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Mullite formation from ethyl silicate and aluminium chlorides

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The formation of mullite via gels prepared from technical ethyl silicate and aluminium chlorides has been studied. Normally, gels prepared specifically with the oxide stoichiometry of mullite ($3Al_2O_3 \cdot 2SiO_2$) do not form the mineral mullite on firing to 1200° C in the absence of a mineralizer. However, when the stoichiometric gel is homogeneous (achieved by acidic or neutral catalysts during the gel preparation) firing at 1200° C can lead to an almost quantitative yield of mullite. For a homogeneous gel, the presence of strontium or caesium salts, or an organo-tin compound such as dibutyltin diacetate or dibutyltin oxide during the gel preparation promotes almost quantitative conversion to mullite at about 1000° C. There is a threshold concentration under which conversion to mullite is incomplete, some cristobalite being formed. For the organo-tin compounds, the type of aluminium chloride is unimportant and the way in which water for the hydrolysis step is added is also unimportant. When the gel is non-homogeneous, the product obtained on firing contains cristobalite and α-alumina or γ-alumina, with little mullite, even if strontium or caesium salts, or organ-otin compounds are present. A ceramic bond is formed from alumina and some other refractory grains during firing.

1. Introduction

This paper presents our combined experience and current "state-of-the-art" in the formation of synthetic mullite from gels. It has long been recognized [1] that mullite, normally formulated as $3Al_2O_3 \cdot 2SiO_2$, can be considered as a solid solution of alumina and silica, formed at a temperature of 1200° C or more. Mullite has also been described [2, 3] as a silica-substituted alumina which can have a range of compositions between $3Al_2O_3 \cdot 2SiO_2$ and $2Al_2O_3 \cdot SiO_2$. $2Al_2O_3 \cdot SiO_2$ is made [4] at a temperature above 1800° C and can be regarded as a metastable form of mullite, mullite being the only aluminosilicate phase in the Al_2O_3–SiO_2 system which is stable at normal atmospheric pressure [5]. Mullite is formed in aluminosilicate refractories on firing to 1200° C or more, which makes the conditions under which mullite is obtained of great significance in refractories technology.

Sintered mullite is prepared [6] commercially by heating a mixture of kaolinite and alumina grains to at least 1650° C. The preparation of pure mullite from a precursor formed by hydrolysing ethyl orthosilicate in the presence of aluminium hydroxide obtained by precipitation from aluminium chloride solution with ammonia has been described [7]. A precursor gel with the oxide stoichiometry of mullite has been prepared [8] from methyl orthosilicate and aluminium *sec*-butoxide. Some other routes to gels with the oxide stoichiometry of mullite have been reviewed by Biddle [9].

In the present work, the conditions under which mullite is formed from gels whose oxide stoichiometry is in the mullite range have been

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investigated, the silica in the gel being derived from ethyl silicate. The formation of mullite from alumina grain, or grain mixtures with mullite oxide stoichiometry, bonded by a gel in which the silica is derived from ethyl silicate has also been investigated. In some experiments, the binding gel also had the oxide stoichiometry in the mullite range. Throughout the work, the ethyl silicate used was "technical ethyl silicate" [10], which is a mixture of ethyl orthosilicate and ethyl polysilicates having a silica equivalent of about 40% w/w. Changes occuring in the gels during drying and firing were observed by differential thermal analysis (DTA) and thermogravimetric (TG) measurements. The structures of the products obtained on firing were characterized by X-ray techniques and also investigated using Mössbauer and IR spectroscopy.

