Bull. Mater. Sci., Vol. 19, No. 2, April 1996, pp. 373–381. © Printed in India.

Crystallization of glass in fireclay refractories: part II: Detailed study on the mullite crystal content of the 'synthetic' glass

S P CHAUDHURI and T DATTA
Special Ceramics Section, Central Glass and Ceramic Research Institute, Calcutta 700032, India

MS received 31 July 1995; revised 2 November 1995

Abstract. A glass of composition similar to that found in fireclay refractories was synthesized and subsequently nucleated with Cr_2O_3, V_2O_5 and TiO_2. These glasses were heat-treated for crystallization of the mullite phase. The mullite content, the crystallization of mullite and the effect of temperature on the rate were investigated. The concentration of the nucleating oxides and the size and charge of their cations influence both the mullite content obtained and the crystallization rate.

Keywords. Fireclay; glass; mullite; nucleation; crystallization.

1. Introduction

Fireclay containing around 20 wt.% Al_2O_3 is poor-grade and not suitable for making refractories. This is due to high concentration of low viscosity glass produced in the refractories. Improvement in the properties of the refractories is, however, possible by increasing the mullite crystal content.

It was shown (MacDowell and Beall 1969) that a glass composition of Al_2O_3–SiO_2 system with 10–30 wt.% Al_2O_3 is prone to crystallization by the nucleation growth process. As the Al_2O_3 content of the poor-grade fireclay products does not usually exceed 20 wt.%, mullite crystals could be precipitated from fireclay glass by incorporating suitable oxides in it and then subjecting it to heat-treatment (Stookey 1959; Bergeron and Risbud 1984).

Earlier, McGee (1966) studied the constitution of fireclay. He concentrated on the mineralogical composition and strength of high-grade fireclay and kaolin clay. That the glassy phase in the fireclay products is a potential source of mullite has not been realized yet. This aspect is very important for poor-grade fireclay to develop high-grade refractory products from them. The present study, therefore, aims at understanding the crystallization of mullite from fireclay glass.

1.1 *Background*

Fireclay refractories of IS-6 and IS-8 qualities are manufactured from fireclays having Al_2O_3 content not less than 30 wt.% and 40 wt.%, respectively. The reserve of such high-grade fireclays in the country is very low at present and the demand of fireclay refractories is met through import. In contrast to this situation, a huge quantity of low-grade (Al_2O_3 content less than 20 wt.% and high flux content) fireclays is left unused or wasted. It is desired to improve the quality of such fireclays and to utilize these for making IS-6 and IS-8 type refractories. The motivation is to employ this otherwise waste material for appropriate useful application and also for import substitution.

The upgrading of low-grade fireclays in terms of hot and cold mechanical strength, thermal-shock resistance and fusion point, may be possible by modification of the large pool of glassy phase in the low-grade fireclay products. The crystallization of the main phase, i.e. mullite, from the synthetic glassy phase resembling that in the products by incorporating nucleating agents and varying time and temperature schedule is, therefore, attempted. The concentration and size of mullite crystals as well as their rates of crystallization and change of size are investigated as the first step and the results are presented in the two papers.

Depending on the information generated from this study the raw low-grade fireclay will be investigated in the second step by mixing selected nucleating agent with it and employing suitable heating schedule for crystallization and growth of mullite phase in the fired products and also by determining their thermomechanical properties as mentioned before.

2. Experimental

2.1 *Analysis of fireclay*

The chemical composition of the fireclay was determined by wet chemical analysis. It was then fired at 1300°C for 1 h and crushed to fine powder. The crystalline phases were identified and estimated by X-ray analysis in a diffractometer (XRD).

The crystalline phases were mostly mullite and quartz. These were estimated by the internal standard technique in XRD (Klug and Alexander 1974). The 2·20 Å and 1·52 Å lines of mullite and 4·26 Å line of quartz were selected for this purpose.

2.2 *Composition of fireclay glass*

Mullite is composed of Al_2O_3 and SiO_2 whereas quartz is only SiO_2. Knowing the concentrations (wt.%) of mullite and quartz and also the composition of fireclay, the amounts of Al_2O_3 and SiO_2 in the crystalline phases were obtained. Therefore, the glass content (wt.%) was determined to be 100-crystal content and its composition was calculated on the assumption that the remaining Al_2O_3, SiO_2 and other oxides combined to yield glass.

2.3 *Synthetic glass preparation*

The glass was synthesized by melting a mixture of glass sand, alumina, Na_2CO_3, $K_2C_2O_4$, Fe_2O_3, TiO_2, $CaCO_3$ and $MgCO_3$ at 1300°C. It was analysed by wet chemical method.

