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Grain growth in high-purity alumina ceramics sintered from mixtures of particles of different sizes

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Abstract

In the present article the assumption has been made that density of ceramics to a significant excent can be controlled by the size distribution function of the powder particles. This assumption has been verified for a series of specimens which were obtained by mixing three alumina powders of different mean size and different diversity in the size of powders particles. A computer program has been developed which helps to select an optimum mixture of the powders assuring a high density of the sintered ceramic.

1. Introduction

Grain growth in alumina ceramics has been the subject of extensive investigation for more than 30 years [1–3]. The control of the grain size of ceramics is of vital importance, since many of their physical, in particular mechanical, properties show a marked dependency on the grains sizes and the size distribution. In certain situations, however, a knowledge of the average behaviour alone is insufficient, and we must know the factors that determine the anisotropy of the grain growth and control not only the grain size and the sizes distribution but also the evolution of the grain shapes and the grains shape distribution [4]. For example, when considering the fracture strength of a ceramic, it is important to know the lengths of the edges of large nonequiaxed (probably abnormal) grains, since these edges may provide preferred sites for the initiation of fracture [5]. So, it is necessary to know the factors that promote anisotropic grain growth [6].

The optimum configuration of a green ceramic body prior to sintering is generally characterised by a high density powder packing of submicrometer, homogeneously arranged particles of nearly spherical shape and with narrow size distribution [7]. Packing of powder particles has been investigated both theoretically [8] and by experiment [9,10]. In our previous study in order to produce a sintered sample with possibly highest density we used three monosized Al_2O_3 powders, differing with the mean particle size, appropriately selected on the based of numerical modelling [11]. The sample was sintered at a temperature of 1500°C; its relative density was 99%. The microstructure of this ceramic indicated that the grain growth had been abnormal.

In the present study we examined how the grains sizes distribution, the evolution of the grain shape and the grain shape distribution of the Al_2O_3 ceramics produced by trimodal powder sintering depend on the sintering time. The experiments were designed so as to minimise the potential effects of a liquid phase and the pore drag [12] on the grain growth characteristics.

2. Experimental

The materials used were monosized powders designated as AKP-15, AKP-30 and AKP-50, manufactured by Sumitomo Co. Ltd. (Table 1 shows the powder properties).

The purity of the powders, as specified by the manufacturer, was 99.99% The content of Si, Ca, F and S impurities did not exceed 40 ppm.

Two series of samples were produced, designated by the symbols “K” and “V”(as in our previous work [11]). In the series “K”, the composition of the powder mixture

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was chosen on the base of numerical simulation according to the "maximum-packing" model. In the series V, the mixture was selected experimentally from the composition triangle (Fig. 1) so as to ensure the maximum density of the sample.

Table 2 gives the proportions of the individual powder fractions calculated by computer modelling based on the model of maximum packing of the powder particles in a unit volume before sintering.

The grain size distributions are shown in Figs. 2 and 3 shows schematically the spatial packing model of the AKP-15, AKP-30 and AKP50 powders. The appropriate weight proportions of the powders, immersed in ethanol, were mixed in a ball mill for 8 h. Then the mixture was subjected to a one-side uniaxial pressure of 13 MPa. All specimens were sintered in air in a furnace

Table 1
Properties of powders

Powder	AKP-15	AKP-30	AKP-50
Alotropy	α	α	α
Purity(%)	> 99.99	> 99.99	> 99.99
Particle size (μ)	0.6–0.8	0.3–0.5	0.1–0.3
Impurities(ppm)			
Cu	< 10	< 10	< 10
Si	< 40	< 40	< 20
Ca	< 40	< 40	< 20
Fe	< 20	< 20	< 20

