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Sintering of CVD Aluminum Oxide–Titanium Dioxide Powders

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SUMMARY

The sintering behavior of co-deposited aluminum oxide–titanium dioxide powder prepared by a flame chemical vapor deposition (CVD) technique was studied in the compositional range of 56–73·5 wt% aluminum oxide. Significant densification was observed between 1100 and 1300°C with the co-deposited powder of stoichiometric composition, or of a slight excess aluminum oxide content. The titanium dioxide crystallites appeared to accelerate the densification when they were sufficient in amount and homogeneously mixed with the aluminum oxide. The excellent sinterability of these powders of relatively lower aluminum oxide content resulted in dense (maximum 95·5% of theoretical) and large-grained (20–50 μm) aluminum titanate ceramics at higher temperatures, while the microstructures of specimens from the mechanically mixed powder or from the co-deposited powder having an excess of aluminum oxide were porous and fine-grained. In the case of the co-deposited powder containing slight excess aluminum oxide, small (1–3 μm) aluminum oxide particles were dispersed on the boundary of β*-*Al_2TiO_5 *grains.*

1. INTRODUCTION

Aluminum titanate (Al_2TiO_5) is known as a ceramic material of low thermal expansion,[1,2] but its application for commercial uses is rather limited,

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mainly due to its very low mechanical strength. The significant thermal expansion anisotropy of aluminum titanate, when the grains are larger than a critical size, causes extensive intergranular cracking and dilation during cooling after densification, which results in a low thermal expansion coefficient but also in low mechanical strength.[3]

In the previous studies on the pressureless sintering of aluminum titanate,[4-6] two categories of starting powder were used: mixed powders of aluminum oxide and titanium dioxide, and synthesized aluminum titanate powders. The latter showed better sinterability and gave a higher bend strength than the former. There still appeared to exist some room for improvement in sinterability and possibly in the mechanical properties, since the maximum density achieved with the synthesized powders was only about 94% of theoretical.[6]

The authors have initiated a chemical vapor deposition (CVD) technique to produce ultrafine sinterable two-component ceramic powders using a combustion flame process.[7] The usefulness of this technique was demonstrated by achieving dense zirconium dioxide-toughened alumina ceramics with a homogeneous zirconium dioxide dispersion from the CVD aluminum oxide–zirconium dioxide powders.[8]

The same technique has been applied to produce aluminum oxide–titanium dioxide powders in the compositional range of 56–73·5 wt % aluminum oxide, resulting in ultrafine ($\simeq$40 nm) spherical particles which contained γ-Al_2O_3 and minute ($\simeq$10 nm) rutile (TiO_2) crystallites.[9] The purpose of this study is to investigate the sintering behavior of the CVD aluminum oxide–titanium dioxide powders.

2. EXPERIMENTAL

Three compositions of the co-deposited aluminum oxide–titanium dioxide powders (55·9, 61·8 and 73·5 wt % aluminum oxide), CVD aluminum oxide (δ-phase) and titanium dioxide (mainly anatase) were produced by the flame CVD technique using the same reaction temperature and time. The average particle sizes of these powders ranged from 30 to 50 nm, and the co-deposited powders consisted mainly of γ-Al_2O_3 particles containing minute ($\simeq$10 nm) rutile crystallites.[9] The three co-deposited powders and the mixture of the CVD aluminum oxide and titanium dioxide powders (adjusted to be 61·8 wt % aluminum oxide) were dispersed into ethanol by ultrasonic agitation and filtered by filter paper (nominal size 7 μm) to remove foreign material. Each of the powder slurries which passed through the filter was centrifuged, dried and calcined at 800 °C for 1 h. The calcination was intended to remove residual chloride ions from the powders because chloride ions are generally known to hinder the densification,[10] but, at the same time, slight changes in crystalline phases were observed. The anatase which existed as a minor phase in the co-deposited powders, transformed to rutile, and the aluminum oxide became more like δ-phase rather than γ-phase.[9]

The calcined powders were ball-milled using a plastic lined mill and plastic media in water, together with a surfactant (Yukanol NCS, Tetsuno Yuka, Japan) for 40 h, dried at 80 °C for more than two days and milled again in a mortar. The powders were uniaxially shaped into pellets, isostatically pressed at 294 MPa, and dried further. Subsequent to the green density measurements, the specimens were preheated at 250 °C for 2 h and at 500 °C for 1 h to remove free water and sintered between 1000 and 1600 °C for 1 h in an air atmosphere by means of a 'Kanthal Super' box furnace. The temperature was raised from 500 °C to the target temperature in less than 20 min, and the furnace was cooled rapidly after sintering by switching off the power.

