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Sintering of High-Density, High-Purity Alumina Ceramics

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Abstract: In the present article the assumption has been made that the density of ceramics can be controlled to a significant extent 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 sizes and diversity in the size of powder 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. Samples could be sintered at 1500 °C to a relative density 99.5% and an average grain size of 0.55–0.69 μm. This proves that particle size distribution (p.s.d.) effect on the density of alumina can be utilized in practice of high-density, high-purity ceramics. © 1997 Published by Elsevier Science Limited

1 INTRODUCTION

In recent years, a continuous development can be observed of technologies for the production of high density sintered materials. A clear tendency in the modifications of these technologies is the search for procedures which employ high purity powders and require lower sintering temperatures. In the case of α-alumina (Al_2O_3) these modifications concern all stages of processing: from synthesis of powders to sintering.

Messing and co-workers have previously described a method for producing high relative density (~98%) α-Al_2O_3 at sintering temperatures of ≈1200 °C.[1–3] The fabrication process involved the preparation of boehmite sol–gel samples containing small additions (≤2.0 wt%) of fine (~0.1 μm) α-Al_2O_3 seed particles. However, it was reported that preparation of boehmite sol–gel monoliths was difficult; gels undergo large shrinkage and tend to crack.

In the study reported in Ref. 4, homogeneous 68% relative density green bodies were used of fine-sized (~0.1 μm), agglomerate-free Al_2O_3 dispersions. It has been shown that samples could be sintered at 1150 °C to a relative density >99.5% and an average grain size of 0.25 μm.[5] In the present article the assumption has been made that the density of ceramics can be controlled to a significant extent 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 sizes and different diversity in the size of powder 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. A satisfactory agreement has been observed between the predictions of the computer program and the properties of the sintered specimens.

2 MATERIALS

High-purity alumina powders (α-$Al_2O_3 \geq 99.99\%$, Si <40 ppm, Fe <20 ppm and Na, Mg and Ca <10 ppm) were used in the present study, supplied by Sumitomo Co. Ltd. The powders, designated as AKP-15, AKP-30 and AKP-50, displayed unimodal distribution of particle size. This is rationalized by the plot in Fig. 1 which depicts histograms of grain section equivalent diameters (see Section 5.2.). It should also be pointed out that the powder particles were of spherical shape.

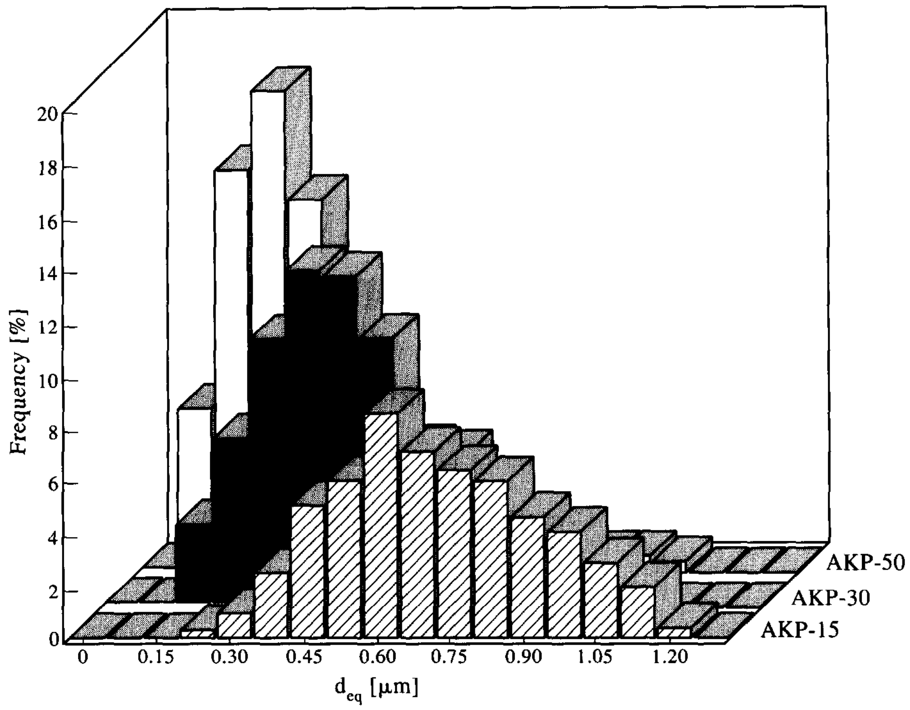

Fig. 1. Particle size distribution functions of the three powders used in the present study. The size of particles has been measured from SEM images.

