ADVANCED CERAMICS WITH DENSE AND FINE-GRAINED MICROSTRUCTURES THROUGH FAST FIRING

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Abstract. Fast firing has been used to produce dense ceramics usually in less than 10 min using conventional furnaces. Most of densification occurs under non-isothermal conditions. The very fast densification rates observed are related to high heat inputs, originated from changes in the internal structure of the sample during fast firing. The amount of energy available for sintering increases by the formation of a dense outer layer which controls the flux of heat to the interior of the compact. High thermal stresses were expected to be generated from high heating rates in fast firing, but no serious manufacturing defect was observed. This fact could be related to the formation of a densification front moving from the outer surface towards the centre of the sample. In this paper, the production of dense, fine-grained ceramics through fast firing is reviewed. The variables that control the microstructure and densification are discussed.

1. INTRODUCTION

The most part of the energy consumed by the ceramic industry is used for firing operations. A reduction of the energy necessary for firing could be obtained by varying furnace design concepts, as well as properties of ceramic bodies allowing higher heat inputs [1].

Most ceramics are known to be refractory. Thermal diffusivity determines the rate of rise of temperature in the centre of a sample which is being heated at the surface. The low thermal diffusivity of the green compact tends to slow down the rate at which heat is transported to the centre of the body during firing [2,3].

Powder compacts may show most of sintering and the highest densification rate during the heating-up period, i.e., under non-isothermal conditions [4]. Rapid densification accompanies fast heating-up [5]. It was found experimentally that the temperature could be raised quite rapidly and the sintering process enhanced to a large extent by fast firing schedules using either conventional furnaces [6], heated by electric resistance or fuel combustion, or alternative techniques, such as microwave (MW) [7,8] or millimeter-wave sintering (mS) [9], spark plasma sintering (SPS) [10], self-propagating high-temperature synthesis (SHS) [11,12] and flash sintering (FS) [13-17].

The denomination "fast firing" has been employed since the 1970´s to both traditional [18-20] and advanced ceramics [21,22]. The rapid thermal treatment in contrast to conventional "slow" firing is usually meant for cycles taking less than 60 min cold-to-cold, sometimes even less than 1 min! Nevertheless, firing cycles in the tile, brick and porcelain industry of up to 6 h have been formerly referred to as "fast" firing [23-25].

Fast fired traditional ceramics include silicate-based bricks and tiles [26-28], and porcelain [29-31], both at laboratory and industrial scales [32]. In

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the latter case, fast firing has been carried out in tunnel [33] or roller kilns [34].

Advanced ceramics sintered in high heating rates have been reported for alumina [21,35-37], zirconia [38,39], ferrites [40-43], barium titanate [44-47], indium tin oxide (ITO) [48], ceria [49], lead iron niobate (PFN) [50], lead magnesium niobate (PMN) [51], lead zirconate titanate (PZT) [52-55], yttrium aluminum garnet (YAG) [56], as well as composites [57,58], glasses [59,60], glazes [61,62], and glass-ceramics [63-65].

When using conventionally heated furnaces, the very high densification rates observed seems to be related to high heat inputs, due to changes in the internal structure of the sample during fast firing [5]. The formation of a dense outer layer during the initial stage of fast firing increases the rate at which heat is transferred to the centre of the body. Increased diffusion caused by the thermal and/or density gradient seems to be the driving force which speeds up ceramic processing rates.

In this paper, the production of dense, fine-grained ceramics through fast firing is reported. MW and SPS techniques are beyond the scope of this review, which is restricted to electrical resistance ovens as heating sources and to advanced ceramics as sintered products. The variables that control the microstructure and densification are discussed.

2. FAST FIRING TECHNIQUES AND EQUIPMENTS

Introducing a green compact in a pre-heated furnace at sintering temperature represents an ultimate heat input. Fast firing has been successfully used to fabricate high-density, fine-grained ceramics [66]. In order to obtain economical benefits through energy saving from the superior densification resulting from firing in a short time at high temperature, there is a need for a specific furnace design.