The densities of the specimens were determined by the weight/dimension measurements; some were confirmed by an Archimedes method using mercury displacement. The relative density calculations were simplified by assuming that the only phases in the theoretically dense specimens were β-Al_2TiO_5 and α-Al_2O_3, though aluminum titanate was not detected in the specimens sintered at temperatures up to 1200 °C. The theoretical densities of β-Al_2TiO_5[11] and α-Al_2O_3[12] were assumed to be 3·702 and 3·987 $Mg\,m^{-3}$, respectively.

X-ray diffraction (XRD) analyses using Cu–Kα were made mainly on the as-sintered surfaces of the specimens and the microstructures were observed by scanning electron microscopy (SEM) on the fractured surfaces.

3. RESULTS AND DISCUSSION

3.1. Phase changes during sintering

Figure 1 shows the change of XRD profile as a function of sintering temperature with the specimens of 61·8 wt% aluminum oxide. Similar changes of XRD profiles were observed with specimens of different compositions, except that the intensities of α-Al_2O_3 and rutile varied according to the composition.

Between 1000 and 1200 °C, the only phases detected were α-Al_2O_3 and rutile. The phase changes of Al_2O_3 from γ or δ to α occurred below 1000 °C, whereas they occurred at temperatures higher than 1000 °C, without titanium dioxide addition[13] or without compaction.[9] Titanium dioxide

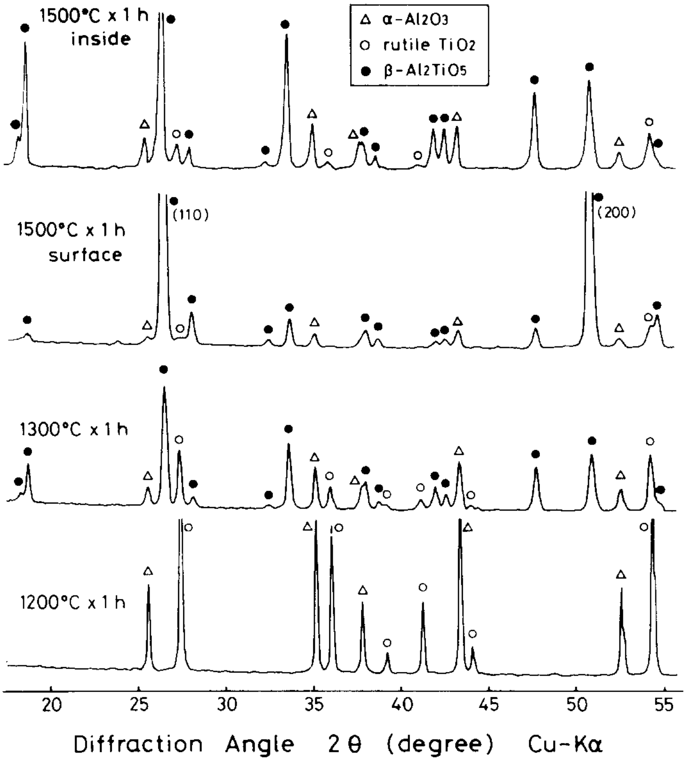


Fig. 1. Phase changes taking place during sintering in the case of powder No. 605 (co-deposited powder, 61·8 wt % aluminum oxide). The XRD measurements were made mainly on the as-sintered surfaces. The inside of the specimen sintered at 1500 °C was measured for comparison.

appeared to accelerate the Al_2O_3 phase changes from γ or δ to α especially when the powder was compacted. This is in contrast to the fact that a zirconium dioxide addition to δ-Al_2O_3 retarded the Al_2O_3 phase change.[13]

