

Effect of  $\text{TiO}_2$  on Characteristics of  $\text{Al}_2\text{O}_3/\text{ZrO}_2$   
Composite Powders

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ABSTRACT

A uniform  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  (ZTA) composite powder was obtained from the hydrolysis of  $\text{Zr/Ti}-(\text{OC}_3\text{H}_7)_4$  in an  $\text{Al}_2\text{O}_3$  slurry, which contains 2.5 mole%  $\text{TiO}_2$ . During calcination, the existence of  $\text{TiO}_2$  hinders the growth and the t $\rightarrow$ m phase transformation of  $\text{ZrO}_2$  particles in ZTA powders.  $\text{TiO}_2$  also enhances the sinterability of ZTA composite powders and increases the remaining tetragonal  $\text{ZrO}_2$  content in sintered ZTA specimen.

INTRODUCTION

Zirconia-toughened-alumina (ZTA) ceramics is used in various mechanical applications[1] because of its high strength and toughness. The sintering behavior and mechanical properties of ZTA ceramics depend on not only the  $\text{Al}_2\text{O}_3$  matrix, but also the  $\text{ZrO}_2$  content, the size of  $\text{ZrO}_2$  grains and the fraction of tetragonal  $\text{ZrO}_2$  [2,3].

The authors [4] have reported that uniform ZTA composite powder from the hydrolysis of  $\text{Zr/Ti}$ -alkoxide in an  $\text{Al}_2\text{O}_3$  slurry, which contain small amounts of  $\text{TiO}_2$ , could lower sintering temperature of ZTA specimen. The aim of the present work is to investigate the effect of  $\text{TiO}_2$  on the characteristics of ZTA composite powders.

EXPERIMENTAL

$\alpha$ - $\text{Al}_2\text{O}_3$  powder (0.5 $\mu\text{m}$  in grain size and 99.99% purity) and zirconium (IV) propoxide were used as the starting materials.  $\text{TiO}_2$  additive was introduced by the addition of tetraisopropyl orthotitanate (TPT). The amount of  $\text{Zr}(\text{OC}_3\text{H}_7)_4$  was adjusted to provide 15 mole%  $\text{ZrO}_2$ , and the amount of TPT provided 2.5 mole%  $\text{TiO}_2$  in the final mixed powder. The concentration of  $\text{TiO}_2$  was kept below the total solubility limit in  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  [5,6]. Alumina powders were thoroughly mixed with predetermined amounts of  $\text{Zr}(\text{OC}_3\text{H}_7)_4$  and TPT in ethanol for 5hr, then hydrolyzed by

adding to it a 12M water/ethanol solution. After mixing for 5hr, the solvent was removed by vacuum drying at 40°C, and the powders were completely dried at 110°C. The dried powders were calcined at 450-1050°C for 1hr, then pressed isostatically under 98MPa to obtain bars with the dimension of 5x5x45 mm. The compacts were heated in air at a rate of 6 °C/min to 1500°C, held for 2hr and cooled down in the furnace. Linear thermal shrinkage was measured by using a non-loading dilatometer. The crystalline phases were identified by X-ray diffraction technique. The relative percentage of tetragonal ZrO<sub>2</sub> was determined as follows [7]:

$$X_t = \frac{I_t(111)}{I_m(11\bar{1}) + I_t(111) + I_m(111)} \times 100\%$$

$I(hkl)$  : intensity of (hkl) plane  
 $m$  : monoclinic phase  
 $t$  : tetragonal phase  
 $X_t$  : relative percentage of t-ZrO<sub>2</sub>

The bulk density of sintered specimen was measured by the Archimedes' method using water as the immersion medium, and expressed in a relative scale as the ratio of bulk density to theoretical density. The microstructure was observed by scanning electron microscope (SEM) and transmission electron microscope (TEM). The symbol AZ represents ZTA with the composition of 15 mole% ZrO<sub>2</sub>, while ATZ represents that of 15 mole% ZrO<sub>2</sub> and 2.5 mole% TiO<sub>2</sub>.

## RESULTS AND DISCUSSION

### 1. Characteristics of composite powders

TEMs of AZ and ATZ powders dried at 110°C (Fig.1(A) & (B)) show that hydrolyzed ZrO<sub>2</sub> gels coat uniformly individual Al<sub>2</sub>O<sub>3</sub> particle, and condense into ultrafine sub-rounded particles after calcination at 850°C (Fig.1(C)(D)). Comparing AZ and ATZ powders calcined at 850°C, it can be seen that the ZrO<sub>2</sub> particle size in ATZ powder is smaller. This result may support that the addition of TiO<sub>2</sub> hinders the ZrO<sub>2</sub> coalescence during calcination.