2.4 *Nucleation and crystallization of synthetic glass*

Glass powder was mixed with Cr_2O_3 (0·5, 1, 1·5 wt%), V_2O_5(1, 3, 5 wt%), TiO_2(8, 10, 12 wt%), $Cr_2O_3 + V_2O_5$(1 + 1, 1·5 + 3, 0·5 + 5 wt%) and $TiO_2 + V_2O_5$(10 + 1, 8 + 5, 12 + 3 wt%) thoroughly in stainless steel pot for 24 h and fired at 1300°C for 1 h in an electric furnace in platinum crucible. Each sample was cooled overnight after switching

off the furnace, finely powdered and its crystallization temperature was determined from the DTA trace. It was around 1150 °C.

Samples were heat-treated at 1110°, 1130°, 1150° and 1170 °C for 5, 15, 25 and 35 h at each temperature and cooled overnight at the end of the run by shutting off the furnace. The temperature was raised at 5–7 C/min.

2.5 *Estimation of mullite*

The X-ray calibration curves were drawn by plotting peak heights of 2·20 Å and 1·52 Å lines of mullite against concentration of mullite for four standard samples. The concentrations of mullite in the heat-treated glass samples were obtained by comparing the peak heights of these samples from the calibration curves.

2.6 *Mullite crystallization rate*

A nucleated glass sample was heat-treated at a fixed temperature for four different time periods. The mullite contents of these samples were plotted against time and the rate was calculated from the slope.

Table 1. Chemical composition (wt.%)

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	LOI
Fireclay (raw) (CA)	56·32	23·03	1·52	1·02	1·22	0·82	1·70	0·95	13·73
Fireclay glass (Calc)	69·40	20·20	2·20	1·50	1·80	1·20	2·50	1·40	—
Synthetic glass (CA)	70·47	19·15	2·00	0·72	2·23	1·70	2·80	1·20	—

CA, Chemical analysis: Calc., calculated.

Table 2. Concentration of mullite in samples containing Cr_2O_3.

Nucleating agent Cr_2O_3	Heating temp. → / Heating time(h) ↓	Conc. of mullite crystals (wt.%) at temp. 1110 C	1130 C	1150 C	1170 C
	5	9·25	9·50	10·25	14·87
	15	10·12	10·56	10·37	12·12
0·5 wt.%	25	10·37	10·44	10·87	11·06
	35	10·37	11·57	11·24	10·06
	5	8·00	8·62	8·75	12·81
	15	8·18	9·06	9·75	10·75
1·0 wt.%	25	11·00	10·31	10·93	10·37
	35	10·37	11·37	11·00	8·74
	5	7·93	8·69	9·06	10·87
	15	8·75	10·37	10·12	9·93
1·5 wt.%	25	7·37	9·12	10·00	8·37
	35	9·75	9·25	9·43	10·24

Table 3. Concentration of mullite in samples containing V_2O_5.

Nucleating agent V_2O_5	Heating temp. → Heating time(h) ↓	Conc. of mullite crystals (wt.%) at temp. 1110°C	1130°C	1150°C	1170°C
	5	11·43	12·31	12·56	12·62
	15	10·25	12·37	11·45	12·06
1·0 wt.%	25	12·12	12·87	10·75	11·25
	35	12·50	13·87	12·89	10·18
	5	11·24	12·12	13·94	14·87
	15	11·75	12·62	13·62	13·50
3·0 wt.%	25	12·75	12·40	12·87	11·25
	35	11·62	13·12	13·25	10·81
	5	12·25	12·31	11·75	12·89
	15	10·18	12·12	10·46	12·43
5·0 wt.%	25	12·37	12·43	11·56	10·87
	35	11·37	12·87	12·43	10·56

Table 4. Concentration of mullite in samples containing TiO_2.

Nucleating agent TiO_2	Heating temp. → Heating time(h) ↓	Conc. of mullite crystals (wt.%) at temp. 1110°C	1130°C	1150°C	1170°C
	5	6·62	7·25	8·62	12·50
	15	8·31	11·00	9·17	9·07
8·0 wt.%	25	7·62	8·81	9·68	9·94
	35	9·12	9·94	9·00	8·31
	5	6·75	7·43	7·75	6·93
	15	5·18	7·12	7·56	6·81
10·0 wt.%	25	8·00	8·25	7·87	6·25
	35	7·50	8·25	8·00	7·00
	5	4·75	6·68	6·75	5·68
	15	4·87	7·12	6·94	6·37
12·0 wt.%	25	6·25	7·00	6·18	6·50
	35	5·75	6·37	6·25	6·43

3. Results

The chemical analysis of the raw fireclay is shown in table 1. This suggests that the Al_2O_3 content of the glassy phase in the fireclay is still less.

