Chapter 3: Firing

3.1. Introduction

Green processing is followed by firing of the compact. During firing particles are bonded and voids between particles shrink. Bonded particles join together to form grains. Whereas bonding and elimination of voids are beneficial processes, as they bring about better mechanical properties, grain growth is detrimental, but unavoidable.

Heat treatment is conventionally divided into 'initial', 'intermediate' and 'final' stages, as illustrated in fig. 3-1. The initial stage is also referred to as 'neck growth'. It ends when particles are intersected by true pores and not mere voids as during the initial stage. No grain growth occurs during the initial stage. The intermediate stage ends when pores are pinched of into isolated pockets. Limited grain growth occurs during the intermediate stage. In the final stage the isolated pockets are eliminated and larger grains grow by incorporating smaller pores. Grains continue to grow after the elimination of pockets. (Coble, 1961).

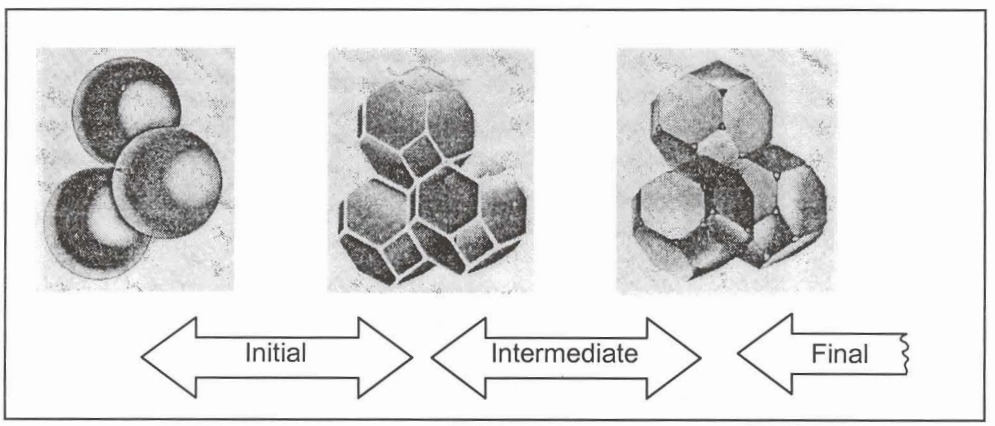

***Fig. 3-1**: The stages of heat treatment. After Coble (1961).*

Heat treatment may be enhanced by the application of either unidirectional pressure ('hot pressing') or isostatic pressure ('hot isostatic pressing' or 'HIPping').

In this work 'firing' is used as a broad term to refer to any form of heat treatment, be it pressureless sintering, hot pressing, or HIPping. The term 'sintering' is used here to specifically refer to pressureless sintering.

No details of the pre-firing processing are given in this chapter. To limit the amount of details only the initial particle size and green density are quoted. These two variables should give a sufficient representation of the pre-firing condition of the compact.

As in the chapter on green processing, literature reviewed here were chosen for its relevance to processing of similar alumina powder to that used in the experimental part of this work. Literature of work on submicron powders was therefore chosen for review.

3.2 Reduction of firing temperature by reducing particle size

Table 3-1 compares some results of pressureless sintering of compacts of submicron particle powders. It illustrates the possibility of reducing sintering temperature by reducing particle size, while still achieving high density. Of special interest is the result of Yeh and Sacks (1988), who claimed to have achieved 100 % relative density in under 2 hours at only 1 150 °C in air.

***Table 3-1**: Particle sizes and sintering temperatures compared. Note that all fired densities are ≥ 95 %.*

Powder		Run-up to sintering	Relative density at start of sintering (%)	Sintering		Relative fired density (%)	Reference
Average particle size (nm)	Characterisation			Temperature (°C)	Time (h)		
60	BET	None	70	1 150	2	100	Yeh and Sacks (1988a)
300	Not stated	Heating at 4 °C/min.	Not stated. Green body formed with dry pressing.	1 450	2	95	Kwon *et al* (1987)
				1 500		97	
				1 550		98	
~ 400	Median Stokes	None	73	1 260	12	96	Yeh and Sacks (1988b)
			65				
			73?	1 340		99	
			65?				
720	Manufacturer	• Ambient to 275 °C in 0.3 h • 0.5 h at 275 °C • 275 to 900 °C in 1 h • 900 to 1600 °C in 0.25 h	80	1600	1.5	98	Cameron and Raj (1990)
			76				