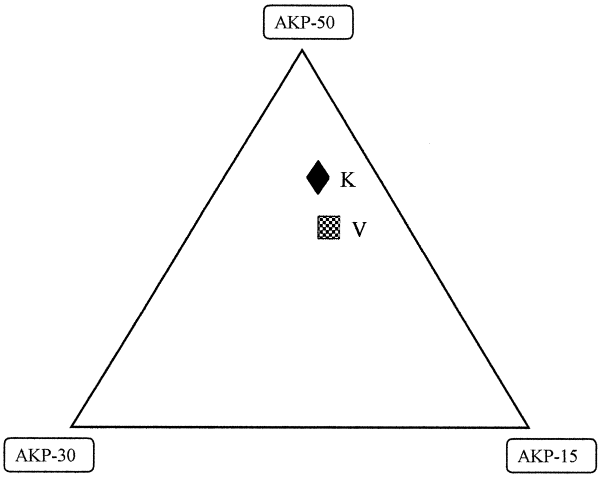


Fig. 1. The composition triangle.

Table 2
Percent fractions of the individual single-module powders

Designation/ powder	AKP-15 (% wt)	AKP-30 (% wt)	AKP-50 (% wt)
K	13	22	65
V	20	30	50

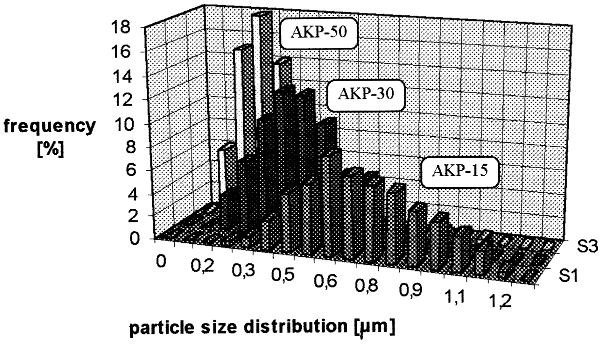


Fig. 2. Particle size distribution of AKP-15, AKP-30 and AKP-50.

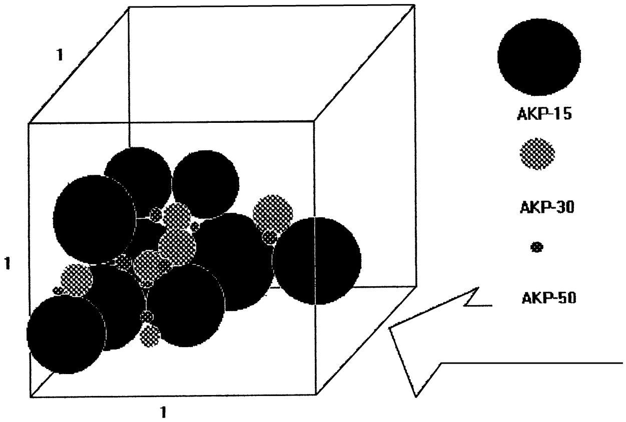


Fig. 3. Model of maximum packing.

Table 3
Sintering process parameters at 1500°C (heating and cooling rate 3°C min^{-1})