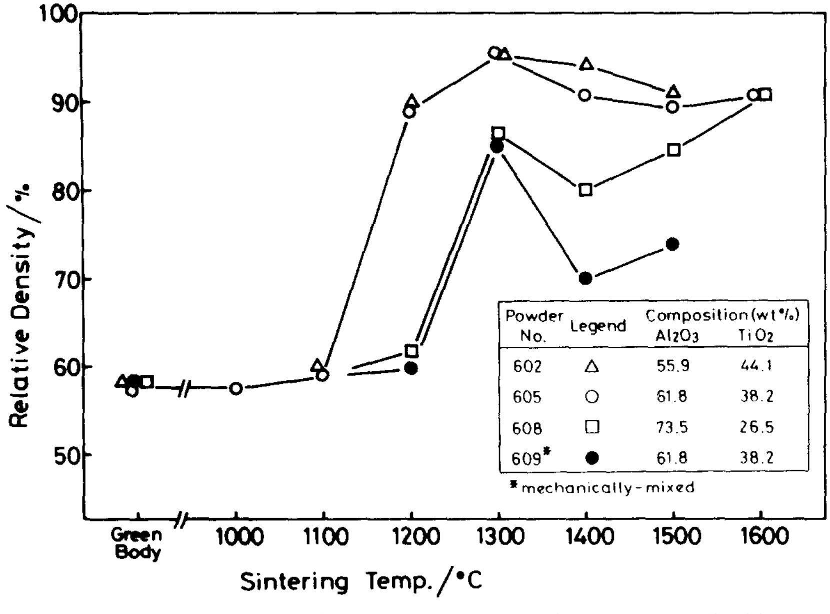
The reaction of α-Al_2O_3 and TiO_2 to form β-Al_2TiO_5 started to occur between 1200 and 1300 °C. The amount of unreacted aluminum oxide and titanium dioxide decreased when the temperature was raised further. The β-Al_2TiO_5 peaks indicated a strong orientation of the crystallites at high temperatures, especially when the composition was close to the stoichiometry of aluminum titanate. The (200) and (110) surfaces, especially the former, of β-Al_2TiO_5 appeared to be preferentially oriented parallel to the sintered surface.

Other phases, such as 'X-phase' reported by Gani and McPherson[14] or 'Y-phase' detected by calcining the co-deposited aluminum oxide–titanium dioxide powders,[9] were not observed.

3.2. Densification behavior

The densification behavior appeared very different from that of conventional ceramic materials and strongly dependent on the powder composition and characteristics. As shown in Fig. 2, significant densification occurred between 1100 and 1200 °C with the co-deposited powders of stoichiometric composition and with those with a slight excess aluminum oxide content (powder Nos 602 and 605). The densification did not proceed at such low temperatures with the co-deposited powder having an excess of aluminum oxide (No. 608) or with the mechanically mixed powder (No. 609).

The formation of β-Al_2TiO_5 appeared to retard densification. At 1300 °C, the formation of β-Al_2TiO_5 was so slow that the densification had progressed significantly before Al_2TiO_5 was formed. At 1400 °C, the densities of specimen Nos 608 and 609 decreased because β-Al_2TiO_5 was formed quickly before sufficient densification could take place. At temperatures higher than 1300 °C more severe microcracking was caused by the further formation of β-Al_2TiO_5 and the development of preferred orientation and, as can be seen in the case of Nos 602 and 605, this resulted in slightly lower densities. Specimen Nos 608 and 609 were densified further between 1400 and 1600 °C, as the driving force for densification became larger, because some porosity remained in these specimens.



Powder No.	Legend	Composition (wt%) Al_2O_3	TiO_2
602	△	55.9	44.1
605	○	61.8	38.2
608	□	73.5	26.5
609*	●	61.8	38.2

* mechanically-mixed

Fig. 2. Densification behavior of CVD aluminum oxide–titanium dioxide powders. Comparisons were made on compositions and between the co-deposited and the mechanically mixed powders.

It appeared advantageous to use the co-deposited powders of stoichiometric composition or of a slight excess aluminum oxide content because higher densities could be achieved before the formation of β-Al_2TiO_5. In comparison with the densification behavior of the synthesized aluminum titanate powder reported by Ohya *et al.*,[6] these co-deposited powders showed superior sinterability. The densities achieved from the co-deposited powders at 1200 °C for 1 h and at 1300 °C for 1 h were 89 % and 95·5 % of theoretical, respectively, which should be compared with 72 % and 78 % at 1300 °C for 2 and 4 h, respectively, achieved by the synthesized powder.

