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Fast Firing of Alumina

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Abstract

Densification behavior and mechanical performance of alumina fast fired at relatively low temperatures were evaluated and compared to those of conventionally sintered alumina. A density of about 99% of the theoretical value and a grain size of 1·2 μm were achieved by firing pure alumina powder compacts at 1350°C for 20 min. Fast fired alumina exhibits room temperature strengths (520 MPa) and Weibull moduli (10·4) nearly comparable to those of conventionally sintered alumina although very high heating/cooling rates were used. A qualitative densification model is presented based on the beneficial effects of transient mismatch stresses.

1 Introduction

Rapid sintering (fast firing), which is known to provide equivalent densities at smaller grain sizes in a less energy-consuming process, has been reported for a number of materials.[1–8] It generally involves rapid insertion of a specimen into a preheated furnace at high temperatures followed by soaking for shorter times than used in conventional sintering. Although the validity of the fast firing concept has been confirmed for several ceramic materials, the mechanism has not been fully identified. Basically the superior densification is attributed to the rapid passage of a specimen through the low temperature regime where grain coarsening dominates into the region where densification mechanisms prevail, resulting in dense products in very short firing times. Using this concept, Johnson[9] modeled rapid initial stage sintering of Ag and found that the heating rate and particle size parameters have a large effect on the sintering behavior. He concludes that rapid sintering and its beneficial effects are uniquely associated to fine particles sizes.

During fast firing, energy is absorbed in the surface of the material which is then transferred into the bulk of the sample by heat conduction. Because thermal conduction takes a finite amount of time, temperature gradients within the sample exist until the sample achieves thermal equilibrium. The importance of temperature gradients in mass transport was stressed by Braudeau *et al.*,[10] and calculations of Searcy[11] suggest that temperature gradients are essential in driving densification during fast firing. Enhanced diffusion is therefore held to be responsible for accelerated sintering in fast firing.

In contrast to these findings, Morgan and Yust,[12] studying the rapid heating of ThO_2 compacts, observed that the increase in densification rate was much greater than the corresponding increase in the diffusion coefficient of the slower diffusing species. They explain their results in terms of material transport by dislocation movement or 'plastic flow'. Furthermore, it is interesting to point out that fast firing and the well known rate controlled sintering concept[13] are somehow in conflict, although both approaches are aimed at the fabrication of advanced ceramics with high density and small grain size. Whereas the first one requires very fast densification rates, the second one is based on the control of densification rates within certain limits through all stages of densification in order to avoid, e.g. premature pore closure, gas entrapment and rapid grain growth.

In the present paper, we focus on fast firing of Al_2O_3 with respect to the benefits in energy savings and production time. Harmer *et al.*[4] have already shown that pure alumina can be fired in 2 min to 95·5% of the theoretical density (T.D.), however, at 1850°C which is a major disadvantage. Therefore, the feasibility of fast firing pure Al_2O_3 at lower temperatures was studied. The intent of the present paper is to further understand fast firing and to compare the mechanical performance of rapidly and conventionally sintered alumina.

2 Experimental Procedure

Commercial Al_2O_3 powder† of high purity (99·99%) and small grain size (~0·2 μm) was used to fabricate bars (4 × 5 × 40 mm) by uniaxial pressing of

†Taimei Chemical Co. LTD, TM-DAR.

the as-received powder at 50 MPa in a steel die followed by cold isostatic pressing at 800 MPa. Green densities of 57% T.D. were attained. The specimens were heated to 200°C prior to firing in order to remove adsorbed water. The fast firing process was carried out at 1350°C using a standard box furnace. To obtain the highest heating rates possible, the samples were introduced rapidly into the preheated furnace. After sintering for various times, the samples were taken out of the furnace and cooled in air. The free cooling to room temperature took about 15 min. Polished specimens cut from samples sintered for 20 min were thermally etched in air at 1300°C for 30 min in order to examine the microstructure and to identify possible strength-determining defects. The average grain diameter was measured using the linear intercept technique.