The fired fireclay had 19 wt% mullite and 8 wt% quartz which accounted for 13·64 wt% Al_2O_3 and 13·36 wt.% SiO_2 in the crystalline phase. The calculated chemical analysis of the fireclay glass is incorporated in table 1. The chemical analysis of the synthetic glass is also given in this table.

The concentrations of mullite in the heat-treated synthetic glass samples are tabulated (tables 2–6). The crystallization rates of mullite in the samples are collected in

Table 5. Concentration of mullite in samples containing ($Cr_2O_3 + V_2O_5$).

Nucleating agent ($Cr_2O_3 + V_2O_5$)	Heating temp. → Heating time(h) ↓	Conc. of mullite crystals (wt.%) at temp. 1110 C	1130 C	1150 C	1170 C
	5	9·37	10·12	9·63	10·31
	15	8·75	10·06	10·81	11·74
(1·0 + 1·0) wt.%	25	10·37	10·75	10·50	9·93
	35	10·25	11·06	9·87	10·24
	5	7·87	10·18	11·12	9·22
	15	8·00	11·00	13·50	9·93
(1·5 + 3·0) wt.%	25	9·50	9·37	8·75	9·81
	35	10·12	10·00	9·75	7·81
	5	10·87	12·43	12·37	11·41
	15	10·00	11·75	10·31	11·31
(0·5 + 5·0) wt.%	25	11·12	11·62	10·81	11·25
	35	10·87	11·12	11·50	11·18

Table 6. Concentration of mullite in samples containing ($TiO_2 + V_2O_5$).

Nucleating agent ($TiO_2 + V_2O_5$)	Heating temp. → Heating time(h) ↓	Conc. of mullite crystals (wt.%) at temp. 1110 C	1130 C	1150 C	1170 C
	5	6·00	6·43	6·18	6·18
	15	7·06	7·57	7·68	6·75
(10·0 + 1·0) wt.%	25	6·50	7·25	6·18	7·12
	35	6·00	6·75	6·18	6·56
	5	6·87	8·12	7·44	6·93
	15	6·24	8·25	7·25	7·43
(8·0 + 5·0) wt.%	25	7·62	7·43	7·62	6·93
	35	7·00	7·93	7·50	7·18
	5	5·75	5·12	5·44	5·08
	15	5·00	7·12	6·58	7·06
(12·0 + 3·0) wt.%	25	6·12	6·25	5·75	5·93
	35	6·38	7·18	7·12	6·09

table 7. The effect of concentration of nucleating agent, time and temperature of heat-treatment on mullite content and the crystallization rate of mullite are revealed here.

The activation energies of mullite crystallization in the samples were estimated from the Arrhenius plots, $\log_{10} K'$ vs $1/T$(K' = rate of mullite crystallization) and recorded in table 8. A typical plot is illustrated in figure 1.

The dependence of concentration of mullite on the radius and charge of cations of Cr_2O_3, V_2O_5 and TiO_2 has been displayed in figures 2 and 3, respectively. The radius and charge of Cr^{3+}, V^{5+} and Ti^{4+} ions are plotted against the average mullite content

Table 7. Rate of crystallization of mullite at different heat-treatment temperatures.

Nucleating agent (N. A.)	Conc. of (N. A.) (wt.%)	Crystallization rate (K'), [(wt.%/min.) × 10^3] at temp.			
		1110°C	1130°C	1150°C	1170°C
Cr_2O_3	0·5	0·83	1·33	0·66	2·50
	1·0	2·33	1·66	1·30	2·30
	1·5	1·20	0·33	1·60	0·33
	1·0	0·55	0·55	0·83	1·11
V_2O_5	3·0	0·33	0·55	0·83	1·66
	5·0	0·48	0·62	1·60	1·33
	8·0	1·40	1·42	0·55	2·25
TiO_2	10·0	0·67	0·48	0·16	0·18
	12·0	0·55	0·21	0·28	1·66
	(1·0 + 1·0)	1·11	0·55	0·83	0·27
(Cr_2O_3 +	(1·5 + 3·0)	1·19	0·14	1·90	0·66
V_2O_5)	(0·5 + 5·0)	0·17	0·71	0·83	0·42
	(10·0 + 1·0)	0·83	0·83	0·14	0·83
(TiO_2 +	(8·0 + 5·0)	0·55	0·15	0·12	0·21
V_2O_5)	(12·0 + 3·0)	0·28	1·10	1·11	0·88

of the samples containing minimum, intermediate and maximum concentrations of the oxides to draw curves 1, 2 and 3, respectively in these figures. Results are summarized in table 9.