To obtain a gel from ethyl silicate, it must first be hydrolysed, and the hydrolysate converted into a gel. Therefore, to obtain a gel with the oxide stoichiometry in the mullite range, the hydrolysis of ethyl silicate must be carried out in the presence of a soluble hydrolysable aluminium compound [11]. Certain four-covalent organotin compounds catalyse the hydrolysis and gelation of ethyl silicate and act as mineralizers in the formation of mullite [12]. Changes in the organo-tin compound on firing have been observed by Mössbauer spectroscopy [13]. Prior addition of strontium salts as $Sr(NO_3)_2$ or caesium salts as CsCl or Cs_2CO_3 to a hydrolysate with oxide stoichiometry in the mullite range gives [14] quantitative conversion to mullite at 1000° C if acid hydrolysis is used. The gels obtained are homogeneous. In contrast, base-catalysed hydrolysis, or adding a base gel an acid hydrolysate decreases mullite formation because a non-homogeneous gel results. The conditions under which the gel is formed are therefore important.

Dibutyltin diacetate increases the amount of mullite formation in ethyl silicate bonded alumina. The size of the alumina grain is important, a smaller particle size increases the amount of mullite formed, whether or not an organo-tin compound is present. This factor also seems significant in ethyl silicate bonded grain mixtures with mullite oxide stoichiometry.

2. Experimental details

2.1. Materials

Technical ethyl silicate (40% SiO_2 equivalent) was used as received from Clino Foundry Supplies Ltd. Representing the structure of technical ethyl silicate as:

$$\mathrm{EtO}\!\left[\mathrm{Si(OEt)_2O}\right]_n\mathrm{Et}$$

analysis by gas/liquid chromatography [9] showed the material to contain a typical distribution of ethoxypolysiloxane oligomers.

Aluminium chlorhydrate was supplied by Wilfred Smith (Fine Chemicals) Ltd, as the anhydrous form (nominally $Al_2Cl(OH)_5$) and also as the hydrate (nominally $(Al_2Cl(OH)_5 \cdot 2H_2O)$. Ammonium acetate solution of pH = 7 was prepared by adding a 10% w/w solution of glacial acetic acid in water (2.8 cm^3) to 50% w/w aqueous ammonium acetate solution (60 cm^3). The pH was adjusted to pH = 8 by further slow dropwise addition of aqueous ammonium acetate solution.

The ethanol used was the UK 74 over proof or the 64 over proof Industrial Methylated Spirit. Distilled water was used throughout, and all other chemicals were of "laboratory reagent" grade. The refractory grains used were as follows: tabular alumina – ALCOA T60 grade; calcined alumina – ALCOA A2 grade or BACO MA95 grade; "superground" alumina – ALCOA A15 or A16 grade; and micronized silica – GASIL 200 grade. Fused and sintered mullite grain, together with a separate fine blend of Bayer alumina and kaolinite, having the equivalent mullite oxide stoichiometry, were supplied by Cawood Refractories Ltd.

2.2. Analytical procedures

X-ray diffraction patterns were obtained from a Debye-Scherrer camera (diameter 12.5 cm) and a Philips TW1130/00 X-ray diffractometer, using Cu$K\alpha$ radiation. A Joyce Loebel BC5 microdensitometer was used to record the optical density of the diffraction pattern obtained, and stored on floppy disc for use with a Commodore CBM-model 4032 computer. The mullite content of the fired samples was estimated by comparing the height and/or peak area of the $2\Theta = 16.4°$ and $2\Theta = 60.8°$ peaks with the height and/or peaks area of the coincident $2\Theta = 35.2°$ and $2\Theta = 35.3°$ peaks due to corundum and mullite respectively. As this ratio approaches unity, the mullite content will approach 100% and the alumina content will become zero as the relative intensity of the $2\Theta = 16.4°$, 60.8°, and 35.3° peaks become equal. The degree of crystallization in gels fired at various temperatures was estimated [13–15] from the ratio of the intensity of the strongest line in the X-ray diffraction pattern of a fully crystallized specimen to the intensity of the same line in the X-ray diffraction pattern of the specimen under study. Peak heights were compared by direct measurement or by means of the computer program MCDASJDMOLLYX together with the diagnostics map BBMOLXMAP [14]. The two methods gave similar results.