3 A MODEL FOR OPTIMUM MIXTURE OF THE POWDERS

A computer program has been developed to model the process of preparing the powder compacts which takes into account the particle size distribution function. This program is based on the two following assumptions:

1. particles have spherical shape;
2. the particles do not deform during the process of compacts preparation.

An algorithm has been employed of a sequential space filling. In this algorithm the biggest particles are closely packed first in a specified volume and then the un-occupied space is filled by slightly smaller particles (Fig. 2). As the "input" data the particle size distribution functions were used and the purpose of the program was to determine such mixtures of the three powders used in the present study for which the algorithm predicts the highest density of the compact. The following optimum composition of the powders has been determined:

AKP – 15 = 13.05%;
AKP – 30 = 21.73%;
AKP – 50 = 65.22%

This composition of the powders is designated as "K" in Table 1 and throughout the text.

Other composition used here are 1, 3, 5 and 6.

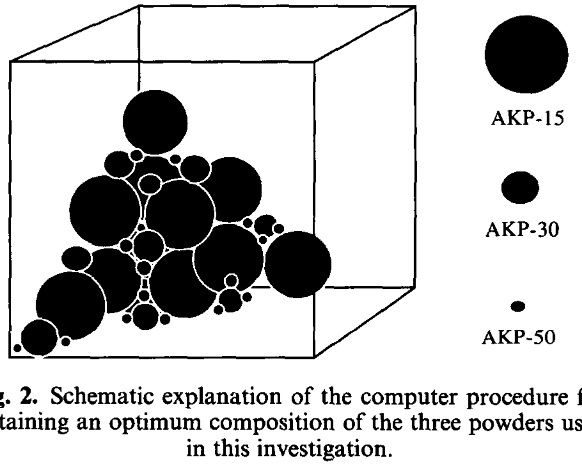

Fig. 2. Schematic explanation of the computer procedure for obtaining an optimum composition of the three powders used in this investigation.

4 FORMING AND SINTERING

Mixtures of the three powders used in the present study are given in Table 1. The list of the examined

Table 1. Compositions of the powder mixtures used in the present study in weight percent

Specimens designations	AKP-15 [weight %]	AKP-30 [weight %]	AKP-50 [weight %]
K	13.05	21.73	65.22
1	10.00	20.00	70.00
3	20.00	20.00	60.00
5	20.00	30.00	50.00
6	10.00	30.00	60.00
15	100.00	0	0
30	0	100.00	0
50	0	0	100.00

compositions includes the optimum composition K and a number of mixtures deviating from K. As reference points, compacts have also been studied of the "input" powders AKP-15, AKP-30 and AKP-50. Powder mixtures were dispersed in alcohol and milled in a ball-mill for 24 h. Dried and granulated mixtures were subsequently compressed under a unidirectional stress of 50 MPa. No additives were used in the process of specimen preparation. Cylindrical specimens were produced with a 10 mm diameter and 10 mm height. These specimens were sintered at 1500 °C in air for 1 h. Heating and cooling rates were 3 °C/min.

5 MEASUREMENTS AND RESULTS

The density of the specimens was measured before and after sintering using an Accu Pyc Micrometrics helium picnometer, which allowed for ±0.001 g/cm^3 precision. The same Micrometrics device has been used to determine the size of the pores.

The microstructure has been studied on sectioned specimen. Diamond pastes have been used for polishing and the grain boundary networks have been revealed by thermal etching at 1200 °C for 2 h. The revealed microstructures were investigated using SEM. The grain size distributions of the samples were measured using the principles of stereology and image analysis (see, for example, Ref. 6).