Designation	Sintering time (h)
K1, V1	2
K2, V2	4
K3, V3	8
K4, V4	16

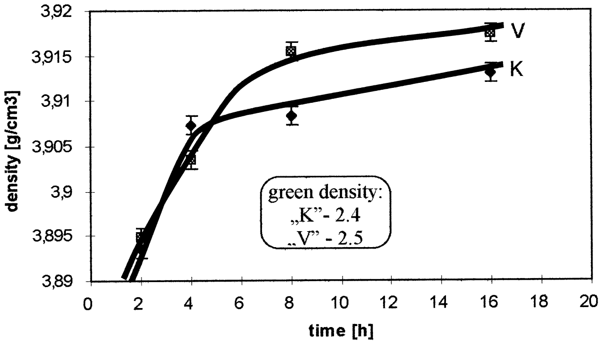
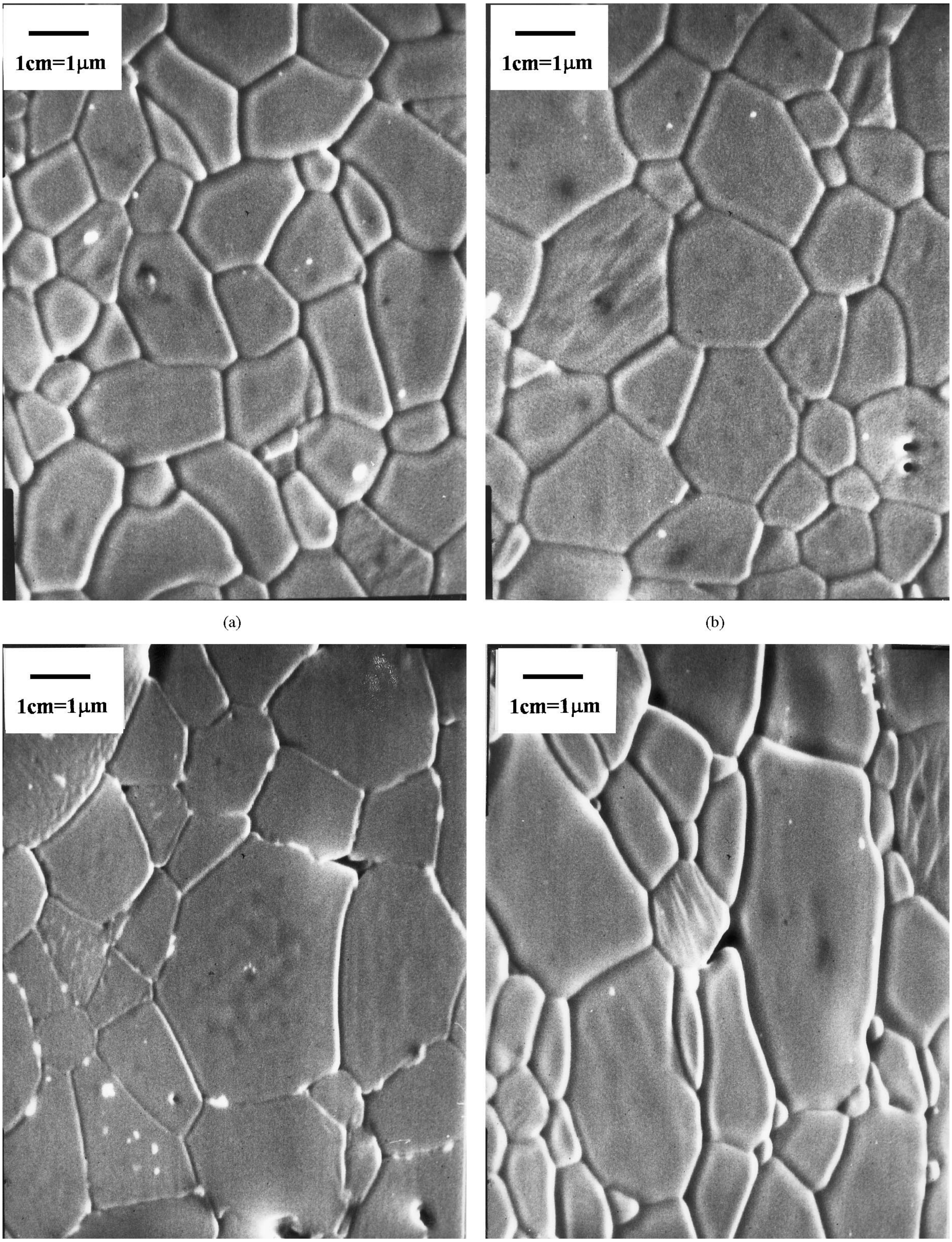


Fig. 4. Variation of the relative density with sintering time.

