研 究

Formation and Sintering of Alkoxy-derived Al_2O_3 - TiO_2 Composite Powders

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In the Al_2O_3 - TiO_2 system, solid solutions of $\text{AlO}(\text{OH})$ gel are formed between 5 and 20 mol% TiO_2 by the simultaneous hydrolysis of aluminium and titanium alkoxides, followed by washing and drying. After dehydration γ - Al_2O_3 solid solutions crystallize slowly from amorphous materials. At higher temperatures, rutile (TiO_2) is formed directly with the transformation of γ - Al_2O_3 phases into corundum. Corundum-rutile composite ceramics with dispersed fine pores generated from the decomposition of Al_2TiO_5 have been fabricated as follows: (1) hot pressing for 2 h at 1350°C under 35 MPa using γ - Al_2O_3 solid solutions, (2) heating for 1 h at 1500°C to achieve the complete formation of Al_2TiO_5 , and (3) annealing for 7 h at 1000°C to decompose of Al_2TiO_5 into corundum and rutile. Their mechanical properties have been examined. The bending strength yields the maximum value of 365 MPa with 15 mol% TiO_2 content whereas the fracture toughness increases from 4.7 to 6.2 $\text{MPa}^{1/2}$ with increasing TiO_2 content.

1 Introduction

Several possible mechanisms have been proposed to explain the mechanical behavior of various ZrO_2 -toughened ceramic materials ¹⁾. Among them two mechanisms are important; one is toughening by microcracking and the other is toughening by stress-induced transformation. As these toughening phenomena are related to the transformation of ZrO_2 and therefore temperature-dependent, the fracture toughness usually decreases at high temperatures. Recently the toughening by crack deflection ²⁾ is attracting much attention because it is insensitive to temperature. The crack deflection toughening can be achieved most effectively by incorporating rod- or disk-shaped particles. However, it is difficult to prepare the particles of high aspect ratio. In the Al_2O_3 - TiO_2 system, aluminium titanate (Al_2TiO_5), which is well-known ceramic with a low thermal expansion and a high melting point ³⁾, is a stable compound only above $\sim 1300^\circ\text{C}$, and at lower temperatures it decomposes into corundum (α - Al_2O_3) and rutile (TiO_2) with a volume shrinkage of

$\sim 10\%$. Because of crack deflection due to dispersed fine pores generated from the decomposition of Al_2TiO_5 , the improvement of toughening will be expected in corundum-rutile composite ceramics. Although many investigators have been undertaken on the preparation of Al_2TiO_5 ceramics with various additives ⁴⁾, little attention has been paid to the sintering of corundum-rutile composite ceramics. Okamura *et al.* ⁵⁾ fabricated composite ceramics consisting of corundum and rutile from TiO_2 -coated powders, but the sintered density was $\sim 90\%$ even with prolonged heating for 20 h at 1280°C . Hori *et al.* ⁶⁻⁷⁾ prepared Al_2O_3 - TiO_2 powders consisting of either γ - or δ - Al_2O_3 and rutile by a flame CVD technique. Even from these sinterable CVD Al_2O_3 - TiO_2 powders, it was difficult to obtain dense composite ceramics. However, by adding a small amount of Na_2CO_3 to the CVD powders, the sinterability was improved and the growth of plate-shaped corundum was observed.

In the present study, solid solutions of $\text{AlO}(\text{OH})$ gel were formed up to 20 mol% TiO_2 by the simultaneous

hydrolysis of aluminium and titanium alkoxides, followed by washing and drying. The present paper deals with the formation of corundum-rutile composite powders and the mechanical properties of composite ceramics with dispersed fine pores generated by utilizing the decomposition of Al_2TiO_5 .

2 Experimental Procedure

As-received aluminium isopropoxide ($\text{Al}(\text{OC}_3\text{H}_7)_3$, 99.999% pure) and titanium isopropoxide ($\text{Ti}(\text{OC}_3\text{H}_7)_4$, 99.999% pure) were used. They were dissolved in 2-propanol. The mixed alkoxides were refluxed for 20 h at 82°C and then hydrolyzed by adding a large amount of distilled water at room temperature. The temperature was slowly raised for 1 h to 75°C while the resulting suspensions were stirred. The hydrolysis products of the various compositions, shown in Table 1, were separated from the suspensions by centrifugation, washed 5 times in hot water, and dried at 120°C under reduced pressure. The powders obtained are termed "starting powders A through D".

