Crystallization of glass in fireclay refractories; part III: Detailed study on the mullite crystal size in the 'synthetic' glass

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Abstract. Poor-grade fireclay products contain substantial amount of glass. A glass of similar composition was synthesized, nucleated and heat-treated for crystallization of mullite. The size and size-distribution of mullite crystals, the rate of change of size and the aspect ratio of the crystals were investigated in relation to the nucleating agents and temperature.

Keywords. Fireclay; glass; mullite; crystal size-distribution.

1. Introduction

It was shown (Chaudhuri and Datta 1996) that the glassy phase in the fireclay products could be crystallized to generate mullite. Besides concentration, other aspects of importance are size, shape and size-distribution of mullite. The communication deals with the study of these microstructural parameters of mullite and the influence of the nucleating agents and heat-treatment temperature on them.

Some earlier investigations (DeVekey and Mazumder 1970; Rogers 1970; Williamson 1970) on other systems, e.g. $CaO-MgO-Al_2O_3$, SiO_2 and $CaO-Al_2O_3-SiO_2$, proved that the crystals which were precipitated from those glasses increased in size with the passage of heating time. Prolonged heating, therefore, caused an increase in the concentration of the crystalline phase as well as an increase in its size. However, the reverse phenomenon was not reported and the size-distribution factor was not taken care of in the studies on glass-crystallization.

2. Experimental

The chemical and phase compositions of fireclay, the chemical composition of fireclay glass and the preparation of the synthetic glass with its chemical analysis were reported in part II (Chaudhuri and Datta 1996). The nucleation and crystallization of the synthetic glass were also described there.

2.1 *Size and size-distribution of mullite*

2.1a *X-ray diffractometry (XRD)*: The size of mullite crystals was determined by following the X-ray line broadening technique (Jones 1938). A powdered glass sample was mixed with pure quartz powder (10 wt.% of the sample). The 1·52 Å line of mullite and 1·817 Å line of quartz were scanned between 60° and 62° (2θ) for mullite and 49° and 51° (2θ) for quartz at $(1/4)°$/min. The pure diffraction broadening at 1/2 height of the mullite peak due to its size was measured and the size was calculated (Henry *et al*

1951) with the equation

$$D_{hkl} = \frac{0 \cdot 9\lambda}{\beta_{1/2}\cos\theta},$$

the symbols have usual meaning.

2.1b   *Scanning electron microscopy (SEM)*:   A glass sample was broken and the broken surface was etched with 40% HF for 1 min at room temperature. The surface

Table 1. Size of mullite crystals in the samples containing Cr_2O_3.

Nucleating agent Cr_2O_3	Heating temp. → Heating time (h) ↓	Size of mullite crystals (μ) at temp.			
		1110°C	1130°C	1150°C	1170°C
0·5 wt.%	5	0·0816	0·0951	0·0762	0·1397
	15	0·2712	0·0922	0·0699	0·1153
	25	0·1317	0·1962	0·1317	0·1085
	35	0·0807	0·1537	0·0756	0·2778
1 wt.%	5	0·1356	0·0738	0·4010	0·1048
	15	0·0815	0·1153	0·0607	0·1153
	25	0·1487	0·1182	0·2305	0·1442
	35	0·2975	0·3547	0·0768	0·1656
1·5 wt.%	5	0·1647	0·3843	0·1072	0·1441
	15	0·1615	0·2305	0·1962	0·2306
	25	0·1845	0·1962	0·0144	0·0023
	35	0·0904	0·0862	0·0768	0·1757

Table 2. Size of mullite crystals in the samples containing V_2O_5.