Fracture strength was measured in 4-point bending according to German standard DIN 51110 but with rectangular bars of reduced length (25 × 4 × 3 mm) and loading spans of 10 and 20 mm. The tensile side was polished to a 3 μm surface finish and the edges were bevelled. The scatter of strength data and Weibull moduli was analyzed as described elsewhere.[14]

3 Results and Discussion

Fast firing of pure alumina by rapid insertion and removal using a preheated furnace includes extremely high heating and cooling rates, and a certain soaking time at maximum temperature. In Fig. 1, final mean densities are summarized as a function of soaking time at 1350°C. A density of 95·4% T.D. was obtained by conventional firing using a heating rate of 15 K min^{-1} and a soaking time of 20 min. Even without densification during the heating period, fast firing yielded final densities of about 99% T.D just by soaking for 20 min. The average grain size is 1·2 μm about 30% smaller than those reported by Seidel *et al.*[14] after conventional sintering using low heating rate (10 K min^{-1}) and soaking for 120 min at 1350°C. The morphology of the microstructure, however, is very close to conventionally sintered pure alumina as shown in Fig. 2. Therefore, the fast firing approach as outlined by Brook *et al.*[4-7] can be used to fabricate highly dense and fine grained alumina within very short periods of time, e.g. cycle time from room temperature to room temperature of ~30 min.

In a strict discussion, however, the density distribution during the initial stages of fast firing must also be considered. For example, Fig. 3 represents a part of the cross section of fast fired alumina after soaking for 8 min at 1350°C showing a dense

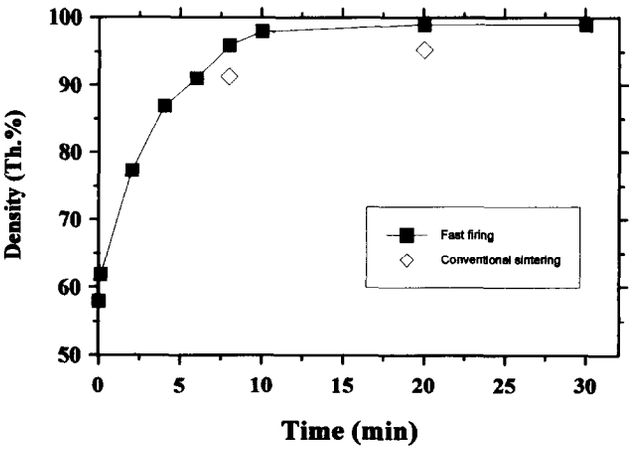

Fig. 1. Average density versus soaking time at 1350°C (note: densities plotted are determined after quenching to room temperature).

Fig. 2. Microstructure of alumina fast fired at 1350°C for 20 min.

outer layer and a porous inner core of the sample as well as a transition from dense to porous within less than 100 μm. Neglecting small gradients within the porous and dense region, the transition can be termed as interface 'porous/dense'. During soaking, this interface migrates from the surface to the center of the sample. Optical microscopy of

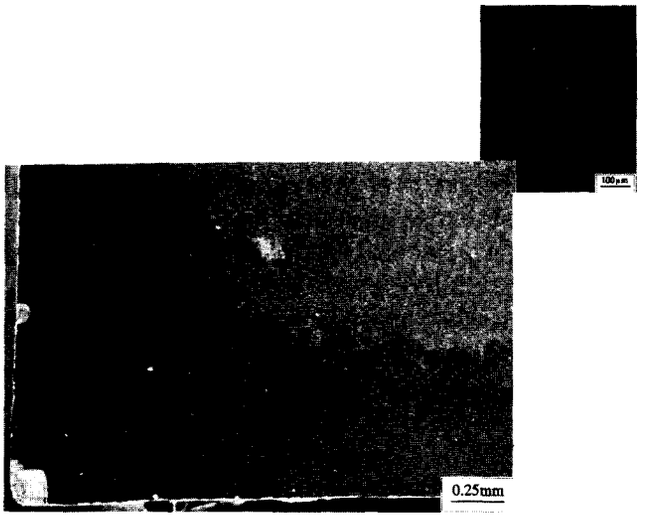

Fig. 3. Cross section of fast fired alumina after 8 min at 1350°C. The interface dense/porous is shown in the upper right at higher magnification.

samples quenched after various soaking times corroborates the evidence for a migrating interface 'porous/dense'. However, micrographic reproduction proved difficult due to low contrast and the small scale of pores and grains. In contrast to fast firing, conventional sintering at 1350°C/8 min using a heating/cooling rate of 15 K min^{-1} results in homogeneous microstructures without density gradient.

