Journal of the European Ceramic Society 16 (1996) 851–855

S0955-2219(96)00004-0
0955-2219/96/$15.00 + .00

Constitution of Porcelain Before and After Heat-Treatment. Part II: Aspect Ratio and Size-Distribution of Mullite

S. P. Chaudhuri & P. Sarkar

Special Ceramics Section, Central Glass and Ceramic Research Institute, Calcutta — 700 032, India

(Received 7 August 1995; revised version received 5 December 1995; accepted 12 December 1995)

Abstract

Porcelain samples were prepared with and without the addition of mineralizers. The samples were then heat-treated for 50 h. The aspect ratio and size-distribution (experimental) of mullite crystals were studied in relation to mineralizer and heat-treatment.

1 Introduction

In a recent communication[1] (Part I) it was shown that variations occurred in the mineralogical composition of chemical porcelain before and after heat-treatment at the crystallization temperature of the glassy phase in the material.

The microstructure of the chemical porcelain samples before and after heat-treatment is presented in this paper. The size, size-distribution and shape of the mullite crystals are emphasized and the influence of the mineralizers is also reported.

2 Experimental Procedure

2.1 Sample preparation

Porcelain samples were prepared from a slip made of clay, quartz and feldspar including additional mineralizers by slip casting. The preparation has been described in Part I.[1]

2.2 Electron microscopy

The polished surface of the sample was etched with HF (40%) for 1 min at room temperature, washed with distilled water and dried. A carbon coated plastic replica was prepared. The plastic was dissolved in acetone, the carbon replica was collected on a metal grid and examined by Transmission Electron Microscope (JEM 200 CX, Resolution 1·4 Å, Mag 6,50,000).

2.2.1 Size and shape of mullite crystals

The electron micrographs were illuminated and the length (l) and breadth (b) of mullite crystals seen in the micrographs were measured by a hair divider and scale. 200 crystals were measured from each sample. The aspect ratio (l/b) of the crystals was then derived.

3 Results and Discussion

A brief description of the samples is given in Table 1. The size-distributions of mullite crystals in a few representative samples are displayed in Figs 1 (a–g) where the histograms and continuous curves stand for the experimental size-distribution. The distribution curves are positively skewed.

The mean size and modal size of the mullite crystals increased simultaneously with rise in the concentration of mullite. Both the crystallization and growth of mullite in porcelain were enhanced due to heat-treatment.

The increase in the size of mullite crystals in the samples after heat-treatment is recorded in Table 2, (here the length of mullite crystal is considered as the size). This shows that the added mineralizers influenced the growth of mullite crystals in the samples. It was observed that TiO_2, at low concentration (2·6 wt%) was the most effective oxide in this respect and about 150% increase in the size of mullite crystals could be achieved. The efficiency of TiO_2 decreased, however, at higher concentration and 23% enlargement was found with 8·0 wt% TiO_2.

Cr_2O_3 marginally improved the size of mullite crystals in the heat-treated sample. Incorporation of small amounts of Fe_2O_3, V_2O_5 and Nb_2O_5 in

Table 1. Description of experimental samples

Sample no.	*Description*
1	Base composition (BC)*
2	BC + 8% TiO_2
3	BC + 3% V_2O_5
4	BC + 2·6% Fe_2O_3
5	BC + 2.6% TiO_2
6	BC + 1·5% V_2O_5 + 1·3% Fe_2O_3
7	BC + 1·5% V_2O_5 + 1·3% TiO_2
8	BC + 2.5% Cr_2O_3
9	BC + 2% Nb_2O_5

* BC = 63% clay + 12% quartz + 25% feldspar.

the base composition also helped grow larger mullite crystals. Mixed mineralizers were also used and found to be effective. One such combination, (V_2O_5 + Fe_2O_3), accelerated the influence of the individual components but the other combination, (V_2O_5 + TiO_2), suppressed their activity (Table 2).

The efficiency of mineralizers can be seen to depend on their fluxing action and on their solubility in the glassy phase of the sample. Therefore, a high concentration of TiO_2 (flux) and the low solubility of Cr_2O_3 appeared to be respon-