Nucleating agent V_2O_5	Heating temp. → Heating time (h) ↓	Size of mullite crystals (μ) at temp.			
		1110°C	1130°C	1150°C	1170°C
1 wt.%	5	0·1770	0·0884	0·1213	0·1263
	15	0·1395	0·0838	0·0775	0·1845
	25	0·3547	0·0683	0·1845	0·1264
	35	0·0809	0·1397	0·1182	0·0872
3 wt.%	5	0·1139	0·0710	0·1229	0·1111
	15	0·1050	0·1317	0·0802	0·1537
	25	0·0911	0·0683	0·1153	0·0645
	35	0·1246	0·1153	0·0693	0·0878
5 wt.%	5	0·0688	0·1317	0·0756	0·1025
	15	0·1629	0·0795	0·0437	0·1845
	25	0·0861	0·1230	0·0838	0·1264
	35	0·0846	0·0768	0·1773	0·1198

Table 3. Size of mullite crystals in the samples containing TiO_2.

Nucleating agent TiO_2	Heating temp. → Heating time (h) ↓	Size of mullite crystals (μ) at temp.			
		1110 C	1130 C	1150°C	1170 C
8 wt.%	5	0·1844	0·3294	0·0560	0·1263
	15	0·1164	0·0922	0·1962	0·3075
	25	0·1125	0·0862	0·3074	0·1264
	35	0·1246	0·0941	0·1182	0·3660
10 wt.%	5	0·3547	0·2196	0·6588	0·0922
	15	0·2562	0·0941	0·1317	0·7686
	25	0·0615	0·1487	0·1441	0·0645
	35	0·1060	0·1962	0·0536	0·2562
12 wt.%	5	0·8384	0·1708	0·1962	0·6588
	15	0·3416	0·3843	0·5693	0·2050
	25	0·0768	0·2713	0·1708	0·0838
	35	0·3689	0·2755	0·7686	0·3827

Table 4. Size of mullite crystals in the samples containing $(Cr_2O_3 + V_2O_5)$.

Nucleating agent $(Cr_2O_3 + V_2O_5)$	Heating temp. → Heating time (h) ↓	Size of mullite crystals (μ) at temp.			
		1110 C	1130 C	1150 C	1170°C
(1 + 1) wt.%	5	0·1419	0·2365	0·0932	0·0887
	15	0·3689	0·0775	0·1153	0·2005
	25	0·1153	0·0795	0·0913	0·0923
	35	0·0895	0·0854	0·0823	0·1178
(1·5 + 3) wt.%	5	0·0932	0·1060	0·0971	0·0756
	15	1·0247	0·0636	0·4611	0·1213
	25	0·0838	0·1085	0·1002	0·1230
	35	0·0698	0·0632	0·0694	0·0971
(0·5 + 5) wt.%	5	0·0688	0·0720	0·1060	0·2427
	15	0·09223	0·0611	0·0838	0·8385
	25	0·1025	0·0795	0·1198	0·1488
	35	0·0951	0·0650	0·0932	0·4521

was gold coated and observed under SEM to take micrographs from different places. The length and breadth of a large number of mullite crystals were measured and also the aspect ratio of each crystal.

The histogram and the distribution curve were drawn for each sample on the same plot. The skewness factor was also calculated (Goulden 1952) from the following:

$$\text{Skewness} = \frac{\text{Mean size} - \text{modal size}}{\text{Standard deviation}}.$$

Table 5. Size of mullite crystals in the samples containing ($TiO_2 + V_2O_5$).

Nucleating agent ($TiO_2 + V_2O_5$)	Heating temp. → Heating time (h) ↓	Size of mullite crystals (μ) at temp.			
		1110°C	1130°C	1150°C	1170°C
(10·0 + 1·0) wt.%	5	0·8384	0·1397	0·1098	0·0454
	15	0·5764	0·0518	0·4611	0·1441
	25	0·0709	0·0801	0·0951	0·6148
	35	0·1947	0·0922	0·6587	0·2186
(8·0 + 5·0) wt.%	5	0·1019	0·0941	0·0932	0·1125
	15	0·6588	0·0726	0·0485	0·4010
	25	0·0461	0·0460	0·1048	0·0838
	35	0·0636	0·0559	0·1774	0·6782
(12·0 + 3·0) wt.%	5	0·2562	0·1441	0·1281	0·2305
	15	0·1845	0·1230	0·0542	0·4392
	25	0·0990	0·0862	0·1677	0·2250
	35	0·3617	0·2635	0·2306	0·4081

Table 6. Rate of size change of mullite crystals in the samples.

