Hot Isostatic Pressing of SnO₂ Prepared by the Hydrazine Method

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SYNOPSIS
Reactive SnO₂ powders have been prepared by the hydrazine method. Their individual particles tend toward a hexagonal morphology with increasing temperature. Well-densified SnO₂ ceramics (99.8% of theoretical) with an average grain size of 0.9 μm have been fabricated by hot isostatic pressing for 2 h at 900°C and 196 MPa. Their Vickers hardness and bending strength are ~14.4 GPa and ~200 MPa, respectively. They exhibit an electrical conductivity of ~5 × 10⁻³ S cm⁻¹ at room temperature.

KEYWORDS
hot isostatic pressing, tin oxide, hydrazine monohydrate, mechanical properties, electrical conductivity

1 Introduction
Tin (IV) oxide SnO₂ (tetragonal, rutile-type structure) is widely used as gas detecting sensors and electrodes for electric glass-melting furnaces. The basic studies for SnO₂ have mainly restricted to single crystals and thin films because of the difficulties in obtaining ceramics with high density. Pure SnO₂ can not be densified by pressureless sintering due to the high vapor pressure of SnO₂ at high temperatures. Therefore, much effort has been devoted to the sintering of SnO₂ with additives such as ZnO, Nb₂O₅, V₂O₅, and Sb₂O₃. On the other hand, Park et al. reported that dense nonadditive SnO₂ ceramics (97.3% of theoretical) were fabricated by hot isostatic pressing for 12 h at 1200°C and 150 MPa. Moreover, pure ceramics with almost full density were prepared by Uematsu in hot isostatic pressing for 1 h at 1300°C and 50 MPa using powders prepared by thermal decomposition of tin oxalate. However, no characterization for dense ceramics, except for microstructures, has been described in the literature.

A new powder preparation method that uses hydrazine monohydrate has recently been developed in many systems. We have successfully prepared reactive SnO₂ powders by applying the same method. The present paper deals with the formation and hot isostatic pressing of SnO₂ prepared by the hydrazine method.

2 Experimental Procedure
Tin metal (Sn, 99.999% pure) and hydrazine monohydrate (NH₂)₂·H₂O were used as starting materials. The former was dissolved in concentrated hydrochloric acid and then adjusted to a concentration of 0.5 mol/L by adding distilled water. A five-necked flask was equipped with a reflux condenser, a dropping funnel, a stirring rod, a thermometer, and a thermocontroller. The solution was introduced in the flask and stirred for 15 min at room temperature, and then, hydrazine monohydrate was added dropwise, with continuous stirring, until the resulting suspension reached pH 9. The resulting suspension was then heated for 2 h at 80°C. The product was separated from the suspension via centrifuging, washed more than ten times in hot water to remove adsorbed hydrazine and chloride ion (tested by adding a AgNO₃ solution), and then dried at 140°C under reduced pressure.

Differential thermal analysis (DTA) was conducted in air at a heating rate of 10°C/min; α-Al₂O₃ was used as the reference. The as-prepared powder and specimens, obtained from DTA runs after cooling, were examined by X-ray diffraction (XRD) using Ni-filtered CuKα radiation. They were observed by transmission electron microscopy (TEM). Sintering was performed by hot isostatic pressing (HIPing) using argon gas as the pressure-transmitting medium. Before HIPing, calcined powders were pressed into pellets at 30 MPa by uniaxial pressing and then isostatically cold pressed at 343 MPa. The green compacts, covered with α-Al₂O₃, were subjected to HIPing for 2 h at 1300°C and 196 MPa. The green compacts, covered with α-Al₂O₃, were subjected to HIPing for 2 h at 1300°C and 196 MPa. The HIPed compacts were examined by XRD and transmission electron microscopy (TEM). The microstructures of the HIPed compacts were examined by transmission electron microscopy (TEM).

1998年12月
powders (~200μm), were sealed in a Pyrex glass tube under a reduced pressure of 1.3 × 10⁻¹³ Pa. HIPping conditions were as follows: (1) heating rate of 600°C/h, (2) increasing pressure rate of 180 MPa/h above 800°C, and (3) sintering for 2 h at 900° to 1200°C under 196 MPa. Bulk densities after polishing with diamond paste were determined by the Archimedes method. Scanning electron microscopy (SEM) was used for microstructural observations.

3 Results and Discussion

3.1 Formation of SnO₂

XRD analysis showed that the as-prepared powder was a mixture of SnO and SnO₂. Figure 1 shows a TEM photograph of the as-prepared powder, indicating that SnO and SnO₂ are needlelike and flake forms, respectively. In the DTA a broad exothermic peak resulting from the oxidation of SnO was observed at ~450° to ~690°C. No significant structural change of the as-prepared powder was recognized on heating up to the exothermic temperature. Powders heated at temperatures above the peak showed the XRD pattern of SnO₂. The lattice parameters of SnO₂ (tetragonal) prepared by heating for 1 h at 700°C were a=0.4738 and c=0.3187 nm, agreeing with data (a=0.4738 and c=0.3188 nm) reported previously. Figure 2 shows TEM photographs for SnO₂ powders heated to various temperatures.
temperatures. Fine particles (~30nm) were observed in powder at 700°C. They grew to ~70 and ~120 nm at 900°C and 1100°C, respectively, and attained ~200 nm at 1300°C. In addition, powders with increasing temperature consisted of particles showing morphology with a thin hexagonal plate.

