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Enhanced densification of pure SnO_2 by spark plasma sintering

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Densification of pure SnO_2 by conventional sintering is known [1, 2] to be very difficult due to the evaporative decomposition of SnO_2 into SnO(g) and $1/2O_2$(g) occurring during sintering. The adsorbed impurities on the surface were also suggested to retard the densification process [3]. Therefore, it has been reported [4] that the fully-dense SnO_2 specimens could be obtained only by hot isostatic pressing. In this investigation, we tried to achieve a full densification of SnO_2 specimen by spark plasma sintering (SPS) which is known to be quite effective for the densification of various materials [5–10]. Although the exact mechanism of the enhanced densification by SPS has not been clarified yet, the surface cleaning by joule heating due to dielectric breakdown [5] would remove the surface impurities. Note also that the SPS is usually carried out at low-temperatures compared with the conventional sintering, so that the evaporation of SnO_2 can be minimized. In this study, therefore, the densification of SnO_2 specimens using SPS process was investigated by varying the SPS conditions and starting powders.

Commercial SnO_2 powders (99.9% purity, Aldrich Chemicals, USA) as well as the powders prepared in the laboratory were used. To prepare the SnO_2 powders, 200 ml of 0.2 M $SnCl_4{\cdot}5H_2O$ (99.9% purity, Aldrich Chemicals) butanol solution was dripped into 400 ml of 0.5 M $(C_2H_5)_2NH$ (diethylamine, 99.9%, J. T. Baker Co.) butanol solution. Ten milliliters of water was additionally dripped into solution for promoting hydrolysis reaction. The precipitate was washed using ethanol until no Cl^- ion was detected. After pulverization, the powders were heat-treated at 250 °C for 1 hr to decompose residual $(C_2H_5)_2NH$, and calcined at 500°C for 1 hr. A key feature to be noted in the powder processing used in this study is the minimization of water consumption to enhance the dispersion of the powders [11]. Transmission electron microscope (TEM, JEM-3000F, JEOL, Japan) was used to observe the agglomerates and particle sizes of each powder. For sintering, the powders were placed in a graphite die (10 mm in diameter) and heat-treated at various temperatures for 5 min under vacuum (∼2.7 Pa) in SPS furnace (Spark Plasma Sintering, ElTek Co., Korea). The pressure and electric current applied during sintering were 37.5 MPa and 1200 A, respectively. The densities of sintered specimens were measured by the standard Archimedes method. Cross-sections of the specimens were mirror-polished for scanning electron microscope (SEM, JSM-5600/JSM-6330F, JEOL, Japan) observation.

Fig. 1 shows TEM photos of commercial and synthesized SnO_2 powders. The difference in primary crystallite size was not so significant; it was 60 nm for commercial powders (Fig. 1a) and 30 nm for synthesized one (Fig. 1b). In contrast, the commercial powders have agglomerates which are much larger than those present in the synthesized one. The average size of agglomerates was determined to be about 800 and 70 nm, respectively. The variation of the relative density and the weight loss obtained from the specimens prepared with a commercial SnO_2 powder was shown in Fig. 2. As can be noted, the densification occurs from the sintering at 1000 °C. The density of the specimen reached the maximum of around 95% of theoretical density at 1050–1100 °C, and then slightly decreased with further increase in sintering temperature. On the other hand, the weight loss began to occur from 1050 °C, and became appreciable at 1100 °C. Based on these results, the optimal sintering temperature for densification of SnO_2 with minimum weight loss is expected to be 1050 °C.

The microstructures of a specimen sintered at 1050 °C for 5 min with 95% of theoretical density are shown in Fig. 3. The specimen was observed to contain many large voids as shown in Fig. 3a, but the regions surrounding the voids are practically fully dense. It was also found that the grains at the porous region were exceptionally large and they exhibited well-developed crystal habit planes (Fig. 3b). Due to the evaporative decomposition of SnO_2 into SnO(g) and O_2(g) [1, 2], the vapor phase inside the isolated pores can be supersaturated during sintering. Furthermore, the thermal conductivity of SnO_2 is relatively low so that the heat evolved by dielectric breakdown during SPS can be piled up at the pore region. In this regard, the grains nearby the pores are expected to have grown excessively by evaporation and condensation process. Indeed, Ahn *et al.* [12] reported that the average grain size of SnO_2 specimen prepared from loosely compacted green body was 7.5 times larger than that from a higher green density.

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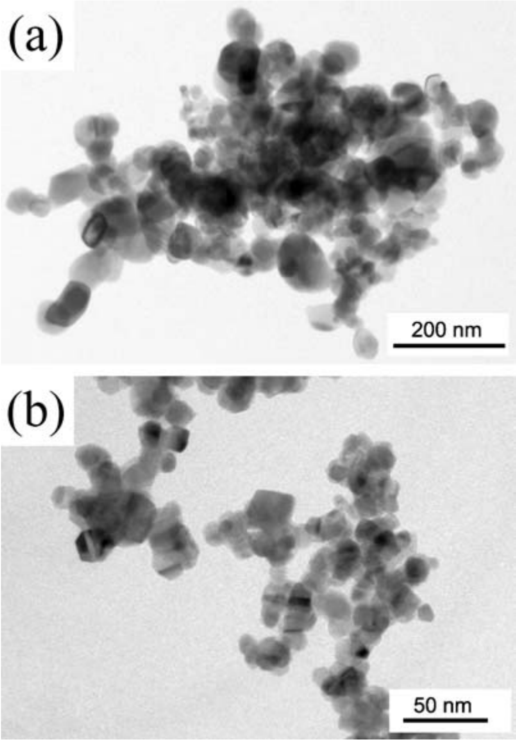

Figure 1 TEM images of agglomerates observed in (a) the commercial SnO_2 powders and (b) the synthesized powders.