In fast firing furnaces, heating requires the highest transfer rate; therefore, heat should be transmitted primarily by radiation. As radiation necessitates exposure of a large area to radiant heat, powder compacts must pass through the furnace one at a time. The reduction in mass of products to be heated (refractory and loading material) per unit of time, contributes to reducing the furnace size and its thermal inertia allowing that all internal chamber faces could be heated to uniformly high temperature.

As the load is only one piece high, the use of furnace furniture is reduced, additional energy savings could be made if the powder compacts can
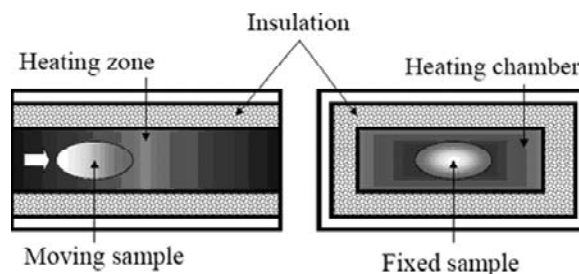

Fig. 1. Schematic representations of the fast firing technique: (a) continuous tubular furnace; (b) intermittent chamber furnace.

be set directly at high temperature without need of additional furniture. A significant reduction in capital costs associated with the use of furniture and the energy needed to heat it could be expected.

The dynamics of the fast firing technique allows observing any detrimental effect of the processing variables on products earlier than in conventional firing, making possible a rapid adjustment in production.

Fast firing of ceramics has been successfully accomplished in both continuous zone-sintering furnaces and intermittent resistive electric chamber furnaces, as shown schematically in Fig. 1.

2.1. Zone-sintering furnaces

Short firing times were achieved for alumina, by using a fast firing zone-sintering process developed by Jones and Miles (Fig. 1a) [67]. Powder compacts were subjected to a non-isothermal treatment, and sintered for a short time when pushed from one end to the other, through a hot zone held at very high temperatures. Through this process, dense and fine-grained ceramics could be fabricated in about 15 min at 1850 °C [63].

In the technique of zone-sintering, the temperature profile of the furnace is very steep and the furnace is not at constant temperature. Samples were pushed at rates ranging between 10^{-4} and 10^{-2} m/s through a short cylindrical furnace (0.02 m diameter, 0.05 m hot zone length). For each maximum temperature of the hot zone, there was an optimum speed of traverse through the furnace for obtaining the highest sintered density [69].

2.2. Intermittent chamber furnaces

In order to obtain the highest possible heating rate, samples have been introduced rapidly into a furnace preheated at the sintering temperature (Fig. 1b). After fast fired for a short period of time (typically 5 to 10 min) the samples were taken out of the furnace and
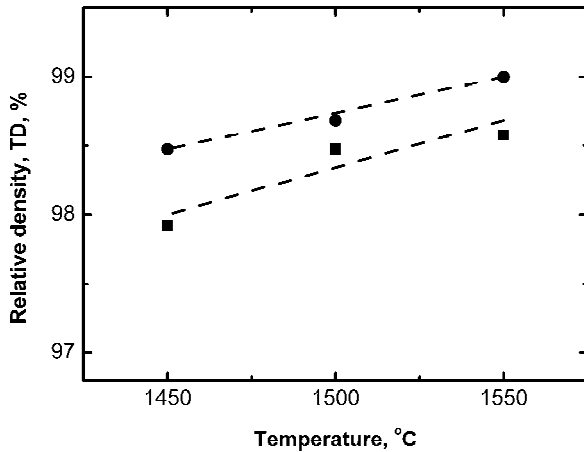
Fig. 2. Relative density-temperature profile of Al_2O_3 compacts fast fired at indicated times (adapted [36]).

Fig. 3. Firing programmes compared: (a) conventional; and (b) fast firing.

air cooled. Cooling to room temperature took about 15 min. In order to reduce the thermal shock and to create a homogeneous heating field, the green compacts were placed in the centre of a box comprising of alumina ceramic foam plates with 80 to 90 vol.% porosity. A commercial submicrometric Al_2O_3 powder was used to prepare fired bodies of relatively high density (>98.5% TD) after firing for 5 or 10 min at temperatures ≤1550 °C, as shown in Fig. 2 [36].