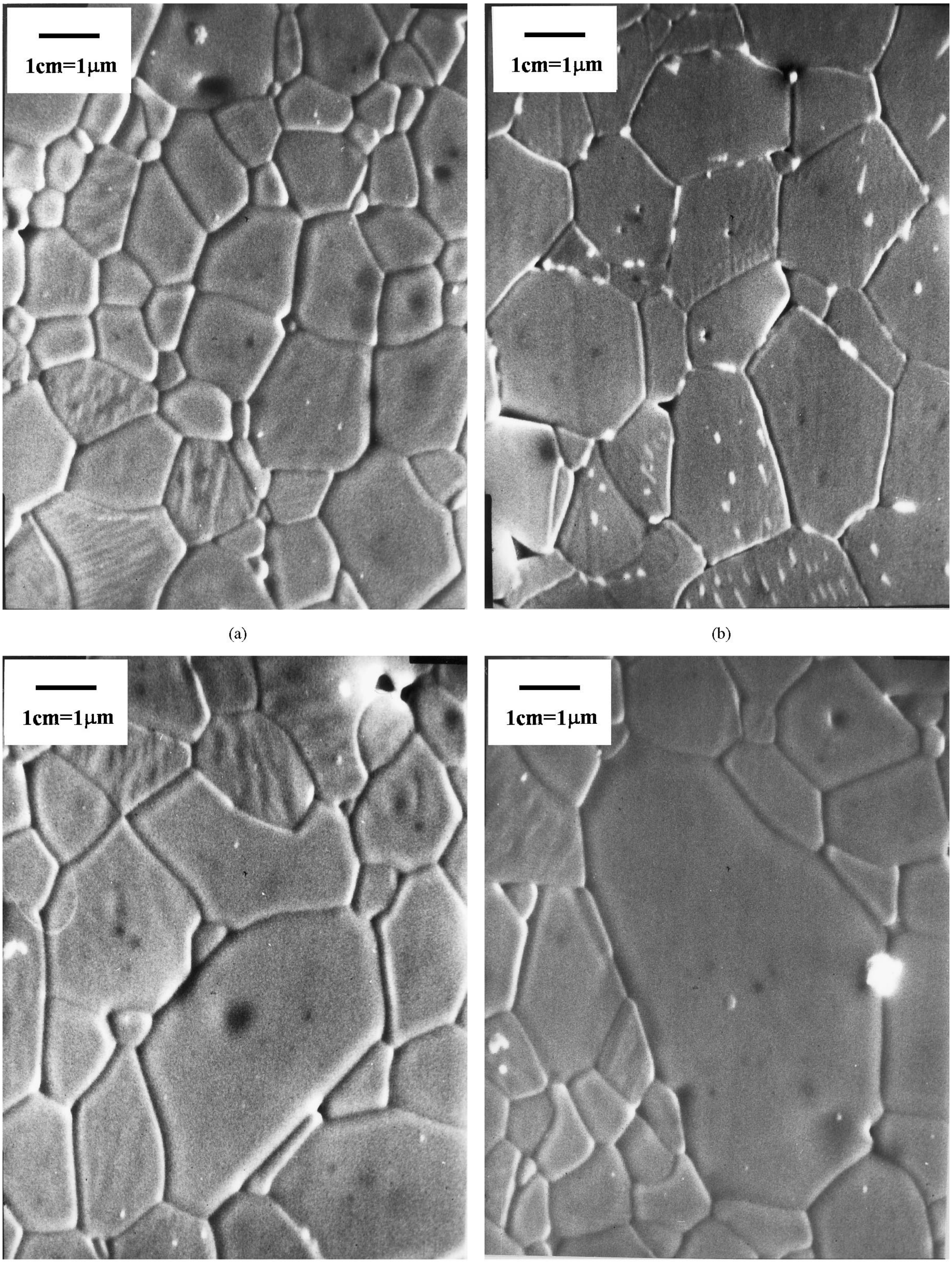


(a) (b) (c) (d)

Fig. 5. Grain structure Al_2O_3:(a) K1,(b) K2,(c) K3,(d) K4.

model LTD 1600 (Lenton Thermal Design Ltd.) by heating to 1500°C and then soaking at this temperature for 2, 4, 8 and 16 h. Heating and cooling rate were 3°C min^{-1}. The designations of the samples and the parameters of their synthesis are given in Table 3.