It is necessary to point out that the creation of an interface 'porous/dense' in fast fired samples is associated with the formation of transient stresses due to the shrinkage mismatch. Considering these stresses, a schematic of our understanding of the densification progress during fast firing is given in Fig. 4 contrasting the migrating densification front with the transient mismatch stresses during a given fast firing experiment at various times. For simplicity, the interface is considered as infinite. In the following, each situation is discussed in turn.

t_0: The green sample is just inserted into the preheated furnace. The surface of the sample is heated to temperatures close to the temperature of the furnace predominantly by radiation heat transfer, whereas the core remains almost at room temperature (assuming heat conduction as the velocity determining mechanism). However, a notable densification and, therefore, transient stresses caused by shrinkage mismatch are not yet formed. Considering the calculations of Searcy[11] the large

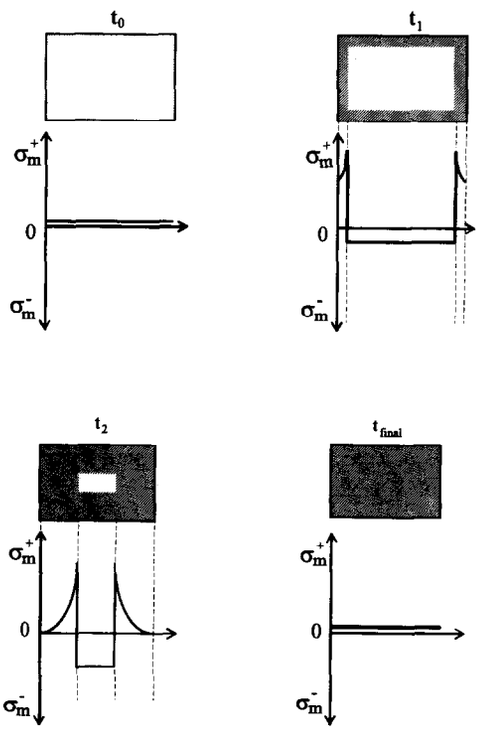

Fig. 4. Schematics contrasting densification progress and transient mismatch stresses during fast firing for the (a) porous compact, (b) initial and (c) medium state during fast firing and (d) final product after prolongated soaking at T_{max}, (note: stress relaxation effects are neglected and the interface is considered as infinitesimal thin).

thermal gradient formed may cause an enhanced mass transport although the following scheme holds also assuming conventional mass transport.

t_1: A small surface layer is densified to a certain extent. Tensile stresses are formed in this layer, however, they are overruled by high sintering potential resulting in a first densification of the outer layer (the rate of densification is neglected for this simplified discussion). The compressive stresses at the interface enhance the densification of the porous region. Due to easy stress relaxation, the stresses are only effective within a small area considering the grain size as characteristic length of microstructure.

t_2: The interface has moved further and, therefore, densification caused by transient stresses proceeds in the interior. The center core, however, is still porous (cf. Fig. 3). The densification already present is associated with volumetric shrinkage of the sample and, therefore, with mass transport from the outer dense to the inner porous part.

t_{final}: The sample is almost fully densified, i.e. after 20 min soaking at 1350°C. Furthermore, transient stresses caused by constrained sintering are diminished due to creep relaxation. The microstructure of the final product (Fig. 2) is similar to conventionally sintered pure alumina.

