950°C for 1 h.

Fig. 8. SEM microstructures showing the polished surfaces for: (a) TiO₂(rutile)-8 wt% CuO sintered at 850°C for 1 h, (b) TiO₂(rutile)-0.5 wt% CuO sintered at 950°C for 1 h. A white phase at a grain boundary or junction is CuO. Thermal etching was carried out at a lower temperature of 50°C than the sintering temperature for 0.5 h.

of the activator. Thus, excess activator beyond what is needed to obtain the equilibrium thickness of the segregated layer provides no benefit for further densification. In our systems, CuO activators at levels beyond the solubility limit, therefore, lie at the grain boundaries as segregated layers and play the role of high diffusion paths for TiO₂

Fig. 9. TEM micrographs for 2 wt% CuO-doped TiO₂ (rutile), sintered at 850°C (a-d) and 950°C (e-h) for 1 h. (c) and (g) are the magnified images for (b) and (f), respectively. (d) and (h) are electron diffraction pattern images for areas marked with arrows for (a) and (e), respectively. Scale bars (nm) are (50, 10, 5) and (100, 5, 2) for (a-c) and (e-g), respectively.

mass transfer. An equilibrium thickness of the segregated layer seems to be formed at the optimum level of 2 wt% CuO. That is why further addition beyond the optimum level provides no additional benefit for densification, as shown in Figs. 3 and 4.

To sum up, segregated CuO supplied high diffusion paths for TiO₂ mass transfer, thus enhancing the grain boundary diffusion. The sinterability at low temperature, at which the volume diffusion can be disregarded, improved because of the enhanced grain boundary diffusion.

4. Conclusions

To simultaneously integrate a circuit and a module of a device, LTCC technology is necessary. TiO₂ is well known for its usefulness in dielectric ceramics. Pure TiO₂, however, requires a very high temperature (>1,200°C) for sintering. For LTCC technology, thus, the TiO₂-CuO system was investigated. Grain boundary diffusion was found to be an active mechanism at low temperatures at which volume diffusion is negligible during sintering. In the current system, maximum density was obtained at the optimal level of 2 wt% CuO. Further addition above the optimum level pro-

Fig. 10. Compositions analyzed by EDS in grain boundary phase (a) and an adjacent grain (b) for sample (f) in Fig. 9. The ratio of Ti to Cu for the grain boundary is 38.6:61.4 in at%. The ratio of Ti to Cu for grain is 98.5:1.5 in at%. As a result, the grain boundary phase is Cu-enriched.

vided no additional contribution to densification. The content of 2 wt% CuO is in the range of the excess solute. The excess CuO built a segregated layer and, thereby, grain boundary diffusion was enhanced. The improved densification at low temperatures resulted from the enhanced grain boundary diffusion. These results, therefore, prove that the TiO₂-CuO system shows the characteristics of activated sintering.

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