5.1 Density of specimens

Figure 3 shows the results of the density measurements. In this figure the density after sintering is plotted against the initial density. It can be noted that the density of the material for optimum composition of the powders is significantly higher than the densities obtained for each powder separately. The same is true for the compositions slightly deviating from the optimum one. The densities for K composition and the related ones vary in the range of 98.71–99.51%. The results of the density measurements are also plotted in Fig. 4, which shows the correlations between density and specimen shrinkage.

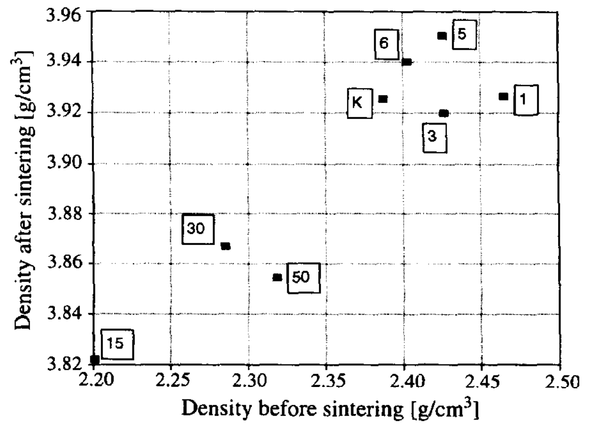

Fig. 3. Results of the density measurements on the specimens before and after sintering, the designations used are from Table 1.

5.2 Size of pores and grains

Figure 5 presents the results of pore size measurements. It can be noted that pores observed in the specimens produced from powder mixtures reveal pores in a relatively narrow size range of 50–70 nm. In contrast, the size of the pores in specimens obtained from the powders range from 60 to 150 nm.

The distribution functions of the grain size (described by equivalent diameter, d_{eq}) for two of the specimens is given in Fig. 6. Mean values of the equivalent diameter, $E(d_{eq})$, are listed in Table 2. This table also lists the mean values of the shape factor, defined as the ratio of d_{max}/d_{eq}, where d_{max} is the length of the maximum chord (see Ref. 6). (Mean values of this shape factor are a sensitive measure of the grain elongation. For well annealed metals $E(d_{max}/d_{eq})$ decreases to 1.24.)

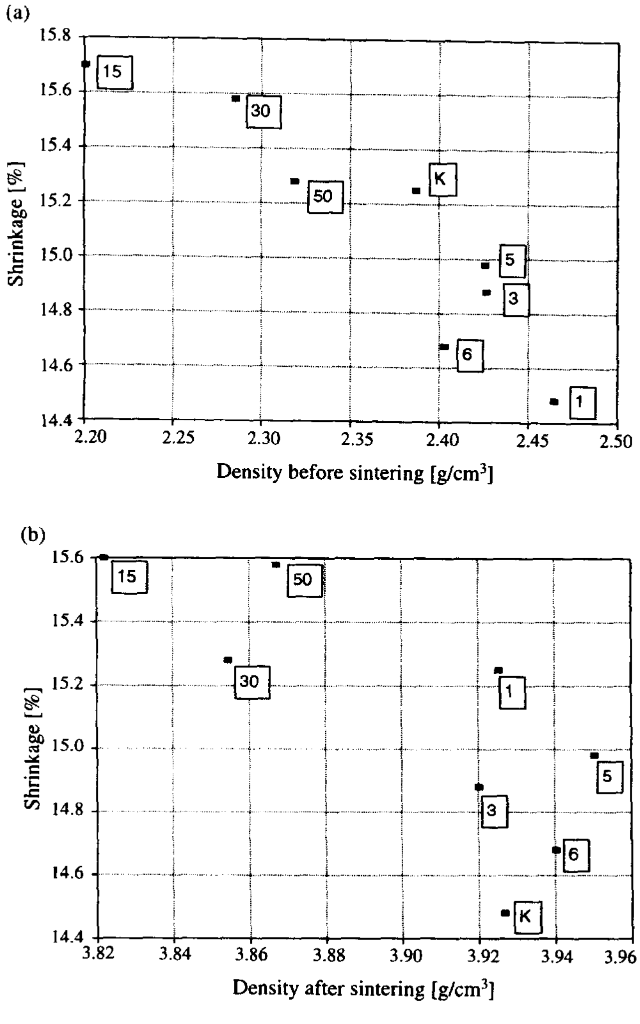

Fig. 4. Results of the shrinkage measurements plotted against the density: (a) before and (b) after sintering.