XRD results of AZ and ATZ powders are shown in Fig.2. The ZrO<sub>2</sub> gels in both powders are amorphous after dried at 110 °C. During heating the crystallization behavior of ZrO<sub>2</sub> is much different for these two powders. In the case of ATZ, amorphous ZrO<sub>2</sub> still remains after calcination at 450°C and only tetragonal ZrO<sub>2</sub> crystallites are formed when calcined between 650-850 °C. While for AZ, both tetragonal and monoclinic ZrO<sub>2</sub> are formed after calcination above 450°C. The results indicate that the addition of TiO<sub>2</sub> also hinders t→m phase transformation of ZrO<sub>2</sub> gel during calcination.

### 2. Sinterability

The instantaneous relative density of powder compacts (Fig.3) was calculated from linear thermal shrinkage using the

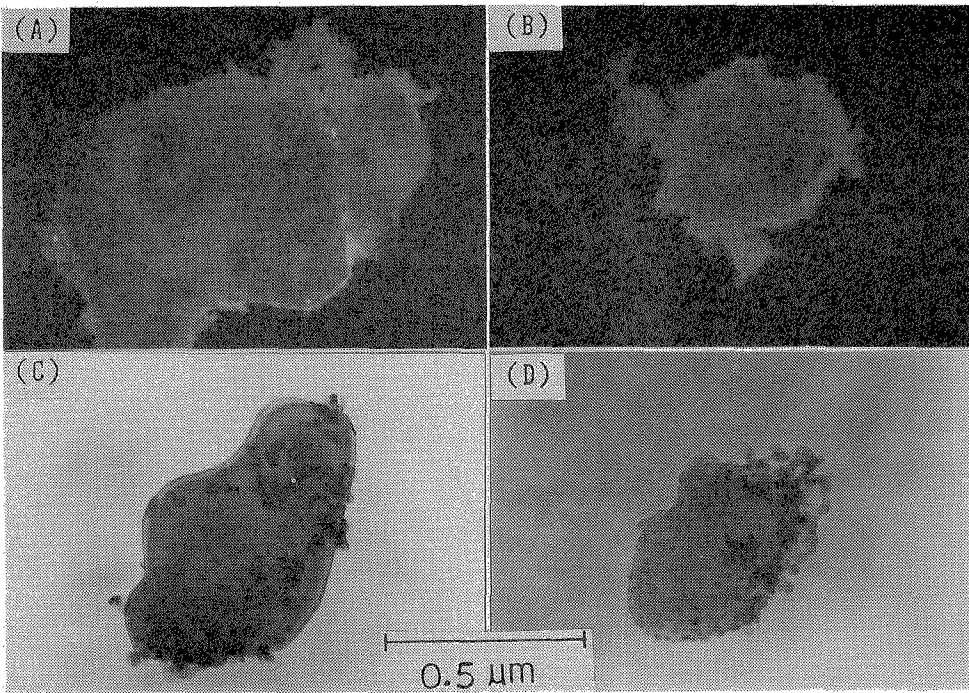


Fig.1. TEMs of AZ and ATZ powders:(A) and (C); AZ, (B) and (D); ATZ, (A) and (B) dried at 110°C, (C) and (D) calcined at 850°C.

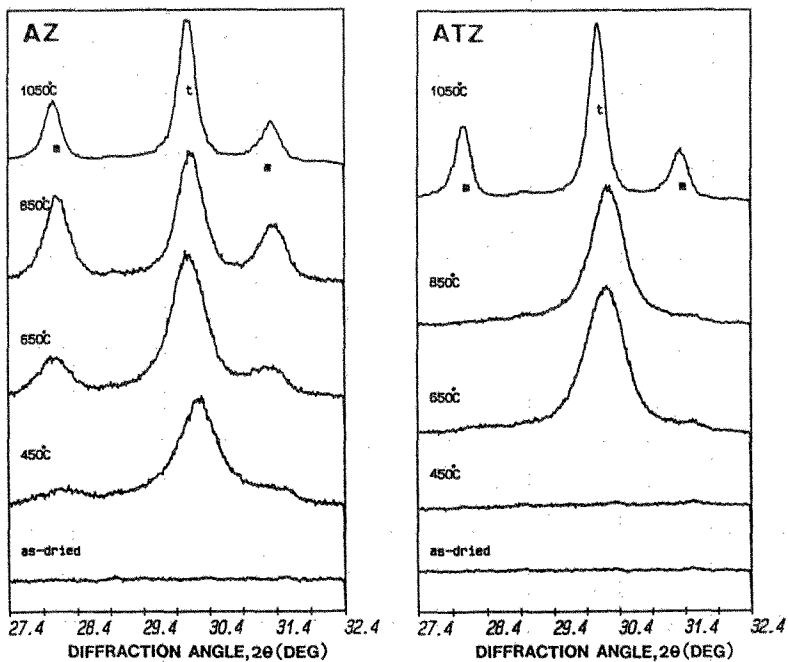


Fig.2. X-ray diffraction patterns of AZ and ATZ specimens calcined at 450-1050°C.

