journal
J. Am. Ceram. Soc., 74 [8] 2011–13 (1991)

Low-Temperature Sintering of Alumina with Liquid-Forming Additives

Liang A. Xue* and I-Wei Chen*

Department of Materials Science and Engineering, The University of Michigan, Ann Arbor, Michigan 48109

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% TiO_2 + 0.1% B_2O_3 + 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[1] *and* to eliminate agglomerates in the green preforms,[2–4] such as by colloidal routes.[5] The second approach is to use sintering aids or additives. Additives in solid solutions can enhance diffusion and hence sintering by increasing defect populations,[6,7] while additives forming a liquid phase can facilitate particle rearrangement and solution/reprecipitation.[8]

For alumina, as an extreme example of the first approach, Yeh and Sacks[9] 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.*[10] used 4 wt% additives (about an equal amount of either TiO_2 + Cu_2O or TiO_2 + MnO_2) to achieve 96% of theoretical density at 1300°C in 1 h. This compares with a more typical sintering temperature of 1500° to 1700°C for high-purity alumina in normal laboratory practice. Further improvement has been made recently by Cannon,[11] 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% TiO_2.

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% TiO_2 + 0.1% B_2O_3 + 0.1% MgO. This composition is similar to that used by Cannon, but the total additive amount is smaller. Of the two minor additives, B_2O_3 seemed to enhance sintering, whereas MgO seemed to improve microstructure uniformity.[12]

The alumina powder was ultrasonically dispersed in distilled water with a surfactant.† Additives were introduced by adding aqueous solutions of $Cu(NO_3)_2$, $Mg(NO_3)_2$, and H_3BO_3 and ethanol solution of $Ti\{O(CH_2)_3CH_3\}_4$ 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[13] (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° 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,[14] using a load range of 4 to 15 kg. Flextural 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,

†Darvan 821A, R.T. Vanderbilt Co., Norwalk, CT.
‡Theta Dilatronic, Theta Industries, Inc., Port Washington, NY.

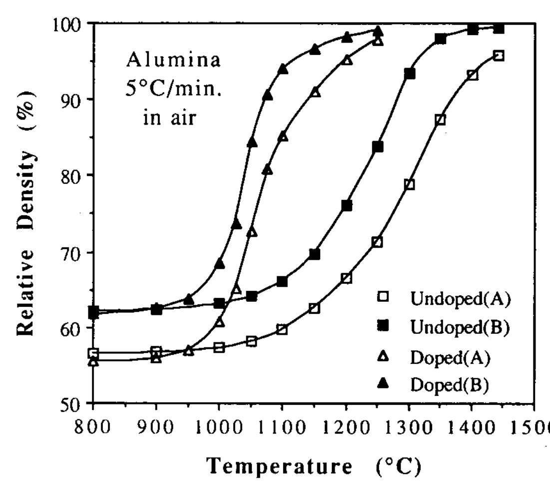


Fig. 1. Sintering curves for doped and undoped alumina. Processes A and B are described more fully in the text.)

C. A. Handwerker—contributing editor

Manuscript No. 197038. Received December 26, 1990; approved April 30, 1991.
*Member, American Ceramic Society.
*TM-D, Taimei Chemicals, Tokyo, Japan.

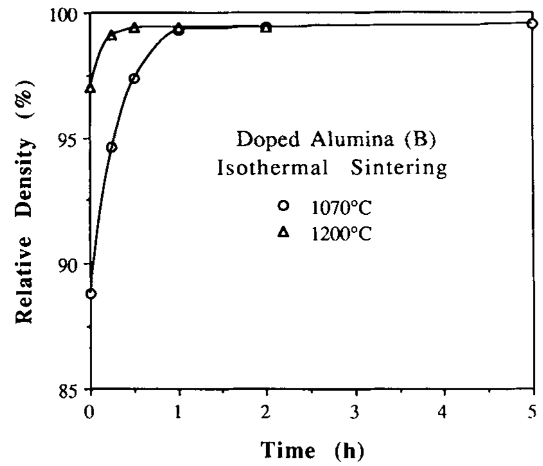


Fig. 2. Sintered density of doped alumina (B) as a function of time for isothermal sintering at 1070° and 1200°C.