The mean values of equivalent diameter, $E(d_{max}/d_{eq})$, for the powder mixtures vary in the range 0.55–0.69 μm. For the constituent powders the following values have been measured: AKP-15 = 0.93 μm, AKP-30 = 0.80 μm, AKP-50 = 0.63 μm.

The shape factors for the powders has been found in the range 1.34–1.37. For the powder mixtures it varies from 1.22 to 1.28.

5.3 Fluctuations in the chemical composition

Large values of the shape factor can be explained by the presence of elongated grains, which in turn indicate abnormal grain growth. A hypothesis has been put forward that this process is influenced by impurity segregation at the grain boundaries. This effect has been studied using an X-ray microprobe (Cameca). The results of this investigation are shown in Fig. 7.

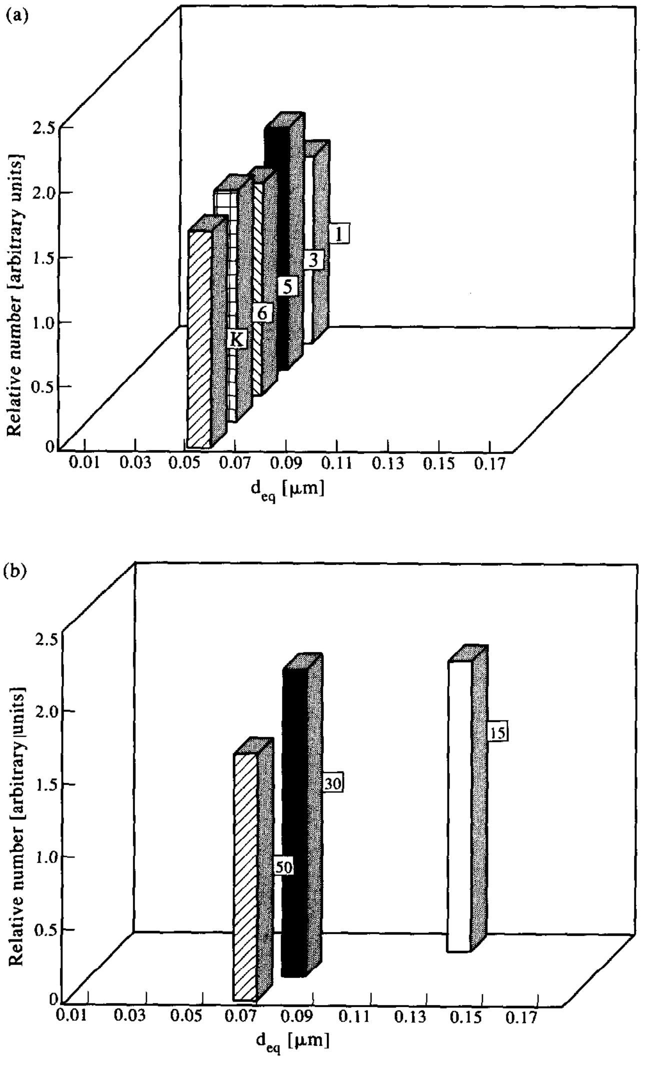

Fig. 5. Relative pore size distribution function for the specimens produced: (a) using the mixtures of the powders, (b) from each of the powders.

6 DISCUSSION AND CONCLUSIONS

The results obtained in the present work demonstrate that the density of sintered α-Al_2O_3 is influenced by the p.s.d. The effect of p.s.d. can be observed already in the case of specimens produced using one of the three powders, AKP-15, AKP-30 and AKP-50, which differed in p.s.d. functions (see Fig. 1) and density (see Fig. 3). However, a more spectacular example of the p.s.d. effect on the density is given by the set of specimens produced from the mixtures of these three powders.

In the present study the optimum composition of the powders was determined, which is expected to result in the maximum density of the powder particles during their densification. The optimum composition of the powders and the composition slightly deviating from this one indeed have yielded higher densities of the sintered material. This proves that the p.s.d. effect on the density of alumina can be utilized in practice for production of high density ceramics.