3.2 Fabrication and Microstructure of SnO2 Ceramics
Calcined powders were prepared by heating for 2 h at 700°C and HIPed as already described. Phases on the fracture surfaces of the sintered compacts consisted of only SnO2. Table 1 shows the bulk and relative densities of SnO2 ceramics. In the calculation of the relative densities, the theoretical density of SnO2 was assumed to be 6.995 g/cm³. Highly sintered SnO2 ceramics were fabricated under the present HIPing conditions. It should be noted that an HIPing temperature as low as 900°C resulted in the ceramics with almost full density.

Figures 3(a) and (b) respectively show SEM photographs for polished and fracture surfaces of SnO2 ceramics HIPed at 900°C. Hardly any pores in the texture were observed (Fig.3(a)), and the ceramics had a microstructure whose average grain size, as determined by a linear intercept method, was 0.9μm. The ceramics HIPed at 900°C to 1200°C consisted of smaller grains (Fig.4 and Table 1) than those (2.4 and 3μm) appeared in the literature. This must be explained in terms of low-temperature and short-time HIPing.

3.3 Mechanical Properties and Electrical Conductivity
Test samples (~3 x 3 x 20mm) for mechanical measurements were cut from sintered SnO2 with a diamond saw and then lapped with diamond paste. Vickers hardness \( (H_v) \) was measured by the microindentation technique with a 2.94-N load. Three-point bending strength \( (\sigma_b) \) was measured with a 16 mm span and a crosshead speed of 0.5 mm/min. As shown in Fig.5, ceramics HIPed at 900°C gave the highest values in which \( H_v \) and \( \sigma_b \) were ~14.4 GPa and ~200 MPa, respectively; the values were higher than those \( (H_v=7-11 \text{ GPa and } \sigma_b=69-103 \text{ MPa}) \) of TiO2 (rutile) ceramics. They decreased linearly with increased HIPing temperature. The results suggest that the mechanical properties, as well as other ceramics, were strongly dependent on the grain size. Matsushita and Yamaib examined the bending strength of SnO2-based composite ceramics with oxide additives, in which the relative densities were ~55-~95% and reported that their strength increased with increased density. The maximum strength of ~140 MPa was obtained in the composite ceramics with 10 wt% Sb2O3 and 2 wt% CuO additions. Highly sintered pure SnO2 ceramics HIPed at lower temperatures were found to show the higher strength than the composite ceramics containing up to 20 wt% Sb2O3 with small amounts of CuO, ZnO, or MnO2.

The electrical conductivity of ~1 mm thick samples with a Pt electrode heated for 1 h at 850°C was measured at room temperature by a two-probe technique using an impedance analyzer at a frequency of 100 kHz. Conductivities showed the value of \( \sim 5 \times 10^{-3} \text{ S \cdot m}^{-1} \), irrespective of grain sizes (0.9–1.7μm), in agreement with the data of doped-ceramics reported in Refs.4 and 6, in contrast to high values of the ceramics with small amount of Sb2O3 and single crystals.

4 Conclusions
The sintering of pure SnO2 occurs mainly by the evaporation-condensation mechanism; dense ceramics can not be obtained by either pressureless sintering or hot pressing. Much works have been focused on the sintering of SnO2 with additives. In the present study, reactive SnO2...
Noriyuki Maeda, Masaru Yoshinaka, Ken Hirota, Osamu Yamaguchi

Fig.4 SEM photographs for fracture surfaces of SnO₂ ceramics HIPed at (a) 1000°C, (b) 1100°C, and (c) 1200°C.

Powders have been prepared by the hydrazine method. Pure SnO₂ ceramics with almost full density, in which the average grain size is 0.9μm, can be fabricated by hot isostatic pressing (900°C/2h/196MPa). Their Vickers hardness and bending strength are ~14.4 GPa and ~200 MPa, respectively. Electrical conductivities exhibit the value of ~5 × 10⁻³ S·m⁻¹ at room temperature.

Acknowledgment
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References
2) Z.M.Jarzebski and J.P.Marton: "Physical Properties of

Table 1 Characteristics of SnO₂ ceramics fabricated by hot isostatic pressing

<table>
<thead>
<tr>
<th>HIPing temperature (°C)</th>
<th>Bulk density (g/cm³)</th>
<th>Relative density (%)</th>
<th>Grain size (μm)</th>
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</thead>
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<tr>
<td>900</td>
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<td>99.8</td>
<td>0.9</td>
</tr>
<tr>
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<td>99.8</td>
<td>1.1</td>
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<td>6.99</td>
<td>99.9</td>
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<tr>
<td>1200</td>
<td>6.99</td>
<td>99.9</td>
<td>1.7</td>
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</tbody>
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Fig.5 (a) Bending strength σ_b and (b) Vickers hardness H_v of SnO₂ ceramics as a function of HIPing temperature.


3) H.E.Matthews and E.E.Kohnke: "Effect of Chemisorbed Oxygen on the Electrical Conductivity


10) Powder Diffraction File, No. 6-0395, Joint Committee on Powder Diffraction Standards, Swarthmore, PA.