Nucleating agent (N.A.)	Conc. of N.A. (wt.%)	Rate of size change (K), [$(\mu/min) \times 10^5$] at temp.			
		1110°C	1130°C	1150°C	1170°C
Cr_2O_3	0·5	16·6	3·3	1·1	2·8
	1·0	40·0	40·0	30·0	3·3
	1·5	4·7	13·3	2·3	17·5
V_2O_5	1·0	5·8	2·3	3·9	7·7
	3·0	1·7	10·0	3·3	8·3
	5·0	8·8	2·9	11·7	5·8
TiO_2	8·0	3·3	6·7	5·0	8·3
	10·0	14·4	8·7	43·3	7·2
	12·0	50·4	16·6	41·7	62·5
($Cr_2O_3 + V_2O_5$)	(1·0 + 1·0)	26·6	13·3	3·3	8·9
	(1·5 + 3·0)	3·3	8·3	33·3	5·5
	(0·5 + 5·0)	5·3	3·3	3·3	4·0
($TiO_2 + V_2O_5$)	(10·0 + 1·0)	40·3	6·7	53·2	35·5
	(8·0 + 5·0)	6·6	4·0	2·5	33·3
	(12·0 + 3·0)	12·5	5·6	5·6	33·3

2.2 *Rate of change of mullite crystal size*

A glass sample containing one concentration of a nucleating agent yielded four samples when heat-treated for four different time periods at one temperature. The size of mullite crystals was then plotted against the time and the rate of size change was determined from the slope.

Table 7. Activation energy of rate of size change of mullite in the samples.

Nucleating agent (N.A.)	Conc. of N.A. (wt.%)	Activation energy (Kcal/mol)
Cr_2O_3	0·5	137·3
	1·0	73·2
	1·5	183·5
V_2O_5	1·0	45·7
	3·0	36·6
	5·0	137·3
TiO_2	8·0	91·5
	10·0	30·5
	12·0	137·3
$(Cr_2O_3 + V_2O_5)$	(1·0 + 1·0)	91·5
	(1·5 + 3·0)	45·5
	(0·5 + 5·0)	36·5
$(TiO_2 + V_2O_5)$	(10·0 + 1·0)	18·3
	(8·0 + 5·0)	91·5
	(12·0 + 3·0)	137·3

Table 8. Aspect ratio of mullite crystals and skewness of size–distribution curves.

Nucleating agent	Range of aspect ratio	Skewness of size distribution curve
Cr_2O_3	1·90 – 3·14	0·235
V_2O_5	2·06 – 3·60	0·032
TiO_2	2·13 – 3·93	0·143
$(Cr_2O_3 + V_2O_5)$	2·37 – 3·33	0·150
$(TiO_2 + V_2O_5)$	2·64 – 4·06	0·014

3. Results

The sizes of mullite crystals in different samples are presented in tables 1–5. The rates of change of crystal size (K) are included in table 6. The temperature dependence of the rate was calculated from the Arrhenius plot,

$$\log_{10}K \text{ vs } 1/T.$$

A representative plot is shown in figure 1. The activation energy values are compiled in table 7. The skewness factors and aspect ratios (min and max in the range) are given in table 8. The influence of radius and charge of cations of nucleating agents on the size of mullite crystals is displayed in figures 2 and 3, respectively and also in table 9. The relationship at the minimum, intermediate and maximum concentrations of the oxides are shown by curves 1, 2 and 3, in figures 2 and 3.

Table 9. Effect of radius and charge of cations of nucleating agents on the avg. size of mullite crystal.

