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Preparation of Zn_2TiO_4 by co-precipitation method and hot-isostatic pressing

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Zn_2TiO_4 powder was prepared by the co-precipitation method using an organic basic, diethylamine solution. X-ray and differential thermal analysis-thermogravimetric (DTA-TG) analyses of the dried coprecipitate showed the intimacy of mixing attained. Although crystallite size was dependent on calcining temperature, the particle size was independent. The optimum density was obtained by calcining at 800° C. The highest density which was obtained by sintering at 1150° C was about 95% theoretical with closed porosity. The pre-sintered samples were hot-isostatically sintered at 1150° C in argon for 2 h under 80 to 150 MPa without any capsule. The density of hot-isostatically sintered samples reached about 100% and they became translucent.

1. Introduction

Hot-isostatic pressing (HIP) is an effective method used to enhance the densification of ceramics [1–3]. HIP is usually carried out in two steps: (1) sintering a specimen to high density without open pores, (2) the specimen is hot isostatically pressed. Ceramics with closed pores are often prepared at relatively low temperature by the co-precipitation method which is effective to prepare sinterable powders [4, 5]. Therefore, it can be supposed that the HIP conditions may be reduced when the powders are prepared by the co-precipitation method.

It is well known that Zn_2TiO_4 is difficult to sinter to high density because of the vaporization of ZnO [6]. Therefore, HIP may be effective to densify Zn_2TiO_4 ceramics whose powder is prepared by the co-precipitation method. In this study, the HIP of powders resulting from the co-precipitation is described.

2. Experimental procedure

As a starting material, reagent-grade ZnO was chosen for the zinc component. A solution containing zinc ions was prepared by dissolving ZnO in 2 N HNO_3. For the titanium component, a solution containing reagent-grade $TiCl_4$ or $TiOSO_4$ was chosen. These two solutions were mixed in a ratio of Zn : Ti = 2 : 1. Both titanium and zinc were precipitated as hydroxides in basic solution. However, ammonium hydroxide was found to be unsuitable to precipitate zinc ions, because it reacts to make soluble $[Zn(NH_3)_6]^{2+}$. Therefore, the mixed solution was titrated to an organic basic, diethylamine solution. During titration, the pH of the solution was kept between 11 and 12. The precipitate was washed, filtered and dried at 120° C.

The precipitate obtained was calcined in air for 2 h at various temperatures from 600 to 900° C. For sintering, the calcined powder was pressed at 50 MPa into discs 12 mm diameter and 6 mm long, and then pressed hydrostatically at 160 MPa. Thereafter it was sintered in oxygen for 2 h at various temperatures from 900 to 1300° C.

The pre-sintered samples were put into an alumina crucible without any capsule. The alumina crucible was introduced into a platinum furnace and placed in a high-pressure vessel. The HIP experiments were done under conditions of 1150° C for 2 h in argon and 80 to 150 MPa.

X-ray diffraction analysis was performed using a Rigakudenki X-ray diffractometer (Cu*Kα*). Thermal analysis was done using Rigakudenki DTA-TG. The surface areas of the calcined powders were measured using a Microtrac Betasorb Model 4200 by the BET method. Particle-size distribution was measured using a Seisin Co. SKA 5000 by the sedimentation method. HIP was carried out by an apparatus manufactured by Kobe Steel Co. Ltd (Cho-ku, Kobe, Japan).

3. Results and discussion

3.1. Preparation of Zn_2TiO_4

X-ray diffraction analysis results suggested that the dried co-precipitate was amorphous, while the precipitate heated at 550° C showed pure Zn_2TiO_4 phase. The dried precipitate of the titanium component was also amorphous but yielded mixed phases of rutile and