3.3 Less aggressive firing by controlling green structure

Roosen and Bowen (1988) found experimentally that green bodies formed through a 'wet' processing route densify more easily than those formed by dry pressing. In fig. 3-2 the temperature of the maximum shrinkage rate of green bodies formed through dry pressing and 'wet' routes are compared. It can be seen that the temperature of maximum shrinkage is more than 50 °C higher for dry pressed green bodies than for 'wet' processed green bodies of a similar green structure. In addition to this, a dramatic drop in temperature of maximum shrinkage occurs below an average pore size of 51 nm for green bodies formed through wet routes. As 'dry' and "wet' data follow the same trend in the relationship between green texture and green density (fig. 2-2), this effect cannot be explained in terms of green density alone. Roosen and Bowen suggest two possible explanations for this effect:

1) Cappilary forces during drying improve the green microstructure as compared to 'dry' processed samples, or

2) Particles are 'cemented' to each other due to hydrolysis during 'wet processing', which enhances densification.

Further evidence for the beneficial effect of using fine textured green bodies are shown in fig. 3-3, where finer textured green bodies are seen to result in higher fired densities under the same firing conditions.

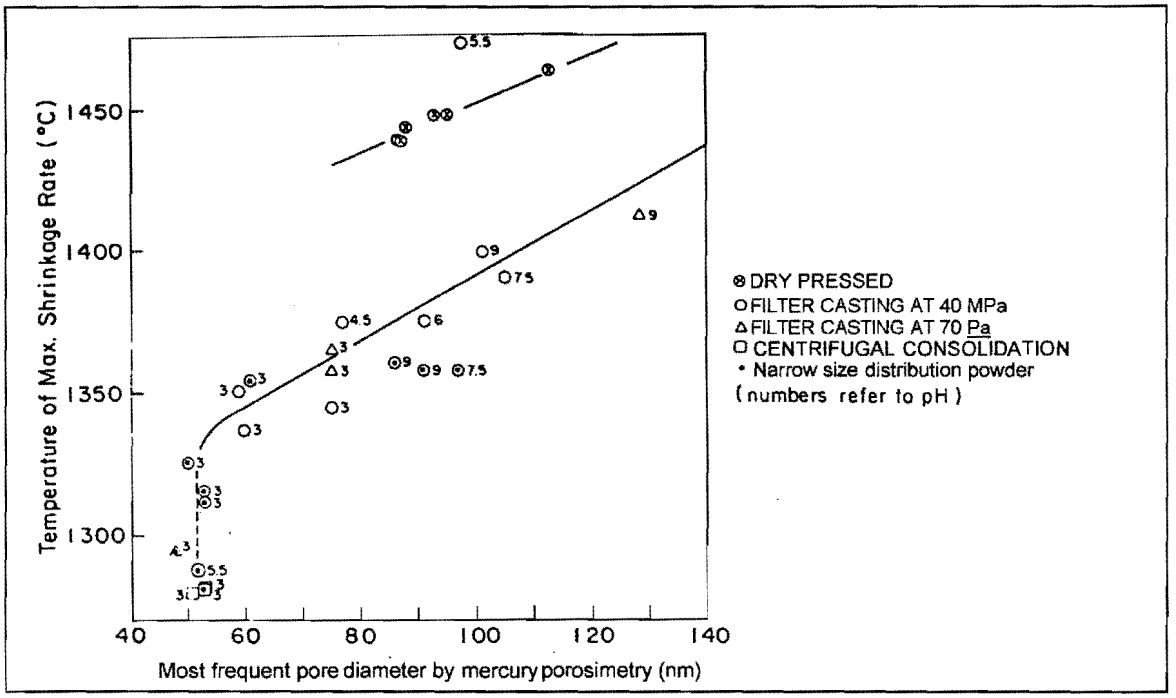

***Fig. 3-2**: Temperature of maximum shrinkage rate compared to green microstructure. Heating rate 10 °C/min. See table2-1 for green processing details not mentioned on graph. (Roosen and Bowen, 1988).*