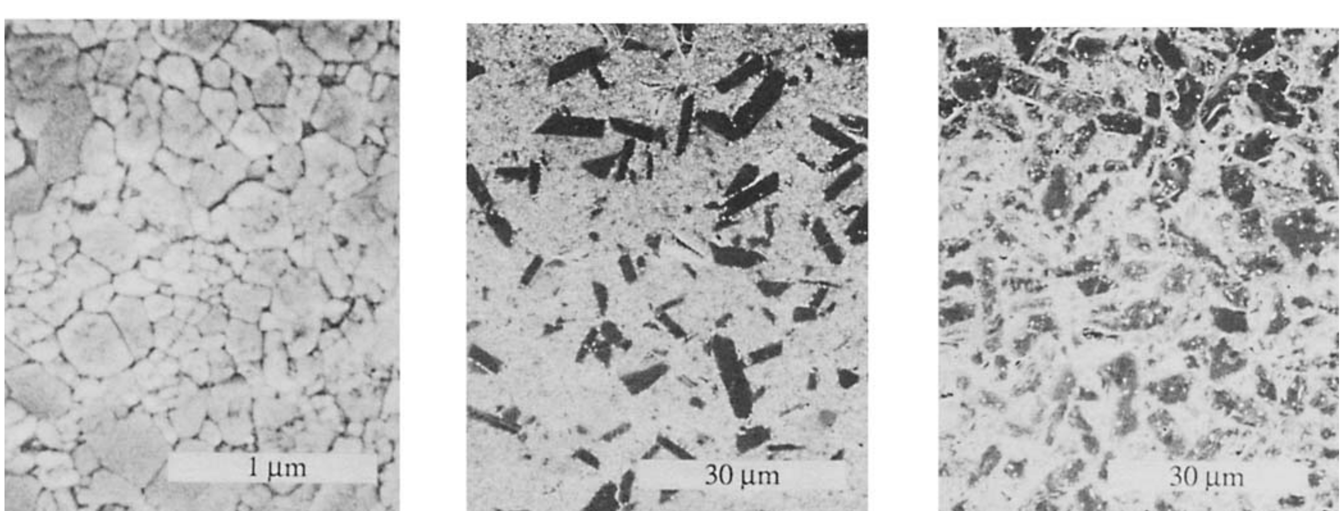
the colloidally processed specimen (B) gives a significantly faster sintering rate than that of the conventionally processed one (A). For instance, the former achieves a density of 98% of the theoretical at 1350°C, while the latter reaches only 95.9% even at 1450°C. For doped alumina, sintering starts 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 above results can be qualitatively understood as follows. First, process A yields a less efficient packing of powders than process B, as evidenced by its lower green density (59% in A as compared to 65% in B).[§] Mercury porosimetry has further shown the presence of a larger average pore size and a broader pore size distribution in process A. These features are known to retard effective sintering.[2,15] Second, a low-temperature eutectic is likely to exist between Al_2O_3, CuO, Cu_2O, TiO_2, MgO, and B_2O_3. The eutectic temperature is probably lower than 1000°C, considering the known eutectic of 1096°C between Al_2O_3–CuO–Cu_2O.[16] To estimate the eutectic temperature range, a DTA run has been conducted at a heating rate of 5°C/min for powder obtained by crushing a piece of the doped alumina (B) cake. An endothermic peak has indeed been found, which starts gradually at ~1040°C and begins to accelerate around 1130°C before peaking at 1167°C. Since the DTA experiment employs loosely packed powder as contrast to the densely packed pellets used in sintering, the endothermic peak would somewhat shift to a lower temperature for the sintering samples. Thus, liquid-phase sintering is probably operative in the doped alumina. Moreover, the presence of a liquid phase is known to render sintering more forgiving to processing flaws introduced by unsatisfactory powder packing processes. Lastly, the codoping of Ti and Cu is also known to increase the solubility of each, due to mutual charge compensation. This may, in turn, allow an additional contribution to enhance kinetics.[11,17]

For the doped alumina (B) the densities achieved after isothermal sintering at two different temperatures are plotted as a function of sintering time in Fig. 2. At 1070°C, 99.3% relative density was obtained in 1 h, which appeared to be the optimal sintering time since longer time did not increase the density much. At 1200°C, the sintering kinetics were so fast that a 99.1% density was reached in 15 min. However, the higher sintering temperature did not result in higher densities for sintering time longer than 1 h.

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;[18,19] therefore, the observed microstructure here is no doubt due to the presence of a liquid phase. Moreover, liquid phases

[§]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 those 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.



(A) (B) (C)

Fig. 3. SEM micrographs of the doped alumina sintered at various temperatures for 1 h: (A) 1070°, (B) 1110°, and (C) 1200°C.

containing compensating dopants (e.g., TiO_2 + CaO, SiO_2 + SrO, and SiO_2 + Na_2O) are found particularly effective in producing elongated, platelike abnormal grains.[19] 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 $\pm$ 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$\cdot$m$^{1/2}$, compared favorably to values of 2.41 to 2.76 MPa$\cdot$m$^{1/2}$ for the undoped alumina. A similar observation has been reported for an alumina/rutile system,[20] where the development of abnormal elongated grains promoted by Na_2O, a liquid phase former, resulted in a significantly higher 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

[1] C. Herring, "Effect of Change of Scale on Sintering Phenomena," *J. Appl. Phys.*, **21** [4] 301–303 (1950).