Nucleating agent (N.A.)	Conc. of N.A. (wt.%)	Radius of cation of N.A. (Å)	Charge of cation of N.A.	Avg. size of mullite crystal (μ)
Cr_2O_3	0·5	0·63	3^+	0·1310
	1·0			0·1640
	1·5			0·1585
V_2O_5	1·0	0·59	5^+	0·1349
	3·0			0·1016
	5·0			0·1079
TiO_2	8·0	0·68	4^+	0·1715
	10·0			0·2254
	12·0			0·3602

Figure 1. Arrhenius plot for rate of size change of mullite (K).

4. Discussion

The results given in tables 1–5 showed that irrespective of time and temperature of heat-treatment, and, the concentration of nucleating oxides, V_2O_5 favoured formation of small crystals and TiO_2 the big crystals. But the crystal size due to Cr_2O_3 stood in between. The use of V_2O_5 in combination with either Cr_2O_3 or TiO_2 helped reduction of crystal size that grew in the presence of Cr_2O_3 and TiO_2 alone.

At any temperature the crystal size decreased with the increase in heating time. Consequently, the rate of size change as reported in table 6 implied the rate of decrease or disappearance of mullite crystals, i.e. higher rate values meant faster decrease of size.

Mullite crystals in the samples are displayed in figures 4a–e. It appeared from this figure and table 6 that except at 1130°C, Cr_2O_3 was responsible for the lowest rate of size
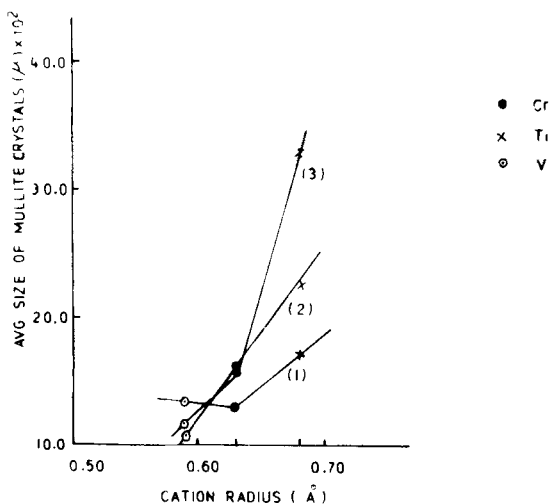
Figure 2. Dependence of average size of mullite crystals on the cation radius of nucleating agent at (1) minimum, (2) intermediate and (3) maximum concentration of it.
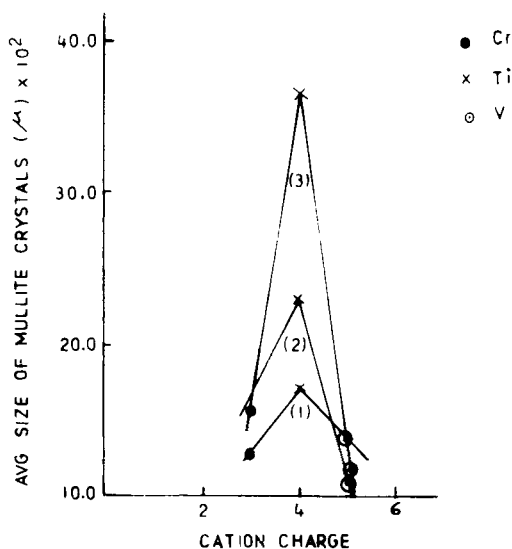
Figure 3. Dependence of average size of mullite crystals on the cation charge of nucleating agent at (1) minimum, (2) intermediate and (3) maximum concentration of it.

change, V_2O_5 for the highest rate and TiO_2 for the rate in between. Therefore, the size of mullite crystals decreased from samples containing Cr_2O_3 to those containing V_2O_5.

The lowest and highest rates of decrease of mullite crystal size with Cr_2O_3 and V_2O_5, respectively are also justified by the highest (131 Kcal/mol) and the lowest (73·2 Kcal/mol) average values of activation energies of rate of crystal size change of the samples with Cr_2O_3 and V_2O_5, respectively. The effect of TiO_2, in this respect, assumed the intermediate position (86·2 Kcal/mol).