Infrared spectra over the range 4000–400 cm^{-1} were recorded using a Perkin-Elmer 397 spectrometer. Samples were prepared by grinding the solid materials with potassium bromide and pressing into disc pellets.

Thermogravimetric analysis up to 1000° C was carried out using a DuPont 950 thermogravimetric analyser. Differential thermal analysis up to 1200° C was carried out using a DuPont 900 temperature analyser. Mössbauer spectra for tin compounds were recorded [13] using ^{119}Sn source in the form $^{119}SnO_2$.

2.3. Preparation and treatment of gels

Non-homogeneous gels were prepared using aluminium chlorhydrate and technical ethyl silicate by the methods A–C in sections *2.3.1.* to *2.3.3.* Homogeneous gels were prepared by the methods D–G in sections *2.3.4.* to *2.3.7.* Gels prepared using organo-tin compounds were by the methods D and H in sections *2.3.4.* and *2.3.8.* Gels incorporating strontium or caesium salts were prepared by the methods J and K in sections *2.3.9.* and *2.3.10.* All gels were dried in air at ambient temperature, and some were then placed in an oven at 60° C. The resultant solids were crushed and fired at 1470° C or 1600° C in a gas/air fired furnace, unless otherwise stated.

2.3.1. Method A

Anhydrous aluminium chlorhydrate powder (16.4 g) was dispersed in a solution of technical ethyl silicate (10.0 g) in ethanol (5 cm^3), giving the molar ratio Al_2O_3:SiO_2 as 2.85:2. Water (5 cm^3) was slowly poured into the paste with rapid stirring. A flocculate interspersed with a cloudy oily fluid formed immediately. The gel obtained was air-dried at ambient temperature for 4 days, dried at 60° C for 3 days, and then fired.

2.3.2. Method B

Technical ethyl silicate (10.0 g) was mixed with 2 cm^3 of a 10% v/v solution of water in ethanol and 1 cm^3 of a 35% v/v solution of water in piperidine. Aluminium chlorhydrate dihydrate (17.7 g) was quickly stirred into the above mixture giving the molar ratio Al_2O_3:SiO_2 as 2.85:2. The dispersion became very viscous after about 90 min, forming a gel during 2 days air drying. After further drying at 60° C for 2 days, the gel was fired.

2.3.3. Method C

Anhydrous aluminium chlorhydrate (17.41 g) was dissolved in water (20.5 cm^3) by adding about 3 g portions with stirring to dissolve before any further solid was added. A solution of technical ethyl silicate (26 cm^3) in ethanol (91.25 cm^3) was also prepared. Ammonium acetate solution of pH = 7 (2 cm^3) was added to the mixture of aluminium chlorhydrate solution (18 cm^3) with the technical ethyl silicate solution (29 cm^3) without warming. The gel time was about 6 min, forming a non-homogeneous gel. Addition of ammonium acetate solution of pH = 8 (2 cm^3) also gave a non-homogeneous gel in 2–3 min. These gels were hygroscopic.

2.3.4. Method D

Anhydrous aluminium chloride (200 g) was refluxed with ethanol (480 g) in a two litre flask. The aluminium trichloride dissolved in about 30 min, refluxing being continued until hydrogen chloride evolution ceased after about 4 h. The solution, now containing an aluminium ethoxide, was cooled to ambient temperature, then technical ethyl silicate (75 g) dissolved in 75 cm^3 of a 10% v/v solution of water in ethanol was added, giving the molar ratio Al_2O_3:SiO_2 as 3.01:2. A clear solution was obtained. Further experiments were carried out with and without the addition of dibutyltin diacetate as a hydrolysis/gelation catalyst. In each case, the solution was refluxed at 80° C for 4 h, giving a resin-like material. This was spread on polyethylene sheeting to aid the removal of hydrogen chloride and solvent, dried at 60° C, and then fired.