Table 1 Chemical composition of starting powders and transformation temperatures of γ - Al_2O_3 solid solutions into corundum

Starting powder	Composition $\text{Al}_2\text{O}_3/\text{TiO}_2$ (mol%)	Transformation temperature (°C)
A	95 / 5	1130 - 1185
B	90 / 10	1085 - 1150
C	85 / 15	1070 - 1145
D	80 / 20	1040 - 1105

Differential thermal analysis (DTA) was conducted in air at a heating rate of 10°C/min; α - Al_2O_3 was used as the reference. The starting powders and specimens, obtained from the DTA runs after quenching, were examined by X-ray diffraction (XRD) using Ni-filtered $\text{CuK}\alpha$ radiation. Sintering was performed by hot pressing. Before hot pressing, calcined powders were uniaxially pressed into pellets 26 mm in diameter and about 9 mm thick under a pressure of 150 MPa using

distilled water (15 wt%) as a binder. The compacts were heated at a heating rate of 300°C/h, and then after soaking for 15 min at 1350°C a pressure of 35 MPa was applied for 2 h. Sintered pellets were heated for 1 h at 1500°C in air to achieve the complete formation of Al_2TiO_5 , and then by annealing for 7 h at 1100°C it was decomposed into corundum and rutile. Bulk densities were verified by the Archimedes method. Relative densities of composite ceramics corresponding to each composition were calculated using 3.99 g/cm³⁸⁾ and 4.25 g/cm³⁹⁾ for the theoretical densities of corundum and rutile, respectively.

3 Results and Discussion

3.1 Identification of Starting Powder and Thermal Analysis

All starting powders showed the XRD patterns of $\text{AlO}(\text{OH})$ gel. Electron microscopic examination was carried out by transmission electron microscopy (TEM). Figure 1 shows an electron micrograph of B. It consisted of highly aggregates and showed primary particles ranging in size from 5 to 10 nm. DTA curves for all starting powders revealed endothermic peaks at 365° to 455°C; these resulted from the dehydration of $\text{AlO}(\text{OH})$ gel containing TiO_2 . As will be described, γ - Al_2O_3 solid solutions were formed from amorphous materials after dehydration. Small exothermic peaks were observed in the temperature range shown in Table 1. They were found to result from the transformation of γ - Al_2O_3 phases into corundum with the formation of

Fig. 1 Transmission electron micrograph of starting powder B (bar=0.05 μm).

rutile. The transformation temperature was shifted at lower temperatures with increasing TiO_2 content. Note that in the Al_2O_3 - TiO_2 system corundum was formed at lower temperatures by transformation of γ - Al_2O_3 solid solutions.

3.2 Heating Process

Phases identified for heated specimens are summarized in Table 2. After dehydration specimens were amorphous. γ - Al_2O_3 phases were confirmed when heated at 550°C and their intensity of the XRD lines increased gradually with increasing temperature. The specimens heated after the exothermic peaks were mixtures of corundum and rutile. Now, the hydrolysis products of $\text{Al}(\text{OC}_3\text{H}_7)_3$ and $\text{Ti}(\text{OC}_3\text{H}_7)_4$ were $\text{AlO}(\text{OH})$ gel and an amorphous material, respectively. Heating of the former yielded corundum above 1225°C via θ - Al_2O_3 from γ - Al_2O_3 . When the latter was heated, anatase (TiO_2) crystallized slowly at $\sim 400^\circ$ to $\sim 600^\circ\text{C}$, although no thermal activity was detected in the DTA. The anatase-to-rutile transformation was observed at 680° to 740°C . In the present study, rutile was formed directly with the transformation of γ - Al_2O_3 phases into corundum. These results suggest that the solid solutions of $\text{AlO}(\text{OH})$ gel and γ - Al_2O_3 containing TiO_2

were prepared from alkoxides. The cell dimensions with compositional changes could not be calculated because of broad and weak XRD lines for both compounds. Solid state reaction between corundum and rutile occurred above 1400°C . The formation of Al_2TiO_5 was completed after heating for 1 h at 1500°C ; mixtures of corundum and Al_2TiO_5 were obtained. Annealing for 7 h at 1100°C for sintered pellets prepared from D was required for the decomposition of Al_2TiO_5 into corundum and rutile.