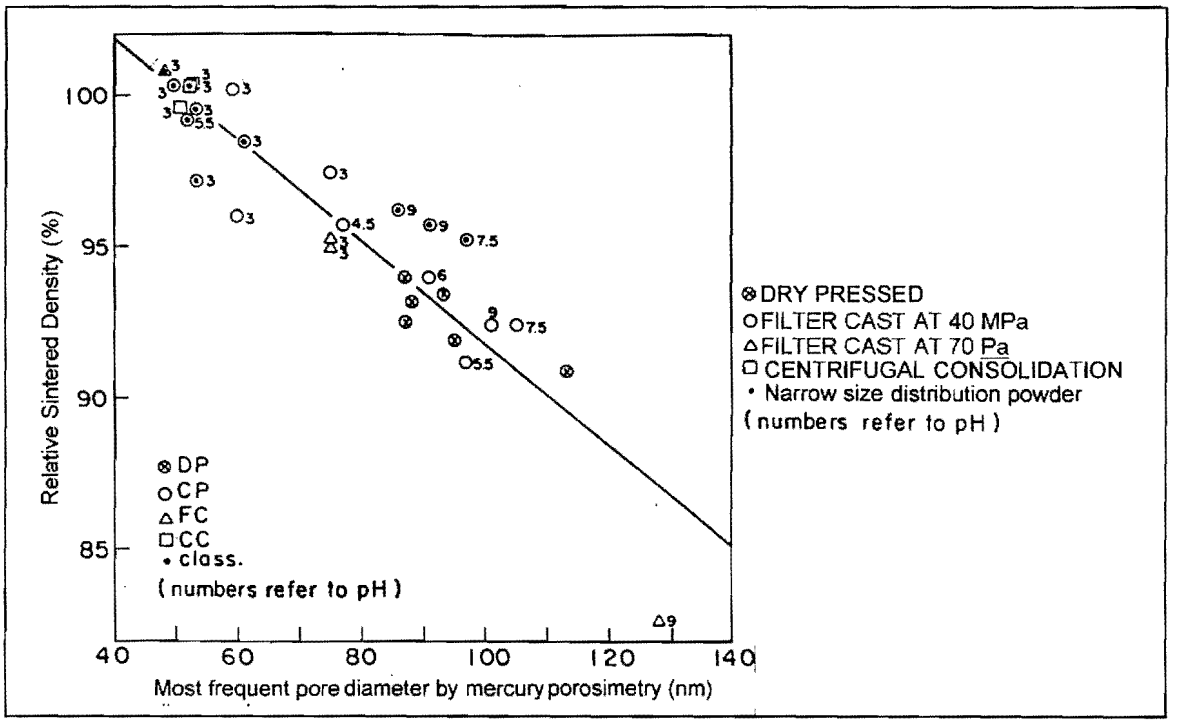

***Fig. 3-3**: Sintered density related to green microstructure. Heating rate 10 °C/min and dwell at 1 500 °C for 30 min. See table2-1 for processing details not mentioned on graph. (Roosen and Bowen, 1988).*

3.4 The influence of powder size distribution on grain size and fired density

As long as finer particles are free to move to fill the voids between larger particles (as in well-dispersed suspensions), broad size distributions lead to more efficient packing of particles in the green body. It is difficult for finer particles to penetrate unfilled voids between larger particles during dry pressing, while more rearrangement of particles is possible during 'wet' processing. In wet processing, smaller particles would therefore be able to penetrate voids between larger particles. This would lead to a greater green density, which should lead to faster densification during firing. However, it is generally accepted that powders with narrow size distribution produce compacts that are superior in terms of having narrow grain size distribution and the ability to densify at lower temperatures. Yeh and Sacks (1988b) criticised this view, citing a lack of evidence. In Yeh and Sacks's work (1988b), a broadly and narrowly distributed powder (fig. 3-4) were dispersed by controlling pH at ~ 4. Both powders have an average particle size of 0.4 μm. The suspensions were slip cast, and the resulting green bodies were sintered at a range of temperatures between 1 180 and 1 340 °C. As can be expected the broadly distributed powder densified faster (fig. 3-5). Contrary to the conventional view though, in this instance it was indeed found that narrow size distribution did not have an advantage above a broad distribution in terms of fired microstructure, showing a similar average grain size and grain size distribution (fig. 3-6 and 3-7).