[2] W. H. Rhodes, "Agglomerate and Particle Size Effects on Sintering Yttria-Stabilized Zirconia," *J. Am. Ceram. Soc.*, **64** [1] 19–22 (1981).

[3] F. F. Lange, "Sinterability of Agglomerated Powders," *J. Am. Ceram. Soc.*, **67** [2] 83–89 (1984).

[4] R.T. Tremper and R. S. Gordon, "Agglomeration Effects on the Sintering of Alumina Powders Prepared by Autoclaving Aluminum Metal"; pp. 153–76 in *Ceramic Processing Before Firing.* Edited by G. Onoda and L. L. Hench. Wiley, New York, 1978.

[5] F. F. Lange, "Powder Processing Science and Technology for Increased Reliability," *J. Am. Ceram. Soc.*, **71** [1] 3–15 (1988).

[6] D.W. Readey, "Mass Transport and Sintering of Impure Ionic Solids," *J. Am. Ceram. Soc.*, **49** [7] 366–69 (1966).

[7] R. D. Bagley, I. B. Cutler, and D. L. Johnson, "Effect of TiO_2 on Initial Sintering of Al_2O_3, *J. Am. Ceram. Soc.*, **53** [3] 136–41 (1970).

[8] W. D. Kingery, "Densification during Sintering in the Presence of a Liquid Phase. I. Theory," *J. Appl. Phys.*, **30** [3] 301–306 (1959).

[9] T.-S. Yeh and M. D. Sacks, "Low-Temperature Sintering of Alumina Oxide," *J. Am. Ceram. Soc.*, **71** [10] 841–44 (1988).

[10] I. B. Cutler, C. Bradshaw, C. J. Christensen, and E. P. Hyatt, "Sintering of Alumina at Temperatures of 1400°C and Below," *J. Am. Ceram. Soc.*, **40** [4] 134–39 (1957).

[11] W. R. Cannon, "High Creep Ductility in Alumina Containing Compensating Additives"; pp. 741–49 in Advances in Ceramics, Vol. 10, *Structure and Properties of MgO and Al_2O_3 Ceramics.* Edited by W. D. Kingery. American Ceramic Society, Columbus, OH, 1984.

[12] M. P. Harmer, "Use of Solid-Solution Additives in Ceramic Processing"; pp. 679–96 in Advances in Ceramics, Vol. 10, *Structure and Properties of MgO and Al_2O_3 Ceramics.* Edited by W. D. Kingery. American Ceramic Society, Columbus, OH, 1984.

[13] L. A. Xue and I-W. Chen, "Deformation and Grain Growth of Low-Temperature Sintered High Purity Alumina," *J. Am. Ceram. Soc.*, **73** [11] 3518–21 (1990).

[14] G. R. Anstis, P. Chantikul, B. R. Lawn, and D. B. Marshall, "A Critical Evaluation of Indentation Techniques for Measuring Fracture Toughness: I, Direct Crack Measurements," *J. Am. Ceram. Soc.*, **64** [9] 533–38 (1981).

[15] M. A. Occhionero and J.W. Halloran, "The Influence of Green Density Upon Sintering"; pp. 89–102 in *Sintering and Heterogeneous Catalysis.* Edited by G. C. Kuczynski, A. E. Miller, and G. A. Sargent. Plenum Press, New York, 1984.

[16] A. M. Cadalla and J. White, "Equilibrium Relationships in the System $CuO–Cu_2O–Al_2O_3$," *Trans. Br. Ceram. Soc.*, **63** [1] 39–62 (1964).

[17] Y. Ikuma and R. S. Gordon, "Effect of Doping Simultaneously with Iron and Titanium on the Diffusional Creep of Polycrystalline Al_2O_3," *J. Am. Ceram. Soc.*, **66** [2] 139–47 (1983).

[18] W. A. Kaysser, M. Sprissler, C. A. Handwerker, and J. E. Blendell, "Effect of a Liquid Phase on the Morphology of Grain Growth in Alumina, *J. Am. Ceram. Soc.*, **70** [5] 339–43 (1987).

[19] H. Song and R. L. Coble, "Origin and Growth Kinetics of Platelike Abnormal Grains in Liquid-Phase-Sintered Alumina," *J. Am. Ceram. Soc.*, **73** [7] 2077–85 (1990).

[20] S. Hori, H. Kaji, M. Yoshimura, and S. Somiya, "Deflection-Toughened Corundum-Rutile Composites"; pp. 283–88 in *Advanced Structural Ceramics.* Edited by P. F. Becher, M.V. Swain, and S. Somiya. Materials Research Society, Pittsburgh, PA, 1987. □