

Mullite Ceramics: Its Properties, Structure, and Synthesis

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Abstract

Besides its importance for conventional ceramics, mullite has become a choice of material for advanced structural and functional ceramics due to its favourable properties. Some outstanding properties of mullite are low thermal expansion, low thermal conductivity, excellent creep resistance, high-temperature strength, and good chemical stability. The mechanism of mullite formation depends upon the method of combining the alumina- and silica-containing reactants. It is also related to the temperature at which the reaction leads to the formation of mullite (mullitisation temperature). Mullitisation temperatures have been reported to differ by up to several hundred degrees Celsius depending on the synthesis method used. The three synthesis methods used to prepare mullite are discussed in this paper together with an overview of mullite, its properties and the current application of mullite.

Keywords: mullite, mullitisation, glassy phase, sol-gel, spray pyrolysis, chemical vapour deposition

Abstrak

Keramik mullite tidak hanya penting dalam penggunaan konvensional, tetapi juga sudah menjadi bahan pilihan untuk aplikasi struktural dan fungsional karena sifat-sifatnya yang menguntungkan. Beberapa keunggulan sifat mullite adalah sifat muai dan konduktivitas panasnya rendah, ketahanan mulur yang tinggi, kekuatan yang terjaga pada temperatur tinggi, dan sifat korosinya yang baik. Mekanisme pembentukan mullite bergantung pada bagaimana proses menggabungkan reaktan yang mengandung alumina dan silika. Mekanisme tersebut juga bergantung pada temperatur reaksi awal yang akan mengarah pada pembentukan mullite (mullitisation). Beberapa penelitian melaporkan terjadinya temperatur mullitisation yang bervariasi hingga beberapa ratus derajat Celsius bergantung pada proses sintesa yang digunakan. Artikel ini menjelaskan tiga proses sintesa yang menghasilkan mullite yang dibahas bersama dengan sifat-sifat dan aplikasi mullite saat ini.

Kata kunci: mullite, mullitisation, fasa glassy, sol-gel, spray pyrolysis, chemical vapour deposition.

1. Introduction

Mullite is an alumino-silicate compound that is used extensively in traditional refractory applications. Most traditional ceramic products have mullite as part of their final phase composition since they usually contain some clay and silicon as starting materials. The microstructures of the materials also contain a relatively low melting glass.

Natural mullite is rare in nature; it is named after one of the few known deposits on the Isle of Mull, United Kingdom. (Bowen and Greig, 1924) The occurrence of this compound on the Isle of Mull is thought to be a result of post-Caledonian volcanic activities in which clay mineral deposits, heated through contact with magma, produced a high

temperature mullite phase. (Bowen, Greig *et al.*, 1924) It was not until the 1970s that the significance of the inherently favourable properties of mullite was recognised, when the mechanical behaviour in compression of mullite specimens, free or nearly free of a glassy phase, was first studied.

Mullite is becoming increasingly important in electronic, optical, and high temperature structural applications, because of its low dielectric constant, good transparency for mid-infrared light and excellent creep resistance. Classical uses of mullite include refractories in the metallurgical industries for electric-furnace roofs, hot metal mixers and low-frequency induction furnaces. In the glass Industries, these refractories are employed in the upper structure of the tank in which the glass is melted and for constructing the drawing chambers. Mullite is frequently used as kiln setting slabs and posts for firing ceramic ware as well as for the linings of high-

Note: Discussion is expected before July, 1st 2005. The proper discussion will be published in "Jurnal Teknik Mesin" volume 7, number 2, October 2005.

temperature reactors. However, during the last decade, the spectrum of actual or potential employment of mullite now includes its use as a matrix material for high-temperature composite development, a substrate in multilayer packaging, protective coatings, turbine engine components, and an infrared-transparent window especially for high-temperature application. (Tummala, 1991; Prochazka and Klug, 1983) One approach to improve the environmental durability of silicon-based ceramics is to apply refractory oxide coatings containing no silica or those with a lower silica activity. Mullite is most promising because of its environmental durability, chemical compatibility, and coefficient of thermal expansion (CTE) similar to that of SiC. Coatings of mullite applied by atmospheric plasma spraying (APS) to SiC ceramic matrix composites provides some degree of corrosion resistance to corrosive industrial environments. (Van Rooode, Price *et al.*, 1988)

These new interests have sparked extensive studies on the synthesis and processing of mullite and mullite-based composites by molecular and/or colloidal methods and also on techniques for producing mullite protective layers.

Mullite rarely occurs in nature, so it is usually synthesised, rather than mined. Various preparation methods and starting materials are used for the synthesis of mullite ceramics. The preparation methods can be classified into three different preparation routes as follows: (1) sinter-mullite, (2) fused-mullite (3) chemical-mullite (high-purity mullite). The synthesis of mullite ceramics together with important processing routes to fabricate monolithic mullite ceramics are described in this paper.

2. Properties of Mullite Ceramics

Mullite has been used for high-temperature exposed parts because of its good creep resistance and high compressive strength at elevated temperature. Flexural strength and creep resistance at elevated temperatures are significantly affected by the presence of glassy boundary inclusions; in the absence of grain boundary glassy phase, polycrystalline mullite retains > 90% of its room-temperature strength to 1500°C, (Mah and Mazdiyasi, 1983; Kanzaki, Tabata *et al.*, 1985; Ismail, Nakai *et al.*, 1986; Ismail, Nakai *et al.*, 1987; Kumazawa, Ohta *et al.*, 1990; Kumazawa, Kanzaki *et al.*, 1988; Ohnishi, Kawanami *et al.*, 1990) with excellent thermal shock resistance, and low thermal conductivity. (Becher, 1991; Somiya and Hirata, 1991; Nixon, Chevacharoenkul *et al.*, 1990) Depending on the microstructural features, the low fracture toughness of mullite, typically of the order of 2 MPam^{1/2} is regarded as a significant factor in limiting the potential applications. Moreover, the

goal of high temperature stability requires the grain boundary to be free from glass. This is particularly difficult to achieve in mullite ceramics because of its low bulk and surface diffusivities, which are the reason for its high temperature stability. The processing of mullite is therefore especially important if a dense ceramic capable of fulfilling its high-temperature potential is to be achieved. Table 1 summarises the range of characteristic properties now being achieved in dense mullite ceramics.