2.3.5. Method E

Anydrous aluminium chlorhydrate (16.4 g) or aluminium chlorhydrate dihydrate (19.7 g) was refluxed with ethanol (60 g) in a 250 cm^3 flask for 3.5 h, during which time the chlorhydrate dissolved. The solution was cooled to ambient temperature, then technical ethyl silicate (10 g

TABLE 1 Effect of dibutyltin oxide on the gelation of technical ethyl silicate–aluminium chlorhydrate and the behaviour of the resulting gel on firing

% w/w of dibutyltin oxide	Yield of dry gel (g)	Gelation characteristics and behaviour of resulting gel on firing
19.1	56	Immediate gelation stopping the stirrer. Gel softened after 25 min, allowing stirring to continue. Hardened to a white solid mass after 4 h. Firing gave cristobalite and good yields of mullite
15.0	52	As above, but slower initial gelation. Softer gel. Firing gave cristobalite and a high yield of mullite
10.5	57	Initial gelation did not stop the stirrer. Two layers formed, top layer a clear thick liquid, bottom layer a white solid. Top layer gelled in a few hours. High yield of mullite on firing
5.5	53	As above, but less white solid was formed. Nearly quantitative conversion to mullite on firing
1.2	49	Formed a clear solution which set to a clear gel in about 48 h. Nearly quantitative conversion to mullite on firing

Data from Rahman [13] and Wakefield [15]. The sintered mullite of Metcalfe and Sant [7] was taken as standard in estimating mullite conversion by X-ray analysis.

dissolved in 10 cm^3 of a 10% v/v solution of water in ethanol) was added, giving the molar ratio Al_2O_3:SiO_2 as 2.85:2. A clear solution was obtained and refluxed for a further 3.5 h. After cooling to ambient temperature, water (14 cm^3) was added dropwise with stirring, and the solution heated to 50° C until gelation occurred within about 10 min. The resulting gel was dried at 60° C, then fired.

2.3.6. Method F

Anhydrous aluminium chlorhydrate (16.4 g) or aluminium chlorhydrate dihydrate (19.7 g) was dissolved in water (20–25 cm^3). Technical ethyl silicate (10.0 g dissolved in 100 cm^3 ethanol) was added, giving a homogeneous solution with the molar ratio Al_2O_3:SiO_2 of 2.85:2. The solution was refluxed for 2 h, giving a viscous solution which set to a gel on standing for 1 day. The gel was dried at 60° C for 7 days, then fired.

2.3.7. Method G

Anhydrous aluminium chlorhydrate (17.41 g) was dissolved in water (20.5 cm^3) by adding with stirring to allow each 3 g portion to dissolve before any further solid was added. A solution of technical ethyl silicate (26 cm^3) in ethanol (91.25 cm^3) was also prepared. A homogeneous gel was obtained by mixing the aluminium chlorhydrate solution (18 cm^3) with the technical ethyl silicate solution (29 cm^3) and warming the mixture (pH = 4.7) to 60° C. Gelation occurred within 40 min.

2.3.8. Method H

Typically, a mixture of dibutyltin oxide (12.76 g) and technical ethyl silicate (19.25 g) was heated for 1 h at 150° C. On cooling, ethanol (62.7 cm^3) was added, and the resulting mixture was slowly added dropwise to a vigorously stirred solution of anhydrous aluminium chlorhydrate (34.89 g) dissolved in water (28.55 g). Gelling occurred immediately, and when the gel had hardened, volatile reaction products and solvent were removed by means of a rotary evaporator at 100° C. Varying the amount of dibutyltin oxide altered the gelation behaviour as shown in Table I.

2.3.9. Method J

A mixture of technical ethyl silicate (19.25 g) and an aqueous solution of strontium or caesium salts was heated for 10 min at 50° C. On cooling, ethanol (67.7 cm^3) was added and the resulting solution added dropwise to a solution of anhydrous aluminium chlorhydrate (34.89 g) dissolved in water (28.55 g). The amounts of material used, the pH of the final mixture and the gelation behaviour are given in Table II. A control sample was prepared without the addition of strontium or caesium salts. The gels obtained were washed with several quantities of distilled water, dried under an infrared lamp for 6 h, then fired at 1000° C for 18 h.

