Simultaneous application of colloidal processing and liquid-forming additives to alumina resulted in a sintered density of 
>99% in 1 h at a temperature as low as 1070°C for a commercial high-purity alumina powder at a total dopant level of 2 mol%. The additives were 0.9% CuO + 0.9% TiO₂ + 0.1% B₂O₃ + 0.1% MgO. At higher temperatures or after prolonged sintering, the doped alumina ceramic developed a duplex microstructure containing large elongated grains and exhibited a relatively high fracture toughness of ~3.8 MPa·m^{1/2} as compared to a value of ~2.6 MPa·m^{1/2} for the undoped alumina. [Key words: sintering, alumina, additives, processing, microstructure.]

I. Introduction

There are two general approaches to enhancing sintering kinetics or lowering the sintering temperature for ceramics. The first is to improve powder processing, that is, to use fine starting powders and to eliminate agglomerates in the green preforms, such as by colloidal routes. The second approach is to use sintering aids or additives. Additives in solid solutions can enhance diffusion and hence sintering by increasing defect populations, while additives forming a liquid phase can facilitate particle rearrangement and solution/reprecipitation.

For alumina, as an extreme example of the first approach, Yeh and Sacks used colloidal processing with a specially classified ultrafine powder to achieve a sintered density of 99.2% at 1150°C in 2 h. On the other hand, Cutler et al. used 4 wt% additives (about an equal amount of either TiO₂ + Cu₂O or TiO₂ + MnO₂) to achieve 96% of theoretical density at 1300°C in 1 h. This compares with a more typical sintering temperature of 1500°C to 1700°C for high-purity alumina in normal laboratory practice. Further improvement has been made recently by Cannon, who achieved a 99% density at 1200°C in 1 h by doping alumina with one of Cutler's additive compositions, i.e., 2 mol% CuO + 2 mol% TiO₂.

The simultaneous application of the above two approaches has not been exploited for alumina. In this paper, we show that they can result in a sintering temperature below 1100°C, and some beneficial effects on the mechanical properties.

II. Experimental Procedure

The starting material was a high-purity (>99.99%) alumina powder with an average particle size of ~0.2 µm. The additive composition expressed in mole percent was 0.9% CuO + 0.9% TiO₂ + 0.1% B₂O₃ + 0.1% MgO. This composition is similar to that used by Cannon, but the total additive amount is smaller. Of the two minor additives, B₂O₃ seemed to enhance sintering, whereas MgO seemed to improve microstructure uniformity.

The alumina powder was ultrasonically dispersed in distilled water with a surfactant. Additives were introduced by adding aqueous solutions of Cu(NO₃)₂, Mg(NO₃)₂, and H₃BO₃ and ethanol solution of Ti(O(CH₂)₃CH₃)₄ to the dispersed suspension of alumina powder. The pH of the mixture was then adjusted to flocculate the suspension. The slurry was dried and calcined at 700°C for 1 h. A portion of the powder thus obtained was dried and then die-pressed under a compaction pressure of 150 MPa into pellets (process A). The rest was dispersed again, by attrition-milling and ultrasonic agitation, then pressure-cast into cakes as described elsewhere (process B). Shrinkage during nonisothermal sintering experiments was recorded in a dilatometer at a heating rate of 5°C/min up to 1450°C. Isothermal sintering experiments were conducted in the temperature range of 1070°C to 1200°C for times up to 5 h.

To measure the hardness and the fracture toughness of the sintered samples, a Vickers indentation technique was employed, using a load range of 4 to 15 kg. Flexural strength measurements were performed in four-point bending for specimens of dimensions 2.0 mm × 3.0 mm × 20.0 mm with a 4-mm inner span and a 17-mm outer span.

III. Results and Discussion

Figure 1 shows sintering curves of undoped and doped alumina, compacted in two processes. For the undoped material,
Isothermal Sintering

![Graph of Doped Alumina (B) Isothermal Sintering](image)

**Fig. 2.** Sintered density of doped alumina (B) as a function of time for isothermal sintering at 1070°C and 1200°C.

the colloidally processed specimen (B) gives a significantly faster sintering rate than that of the conventionally processed one (A). For instance, the former achieves a density of 98% of the theoretical at 1350°C, while the latter reaches only 95.9% even at 1450°C. For doped alumina, sintering starts at a much lower temperature and seems to be much less sensitive to the variation of compacting processes. Nevertheless, the colloidal process (B) still has an advantage over the other process. For example, at 1200°C the colloidal processed sample reaches a density of 98.2%, a value the conventionally processed sample would obtain only after an 80°C temperature increase, i.e., at 1280°C.

The relative density curves in Fig. 1 are calculated from the end densities and the dilatometry traces, assuming isotropic linear shrinkage for the specimens. However, the measured shrinkage in the thickness direction is larger than that in the radial direction by about 1%. Therefore, the calculated starting densities in Fig. 1 are lower by about 3% than the actual green densities. This deviation, although noticeable in the low density range, does not affect the comparison of the relative density data.

The microstructure of a doped alumina (process B) sintered at 1070°C for 1 h is shown in Fig. 3(A), which features a very fine grain size (average grain size 0.33 μm) almost free of porosity (ρ = 99.3%). If the sintering temperature is raised or prolonged isothermal heating is used, however, a new duplex microstructure is developed. This is shown in Fig. 3(B), for a sample sintered at 1110°C for 1 h, which has a substantial amount of large, elongated abnormal grains, of a size around 20 μm with an aspect ratio 3 to 10, embedded in a fine-grained (0.38 μm) matrix. These elongated grains become entirely dominant at an even higher sintering temperature, as can be seen in Fig. 3(C), for a sample sintered at 1200°C. Abnormal grain growth at such a low temperature is rare in high-purity alumina, and strongly faceted abnormal grains are frequently observed in liquid-phase-sintered alumina; therefore, the observed microstructure here is no doubt due to the presence of a liquid phase. Moreover, liquid phases
containing compensating dopants (e.g., TiO$_2$ + CaO, SiO$_2$ + SrO, and SiO$_2$ + Na$_2$O) are found particularly effective in producing elongated, platelike abnormal grains. The two major additives in the present study, TiO$_2$ and CuO, are a compensating pair to alumina.

Some beneficial effects of such a duplex microstructure on mechanical properties have been observed in this study. Flexure strength for specimens shown in Fig. 3(B) is 396 ± 41 MPa, about the same as for an undoped alumina with an average grain size 0.5 µm. More encouragingly, the fracture toughness is between 3.60 and 4.17 MPa.m$^{1/2}$, compared favorably to values of 2.41 to 2.76 MPa.m$^{1/2}$ for the undoped alumina. A similar observation has been reported for an alumina/rutile system, where the development of abnormal grains promoted by Na$_2$O, a liquid phase former, can also be promoted by doping which results in an improved fracture toughness.

IV. Summary

Both colloidal processing and the use of additives can reduce the sintering temperature of alumina, the latter being more effective. When these two approaches are combined, a commercial high-purity alumina powder can be sintered to a relative density of 99.3% at 1070°C in 1 h, at an additive concentration of no more than 2 mol%. A duplex microstructure can also be promoted by doping which results in an improved fracture toughness.

References