It should be noted that the optimum composition of the powders, designated as K, assures 98.88% dense alumina after sintering at 1500 °C (for 1 h). This is not the maximum density obtained in the present experiments, which was measured for the specimen designated 5 (99.5%). Such a discrepancy between the experimental data and the model used in the present study indicates its too simplistic character.

The sintered specimens have, in general, shown little grain growth, as indicated by the mean values of the equivalent diameter, $E(d_{eq})$, varying in the range 0.55–0.69 μm.

The microstructural observations revealed a significant elongation of some of the grains. Their presence lead to a relatively large mean value of the shape factor, d_{max}/d_{eq}, used in the present study. The parameter $E(d_{max}/d_{eq})$ has been found in the range 1.34–1.37. Measurements of local concentrations of impurities, carried out by means of a micro-probe, suggest that this phenomenon can be explained in terms of an abnormal grain growth stimulated by the presence of SiO_2 and/or CaO. These two oxides can form a low-melting point eutectic with α-Al_2O_3, and can locally change the sintering conditions. Since the segregation of these compounds takes place on specific crystallographic planes of α-Al_2O_3,[7–9] the resulting growth of grains is highly directional and leads to elongation of the grains which assume a plate-like shape.

The following conclusions can be drawn from the results obtained in the present study.

1. The density of sintered α-Al_2O_3 can be improved by a proper choice of the particle

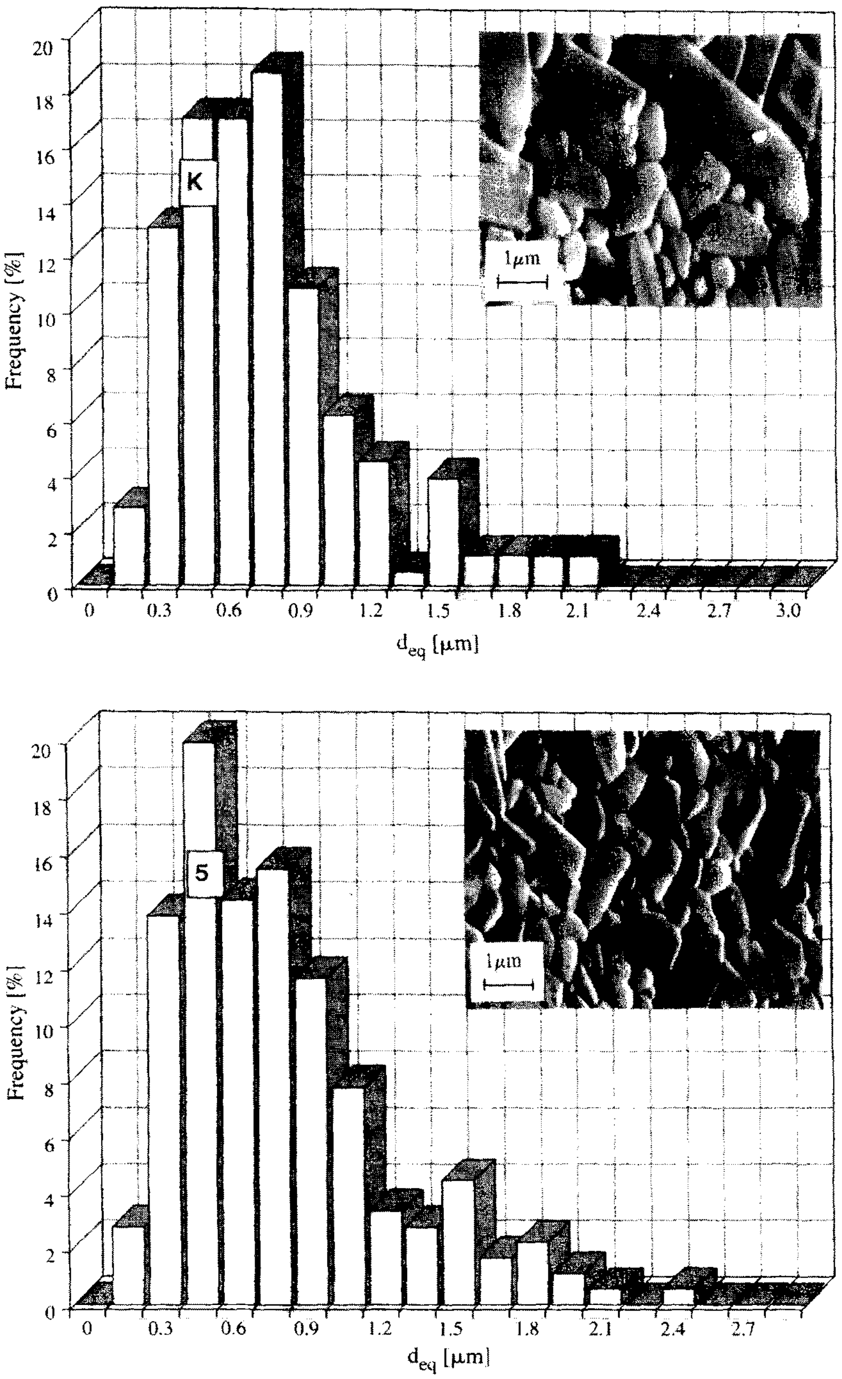

Fig. 6. Grain size distribution functions, d_{eq}, for grain sections, for the specimens designated as: (a) K and (b) 5. The inserts show characteristic features of the microstructures observed in these specimens.

size distribution function. A simple model of purely geometrical nature proved to be useful in the search for the optimum distribution function.

2. Methods based on the choice of the particle distribution size make it possible to obtain high density α-Al_2O_3 sintered at a temperature which does not trigger the process of intensive grain growth. Some growth of grains observed in the present study can be explained in terms of an impurities effect.

Table 2. The mean values of the grain size, $E(d_{eq})$, and the mean value of shape factor, $E(d_{max}/d_{eq})$

Specimen designation	$E(d_{eq})$ [μm]	$E(d_{max}/d_{eq})$
K	0.66	1.35
1	0.55	1.36
3	0.57	1.34
5	0.69	1.37
6	0.61	1.36
15	0.93	1.22
30	0.80	1.26
50	0.63	1.28

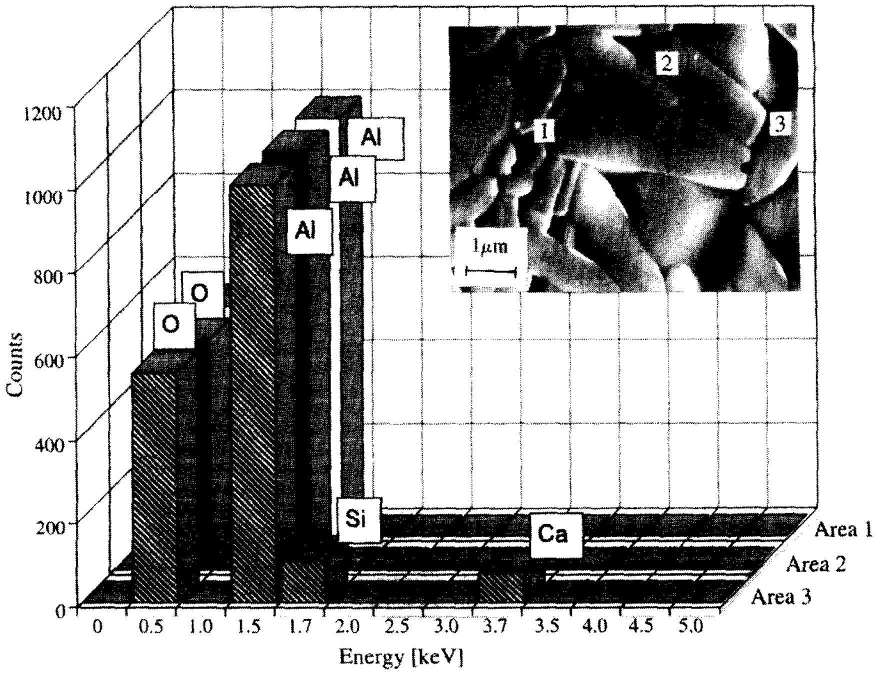

Fig. 7. Results of the micro-probe studies of the chemical composition of the regions around elongated grains. Locations of the three areas which have been studied are shown in the insert.

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