3. HEAT TRANSFER PHENOMENA

The common firing schedule in conventional sintering involves the use of a constant heating rate to maximum temperature (T_{max}) and a dwell time at this temperature until the required properties are obtained (Fig. 3a). In fast firing, instead, the heating rate is some orders of magnitude higher than in conventional sintering and there is no need for an isothermal hold at the sintering temperature (Fig. 3b).

In conventional sintering, both convection and radiation are present. Heat transfer by convection provides the major contribution at lower temperatures, and heat transfer by radiation is most important at higher temperatures, typically where sintering occurs (>1000 °C).

The rate of heating is governed primarily by the rate of heat transfer from the furnace to the specimen. The heat transfer process may be described by:

$$q = \left(h_c + h_r \right) A \Delta T, \tag{1}$$

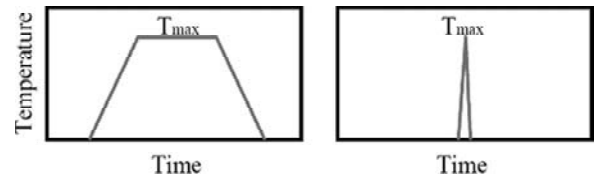where A is the surface area of heat transfer, h_c and h_r are the heat transfer coefficients by convection

and radiation, respectively; and ΔT the temperature difference between the body surface and the surrounding fluid at bulk temperature, and between the body surface and the font of radiation, respectively for convection and radiation.

Temperature gradients within the body depends on the rate of heat input at the surface; hence, the faster the heating rate, the greater the temperature gradient. If the surface temperature increases rapidly, internal temperatures lag significantly behind. The limit of densification rate is determined by the ability of the sample to diffuse heat. If sufficient time is not allowed for heat to penetrate into the body, the resulting steep temperature gradient might originate body damage, in the form of cracks and microcracks.

Fast firing is accomplished mainly by radiation. As powder compacts are placed in or pushed through a region of high temperature, its surface is exposed to radiation. Radiation coefficients are much higher than convection coefficients. The amount of heat transferred by radiation is proportional to the difference of the fourth power of the temperatures of the transmitting and receiving bodies, furnace and samples, respectively. Thus, the amount of heat transferred to the sample is higher the hotter the temperature of the furnace.

When a green compact at room temperature is inserted in a pre-heated furnace or travels through a hot zone, a large temperature gradient appears between the surface and the inside, as consequence of the low thermal diffusivity [70]. As shown in Fig. 4, if the furnace temperature is high enough to produce dense Al_2O_3 under conventional schedules, a dense outer layer is formed after a period of time enough to increase its surface to the furnace temperature. These structural changes strongly affect the densification rate, due to the high thermal diffusivity of dense alumina when compared to a green compact. The formation of a dense Al_2O_3 layer at the interface air/green compact has a significant effect on the temperature distribution and the resulting density profile. As it controls the flux of heat to the interior of the compact, there is a significant increase in the amount of energy available to
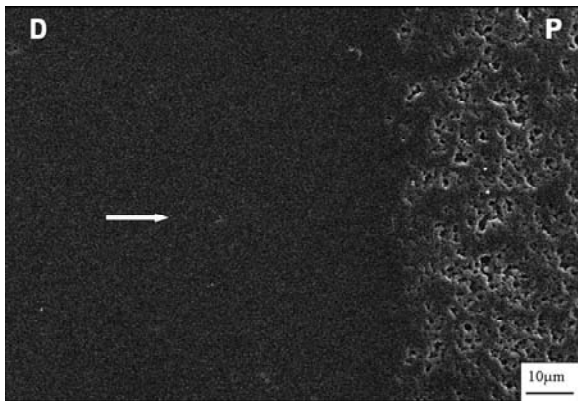
Fig. 4. Scanning electron micrograph of a cross section of fast fired Al_2O_3, showing the densification front moving from the dense outer surface (D) towards the porous centre of the sample (P), see [5].

densification. High densification rates observed during fast firing seem to be related to these changes in the internal structure of the sample. This phenomenon is not considered a complementary sintering mechanism but may contribute to the enhancement of sintering. As radiation could enhance diffusion, at least for surfaces that are "seen" by the source of radiation, remains the question if radiation is contributing directly to rapid densification or is merely a heat transfer medium.