The reason for the low-temperature densification with these powders can be attributed to the existence of ultrafine titanium dioxide crystallites. As Yan and Rhodes[15] showed, titanium dioxide powders can be sintered at very low temperatures, especially when they are small in size and agglomerate-free. The rutile crystallites contained in the γ- or δ-Al_2O_3 particles are more effective at increasing the sinterability of aluminum oxide–titanium dioxide mixture than independent titanium dioxide particles mechanically mixed with aluminum oxide, not only because of their smaller sizes but also because of the better contact with aluminum oxide as hypothesized in the following. The rutile crystallites are probably swept out to the surface of the particles when Al_2O_3 transforms from γ (or δ) to α, and then the densification is strongly enhanced by these titanium dioxide crystallites on the surface of aluminum oxide particles. It appears important to obtain a sufficient amount of fine titanium dioxide crystallites attached to the surface of aluminum oxide particles, since the densification does not proceed at such low temperatures when the amount of titanium dioxide is small (No. 608) or when the powder is mechanically mixed (No. 609).

3.3. Microstructural observations

Figure 3 shows the scanning electron micrographs (SEMs) of the fractured specimens. The dependence of microstructure on sintering temperature was compared in the case of 61·8 wt % aluminum oxide (No. 605). At 1200 °C (Fig. 3(a)), the microstructure consisted of small ($\simeq 1\ \mu m$) aluminum oxide and titanium dioxide grains and appeared fairly dense despite the low sintering temperature. At 1300 °C (Fig. 3(b)), as the result of β-Al_2TiO_5 formation, the microstructure consisted of large (average $\simeq 50\ \mu m$) aluminum titanate grains and intergranular microcracking, while high density was achieved. The excess aluminum oxide appeared to be dispersed mostly as small (average $\simeq 3\ \mu m$) particles on the grain boundaries. Despite the high density and the large aluminum titanate grain sizes, the microcracking was not very severe, probably due to the incompleteness of the reaction between Al_2O_3 and TiO_2 to form β-Al_2TiO_5. At 1500 °C