2.3.10. Method K

Mullite precursor gels were also prepared [14, 16] by mixing 19.25 cm^3 of a stock solution contain-

TABLE II Mullite precursor gels incorporating strontium and caesium salts

Catalyst	% v/v	pH	Gelation behaviour	Firing conditions and X-ray results
$Sr(NO_3)_2$	1.89	5.4	Turbidity appeared on adding ethanol, which disappeared with aluminium chlorhydrate soln. Gel time about 20 h reduced to 1.5 h on warming to 60° C	Transformation of γ-Al_2O_3 to α-Al_2O_3 promoted at 1000° C
$Sr(NO_3)_2$	5.5	5.3	As above. Gel time 20 min at 60° C	Fired 14 h at 775° C, no crystallites. Fired 1 h at 900 or 1000° C, gave mullite and γ-alumina. Only mullite after 18 h at 1000° C
$Sr(NO_3)_2$	5.5	5.3	Gelling was accelerated by dilute ammonia solution	X-ray diffraction pattern showed cristobalite, γ-alumina, and SrO with less mullite formation
$Sr(NO_3)_2$	10.4	5.0	Gel time 1 min at 60° C	Fired at 1000° C for 18 h. Gave γ-alumina, α-alumina, SrO, and trace of mullite
CsCl	0.52	5.3	Gel time 1.5 h at 60° C	Higher % Cs promotes formation of cristobalite. Cs_2O detected in fired gels containing higher % Cs
CsCl	0.97	5.3	1.5 h at 60° C	
CsCl	1.9	5.3	1 h at 60° C	
CsCl	2.95	5.3	40 min at 60° C	
Cs_2CO_3	2.88	5.7	45 min at 60° C	Similar to $Sr(NO_3)_2$ Increasing % Cs converts γ-alumina to α-alumina. Complete conversion to mullite with 2.88% Cs_2CO_3
Cs_2CO_3	8.0	5.8	Immediate gelation	
Cs_2CO_3	18.0	6.1	Immediate gelation	

Data from Sharf el Deen [14].

ing: technical ethyl silicate (75 cm^3); 1:1 v/v dicyclohexylamine:piperidine (1.5 cm^3); and water (0.15 cm^3), with a solution of $Sr(NO_3)_2$ or Cs_2CO_3 in 2 M HNO_3. This mixture was added dropwise to a solution of anhydrous aluminium chlorhydrate (34.9 g) in water (28.55 g), giving non-homogeneous gel formation immediately. The amounts of $Sr(NO_3)_2$ added gave 1.9, 5.5 and 10.4% w/w, and those for Cs_2CO_3 gave 1.95, 2.9, 8.0 and 15% w/w.

2.4. Binding of refractory grains

2.4.1. Refractory blocks

These were made by casting a slurry of refractory grains and the appropriate gel-forming system [9] comprising technical ethyl silicate, aqueous ethanol, and either dibutyltin oxide, piperidine or dicyclohexylamine, into a wooden mould 7.5 x 2.5 x 2.5 cm, allowing the slurry to set, then removing the casting from the mould. The casting was air-dried, baked to remove volatiles, and then fired to form a refractory block.

2.4.2. Alumina–ethyl silicate systems with mullite oxide stoichiometry

Technical ethyl silicate (40.0 g), ethanol (5.5 cm^3) and either 1 M HCl (10 cm^3) or water (10 cm^3) and dibutyltin diacetate to give the molar ratios set out in Table IV below were mixed then slurried with dried superground alumina (42.8 g) and allowed to set over a 2 h period. The set slurry was dried in air for 14 days, then fired at 1600° C.