The density before and after sintering of the specimens was measured using an Accu Pyc 1330 V1.02 helium picnometer with an accuracy of 0.05%, after each sintering cycle as specified in Table 2. The microstructure of the specimens was observed on the cross-sections of



(a) (b)

(c) (d)

Fig. 6. Grain structure Al_2O_3: (a) V1, (b) V2, (c) V3, (d) V4.

the samples using SEM (Tesla 100) and TEM (Philips 400); prior to the density determination, the cross-sections were ground, polished and etched thermally ($T = 1500°C$, $t = 1.5$ h). In the latter case, a light sputter-coating of copper was used to avoid specimen charging effects. The grain size was measured by computer image analysis [13], taking the average diameter $E(d)$ to be its measure. $E(d)$ is defined as the diameter of a circle whose area corresponds to the surface area of the grain being measured ($d = (4A/\pi)^{1/2}$ where A is the grain area).

For each sample, the average value of the circularity coefficient $E(\alpha)$ (α is elongation sensitive shape factor d_{max}/d, where d_{max} is maximum grain diameter) was calculated.

3. Results

The variation of the measured values of the density with increasing sintering time is plotted in Fig. 4. At a sintering time of 2 h, the two series of samples have similar densities. Above 2 h, the rate of densification of the specimens increases in samples of both the series.

The microstructures of the sinters of the K and V series are shown in Figs. 5(a)–(d) and 6(a)–(d).

Fig. 7 shows the variation of the average grain size $E(d)$ as a function of the sintering time. The curve $E(d) = f(t)$ has a similar course to the curve that represents the variation of density with sintering time. The V samples were densified much more quickly and their average grain size $E(d)$ was greater. By way of examples, Fig. 8(a) and (b) shows TEM micrographs of the specimens obtained. The Al_2O_3 grain boundaries developed with increasing sintering time, but the grain shapes tended to become anisotropic.

Fig. 9 shows the time variation of the average value of the shape factor $E(\alpha)$. In the "K" samples, the grain shapes showed greatest anisotropy after sintering for 2 h and in the "V" samples—after 4 h. In mixture designated as "K" was more AKP-50 than in "V". AKP-50

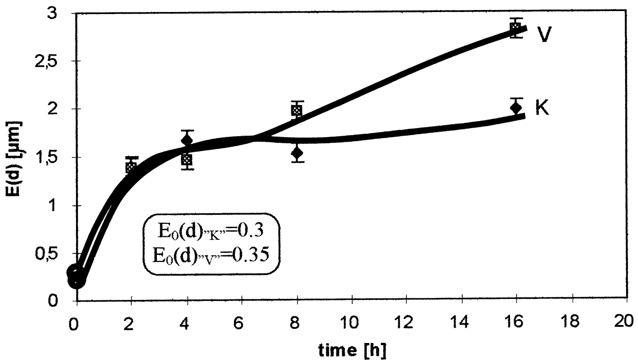


Fig. 7. Variation of the grain size with sintering time.