It was observed that TiO_2 helped in the crystallization of longer needles of mullite as compared to those crystallized by V_2O_5 and Cr_2O_3 in the samples. This is realized from the aspect ratios (table 8) that decreased from TiO_2 to Cr_2O_3.
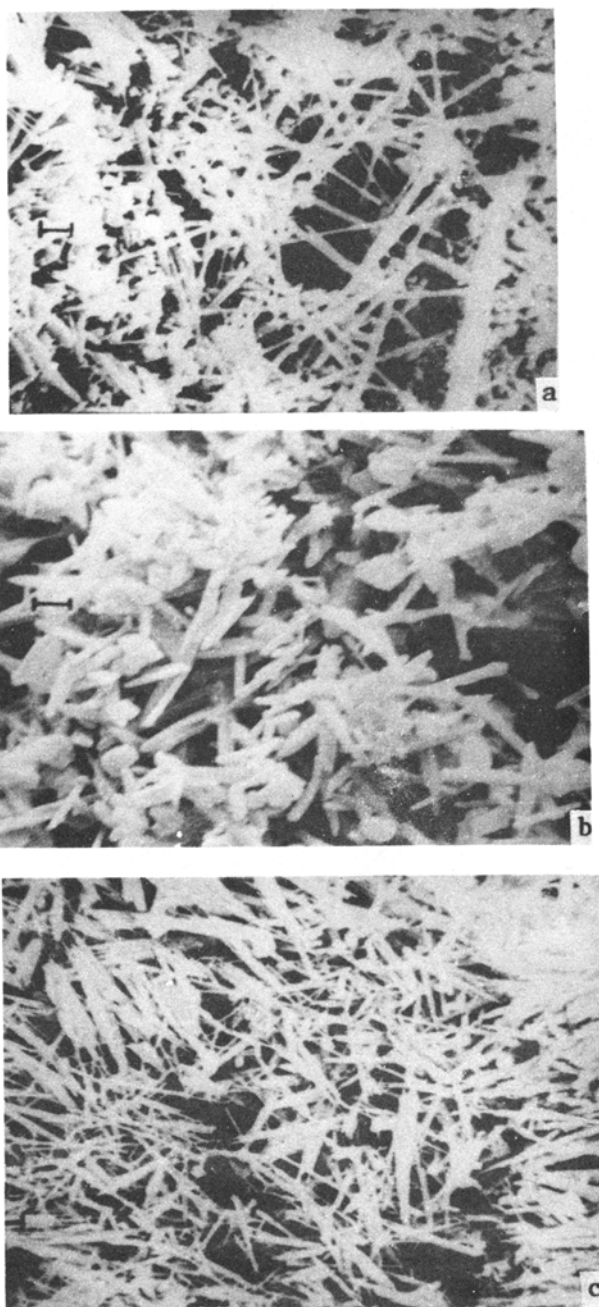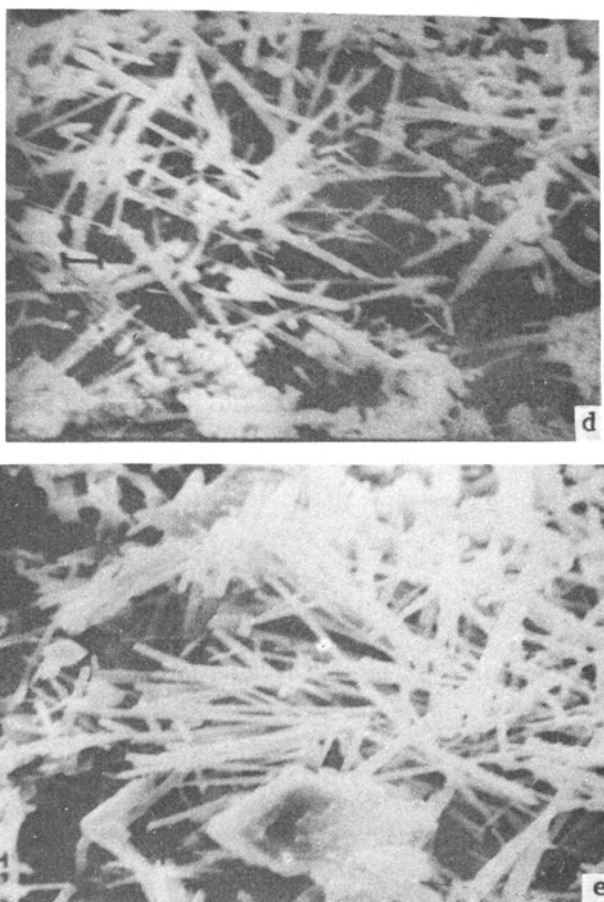