4. Discussion

It appears from tables 2–6 that, irrespective of experimental conditions, V_2O_5 is the most efficient mullite builder followed by Cr_2O_3 and TiO_2. It is also noteworthy that heat-treatment at 1130°C for V_2O_5 containing samples, 1150°C for TiO_2 containing samples and 1170°C for Cr_2O_3 containing samples seemed very suitable for crystallization of mullite. But higher temperature caused reduction in mullite content and better efficiency was observed at low concentration of the oxides.

It is also interesting to note that the addition of V_2O_5 to either Cr_2O_3 or TiO_2 reduced the heat-treatment temperature from 1170°C in case of Cr_2O_3-containing samples and from 1150°C in case of TiO_2-containing samples to 1130°C in each case without sacrificing the amount of mullite crystallization with only Cr_2O_3 or only TiO_2. This has been the special advantage achieved by employing the mixed nucleants.

So far as their properties are concerned, Cr_2O_3 is a very refractory oxide and dissolves in glass to a very small amount. But V_2O_5 and TiO_2 are both fluxing oxides and enter the glass in reasonable amounts (Morey 1938). The viscosity of the glass is, therefore, influenced by the amount of the oxides dissolved in it. While V_2O_5 and TiO_2 reduced glass viscosity, Cr_2O_3 increased the same. Again V_2O_5 caused more reduction than TiO_2. Depending on their melting points, the concentrations of these oxides in glass increased from Cr_2O_3 to TiO_2.

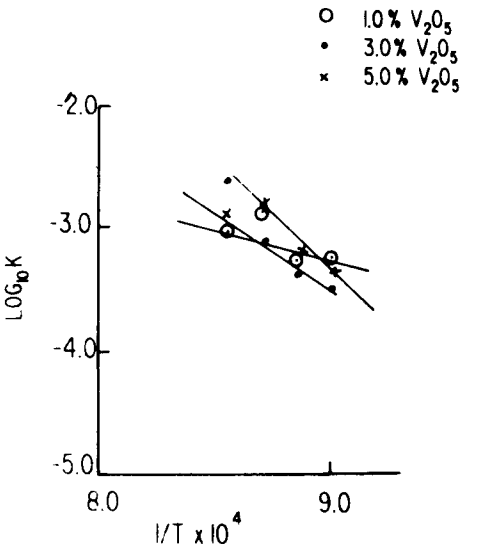

Figure 1. Arrhenius plot for rate of mullite crystallization (K').

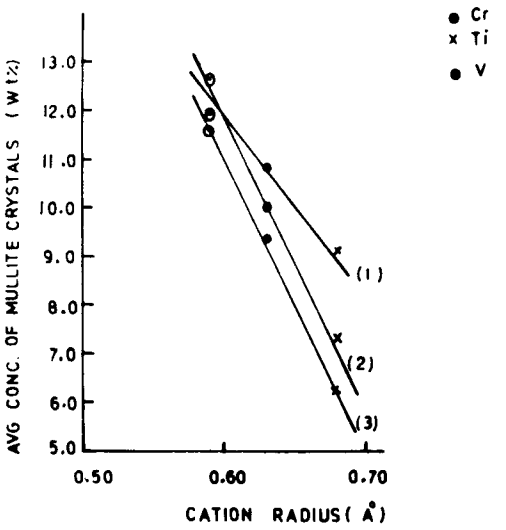

Figure 2. Dependence of average concentration of mullite on the cation radius of nucleating agent at (1) minimum, (2) intermediate and (3) maximum concentration of it.

These facts were mainly responsible for varying degrees of effectiveness of these oxides for crystallization of mullite from glass. So, 0·5 wt.% Cr_2O_3 was found to be most efficient but only at 1170°C. However, 1 wt.% V_2O_5 and 8 wt.% TiO_2 showed best performance at 1130°C. Similar reasons are applicable for the best results obtained from the use of ($Cr_2O_3 + V_2O_5$) and ($TiO_2 + V_2O_5$) mixtures.

The nucleation and crystallization of glass needs generation of sufficient number of nuclei within it and lowering of free energy at glass-nucleus interface (Williamson 1970).