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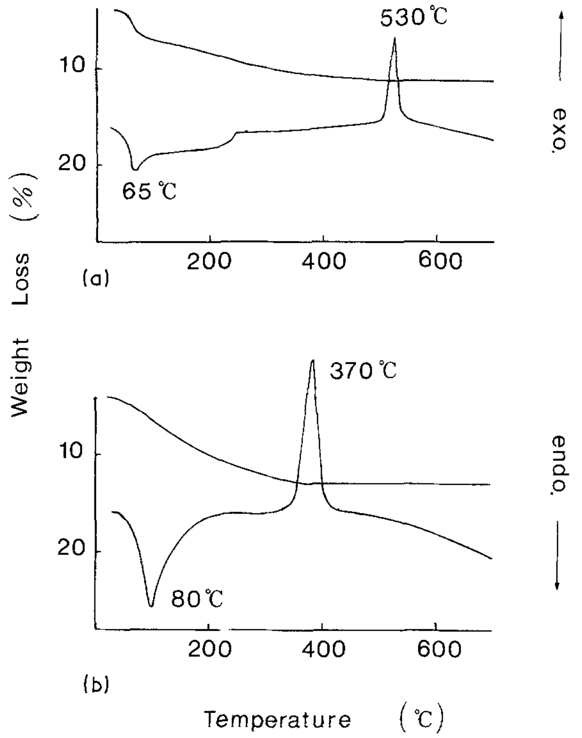

Figure 1 Results of DTA-TG; (a) dried co-precipitate; (b) dried precipitate of the titanium component. Heating rate = 10° C min^{-1}.

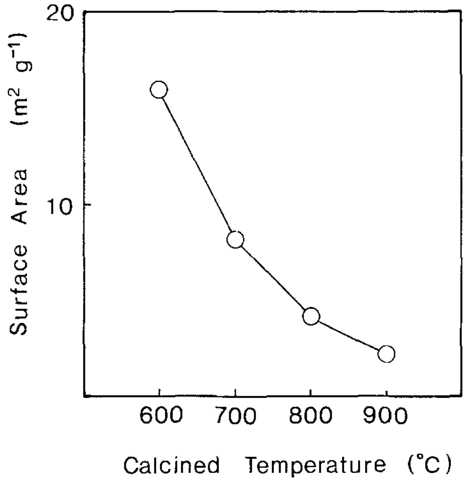

Figure 2 Specific surface area of the calcined powder.

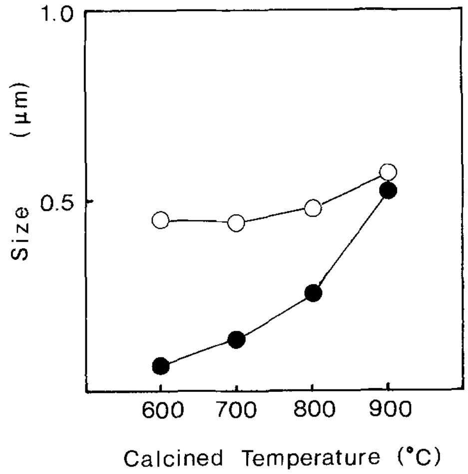

Figure 3 Average particle size (○) and crystallite size (●).

Figure 4 Transmission electron micrographs of Zn_2TiO_4 powders calcined at 800° C.

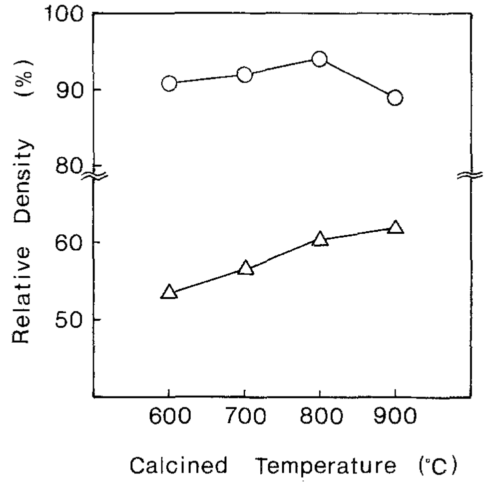

Figure 5 The effect of calcination temperature upon (○) unfired and (△) sintered (1250° C, 2 h) of Zn_2TiO_4 compacts.