method described by Wang et al. [8]. The instantaneous densification rates obtained by differentiating the curves shown in Fig.3, are presented in Fig.4. For both specimens, the start of densification occurs at about 1250 °C. However, the densification rate of ATZ was raised up to 2.6 %/min at 1470 °C, though the maximum densification rate of AZ was only about 0.5 %/min at 1500 °C. Furthermore, when specimens were held at 1500 °C for 0.5hr, the instantaneous relative density of ATZ is 99%, but only 80% for AZ specimen.

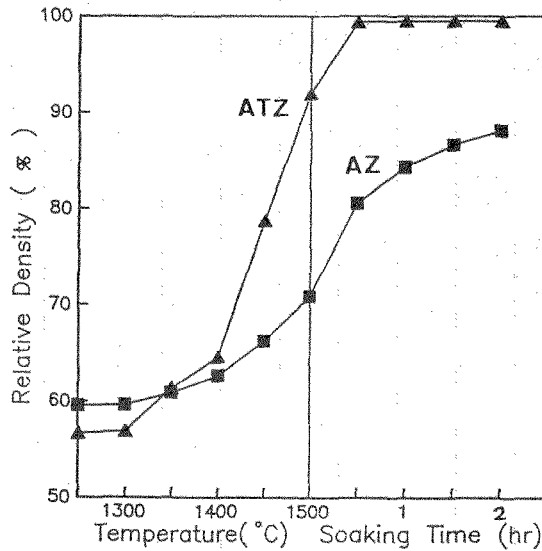


Fig.3. Relative densities of AZ and ATZ specimens.

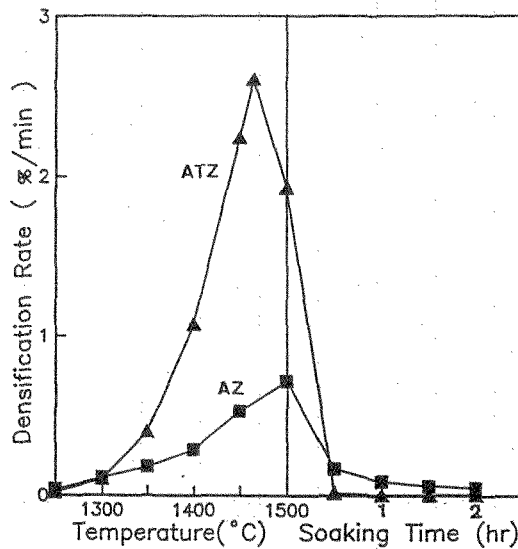


Fig.4. Densification rate of AZ and ATZ specimens.

Figure 5 illustrates the relationship between the relative density of sintered bodies at 1500°C for 2hr and the calcination temperature of the powders. The relative density increases with increasing calcination temperature upto 850 °C. The relative density of ATZ is higher than that of AZ under the every calcination condition. The ATZ specimens calcined between 650-850 °C were densified to 99% relative density.

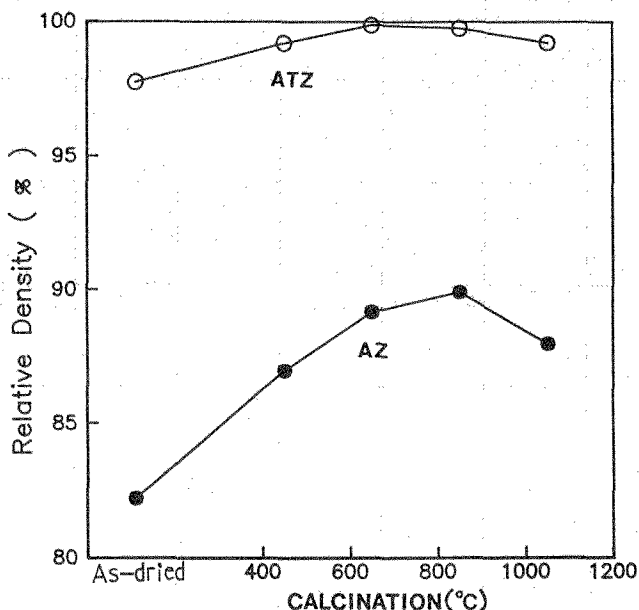


Fig.5. Relative densities of AZ and ATZ specimens with different calcination temperature.