4. FORMATION OF A DENSIFICATION FRONT

After the formation of a measurable and dense layer at surface of the sample, its thermal diffusion controls the heat flux to the interior of the compact. The thermal diffusivity (α) of the dense outer layer determines the rate of temperature rise in the interior of the compact:

$$\alpha = k / \rho c_p, \qquad (2)$$

where k is the thermal conductivity; ρ, the density; and c_p, the specific heat capacity of the material.

The thermal diffusivity represents the ratio of heat conducted through a material to the heat stored per unit volume. Thermal diffusivity is both a function of density and temperature. The specific heat capacity increases with temperature and the thermal conductivity decreases with temperature indicating that thermal diffusivity decreases with temperature. As a green compact at room temperature is inserted in a pre-heated furnace or goes through a hot zone at high temperature, and the surface of the sample has not already reached the sintering temperature, i.e., density remains approximately constant and

equal to the green density, heat tends to accumulate at the surface. As the surface of the sample reaches a temperature high enough, densification begins, absorbing some amount of energy (~150 kcal/mol in the case of Al_2O_3) [71], which further hinders the flux of heat to the interior of the compact. After the formation of a dense layer at surface of the sample, the surplus of heat can diffuse to the interior of the compact. As the time required for heat to diffuse through the porous compact is higher than the time required for full densification, a densification front is formed just at the heat front moving into the material.

As heat emerges from the dense alumina layer, it is consumed at the front by heating up and by the sintering mechanisms, i.e., the velocity of advance of the densification front is controlled by heat diffusion through the dense layer. The difference between the thermal diffusivity of the dense layer (α_d) and the porous core (α_p) determines the form of the densification front. The higher the α_d/α_p ratio, the sharper the densification front [72].

The effect of porosity on the thermal conductivity of sintered alumina has been first investigated by Coble and Kingery [73]. As the thermal conductivity decreases rapidly with the increase in porosity, a relatively high value of ~5 is expected for the α_d/α_p ratio. Simultaneously, it could be speculated that as the core has not been affected by the temperature until is reached by the sintering front, its thermal diffusivity could be significantly low.

An increase in thermal conductivity of ceramic powders has been determined to be a consequence of thermal treatments [74,75]. Healing of microcracks within the particles during heating, relaxation of pressure of the contact surface between particles (necks), and increase in the degree of crystallization could be responsible for this behaviour.

In conventional sintering schedules, considerable time is spent at relatively high temperatures before sintering. In fast firing, due to the short time required for heating up, the core is more likely to remain unmodified and to retain the thermal characteristics of the as-received powder. If it is so, a lower than expected thermal diffusivity at the sintering front could favour heat storing instead of heat diffusion, increasing locally the amount of energy available for sintering.

Simultaneously, the presence at the sintering front of powder, which has not experienced a previous thermal history, may contribute to the enhancement of sintering. In conventional sintering, as demonstrated by Greskovich and Lay [76], much of
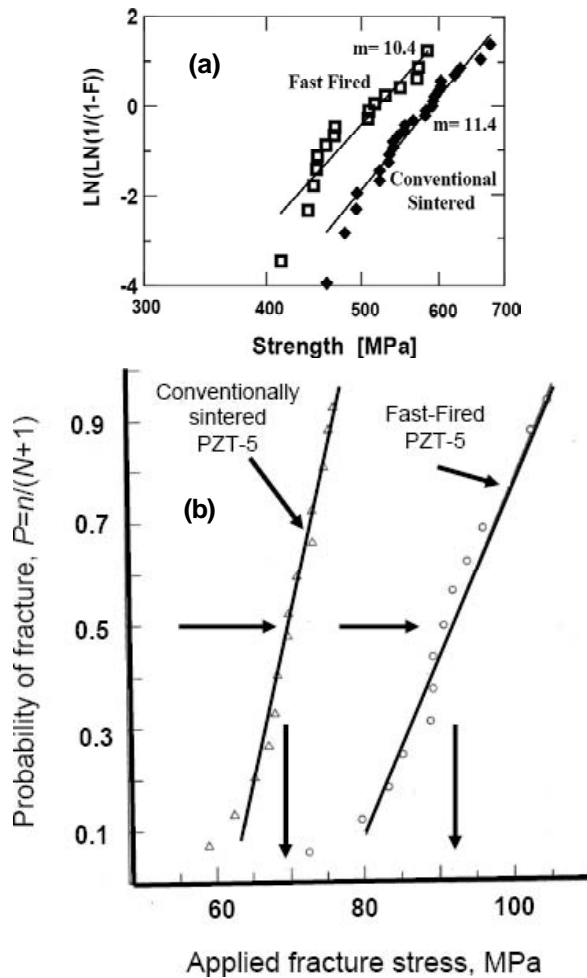
Fig. 5. Weibull plot of conventional and fast fired ceramics: (b) reaction-bonded aluminium oxide (RBAO) [57], and (a) lead zirconate titanate (PZT), adapted from [52].