2.4.3. Refractory grain systems with mullite oxide stoichiometry

Anhydrous aluminium chlorhydrate (16.4 g) or aluminium chlorhydrate dihydrate (19.7 g) dissolved in water (25 cm^3) was added to 26.3 or 29.7 g of a homogenized mixture of superground or calcined alimina (45.9 g) and micronized silica (18.0 g). To the resulting suspension was added a solution of technical ethyl silicate (10.0 g) in ethanol (80 cm^3) followed by a 35% v/v water in piperidine solution (1.0 cm^3). During setting, which required 15 min, the suspension was warmed on a stirrer/hotplate to a maximum temperature of 50° C and when set, was air dried for 7 days then fired. In a similar experiment, a blend of Bayer alumina and kaolinite was used instead of the alumina–silica mixture.

3. Results and discussion

Table III gives the data for the conversion to mullite on firing non-homogeneous and homogeneous precursor gels. The firing cycle was: (a) ambient temperature to 1600° C over 4 h; (b) hold at 1600° C for 1 h; and (c) cool from 1600° C to ambient temperature in 4–5 h. The homogeneous gels gave an almost quantitative conversion to mullite. No difference in the X-ray data for the tin-added and tin-free specimens were observed. The infrared spectra of the fired gels and Cawood sintered mullite were very similar. All spectra had broad bands centered at 1150, 900, 725, 550 and 450 cm^{-1}. No differences in the spectra of tin-added and tin-free specimens were observed.

Mullite precursor gels made using dibutyltin oxide (Table I) crystallize progressively from 700 to 900° C [15] and convert to mullite on firing at 1470° C. Precursor gels obtained from preparations containing 15.0 and 19.1% w/w dibutyltin oxide were non-homogeneous and gave some cristobalite on firing together with a high yield of mullite. Use of excess dibutyltin oxide, therefore, promotes non-homogeneous gelation with cristobalite formation on firing. When, however, a small amount of organo-tin compound is used to prepare the mullite precursor gel, mullite formation is inhibited. There seems to be a "threshold" value above which the formation of mullite is promoted. The reason for this is not clear. It is known [17] that stannic silicates and stannic aluminates are not formed at temperatures above 1200° C, indicating that the behaviour observed is inconsistent with fluxing or exchange mechanisms. The X-ray diffraction data did not show the presence of cassiterite, but ^{119}Sn Mössbauer spectroscopy did indicate [13] the presence of a tin(IV) oxide species, presumably amorphous. Dilatometric studies [15] indicated that the pores present in precursor gels obtained from preparations containing dibutyltin oxide were stable and inhibited densification. The activation energy for densification was found to be between 12 and 42 kJ mol^{-1}.

DTA results [14] for mullite precursor gels obtained via acid hydrolysis procedures are similar to DTA results obtained when caesium or strontium salts are present during the preparation of the gel. The endotherm observed at 240–250° C, which is particularly prominent in non-homogeneous gels, is most likely due to the decomposition of species resulting from aluminium chlorhydrate. The DTA results [14] for aluminium chlorhydrate show a strong endotherm at about 260° C. When caesium or strontium salts are present, other weak endotherms observed below and above 250° C could be due to the dehydration of species derived from caesium carbonate [18] or from strontium nitrate [19]. Another prominent endotherm commencing at 460° C with a peak at 700° C is probably due to the decomposition and melting of any remaining Cs_2CO_3 or $Sr(NO_3)_2$. The effect also indicates the start of reaction between the various phases present. In contrast, DTA results [20] for gels obtained from technical ethyl silicate by base-catalysed hydrolysis and gelation show an endothermic reaction below about 150° C, associated with a loss of volatiles, also an exothermic reaction at about 300° C, associated with oxidation of volatiles, or alteration in the gel structure.