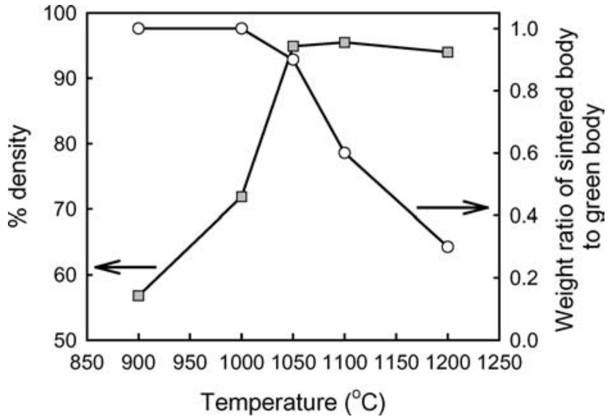

Figure 2 Variation of the relative density and the weight loss with the sintering temperature.

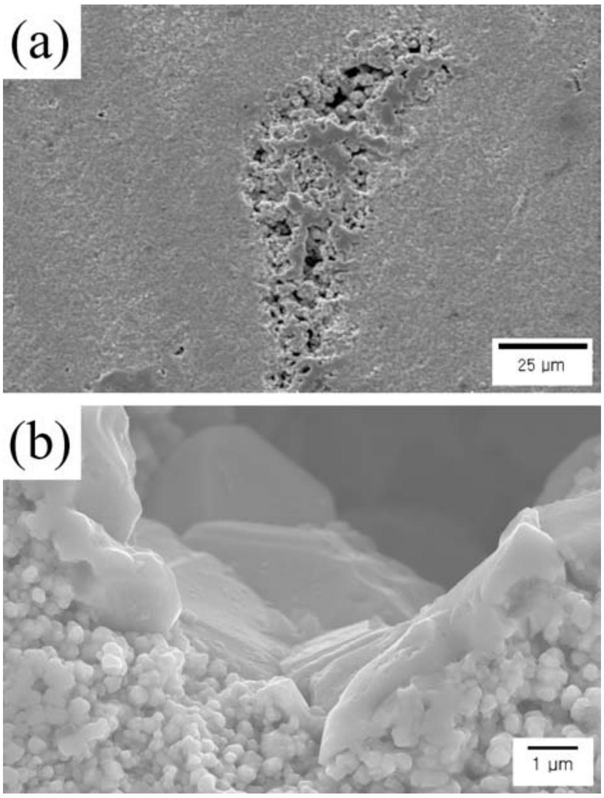

Figure 3 Microstructures of the specimen sintered at 1050°C; (a) low magnification and (b) high magnification of the pore region.

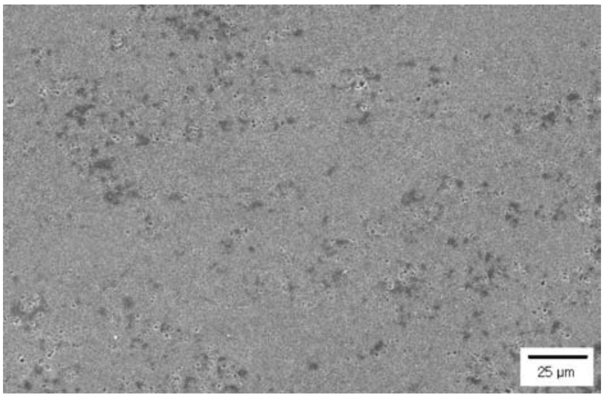

Figure 4 Microstructure of the specimen prepared with a synthesized SnO_2 powder at 1050°C.

In many ceramic systems such as SiC [13], Si_3N_4[13], In_2O_3 [14], ITO [15], ZrO_2 doped Al_2O_3 [16], *etc*., the large pores surrounded by dense regions have been observed to appear particularly when the initial powders were agglomerated [14, 16]. When the green compact is prepared with powders containing agglomerates, the large voids are formed at the initial stage of sintering because the densification within the agglomerates is much faster than that of the matrix. This would be the case observed in the specimen shown in Fig. 3. Indeed, the specimen prepared with a rather well-dispersed synthesized SnO_2 powders showed an enhanced densification without any large pores. Fig. 4 shows a typical microstructure of the specimen treated at 1050 °C for 5 min prepared with synthesized powders. Not only the size of pore was markedly reduced but also the overall microstructure became homogeneous. In this case, almost full densification (>99%) was achieved. This shows that a full densification of pure SnO_2 can be achieved by employing SPS when the well-dispersed powders are used.

In summary, the densification of pure SnO_2 powder compacts was observed to be enhanced by SPS. When commercial SnO_2 powders containing agglomerates were used, however, large voids remained in the microstructure. The difference in densification between agglomerates and the matrix is expected to cause the formation of large voids. With the well-dispersed SnO_2 powders were used, full densification could be achieved by SPS.

Acknowledgments

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