the initial surface area can disappear during initial heating of alumina before measurable densification takes place. In fast firing, an increment of the sintering rate could be expected, since the driving force and the diffusion distance remain almost unchanged until reached by the sintering front.

Therefore, high densification rates observed during fast firing seem to be related to a change in the internal structure of the sample by the formation of a densification front. An enhancement of sintering may be achieved by (a) a significant increase the amount of energy available at the densification front, as a consequence of its high thermal diffusivity when compared to a green compact, (b) the presence at the sintering front of powder, which has not experienced a previous thermal history, (c) a considerable vacancy gradient at the sintering front, enhancing diffusion via vacancies.

5. STRESS-RELATED PHENOMENA

As the densification rate is a function of local temperature and time, the presence of steep thermal gradients within the sample and the continually changing physical-chemical parameters related to the material during fast firing make a reliable calculation very difficult.

During conventional firing, the tensile stresses originated by the use of high heating rates may cause failure of the material during heating. As the green compact has a low thermal diffusivity, a large temperature gradient appears between the surface and the interior. Differential thermal expansion causes tensile stresses on the surface and compressive stresses in the centre. Since the strength of the green compact is low, at high heating rates the tensile stresses might cause failure.

The ability of the sample to withstand the internal stresses produced by fast firing remains to be explained. Fracture strength and Weibull moduli of fast fired Al_2O_3 [36], lead zirconate titanate ceramics (PZT) (Fig. 5a) [52], as well as fracture strength of reaction-bonded aluminium oxide (RBAO) (Fig. 5b) [57], are similar or higher comparing to conventionally sintered ceramics. This indicates that there is no remarkable change of the defects character when compared to conventional sintering.

If the stress exceeds the strength of the material, then some stress relief mechanism has to take place. In conventional sintering, during the heat up period, using slow to moderate heating rates, the creep rate is comparable to the densification rate which implies that the tensile stresses build during sintering are relaxed quickly [77]. During rapid shrinkage in fast firing, the possibility of stress relief by plastic deformation may also be considered. Both lattice and boundary diffusivities are enhanced by a fine-grained microstructure in a high temperature region, what gives the basic conditions to promote superplastic deformation.

The ability a powder compact of withstanding rapid heating during fast firing, resulting in dense and crackles products, could be related to the presence of a thermal/densification front. A thermal/densification front was observed in fast firing in intermittent, as well as in continuous furnaces. In the technique of zone sintering, as samples are pushed through the furnace, a front of temperature/densification is formed. As the sample passes through the short hot zone, held at high temperature, a front end of the sample fully fired and dense together with a rear end unfired can be found, and intermediate densities are present in the middle section.

After fast firing an almost fully densified sample shows increased tensile strength and thermal conductivity, so that it is not likely that a crackless sintered sample produced by fast firing will rupture during cooling in air. The stresses resulting from the sudden cooling of fast fired samples may also have desirable effects on final product [78].