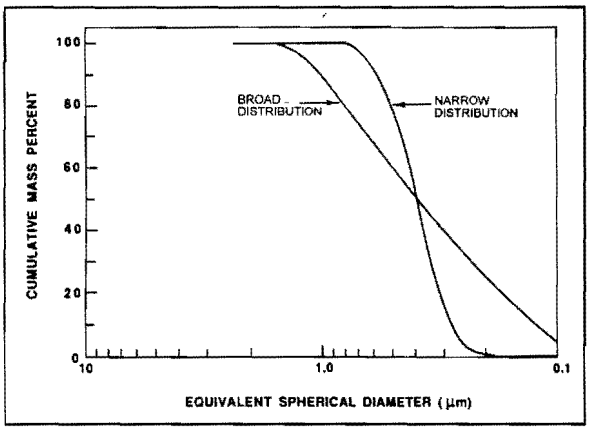

***Fig. 3-4**: X-ray sedimentation data for the powders used by Yeh and Sacks (1988b). Note that <u>different</u> powders was actually used; the difference in distribution is not due to different suspension preparation routes, i.e. the difference was not due to differences in the breakdown of agglomerates.*

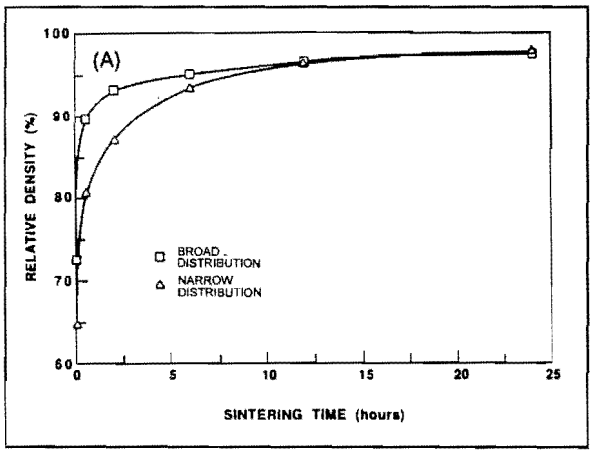

***Fig.3-5**: A comparison between the densification of green compacts prepared from powders with broad and narrow size distribution. The compacts were sintered at 1 260 °C. (Yeh and Sacks, 1988b.) Note the difference between starting, i.e. green density, of the two compacts.*

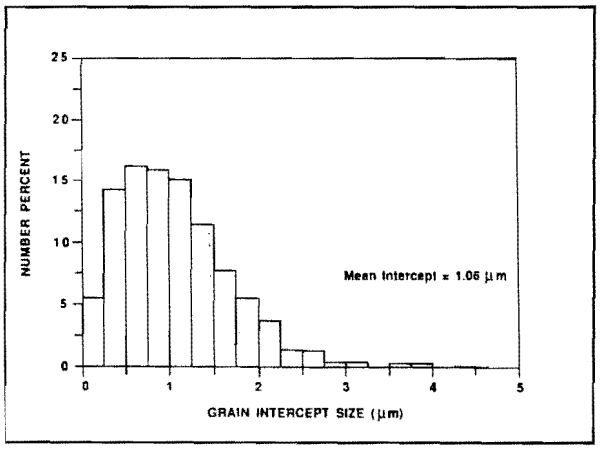

***Fig. 3-6**: Histogram for a sample sintered for 48 h at 1 340 °C prepared with powder with a narrow size distribution (Yeh and Sacks, 1988 b).*