### 3. Microstructure of sintered bodies

Figure 6 shows scanning electron micrographs of polished and thermally etched surface of the AZ and ATZ specimens calcined at 850 °C and then sintered at 1500°C for 2hr. It can be seen that the AZ specimen has small grain size and a porous structure as compared to the large grain size and dense structure of the ATZ specimen. The value of  $X_t$  analyzed from the surface of sintered specimens as a function of calcination temperature is shown in Fig.7. It is shown that ATZ specimen calcined at 850°C has the highest  $X_t$  value of 96%. The above results suggest that the stability of t-ZrO<sub>2</sub> within Al<sub>2</sub>O<sub>3</sub> matrix does not depend simply on the constraint of Al<sub>2</sub>O<sub>3</sub> matrix or grain size effect. The presence of TiO<sub>2</sub> also has significant effects on the retention of t-ZrO<sub>2</sub>. It is believed that higher t-ZrO<sub>2</sub> content can efficiently improve the toughness of ZTA ceramics due to the phenomena of transformation toughening or microcrack toughening, both of which need further study.

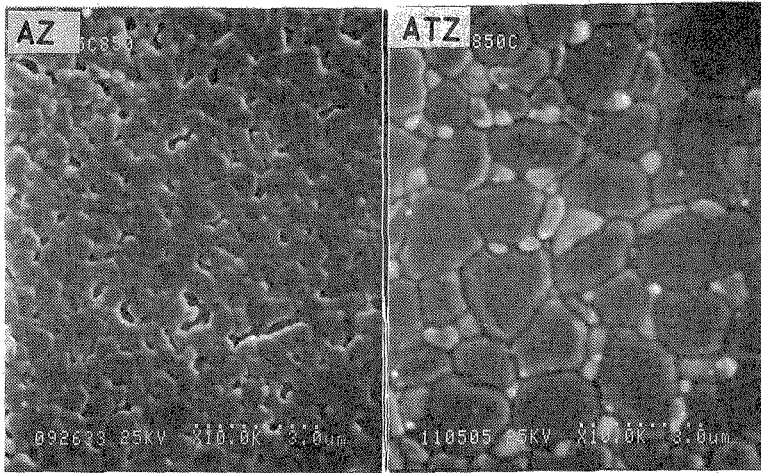


Fig.6. SEMs of AZ and ATZ specimens calcined at 850°C then sintered at 1500°C for 2h.

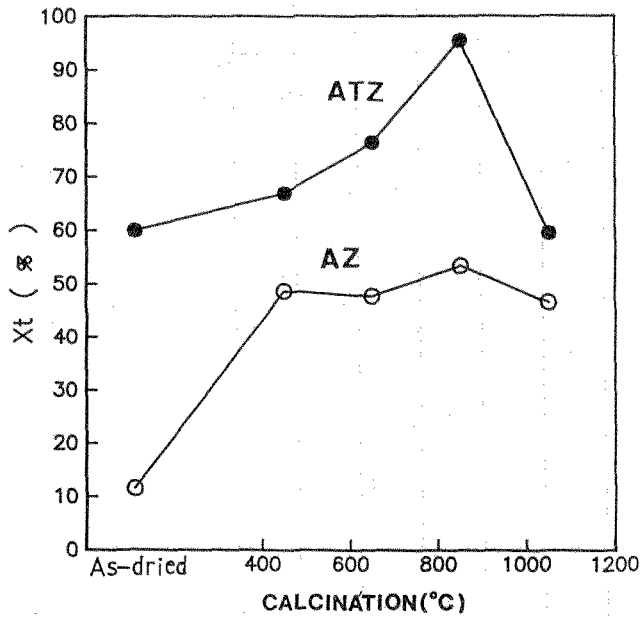


Fig.7. Tetragonal zirconia percent of specimens as a function of calcination temperature.

## CONCLUSION

$\text{Al}_2\text{O}_3$  powder,  $\text{Zr}(\text{OC}_3\text{H}_7)_4$  and  $\text{Ti}(\text{OC}_3\text{H}_7)_4$  were used to synthesize ZTA composite powder, which contains 15 mole%  $\text{ZrO}_2$  and 2.5 mole%  $\text{TiO}_2$ . The addition of  $\text{TiO}_2$  had significant influence on the forming of crystalline phases from  $\text{ZrO}_2$  gels, the growth and the t $\rightarrow$ m phase transformation of  $\text{ZrO}_2$  particles during calcination.  $\text{TiO}_2$  also enhanced the sinterability of ZTA composite powders. The sintered specimen with relative densities >99% could be obtained under condition of 850 °C/1h calcination and 1500 °C/1h sintering. Furthermore,  $\text{TiO}_2$  improved the retention of tetragonal  $\text{ZrO}_2$  phase in the sintered ZTA body.

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