6. MASS TRANSPORT

In the absence of a chemical potential gradient, the presence of temperature gradient results in mass transport due to thermal diffusion [79,80]. As the energy flows from high to low temperature in a temperature gradient, so is the direction of movement of matter. The mechanisms of matter transport under thermal gradients are still under discussion. Braudeau *et al.* [81] reported that the matter transport of alumina is faster under temperature gradient than in isothermal experiments performed at the same temperatures. Searcy [82] proposed an initial-stage vapour transport temperature gradient mechanism. Beruto *et al.* [83] found that temperature gradients supplement surface energy diffusion changes in driving sintering and related processes not only by vapour transport but also by a surface, grain-boundary, or bulk diffusion path. Regardless of the mechanism, the presence of temperature gradients enhances matter transport towards regions of lower temperatures, i.e., matter is transported inwards to cooler porous regions.

Mass transfer for sintering is due to atomic diffusion *D*, according to the Arrhenius equation:

$$D = D_0 \exp\left(-Q_d / RT\right), \tag{3}$$

where D_o is the temperature-independent pre-exponential; Q_d, the activation energy for diffusion; R, the gas constant; and T, the absolute temperature.

The activation energy Q_d represents the amount of energy necessary to break the bonds between an atom and its nearest neighbour atoms and move it to the next position, which may be a vacancy in the lattice.

Moreover, when the vacancy diffusion [84] is considered:

$$D = C_v D_v, \tag{4}$$

where *D* is the coefficient of self diffusion (when all atoms that exchange position are of the same type); C_v is the vacancy concentration; and D_v is the coefficient of vacancy diffusion.

Since C_v is temperature-dependent, along a temperature gradient *dT/dx* there is a concentration gra-
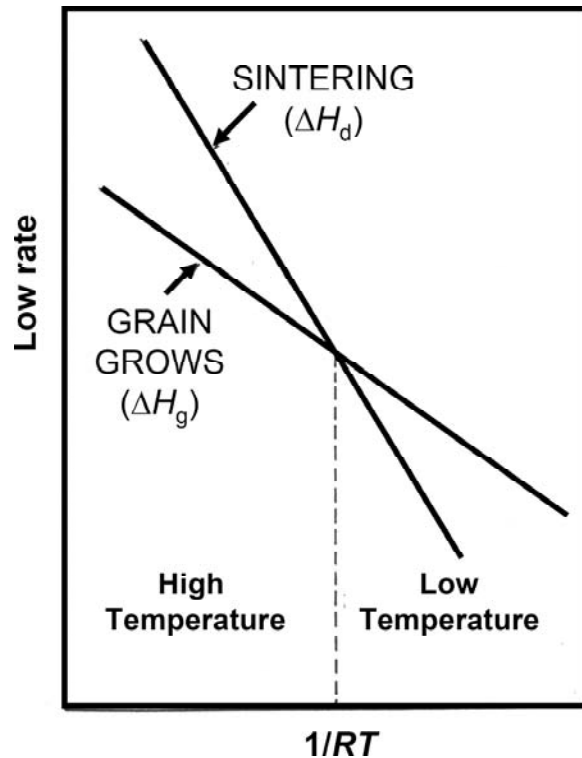

Fig. 6. Densification and grain growth as a function of temperature, replotted from [2].

dient dC_v/dx, which has a strong effect on mass transfer through volumetric self diffusion of atoms. Thus, the higher the concentration gradient, the higher the vacancies diffusion.

The number of vacancies in thermodynamic equilibrium N_v is temperature-dependent according to:

$$N_v = N \exp\left(-Q_v / k_B T\right), \tag{5}$$

where *N* is the total number of positions in the lattice; Q_v is the necessary energy for producing a vacancy; and k_B is the Boltzmann constant.

In this case, there is preferential vacancy diffusion from the lowest to the highest temperature and, as a consequence, a preferential atomic diffusion in the opposite sense, i.e., from the core to the surface, which is hotter. This might explain the higher densification in the presence of a higher thermal gradient and the existence of a densification front which moves along the gradient, i.e., from the highest to the lowest temperature, corresponding to the sense surface to the core of the sintering sample.

