研 究

Hot Isostatic Pressing of SnO_2 Prepared by the Hydrazine Method

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Received July 29, 1998

SYNOPSIS

Reactive SnO_2 powders have been prepared by the hydrazine method. Their individual particles tend toward a hexagonal morphology with increasing temperature. Well-densified SnO_2 ceramics (99.8% of theoretical) with an average grain size of $0.9\mu\text{m}$ have been fabricated by hot isostatic pressing for 2 h at 900°C and 196 MPa. Their Vickers hardness and bending strength are $\sim 14.4\text{ GPa}$ and $\sim 200\text{ MPa}$, respectively. They exhibit an electrical conductivity of $\sim 5 \times 10^{-3}\text{ S}\cdot\text{cm}^{-1}$ at room temperature.

KEY WORDS

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

1 Introduction

Tin (IV) oxide SnO_2 (tetragonal, rutile-type structure) is widely used as gas detecting sensors and electrodes for electric glass-melting furnaces. The basic studies for SnO_2 have mainly restricted to single crystals and thin films because of the difficulties in obtaining ceramics with high density¹⁾. Pure SnO_2 can not be densified by pressureless sintering due to the high vapor pressure of SnO_2 at high temperatures^{1,2)}. Therefore, much effort has been devoted to the sintering of SnO_2 with additives such as ZnO ^{1,3)}, Nb_2O_5 ⁴⁾, V_2O_5 ⁵⁾, and Sb_2O_3 ⁶⁾. On the other hand, Park *et al.*⁷⁾ reported that dense nonadditive SnO_2 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 Uematsu⁸⁾ 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^{7,8)}.

A new powder preparation method that uses hydrazine monohydrate has recently been developed in many systems⁹⁾. We have successfully prepared reactive SnO_2 powders by applying the same method. The present paper deals with the formation and hot isostatic pressing of SnO_2 prepared by the hydrazine method.

2 Experimental Procedure

Tin metal (Sn, 99.999% pure) and hydrazine monohydrate

$((\text{NH}_2)_2\cdot\text{H}_2\text{O})$ were used as starting materials. The former was dissolved to 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 AgNO_3 solution), and then dried at 140°C under reduced pressure.

Differential thermal analysis (DTA) was conducted in air at a heating rate of $10^\circ\text{C}/\text{min}$; $\alpha\text{-Al}_2\text{O}_3$ 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 $\text{CuK}\alpha$ 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 98 MPa by uniaxial pressing and then isostatically cold pressed at 343 MPa. The green compacts, covered with $\alpha\text{-Al}_2\text{O}_3$

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powders ($\sim 200\mu\text{m}$), were sealed in a Pyrex glass tube under a reduced pressure of 1.3×10^{-1} Pa. HIPing 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 SnO_2

XRD analysis showed that the as-prepared powder was a mixture of $\text{SnO}^{(10)}$ and $\text{SnO}_2^{(11)}$. Figure 1 shows a TEM photograph of the as-prepared powder, indicating that SnO and SnO_2 are needlelike and flake forms, respectively. In the DTA a broad exothermic peak resulting from the oxidation of SnO was observed at $\sim 450^\circ$ to $\sim 690^\circ\text{C}$. 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 SnO_2 . The lattice parameters of SnO_2 (tetragonal) prepared by heating for 1 h at 700°C were $a=0.4738$ and $c=0.3187\text{ nm}$, agreeing with data ($a=0.4738$ and $c=0.3188\text{ nm}$) reported previously⁽¹¹⁾. Figure 2 shows TEM photographs for SnO_2 powders heated to various

Fig.1 TEM photograph of as-prepared powder.

Fig.2 TEM photographs of SnO_2 powders heated to (a) 700° , (b) 900° , (c) 1100° , and (d) 1300°C .

temperatures. Fine particles (~30nm) were observed in powder at 700°C. They grew to ~70 and ~120 nm at 900° 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/cm³¹¹⁾. 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° to 1200°C consisted of smaller grains (Fig.4 and Table 1) than those (2.4 and 3μm)^{7,8)} 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 × 3 × 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 (σ_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 σ_b were ~14.4 GPa and ~200 MPa, respectively; the values were higher than those (H_v =7–11 GPa and σ_b =69–103 MPa) of TiO₂ (rutile) ceramics¹²⁾. 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 Yamai⁶⁾ 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 MnO₂⁶⁾.

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 $\sim 5 \times 10^{-3} \text{ S} \cdot \text{m}^{-1}$ 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 Sb₂O₃¹³⁾ and single crystals¹⁴⁾.

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

Fig.3 SEM photographs for (a) polished and (b) fracture surfaces of SnO₂ ceramics HIPed at 900°C.

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

This work was supported by a grant to Research Center for Advanced Science and Technology at Doshisha University from the Ministry of Education, Japan.

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Table 1 Characteristics of SnO₂ ceramics fabricated by hot isostatic pressing

HIPing temperature (°C)	Bulk density (g/cm ³)	Relative density (%)	Grain size (μm)
900	6.98	99.8	0.9
1000	6.98	99.8	1.1
1100	6.99	99.9	1.4
1200	6.99	99.9	1.7

Fig.5 (a) Bending strength σ_b and (b) Vickers hardness H_v of SnO₂ ceramics as a function of HIPing temperature.

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