TABLE III Mullite conversion of non-homogeneous and homogeneous precursor gels

Gel type	Preparation	Mullite conversion (%)
Non-homogeneous	Gelled by water	23.2
Non-homogeneous	Gelled by organic base	53.8
Homogeneous	$AlCl_3$ in ethanol	Almost quantitative
Homogeneous	Aluminium chlorhydrate in ethanol	Almost quantitative
Homogeneous	Aluminium chlorhydrate in ethanol	Almost quantitative
Homogeneous	$AlCl_3$ in ethanol with dibutyltin diacetate	Almost quantitative
Non-homogeneous*	Ammonium acetate pH = 7	Low
Non-homogeneous*	Ammonium acetate pH = 8	Low
Homogeneous*	Gelled by heat, pH = 4.7	Almost complete

*Gels prepared from the same hydrolysate. The fused mullite and sintered mullite of Sargeant *et al.* [6] taken as standard in estimating % mullite conversion. Data taken from Biddle [9], Rahman [13] and Wakefield [15].

TGA data for gels prepared with $Sr(NO_3)_2$ showed that more than 90% of the total weight loss occurred below 700° C, whereas the TGA data for gels prepared with Cs_2CO_3 showed a significant increase in the rate of weight loss both at 750° C and at 890° C. However, when these were heated overnight at 600° C, the TGA data showed no further weight loss on heating from ambient temperature to over 890° C, indicating that the weight loss at 890° C is due to volatilization of Cs_2O. Pre-firing at 850° C has been stated [21] to "fix" caesium in the system $Cs_2O-Al_2O_3-SiO_2$. The gels containing caesium were, therefore, heat treated as follows: the gel was heated at 600° C for 18 h; followed by heating at 800° C for a further 18 h; and then followed by heating above 850° C to allow any crystallites to form. The results obtained on X-ray analysis are given in Table II.

For gels containing strontium, only that prepared with 5.5% w/w $Sr(NO_3)_2$ showed a sharp DTA exotherm at 1130° C after the second strong endotherm. This would seem to indicate a sudden crystallization of reaction products in contrast to the normal slow crystallization over a wide temperature range. This was confirmed by heating the gel sample to 1200° C for 1 h. The X-ray powder diffraction pattern showed the presence of crystalline mullite [14].

In order to show the effect of an acid hydrolysis procedure on mullite formation in the presence of strontium salts, the gelation was accelerated by aqueous ammonia solution. The resulting gel was non-homogeneous. The use of ammonia as gelation agent caused the appearance of cristobalite, γ-Al_2O_3, and SrO in the X-ray diffraction pattern on firing and less mullite formation (see Table II). Hydrolysis and gelation when the mixture of organic bases was present gave a non-homogeneous gel and caused the appearance of γ-alumina, α-alumina, cristobalite, and a trace of SrO in the X-ray diffraction pattern on firing, but no lines assigned to mullite were present. Mullite is also not formed from a precursor gel (homogeneous or non-homogeneous) on heating up to 1200° C in the absence of a mineralizing agent. For a homogeneous gel made via an aluminium salt, the presence of strontium, caesium, or organo-tin compounds promotes quantitative conversion to mullite at about 1000° C. There is a threshold concentration, under which the conversion is incomplete, some cristobalite being formed. For the organo-tin compounds, the type of aluminium salt is unimportant, and the way in which water is introduced is also not important. For a non-homogeneous gel, the product formed on firing contains cristobalite and alumina (α or γ) with little mullite, even if strontium, caesium, or organo-tin compounds are present. When organo-tin compounds are present, slow, even, gelation occurs and increases the amount of mullite formation.