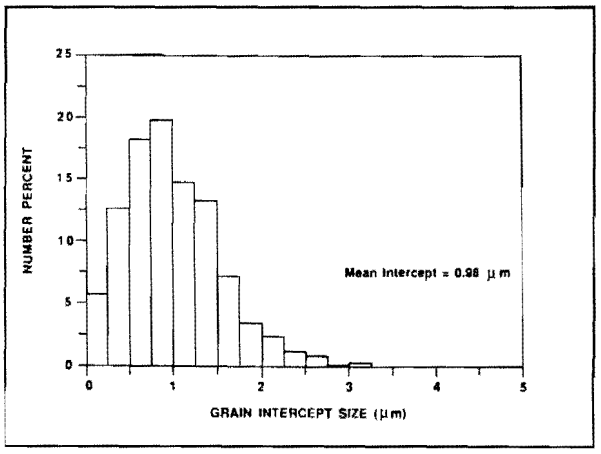

***Fig. 3-7**: Histogram for a sample prepared as in fig. 3-5, but with broad size distribution powder (Yeh and Sacks, 1988 b).*

3.5 The effect of pressure (under HIP) on grain size

Applied pressure during sintering provides an additional means of reducing firing temperature and time. Pressure speeds sintering up by enhancing interparticle contact. Unfortunately, enhanced interparticle contact also aids grain growth.

A specific case of grain growth enhancement by pressure is given by Besson and Abouaf (1991) (fig. 3-8 and 3-9). Their relative green density was 51 % and initial grain size was 0.25 µm. The heating rate up to the constant dwell temperature was 20 °C/min. Grain size showed a linear increase with increasing pressure (fig. 3-8), and an asymptotic increase with time (fig. 3-9).

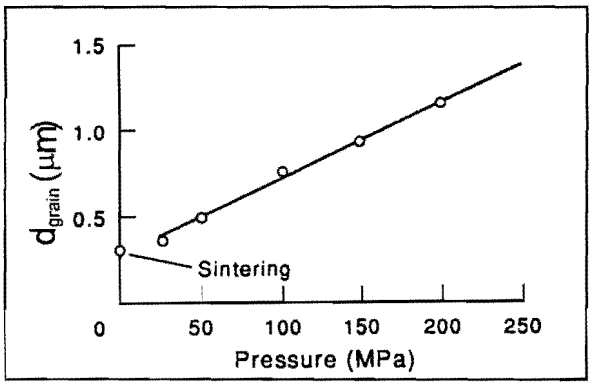

***Fig. 3-8**: Grain size as a function of pressure during HIPping for a dwell of 1 h at 1 300 °C. Final relative density for all data, except at zero pressure, was > 96 %. (Besson and Abouaf, 1991).*

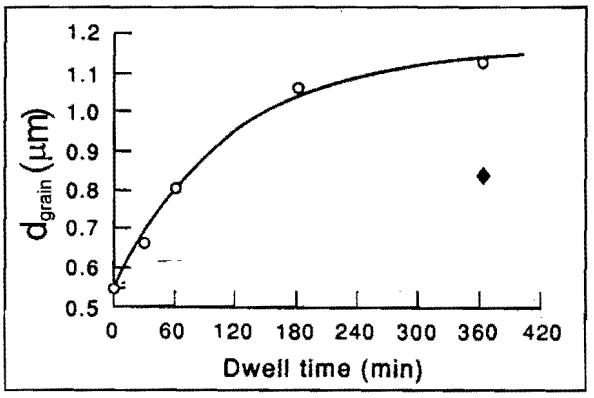

***Fig. 3-9**: Grain size as a function of dwell time during HIPping at 100 MPa and 1 300 °C. ♦ represents the grain size after pressureless sintering. Final relative density for all data was > 96 %. (Besson and Abouaf, 1991)*

3.6 The influence of the temperature and pressure profile (under HIP) on fired density

To provide a quantitative basis of comparison for HIPping results, HIPping data from several sources are collected in fig. 3-10 to 3-13. The progress of density for a variety of conditions is given. A summary of experimental conditions and references for the data presented in fig. 3-10 to 3-13 are given in table 3-2. The data represented for actual HIPping are for relatively large particle sizes, with the result that they are not quite comparable to nano-sized particles. Compacts of nano-sized powders can be expected to densify much faster under the same conditions.