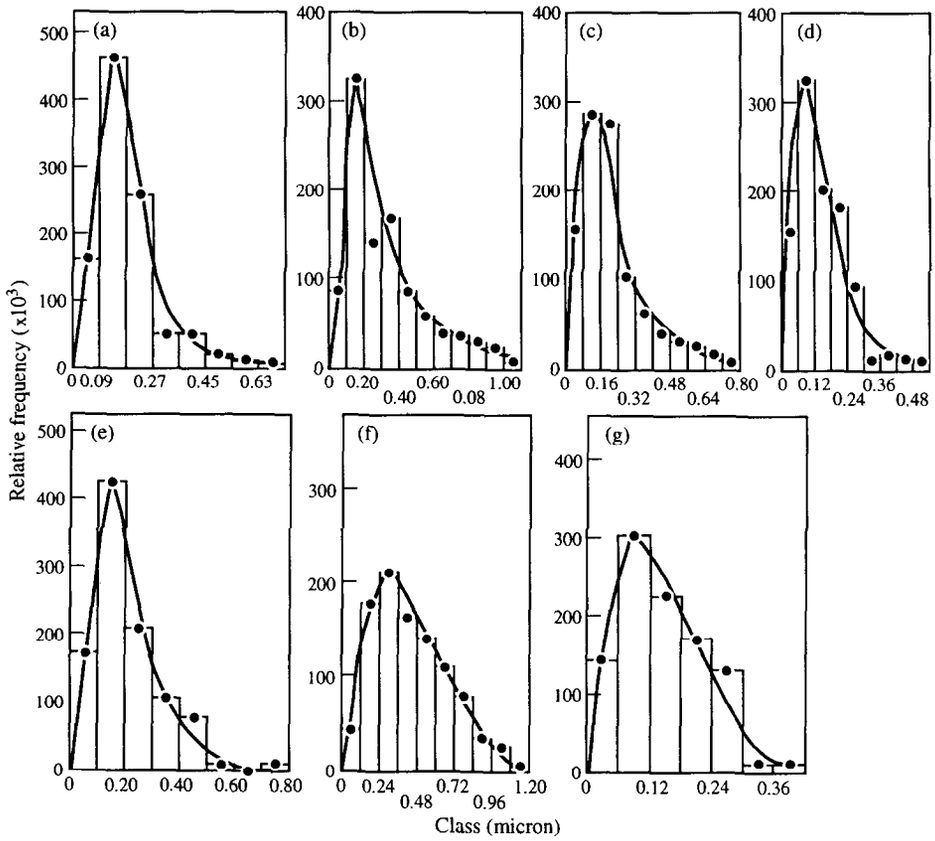


Fig. 1. Size-distribution (experimental) of mullite crystals in porcelain samples: (a) BC + 8·0 wt% TiO_2; (b) BC + 3·0 wt% V_2O_5; (c) BC + 1·5 wt% V_2O_5 + 1·3 wt% Fe_2O_3; (d) base composition; (e) BC + 2·0 wt% Nb_2O_5; (f) BC + 2·6 wt% TiO_2; (g) BC + 8·0 wt% TiO_2. (e) and (g) before heat-treatment and (a), (b), (c), (d) and (f) after heat-treatment.

Table 2. Average size (length) of mullite crystals measured by TEM

Sample no.	*Concentration of mineralizer* (wt%)	*Sample before heat-treatment (B)* (μ)	*Sample after heat-treatment (A)* (μ)	*Increase in average size after heat-treatment* (%)
1	—	0·1364	0·1443	5·8
2	8·0% TiO_2	0·1460	0·1791	22·7
3	3·0% V_2O_5	0·2428	0·3228	32·9
4	2·6% Fe_2O_3	0·1258	0·1772	40·9
5	2·6% TiO_2	0·1790	0·4473	149·9
6	1·5% V_2O_5 + 1·3% Fe_2O_3	0·1298	0·2086	60·7
7	1·5% V_2O_5 + 1.3% TiO_2	0·1233	0·1500	21·7
8	2·5% Cr_2O_3	0·1306	0·1411	8·0
9	2·0% Nb_2O_5	0·2084	0·2550	22·4

Table 3. Average values of aspect ratio (*l/b*) of mullite crystals

Sample no.	*Conc. of mineralizer (wt%)*	*Sample before heat-treatment (B)*	*Sample after heat-treatment (A)*	*Increase in (l/b) after heat-treatment (%)*
1	—	3·1	3·7	19·4
2	8·0% TiO_2	3·5	3·7	5·7
3	3·0% V_2O_5	3·7	5·2	40·5
4	2·6% Fe_2O_3	2·7	4·0	48·1
5	2·6% TiO_2	3·9	6·9	76·9
6	1·5% V_2O_5+ 1·3% Fe_2O_3	3·1	4·1	32·3
7	1·5% V_2O_5 + 1·3% TiO_2	2·8	3·4	21·4
8	2·5% Cr_2O_3	2·9	3·6	24·1
9	2·0% Nb_2O_5	3·7	4·0	8·1

Table 4. Values of skewness of experimental size-distribution curves

Sample no.	*Skewness*	
	Before heat-treatment (B)	*After heat-treatment (A)*
1	0·5701	0·5484
2	0·5549	0·3213
3	0·5270	0·7296
4	0·6110	0·4165
5	0·3962	0·6506
6	0·4985	0·3799
7	0·5561	0·2433
8	0·6176	0·2766
9	0·4182	0·4220

sible for the poor growth of mullite crystals in these samples. At low concentration, TiO_2 was a very good mineralizer. Nb_2O_5 is a good nucleating agent and, thus, improved growth of mullite crystals.