Acid catalysed hydrolysis in the presence of strontium or caesium salts gives homogeneous precursor gels when the hydrolysates are gelled by heat. Consequently, the conversion to mullite on firing is good. However, base-catalysed gelation of this acid hydrolysate, or hydrolysis and gelation when the mixture of organic bases is present, can give a non-homogeneous precursor gel and in consequence the conversion to mullite on firing is low. The formation of mullite from gels prepared using technical ethyl silicate and hydrolysable aluminium compounds in the presence of strontium or caesium salts depends on several factors [14]. Principally, the type and amount of the cation added, secondly the chemical composition and pH of the system which decide whether the gel will be homogeneous or non-homogeneous, and thirdly the firing conditions of time and temperature. The aluminium salts used to prepare precursor hydrolysates will give acid solutions. The addition of a base (ammonia or amine) must first precipitate a hydrous alumina species prior to the ethyl silicate hydrolysate gelling. Therefore, the gel formed will not be homogeneous. This will normally occur with an acid hydrolysate or in a basic hydrolysis procedure. However, by careful adjustment of conditions, an acid hydrolysate of mullite oxide stoichiometry can be caused to gel by a base to give a homogeneous gel suitable for binding refractory grains [9, 11, 12]. This gel has been used to bind alumina, mullite, and sillimanite grains. A selection of large and small refractory shapes has been made, including a large single piece well-block in sintered mullite grain, for a ladle fitted with a sliding-gate system to be used in steel casting.

Refractory blocks made from an ethyl silicate bonded coarse tabular alumina grain gave on firing to 1600° C a ratio of alumina to mullite of about 50:1, unaffected by the type or amount of gelation catalyst. Refractory blocks made from ethyl silicate bonded superground alumina gave on

TABLE IV "Superground" alumina–technical ethyl silicate systems with mullite oxide stoichiometry. Estimation of mullite formation on firing by means of X-ray diffraction technique

Molar ratio $Bu_2Sn(OAc)_2:SiO_2$	%w/w SnO_2 after firing	Peak area by integration (A) mullite $2\theta = 40.8°$ line	Peak area by integration (B) mullite–alumina $2\theta = 35.2°$ and 35.3° coincident line	Normalized intensity A ÷ B
0.09:1	5.65	16.2	38.7	0.419
0.11:1	7.52	24.9	33.0	0.750
0.21:1	12.53	26.8	27.2	0.986
Nil (HCl soln)	nil	23.7	34.8	0.681
Sintered mullite standard [6].	nil	41.8	41.9	0.998

Data from Biddle [9].

firing to 1600° C a ratio of alumina to mullite of about 20:1, again unaffected by the type or amount of gelation catalyst, indicating the effect of particle size of the alumina on the amount of mullite formed. For superground alumina–ethyl silicate systems with mullite oxide stoichiometry, the data given in Table IV shows that a small amount of organo-tin compound reduces the amount of mullite formed on firing. No cassiterite or cristobalite was detected. Fine alumina–silica grain systems with mullite oxide stoichiometry formed mullite in abundance on firing. With superground alumina, small amounts of residual α-alumina were detected by X-ray diffraction analysis. For calcined alumina, a large amount of mullite was formed, some α-alumina remaining. This would be expected, as calcined alumina has the larger particle size. The Bayer alumina–kaolinite blend on firing gave a material with a high mullite and low α-alumina content. The results with refractory grains show the formation of a ceramic bond between the gel and the grains during firing, in agreement with work previously reported [20].

4. Conclusions

1. In the absence of a mineralizer, mullite is not formed from a gel having mullite oxide stoichiometry prepared from technical ethyl silicate and an aluminium chloride on firing up to 1200° C.

2. When the gel is homogeneous, the presence of strontium, caesium, or organo-tin compounds such as dibutyltin diacetate or dibutyltin oxide during the gel preparation, promotes almost quantitative conversion to mullite at about 1000° C. There is a threshold concentration, below which the conversion is incomplete, some cristobalite being formed. With organo-tin compounds, the type of aluminium chloride used is unimportant, and the way in which water is introduced is also unimportant.

3. When the gel is non-homogeneous, the product obtained on firing contains cristobalite and α-alumina or γ-alumina, with little mullite, even if strontium, caesium, or organo-tin compounds are present.

4. Acid-catalysed hydrolysis gives homogeneous gels, showing good conversion to mullite, when the hydrolysate is gelled by heat. However, base-catalysed gelation of the acid hydrolysate can give a non-homogeneous gel, and in consequence, the conversion to mullite is low.

5. The results with refractory grains show the formation of a ceramic bond between the grains and the gel during firing.

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