Note that full density sets in rather fast, in less than 20 minutes at 100 MPa (fig. 3-11). It is therefore critical to only HIP for the time necessary for densification, as the only effect on longer HIPping would be grain growth.

***Table 3-2**: The green bodies used in the HIPping results depicted in fig. 3-9 to 3-12.*

Pressure (MPa)	Green body			Reference
	Particle size (nm)	Particle size method	Density at start of densification (% relative)	
50 and 200	500	BET	48?	Uematsu *et al* (1990)
	1 000		56?	
100	< 500	Initial grain size	Not stated	Shin, Orr, and Schubert (1990)
Sintering	60	BET	70	Yeh and Sacks (1988a)
	~ 400	Median Stokes	73	Yeh and Sacks (1988b)

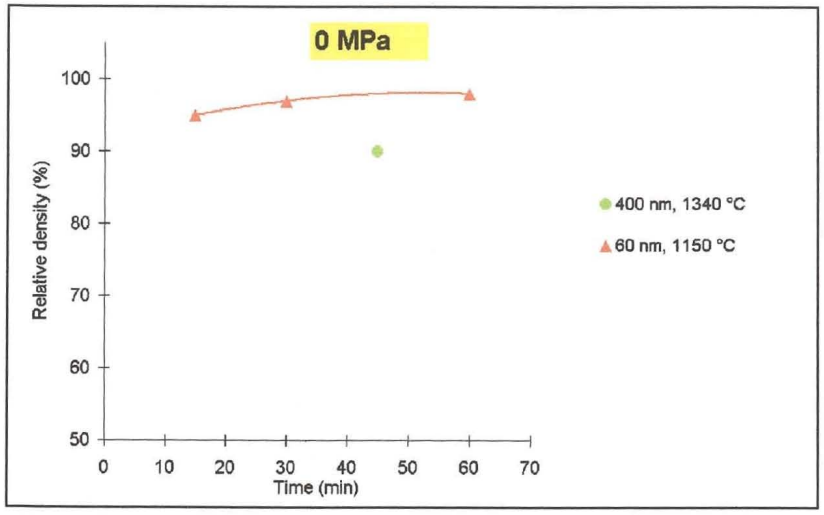

***Fig. 3-10**: Sintering of submicron alumina for comparison with HIPping in fig. 3-10 to 3-12.*

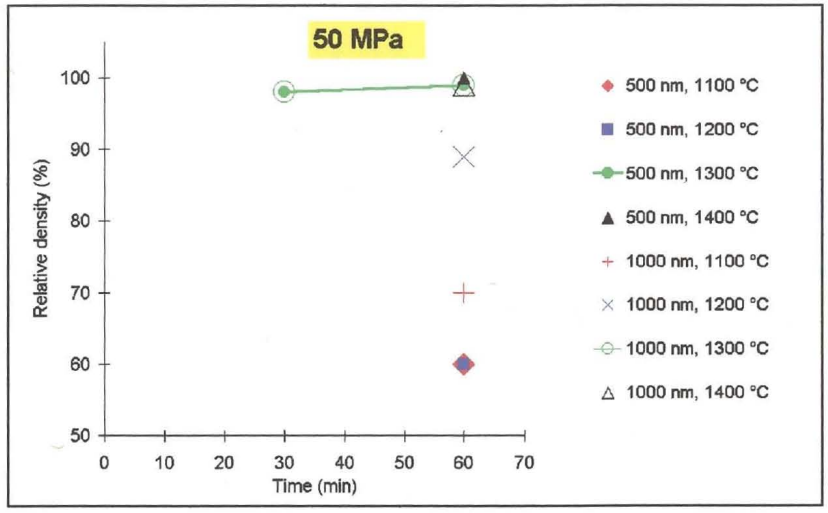

***Fig. 3-11**: HIPping of submicron alumina at 50 MPa.*

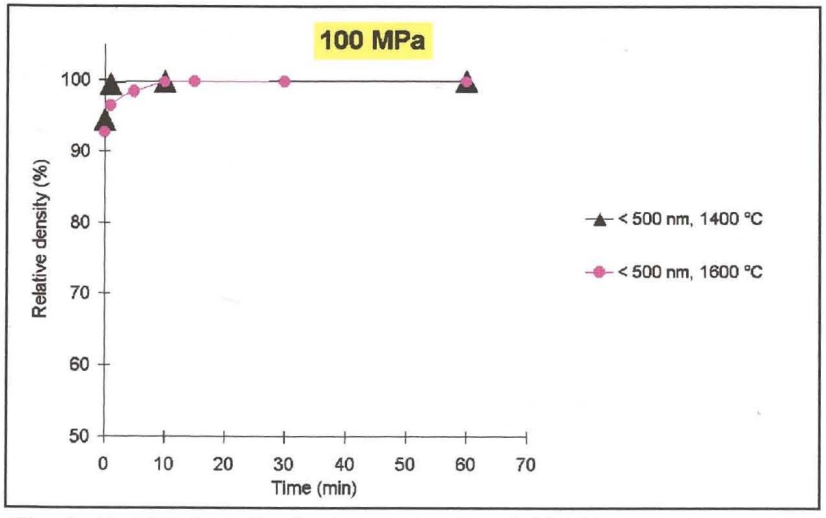

***Fig. 3-12**: HIPping of submicron alumina at 100 MPa.*

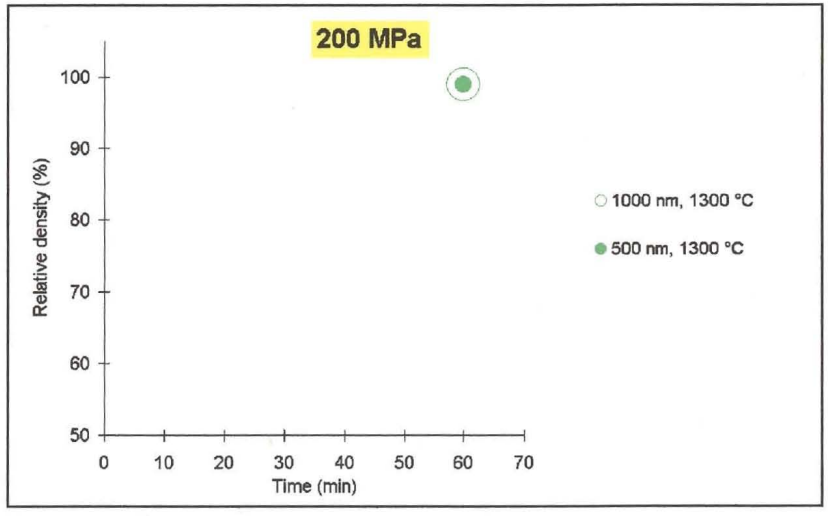

***Fig. 3-13**: HIPping of submicron alumina at 200 MPa.*

3.7 The influence of sintering additives on fired microstructure and density