Figure 4. a–c.

Figure 4. SEM micrographs of samples containing (a) Cr_2O_3, (b) V_2O_5, (c) TiO_2, (d) $(Cr_2O_3 + V_2O_5)$ and (e) $(TiO_2 + V_2O_5)$ (Bar = 1.0μ).

The size-distribution of mullite crystals in all the samples was found to be asymmetric. The asymmetry changed with the nature of the nucleating oxides used for crystallization. It was measured by the skewness factor (table 8) and the values indicated that the effect of these oxides on asymmetry followed the series

$$Cr_2O_3 > TiO_2 > V_2O_5.$$

Compactness of crystal arrangement varies with the asymmetry. So, the effect of the oxides on compactness of crystal arrangement in samples followed the above series.

The cations of the nucleating oxides served as islands in the glass to precipitate crystals on them and thus crystal size was dependent on cation size. The smallest V^{5+} ion and the largest Ti^{4+} ion therefore, initiated growth of the smallest and the largest crystals, respectively while Cr^{3+} ion favoured formation of crystals of medium size (figure 2, table 9).

Except in some unusual cases, the higher valency, cations are smaller in size (Moeller 1952). The crystal size–cation charge relationship (figure 3) is opposite to that found in figure 2.

In this study (described in parts II and III) it was desired to estimate the concentration of mullite and to measure the size (and size-distribution) of mullite crystals simultaneously in the samples as well as the rates of change of concentration of mullite and its size. Unlike other work, it was observed that in a sample while concentration of mullite increased the size of mullite crystal decreased.

The rate of crystallization of mullite (K') was of the order of ($\times 10^{-3}$)wt.% per min (table 7 of Part II) but the rate of change of size of mullite crystal (K) was of the order of ($\times 10^{-5}$)μ per min (table 6 of Part III). The rate of rise of concentration of mullite was 100 times faster than the rate of decrease of size of mullite crystal and, therefore, generation of mullite from glass always far exceeded the dissolution of mullite in the same glass. These two rates would gradually come to equilibrium after prolonged heat-treatment of the sample.

The equilibrium microstructure of the sample should consist of good concentration of mullite crystals of small size. Such microstructure is very favourable for good mechanical and thermal properties of a ceramic body.

This expectation is partially fulfilled in this investigation.

5. Conclusions

(1) The size of mullite crystals increased from V_2O_5-containing sample to TiC_2-containing samples. Irrespective of nucleating agent and heat-treatment temperature, the crystal size decreased with longer heating time.
(2) The rate of reduction of crystal size was influenced by the nucleating agent.
(3) The size-distribution of mullite crystals was asymmetric in all the samples and asymmetry (skewness factor) decreased from Cr_2O_3 to V_2O_5.
(4) The acicularity of mullite crystals (aspect ratio) decreased from samples containing TiO_2 to those containing Cr_2O_3.
(5) A nucleating agent of smaller cation (such as V^{5+}) helped crystallization of smaller mullite crystals.

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