7. OBTAINING FINE-GRAINED MICROSTRUCTURES

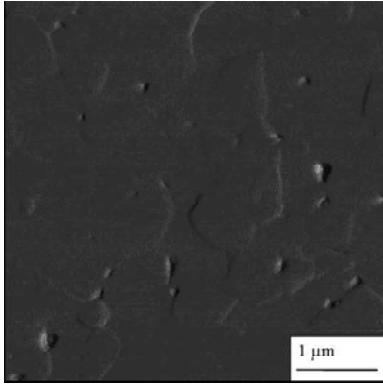In order to improve the properties of ceramics for either structural or functional applications, reducing

Fig. 7. Atomic force microscopy (AFM) of alumina fast fired at 1550 °C for 5 min.

the grain size and limiting the formation of defects are important. During the heat up period a considerable microstructural development and the major part of densification of a powder compact takes place. Young and Cutler [85] suggested that, in constant heating rate experiments, there may be distinct temperature regions in which grain-boundary or volume diffusion may dominate over surface diffusion. To achieve small grain size in fired ceramics, without the use of additives as grain growth inhibitors, may be achieved by establishing conditions under which mass transport mechanisms leading to densification are favoured relative to those leading to grain boundary migration.

In those cases where the densification and grain growth involve different transport mechanisms, the grain size-density relation is dependent on the ratio between the diffusion coefficient for grain boundary (D_{gb}) and diffusion coefficient for surface diffusion (D_s). Considering similar diffusion layer thickness for both mechanisms, low grain growth occurs if the diffusion coefficient ratio favours the densifying mechanism i.e., $D_{gb} \gg D_s$. [86] The densification and grain growth process are exponentially related to the temperature by equations of the form [2]:

$$\rho = \rho_0 \exp\left(-\Delta H_d / RT\right), \tag{6}$$

$$G = G_0 \exp\left(-\Delta H_g / RT\right), \tag{7}$$

where ΔH_d and ΔH_g are the enthalpies associated with the densification rate, ρ, and grain growth rate, G, respectively, being ρ_0 and G_0, the correspondent pre-exponential coefficients.

If favourable temperature conditions can be selected on the basis of ΔH_d and ΔH_g ($\Delta H_d \gg \Delta H_g$), coarsening could be minimized spending as short time as possible in the low temperature region (Fig. 6) [2]. For compositions where the activation

enthalpy for the densification process is high relative to that for grain growth, samples with finer grain microstructure can be produced by high-temperature, short-time firing cycles.

In general, this assumption can only be verified empirically because of the unavailability of requisite thermodynamic data. Corindon (α-alumina) is one of the few exceptions and, on the basis of diffusion data from the literature, it appears to be a suitable candidate for fast firing. As the heating rate is an intrinsic part of sintering conventional schedules, avoiding grain growth seems to be a difficult task in conventional sintering. If grain growth occurred before sintering was complete, the larger pore/boundary distances lower the density rate. In the fast firing technique, as the powder compact is heated rapidly to the maximum temperature, as fast as heat can be absorbed, densification can occur prior to substantial grain growth, as shown in Fig. 7. An isothermal hold at maximum fast firing temperature beyond the time required for achieving thermal uniformity throughout the sample seems not to be necessary.

8. CONCLUSIONS

High density and fine-grained microstructures can be achieved through fast firing of ceramics.

It is possible to control the process responsible for the rates of densification and grain growth, by controlling the time/temperature conditions employed during sintering of the powder compact.

Fast firing provides an opportunity to carry a compact through the temperature range where surface diffusion-controlled coarsening occurs readily to a regime where the densifying mechanisms of grain boundary and lattice diffusion predominate.

An isothermal hold at the sintering temperature beyond the time required for achieving thermal uniformity throughout the sample is no longer necessary.

Heat transfer phenomena play a role speeding up ceramic processing rates. High densification rates observed during fast firing in conventional chamber furnaces seems to be related to a change in the internal structure of the sample.

The presence of high thermal gradients during fast firing is responsible for the formation of a densification front.

The formation of a dense outer layer controls the flux of heat to the interior of the compact, and increases the amount of energy available for sintering.

Although the understanding of the mechanism governing densification and microstructural development is rather limited, fast firing processes offer a promising route for the fabrication of bulk ceramics

Research activities in the fast firing technique have formed the basis for a sintering process that has the potential for simultaneously improving materials' properties and reducing manufacturing costs.

ACKNOWLEDGEMENTS

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