SINTERING OF MULLITE

M. D. Sacks and J. A. Pask
University of California
Berkeley, CA 94720

INTRODUCTION

Despite technological importance, limited information is available on the correlation of major processing variables with the sintering behavior and microstructure development of aluminum silicates containing mullite as the principal phase. Recent studies illustrate the excellent mechanical properties of mullite and the importance of controlled processing in achieving desired properties.¹,²

The character of mullite bodies depends on the Al₂O₃/SiO₂ ratio, the degree of mixing achieved, the firing conditions (time, temperature, atmosphere), and the kind of impurities. Mullite is usually prepared by thermally decomposing aluminum silicates such as clay and sillimanite minerals. Alumina may be added to reduce the amounts of siliceous phase. Reviews on mullite formation and processing are given by Grofcsik,³ Davis,⁴ and Sacks.² Various kinds of Al₂O₃/SiO₂ mixtures are commonly sintered at high temperatures. Mixtures of α-quartz, silicic acid, β-cristobalite or fused silica with α-alumina, bauxite, diaspore (HA1O₂), gibbsite (Al(OH)₃) or AlF₃ have been reported.²,³,⁴

In these approaches, alumina and silica are not mixed on a molecular scale and, because of low diffusivities, normally result in incomplete reactions despite high firing temperatures. Pressure sintering has been used to achieve higher densities and avoid the associated large grains.⁵,⁶,⁷ In order to achieve better composition control, complete reaction, and a fine-grain powder, a number of chemical and gel preparation techniques have been developed to form mullite powder.²,³,⁴
In the present study, several processing schemes are utilized to study the effects of overall Al₂O₃/SiO₂ composition, powder surface area, and sintering atmosphere on the sintering kinetics and microstructure development of mullite.

EXPERIMENTAL

"Powder" Process. Starting materials were Alcoa Aluminum Co. A-14 (α-Al₂O₃) and Illinois Minerals Co. silica flour (α-quartz) which had purities of ~99.8% and ~99.5%, respectively. Compositions ranged from 60 wt% Al₂O₃/40 wt% SiO₂ to 90 wt% Al₂O₃/10 wt% SiO₂.

Mixing and de-agglomeration were achieved by wet (isopropanol) milling in (1) a porcelain ball mill (mixing condition "I") or (2) a teflon-lined vibratory mill (mixing condition "P"). After stir-drying and screening (-120 mesh), mixtures were calcined at 1700°C for 8 h to form mullite, mullite and glass, or mullite and Al₂O₃ (depending on the overall Al₂O₃/SiO₂ ratio). Experiments with the mixture 73 wt% Al₂O₃ showed that calcination time and temperature did not affect subsequent sintering as long as the mullite reaction was complete.

After calcination, the mixture was subjected to coarse crushing in a mechanically operated mortar and pestle and wet (isopropanol) vibratory milling (grinding condition "P"). Unless noted otherwise, grinding time was 5 h. After stir-drying and screening (-120 mesh), powders were calcined at 800°C for 1 h to burn out any organics. Powder mixtures were labeled according to composition and mixing/grinding conditions, e.g., 73IP refers to a 73 wt% Al₂O₃ composition mixed by condition "I" and ground by condition "P". X-ray diffraction and microscopy have shown the most significant contamination in processing to be Al₂O₃ introduced by impact collisions during vibratory milling; thus, PP compositions have the largest Al₂O₃ contamination.

Powder compacts were die formed under uniaxial pressure (17 MN/m²) followed by isostatically pressing at (170 MN/m²).

"Gel" Process. The gel process utilized colloidal size reactants to reduce the time and/or temperature required to complete mullite formation. Aqueous colloidal suspensions of alumina and silica were intimately mixed. To prevent segregation, mixtures were gelled by pH adjustment or by evaporation of water. Details of the process have been described by Ghate. A 73 GP composition was used in kinetic studies. Raw materials were Atomergic Chemicals Corp. GZ5, a γ-Al₂O₃ of ~99.95% purity, and Ludox AS, a dispersion of silica particles of ~99.5% purity. Complete reaction occurred on calcining the gel powders at 1450°C for 24 h.