In summary, besides the densification mechanism mentioned generally for fast firing, transient stresses play an important role improving densification. We should point out that subleties like densification by stress induced diffusion are not included here and may provide an additional effect for the very fast densification observed. Specimen composition and size effects are also not included since these do not effect the basic influence of transient stresses, however, they can be used to improve our understanding of fast firing. For instance, the specimen thickness can be used to calculate the rate of interface movement. Considering the present results (cf. Fig. 1), we can estimate an interface movement of 4 $\times 10^{-6}$ ms^{-1}. For a quantitative analysis, one would have to face for example the rate of heat transfer to the surface, the heat conduction within the sample as well as stress relaxation kinetics. Calculations of heat conductivity, however, are particularly difficult due to non constant parameters during fast firing, i.e. pore size distribution.

Nevertheless, while appreciating that we present a simplified picture of fast firing, the results can be linked to previous work. For instance, Johnson[9] concluded in his review that rapid sintering is a phenomena unique to fine particle sizes. Considering the model presented, it is obvious that reactive fine particles are required in order to overrule the tensile stresses in the dense region by high sintering potential as well as to enhance stress relaxation by creep phenomena.

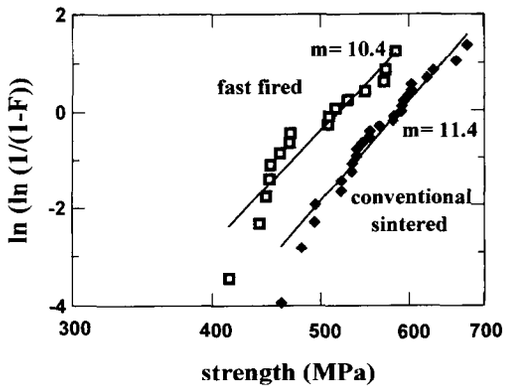

Fig. 5. Bending strength distribution (Weibull plot) of alumina fast fired at 1350°C for 20 min and conventional alumina sintered at 1350°C for 2 h.[14]

The preliminary results of fracture strength of fast fired alumina indicate that there is almost no severe strength degradation when compared to conventionally sintered alumina. Fig. 5 shows the strength distributions of fast fired and conventionally sintered alumina,[14] with an average strength of 520 and 564 MPa and Weibull moduli of 10·4 and 11·4, respectively. The solid lines through the strength data are curves representing the fit on the basis of a two parameter Weibull approach.

Polished surfaces investigated reveal defects of about 10–15 μm in the form of voids, as shown in Fig. 6, probably originating from powder agglomerates in the green compact. However, there is no indication of a change of the defect character when compared to conventional sintering. The small drop in strength and the corresponding increase in flaw size may be attributed to the transient tensile stresses in the surface region during fast firing, resulting in an expansion of flaws already present prior to heat treatment. With this hypothesis, nearly defect-free green bodies as well as further enhanced stress relaxation by creep is required for obtaining high strength alumina by fast firing.

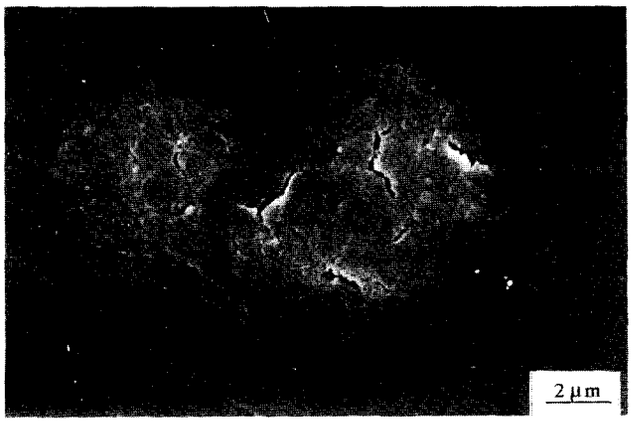

Fig. 6. SEM micrograph of polished surface showing typical defects in fast fired alumina.

4 Conclusions

Using fine reactive powders, the fast firing approach can be used to fabricate alumina within very short production times at low temperature. Transient stresses caused by constrained sintering are formed during fast firing. These stresses accelerate densification and enhance the formation of a dense, fine grained microstructure. The mechanical performance of the final product is, in first approximation, comparable to conventionally sintered alumina.

Acknowledgement

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