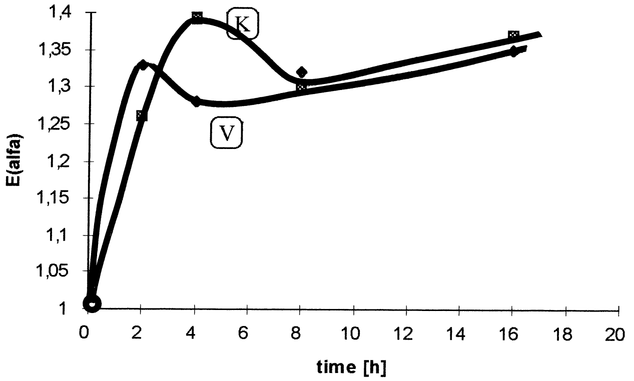
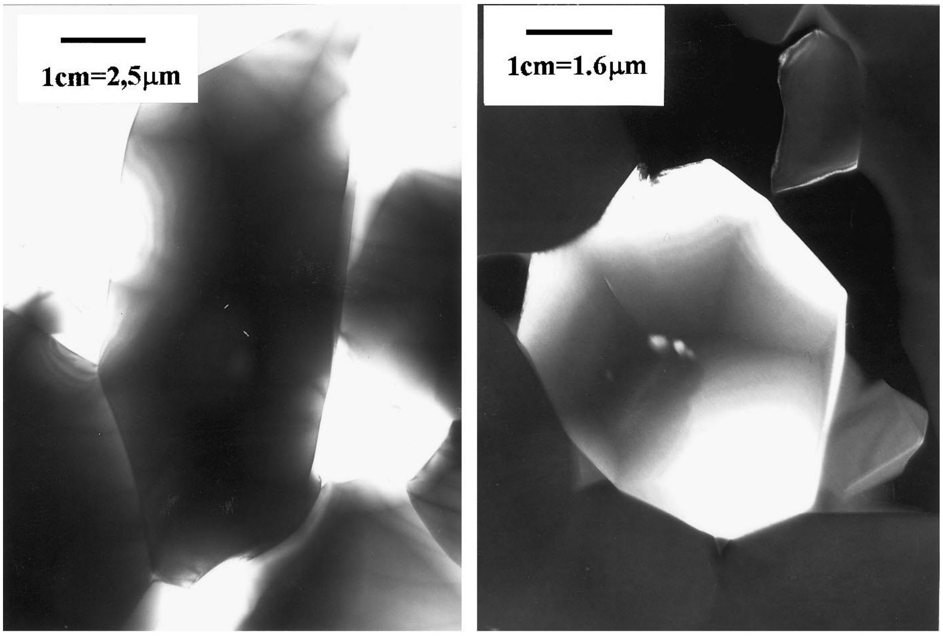


Fig. 9. Shape factor as a function of the sintering time.



(a) (b)

Fig. 8. Example of the microstructure (by TEM) of the (a)"K"and (b)"V"samples after 2 h of sintering.

contain smallest particles from all type of monosized powders used in this experiment. The growth kinetics of the average grain for both the experimental Al_2O_3 series is shown in Fig. 10. The plots of $E(d)$ and $E(\alpha)$ versus sintering time obey the grain growth law [12]:

$$[E(d)]^3 - [E(d_o)]^3 = k * t \qquad (1)$$

where $E(d)$ is the average grain size after time t, $E(d_o)$ is the initial average grain size, t is the sintering time in s and k is a constant. The average value of k for the series K α-Al_2O_3 was 1×10-$^{22}\mathrm{m}^3\,\mathrm{s}^{-1}$ and for the series V-3×10-$^{22}\mathrm{m}^3\,\mathrm{s}^{-1}$ (Table 4).

4. Discussion

Our study confirms that by sintering of powders in a trimodal system we can produce specimens of very high density at a relatively low temperature. Whereas the course of the densifying process in time differs in both types of mixtures.

Up to 4 h sintering both mixtures, V and K behave similar: their rate of densifying and they rate of grain size growth are the same. During longer sintering time than 4 h up to 16 h the specimens V became more dense and their grains growth greater than in specimen K.

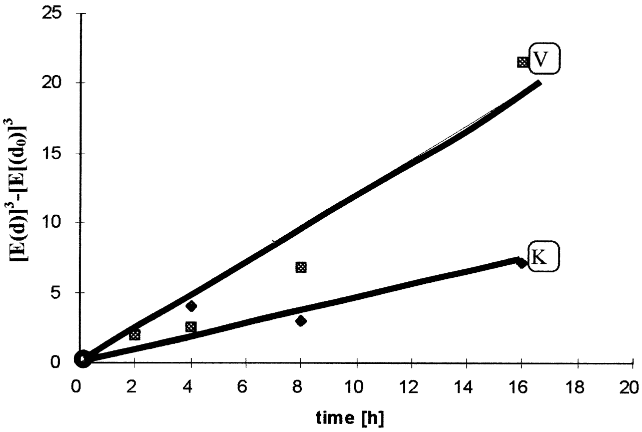


Fig. 10. Rate of growth of the average grain size as a function of sintering time.