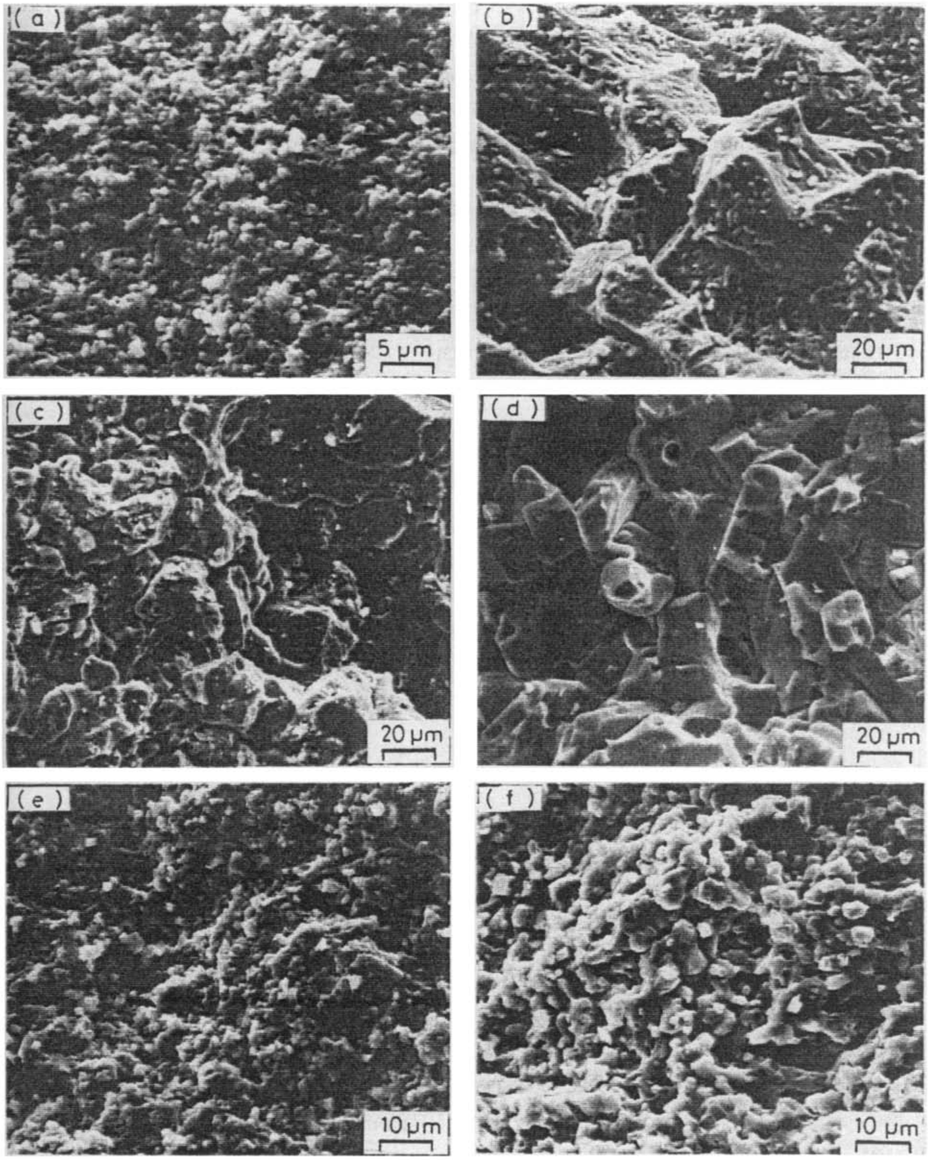


Fig. 3. Scanning electron micrographs of fractured specimens. (a), (b) and (c), No. 605 (61·8 wt % Al_2O_3) sintered at 1200, 1300 and 1500 °C for 1 h, respectively. (d), (e) and (f), sintered at 1500 °C for 1 h from No. 602 (55·9 wt % Al_2O_3), No. 608 (73·5 wt % Al_2O_3) and No. 609 (61·8 wt % Al_2O_3, mechanically mixed), respectively.

(Fig. 3(c)), the grain sizes were smaller (average 20–30 μm) and microcrack density was higher than those at 1300 °C. The reason can be attributed to the higher density of nucleation sites of β-Al_2TiO_5 resulting from the larger chemical driving force. The excess aluminum oxide was also dispersed on the grain boundaries but in smaller particle sizes. It appeared that the sintering schedule strongly influenced the microstructure.

The dependence of microstructure on the composition and powder characteristics was compared between specimens sintered at 1500 °C for 1 h in Figs 3(c), (d), (e) and (f). The specimens sintered from the co-deposited powder of stoichiometric composition (Fig. 3(d), 55·9 wt % aluminum oxide) showed almost the same aluminum titanate grain sizes and microcrack density as those of slight excess aluminum oxide, but the surfaces of aluminum titanate grains with the stoichiometric composition were very smooth, whereas those having a slight excess of aluminum oxide (Fig. 3(c)) were spotted and rugged, due to fine aluminum oxide particles. The specimens sintered from co-deposited powder of 73·5 wt % aluminum oxide (Fig. 3(e)) showed a porous microstructure of small grains. The existence of an excess of aluminum oxide prevented the densification and, at the same time, suppressed the grain growth. The specimens sintered from the mechanically mixed powder of 61·8 wt % aluminum oxide (Fig. 3(f)) showed a noticeably porous microstructure due to the poor sinterability. The co-deposited powder of the same composition achieved much higher density, as is apparent when Figs 3(c) and (f) are compared.

4. CONCLUSIONS

The co-deposited aluminum oxide–titanium dioxide powders of stoichiometric composition and with a slight excess aluminum oxide content showed excellent sinterability which could be attributed to the fact that there were sufficient titanium dioxide crystallites present which were very small in size and homogeneously mixed with the aluminum oxide. The microstructures of specimens sintered from these highly active powders at the higher temperatures appeared to be influenced by the amount of excess aluminum oxide and also by the density of nucleation sites for aluminum titanate formation.

These highly active powders can give more flexibility of processing parameters in controlling the microstructures and properties of aluminum titanate. Further study is in progress as to how the processing parameters, especially the sintering schedule, can affect the microstructures and properties.

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