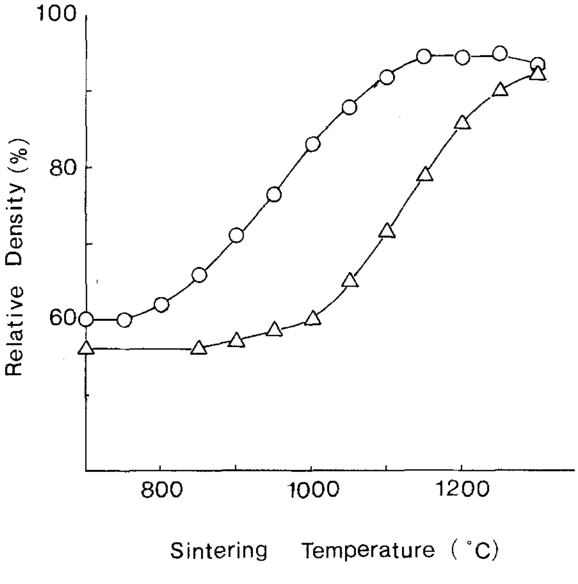

Figure 6 The change in sintered density of the powders prepared by (○) co-precipitation method and (△) solid-state reaction.

TABLE I HIP results

Sample no. (preparation)	HIP condition		Before HIP		After HIP	
	Temperature (° C)	Pressure (MPa)	Density (%)	Grain size (μm)	Density (%)	Grain size (μm)
1 (c.p.*)	1150	80	95	2.8	100	3.0
2 (c.p.)	1150	120	95	2.8	100	3.2
3 (c.p.)	1150	150	95	2.8	100	3.5
4 (s.s.†)	1150	150	93	6.8	95	7.0

*c.p. coprecipitation.
†s.s. solid state reaction.

anatase after heating to 550° C. The only dried precipitate of the zinc component was ZnO.

Differential thermal analysis-thermogravimetry (DTA-TG) was performed on the precipitates of the individual metal components as well as on the co-precipitate for comparison. The results of DTA–TG are shown in Fig. 1. The weight loss of the dried co-precipitate ended about 530° C with an exothermic peak, and the weight loss of the titanium component ended about 370° C with an exothermic peak. On the other hand, the dried precipitate of the zinc component showed a small weight loss (about 1%) and showed no peak until 700° C. The thermal behaviour of the co-precipitate was different from the precipitates of individual metal components, and this result is in close agreement with the X-ray data.

These results showed the intimacy of mixing attained by the co-precipitation method and the effectiveness of using an organic basic solution instead of ammonium solution.

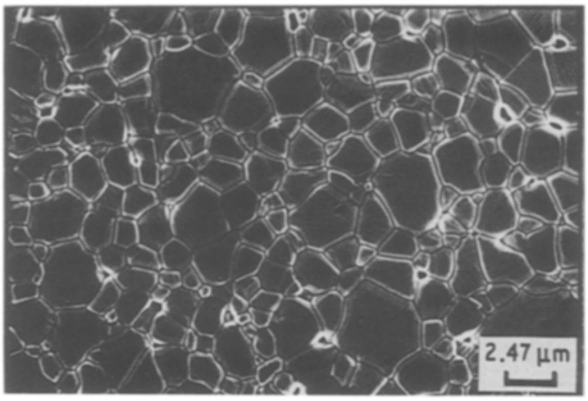

Figure 7 Scanning electron micrographs of Zn_2TiO_4 compact sintered at 1150° C.

3.2. Powder characterization and sintering

The specific surface areas of Zn_2TiO_4 powders calcined in the temperature range 600 to 900° C for 2 h are shown in Fig. 2. A continuous decrease in the surface area with increasing temperature is seen.

The average particle size of the calcined powders and their crystallite size estimated from surface area measurements are shown in Fig. 3. The average particle size was about 0.5 to 0.6 μm, i.e. particle growth did not occur. On the other hand, the crystallite size increased rapidly. The particle size of the calcined precipitate at 600° C was about eight times the crystallite size. However, the particle size of the calcined precipitate at 900° C was nearly equal to the crystallite size.

The crystallite size of the calcined precipitate at 600° C is seen to be about 0.1 μm and that of the calcined precipitate at 900° C is seen to be about 0.5 μm. The results of the tranmission electron microscopy (TEM) are shown in Fig. 4. The results of TEM observation agreed with the crystallite size estimated from the surface area measurement. These results show the agglomeration of the powder. Therefore, sintering appeared to occur within aggregates during the heat treatment to 900° C. Such an agglomeration is often seen in powders prepared by a co-precipitation.