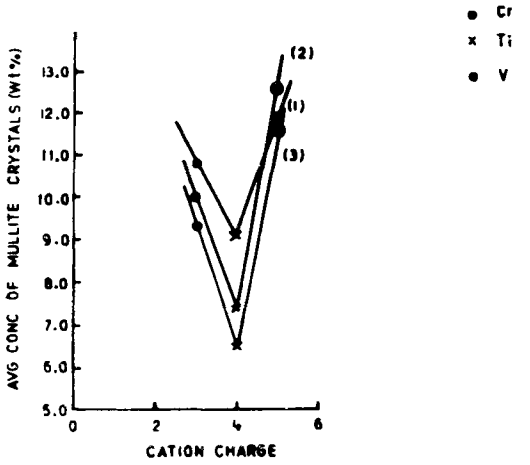

Figure 3. Dependence of average concentration of mullite on the cation charge of nucleating agent at (1) minimum, (2) intermediate and (3) maximum concentration of it.

Table 8. Activation energies of crystallization of mullite in the samples.

Nucleating agent (N. A.)	Conc. of N. A. (wt.%)	Activation energy (Kcal/mol)
Cr_2O_3	0·5	61·1
	1·0	45·8
	1·5	73·2
	1·0	23·0
V_2O_5	3·0	61·1
	5·0	81·1
	8·0	45·8
TiO_2	10·0	91·5
	12·0	61·1
	(1·0 + 1·0)	61·1
$(Cr_2O_3 + V_2O_5)$	(1·5 + 3·0)	73·2
	(0·5 + 5·0)	61·1
	(10·0 + 1·0)	30·5
$(TiO_2 + V_2O_5)$	(8·0 + 5·0)	45·6
	(12·0 + 3·0)	46·0

The crystallization of glass is enhanced by the increase in the nuclei number and decrease in the interfacial energy.

Among the three oxides, the radii (Moeller 1952; Day and Selbin 1962) of Cr^{3+}, V^{5+} and Ti^{4+} ions are 0·63 Å, 0·59 Å and 0·68 Å, respectively. Therefore, maximum number of nuclei were available from V_2O_5, minimum from TiO_2 and intermediate from Cr_2O_3. In unit volume of glass, V_2O_5 offered the highest number of sites for mullite crystallization which decreased from Cr_2O_3 to TiO_2. The amount of mullite crystallized decreased from V_2O_5-containing samples to TiO_2-containing samples (table 9).

The low activation energy of mullite crystallization of the V_2O_5-containing glass samples also suggests that V_2O_5 is superior to Cr_2O_3 and TiO_2 as nucleating agent.

Table 9. Effect of radius and charge of cations of nucleating agents on average concentration of mullite.

Nucleating agent (N. A.)	Cations radius (Å)	Cation charge	Conc. of (N. A.) wt.%	Avg. conc. of mullite wt.%
			0·5	10·81
Cr_2O_3	0·63	3	1·0	10·00
			1·5	9·32
			1·0	11·93
V_2O_5	0·59	5	3·0	12·58
			5·0	11·80
			8·0	9·06
TiO_2	0·68	4	10·0	7·29
			12·0	6·24

5. Conclusions

(1) The glassy phase in fireclay refractories can be partially crystallized to obtain mullite by nucleating the glass with Cr_2O_3, V_2O_5 and TiO_2 followed by heat-treatment.
(2) The most efficient nucleating agent for crystallization of mullite from fireclay glass was V_2O_5 which was followed by Cr_2O_3 and TiO_2. Addition of V_2O_5 to either Cr_2O_3 or TiO_2 improved the efficiency of each.

Acknowledgement

One of the authors (TD) is grateful to CSIR, New Delhi for financial assistance to carry out this study.

References

Bergeron C G and Risbud S H 1984 *Introduction to phase equilibria in ceramics* (Columbus: American Ceramic Society) p. 38
Day M C and Selbin J 1962 *Theoretical inorganic chemistry* (New York: Reinhold Publishing Co.) p. 101
Klug H P and Alexander L E 1974 *X-ray diffraction procedures for polycrystalline and amorphous materials* (New York: Wiley) 2nd ed.
MacDowell J F and Beali G H 1969 *J. Am. Ceram. Soc.* **52** 17
McGee T D 1966 *J. Am. Ceram. Soc.* **49** 83
Moeller T 1952 *Inorganic chemistry—an advanced text book* (New York: Wiley) p. 127
Morey G W 1938 *The properties of glass* (New York: Reinhold Publishing Co.) p. 135
Stookey S D 1959 *Indust. Engg. Chem.* **51** 805
Williamson J 1970 *Miner. Mag.* **37** 758