Table 4
Experimental values of the growth constant

Material	K in undoped Al_2O_3(m^3/s)	K in MgO-doped Al_2O_3(m^3/s)
Al_2O_3[12]	5.16×10^{-20}	1.28×10^{-20}
Al_2O_3 + liquid phase [13]	1.74×10^{-19}	3.90×10^{-20}
Current work	1.00×10^{-22} (series "K") 3.00×10^{-22} (series "V")	—

The average of the shape factor $E(\alpha)$ raises during sintering time, but the $E(\alpha)$ dependence on time is different for K and V series (Fig. 8). The great value of the $E(\alpha)$ growth rate and characteristic broad peak appearance in the curves indicates a tendency to abnormal growth of the grains of both series.

This tendency is most pronounced at short sintering times (2 h for the K series and 4 h for the V series). The tendency to a "super-abnormal" growth of a certain small number of grains seems to be a characteristic feature of the trimodal range sintering. This suggestion is based on the observation that, locally in the microstructure of the sinters obtained we can find grains whose surface areas exceed manifold the surface areas of the adjacent grains (this was discussed in our earlier paper [11]). This local abnormal growth seems to be due to the impurities, such as SiO_2 and CaO, present in the powder, and more precisely to their aggregations which under the sintering conditions form liquid phases.

The differences in the behaviour between the "K" series and "V" series can be attributed to the different proportions of the monosized powders (Fig. 1) of different grain sizes. In the powder mixture of the K series, the ratio of the number of the finest particles (AKP-50) to the largest (AKP-15) particles was greater than that in the "V" series. This difference can also explain the fact that, initially, both the average grain size $E(d)$ and the density increase more quickly in K samples than in V samples. The initial rapid growth of the grains may proceed by the finest powder grains coalescing with the growing grains with the participation of the liquid phase. After 4 h of sintering, the process is slowed probably because most of the finest grains have already been consumed and, thus, the grain size range has been narrowed — from this moment on, the individual grains grow freely. In the "V" samples, the grain growth was fluent and regular, since here the difference in the proportions of the finest and largest powder particles was smaller than that in K samples (Fig. 11).

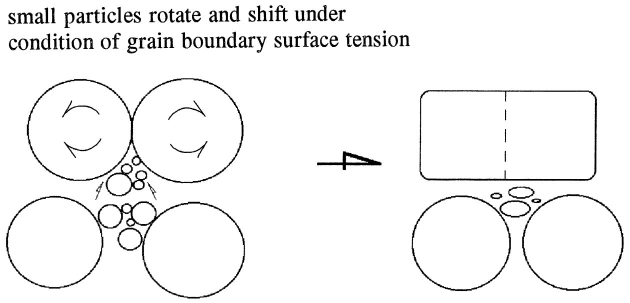


Fig. 11. Schematic explanation of the formation of abnormally long grain.

Using relationship (1) we determined the kinetics of the grain growth in the samples and compared the results with those reported in the literature (Table 3). The values of k obtained for the α-Al_2O_3 sinters produced in the trimodal system described in these work are 100 times larger than those *k* reported by Rodel and Glaeser [Fig. 11] the same material produced under similar conditions in one modal powder system (with wide grain size distribution).

5. Conclusions

1. The density of the ceramics obtained in trimodal system depends on grain growth process, which influences the shapes of grains.
2. Great difference in size of powders of a mixture enhances the dynamics of the grain growth (the grains grow rapidly in a relatively short time), which may result in local abnormal or "super-abnormal" grain growth.
3. The sintering process in trimodal system may be represented in a model illustrated in Fig. 11. Small particles rotate and shift under influence of grain boundary surface tension of large particles.

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