3.3 Fabrication of Corundum-Rutile Composite Ceramics

The starting powders were calcined for 1 h at 900°C . The calcined powders consisted of γ - Al_2O_3 solid solutions. The fabrication was performed by the sintering method described in the section of experimental procedure. Table 3 shows the bulk and relative densities of corundum-rutile composite ceramics. Relative densities increased with increasing TiO_2 content. These values were higher than those of composites reported previously⁵⁻⁶. The improvement of sinterability is probably due to a homogeneous distribution of corundum and rutile resulting from preparation conditions. Scanning electron

Table 2 Phases identified for specimens quenched after heating to various temperatures

Starting powder	Temperature ($^\circ\text{C}$)			
	550 - 1000	1100	1200 - 1300	1400
A	γ - Al_2O_3 (ss)	γ - Al_2O_3 (ss)	corundum rutile	corundum rutile
B	γ - Al_2O_3 (ss)	corundum rutile	corundum rutile	corundum rutile
C	γ - Al_2O_3 (ss)	corundum rutile	corundum rutile	corundum rutile Al_2TiO_5
D	γ - Al_2O_3 (ss)	corundum rutile	corundum rutile	corundum rutile Al_2TiO_5

Note: ss = solid solution.

Table 3 Bulk and relative densities of corundum-rutile composite ceramics

Starting powder	Density (g/cm ³)	Relative density (%)
A	3.72	93.1
B	3.75	93.6
C	3.80	94.6
D	3.86	95.8

microscopy (SEM) was utilized for the microstructural observation of composite ceramics. Figure 2 shows the SEM photographs for fracture surfaces before and after annealing of composites fabricated from C. The texture of composites (corundum + Al₂TiO₅) before annealing showed that Al₂TiO₅ with an average grain size of $\sim 1 \mu\text{m}$

(a)

(b)

Fig. 2 Scanning electron micrographs of (a) corundum-Al₂TiO₅ and (b) corundum-rutile composite ceramics fabricated from starting powder C (bar=2 μm).

was located in grain boundaries of corundum ($\sim 4 \mu\text{m}$). On the other hand, composites (corundum + rutile) after annealing consisted of fine corundum ($\sim 0.2 \mu\text{m}$) and rutile ($\sim 0.2 \mu\text{m}$) formed by decomposition of Al₂TiO₅ and original corundum ($\sim 4 \mu\text{m}$).

3.5 Mechanical Properties of Composite Ceramics

After test samples (3 by 20 by 3 mm) for mechanical measurements were cut from corundum-rutile composite ceramics with a diamond saw, they were lapped with a diamond powder. Three-point bending strength was measured using a 16 mm span and a cross-head speed of 0.5 mm/min. The fracture toughness (K_{IC}) measurements were made by the indentation fracture (IF) technique¹⁰⁻¹¹⁾ with 196 N Vickers load and also by the indentation strength-indentation (ISB) technique¹²⁾ with 100 N Vickers load and three-point bending test. Figure 3 shows the bending strength and fracture toughness as a function of TiO₂ content. The former gave the maximum value of 365 MPa with 15 mol% TiO₂ content whereas the latter increased monotonically with increasing TiO₂ content. The strength and fracture toughness of pure corundum sintered for 1 h at 1550°C are 430 MPa and 2.6 MPa^{1/2}, respectively¹³⁾. The strength of rutile is ~ 150 MPa¹⁴⁾. Accordingly, the decrease of strength in composites containing 20 mol% TiO₂ must be responsible for the adding of excess TiO₂. The fracture toughness with increasing TiO₂ content can be explained by the increase of dispersed fine pores introduced in composites. However, there was a difference between K_{IC} values by the IF method and by the ISB method. As the IF method depends on the observation of crack extension on the sample surface, it is very sensitive to the surface condition. In the present study, it was relatively difficult to obtain the samples with smooth surfaces, especially those with lower density. The absence of smooth surfaces proved that the crack extension was hindered and/or the measurement of crack length was made more difficult. The ISB method is more reasonable in this situation because it is not so much influenced by the surface condition as the IF method. Actually the deviation of K_{IC} values by the ISB method were smaller. Therefore, it seems reasonable

Fig. 3 Bending strength and fracture toughness of corundum-rutile composite ceramics as a function of TiO_2 content.

to conclude that the values measured by the ISB method is correct. Thus the toughening by crack deflection could be achieved in corundum-rutile composite ceramics.

4 Conclusions

Solid solutions of $\text{AlO}(\text{OH})$ gel which yield corundum-rutile composite powders with a homogeneous distribution at low temperatures are formed between 5 and 20 mol% TiO_2 by the alkoxy-method. Corundum-rutile composite ceramics with dispersed fine pores generated from the decomposition of Al_2TiO_5 have been fabricated and their mechanical properties have been examined. The bending strength gives the maximum value of 365 MPa with 15 mol% TiO_2 content.

The fracture toughness increases from 4.7 to 6.2 $\text{MPam}^{1/2}$ with increasing TiO_2 content.

5 References

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