The aspect ratio of the mullite crystals in the heat-treated samples was always higher than in the unheat-treated ones. Irrespective of the added mineralizers, mullite crystals became more acicular in the samples after heat-treatment. In this regard, small amounts (2·6 wt%) of TiO_2 showed excellent performance (Table 3).

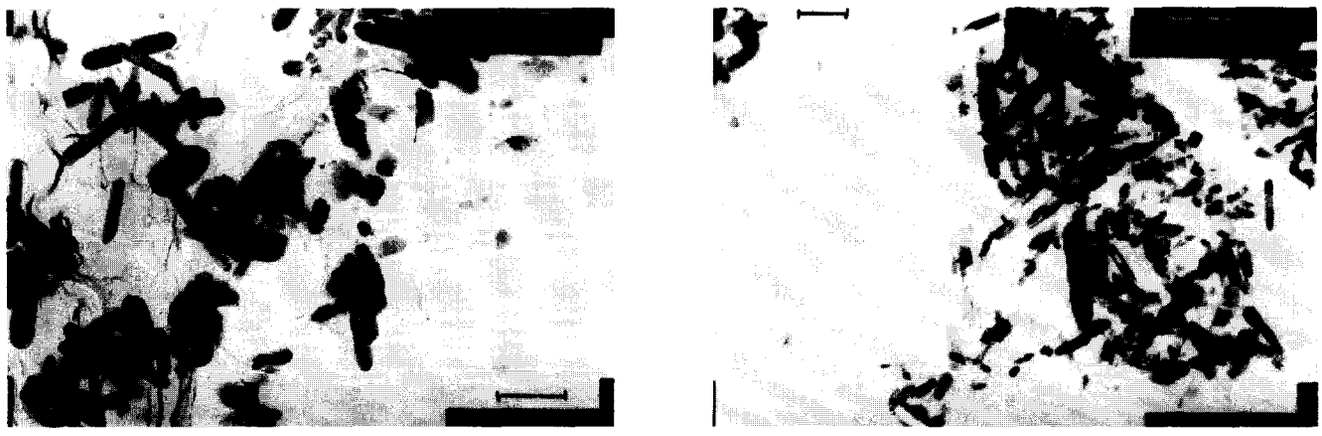
It was observed (Table 4) that the effect of heat-treatment was to reduce skewness, i.e. the size-distribution of mullite crystals in the samples became more symmetric as a consequence of heat-treatment.

A few TEM micrographs of selected samples are portrayed in Figs 2 (a–e) to illustrate the effect of heat-treatment. Each sample is represented by two micrographs labelled B and A for before and after heat-treatment conditions, respectively.

4 Conclusions

(1) Heat-treatment of porcelain samples caused mullite crystals to grow particularly in length (higher aspect ratio).

(2) The size-distribution of mullite crystals in porcelain samples was asymmetric but became more symmetric after heat-treatment.



B(a) A(a)

Fig. 2 TEM micrographs of selected porcelain samples: (a) Base composition; (b) BC + 8.0 wt% TiO_2; (c) BC + 2·6 wt% TiO_2; (d) BC + 1·5 wt% V_2O_5 + 1·3 wt% TiO_2; (e) BC + 2·0 wt% Nb_2O_5. BC = Base composition, bar = 0·2 μ, B = before heat-treatment, A = after heat-treatment.

B(b)

A(b)

B(c)

A(c)

B(d)

A(d)

B(e)

A(e)

Fig. 2. Continued

(3) At low concentration level, TiO_2 was the most efficient mineralizer in promoting large acicular mullite crystals.

Acknowledgements

The authors thank Dr B. K. Sarkar, Director of the Institute for his permission to publish the paper. P. Sarkar is grateful to Council of Scientific and Industrial Research, India for a research fellowship granted to him to carry out this investigation.

Reference

1. Chaudhuri, S. P. & Sarkar, P., Constitution of porcelain before and after heat-treatment. Part I: Mineralogical composition, *J. Euro. Ceram. Soc.*, **15** (1995) 1031–5.