The effect of calcination temperature on the densities of unfired and sintered (1250° C, 2 h) Zn_2TiO_4 compacts is shown in Fig. 5, in which the density of the unfired compacts increased in this temperature range. However, the highest density was obtained for samples calcined at 800° C.

Fig. 6 shows the changes of the sintered density in the powder prepared by both co-precipitation and solid-state reaction for comparison (reagent grade ZnO and TiO_2 were ball milled in ethanol for 20 h and

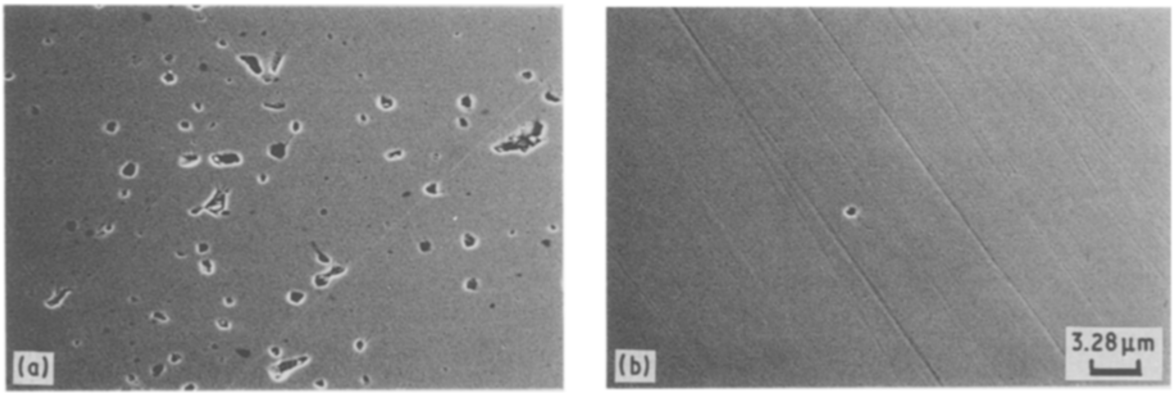

Figure 8 Typical scanning electron micrographs of samples (a) before HIP and (b) after HIP.

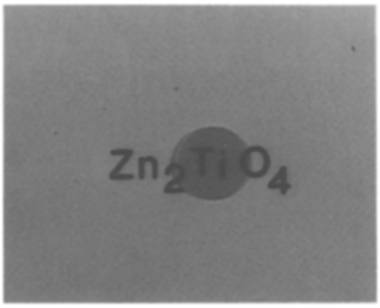

Figure 9 Polished sample (0.3 mm thick) after HIP at 1150° C for 2 h in argon under 120 MPa.

calcined at 1000° C). The rapid shrinkage began about 900° C with the highest relative density was about 95% for the co-precipitated powders. Fig. 7 shows a scanning electron micrograph of the Zn_2TiO_4 which was sintered at 1150° C. Its average grain size was about 2.8 μm with closed porosity. On the other hand, the density of the samples prepared by solid state reaction did not reach 95% theoretical.

3.3. HIP

The pre-sintered samples prepared by co-precipitation and solid-state reaction were sintered by HIP at 1150° C for 2 h in argon under 80 to 150 MPa without any capsule. After HIP, the colour of these samples was black and their electrical resistance was lower. Perhaps these would be reduced during HIP by the fireproof materials used in the heater unit. The samples were annealed at 800° C in air for 1 h, and they turned white.

Table I shows the results of the HIP experiments. Because of the hot-isostatic sintering, the relative densities of the samples prepared by co-precipitation increased to about 100%. Figs 8a and b show typical scanning electron micrographs before and after HIP. The elimination of pores led to an appreciable increase in transparency. Fig. 9 shows the polished sample (0.3 mm thick) after HIP under 120 MPa. SEM observation of the thermally etched samples showed that the grain size did not significantly change during HIP. On the other hand, the relative densities of the samples prepared by solid-state reaction did not increase to full density.

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