Magnesia (MgO) and titanium oxide (TiO_2) are commonly used as additives to alumina to improve densification. However, no data were found on the effect of these additives when sintering submicron powders below 1 600 °C.

Dörre and Hübner (1984) also states that MgO inhibits grain growth while TiO_2 promotes it. Whereas this is true of conventional sintering of particles in the micron range at c. 1 600 °C, Dörre and Hübner do not give any specific results for smaller particles at lower temperatures.

Ikegami, Kotani, and Eguchi (1987) conducted work with particles of c. 330 nm (by BET) in diameter. They increased temperature steadily at 10 °C/min to temperatures of up to 1 600 °C followed by quenching (no dwell). For these heating conditions their findings were as follows:

- The rate of densification in the initial and intermediate stages was affected in the order:
  TiO_2 added >> No additives ≈ MgO added.
- Grain sizes at densities greater than 90 % relative were c. 7 μm or larger.
- Grain sizes (not at full density) achieved between 900 and 1 600 °C were in the order:
  No additives ≈ TiO_2 > MgO.

Under the same conditions as above, but with an additional dwell of 1 h at 1 600 °C they found that final density achieved was in the order:

No additives (97 to 98 % relative density),
MgO added (97 to 98 % relative density),
TiO_2 added (99 % relative density).