Table 1. Typical Properties of Mullite Ceramics. (Lee and Rainforth, 1994)

Density (g cm ⁻³)	3.16-3.22
Hardness (GPa)	
At RT	13-15
At 1000°C	10
RT fracture toughness K _{IC} (MPam ^{1/2})	1.5-3
Young's Modulus (GPa)	140-250
Bend strength (MPa)	150-500
Thermal expansion coefficient (x10 ⁶ K)	3.1-4.1 //a
300-900°C	5.6-7.0 //b
	5.6-6.1 //c
Thermal conductivity (Wm ⁻¹ K ⁻¹)	
At 100°C	6.07
At 600°C	4.31
At 1000°C	3.98
At 1400°C	3.89

The slow diffusion kinetics which make the material so difficult to sinter also impart excellent high temperature microstructural stability. This behaviour is in marked contrast to some other ceramics such as hot pressed silicon nitride (HPSN) which contains sufficient glassy phase at the grain boundaries. The grain boundary glass has a critical effect on high-temperature properties. Rapid softening of the glass and microcracking can occur as the test temperature is raised, degrading high-temperature strength loss. In contrast, mullite usually only has a minimal grain boundary glassy phase, if any, reducing the damaging effects of grain boundary sliding and micro-cracking. Bend strength values can vary from as low as 120 MPa to over 400 MPa. The differences can be partly explained in terms of the density achieved, the morphology of the grains and the presence of additional crystalline and amorphous phases.

In the polycrystalline form, the most essential requirement for retaining the strength of mullite at elevated temperatures appears to be the elimination of glassy boundaries. As shown in Fig. 1, two typical curves are observed. The first type shows a significant increase in strength at about 1300°C. The second shows no distinct maxima and decrease

slightly with increasing temperature. When polycrystalline mullite contains a small amount of glassy phase at the grain boundaries, a noticeable increase in strength occurs above the softening temperature of the glassy inclusions. The increase in strength was considered to be associated with some form of stress relaxation and/or crack healing by softening of the glassy phase at high temperatures. When the glassy phase is crystallised to form cristobalite, the peak in strength disappears, but the resulting mullite-cristobalite composite now retains its strength up to 1400°C. (Kumazawa, Ohta *et al.*, 1990) The initial increase in strength corresponds to a similar increase in fracture toughness caused by the blunting of the cracks with the viscous phase. (Kumazawa, Kanzaki *et al.*, 1988; Kumazawa, Ohta *et al.*, 1990)

Dokko *et al.* (1977) were the first to show the high creep resistance of mullite. Single crystals tested up to 1500°C and under stress levels of 900MPa, no plastic deformation was observed. (Dokko, Pask *et al.*, 1977) There is limited creep data on mullite and some disagreement as to the creep mechanisms. Ohnishi *et al.* considered that Coble creep occurred in a sol-gel derived mullite. (Ohnishi, Maeda *et al.*, 1990) However, Dokko *et al.* identified a Nabarro-Herring mechanism. (Dokko, Pask *et al.*, 1977) Once again differences may be partly explained by the processing techniques employed.

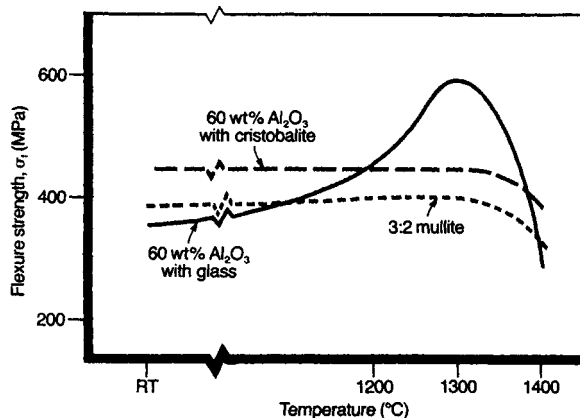


Figure 1. Flexural strength as a function of temperature for mullite and mullite composites. Phase-pure mullite retains > 90% of its strength at 1400°C. Glass containing mullite, however, starts losing its strength above 1300°C after an initial increase due to the presence of the viscous phase. After the crystallisation of this phase to cristobalite, the behaviour resembles that of phase-pure mullite. (Kumazawa, Kanzaki *et al.*, 1988; Kumazawa, Ohta *et al.*, 1990)

3. Structure of Mullite

3.1 Crystal Chemistry of Mullite

The crystal structure of mullite (nominally $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is orthorhombic with the space group Pbam and unit cell dimensions $a = 0.7540$ nm, $b = 0.7680$ nm and $c = 0.2885$ nm for the stoichiometric composition. (Angel and Prewitt, 1986) An [001] projection of an ideal unit cell is shown in Fig. 2, from which it can be seen that mullite consists of chains of AlO_6 octahedra at the edges and centre of the unit cell, running parallel to the c -axis. These chains are joined by $(\text{Al},\text{Si})\text{O}_4$ tetrahedra forming double chains, which also run parallel to the c -axis.

Mullite possesses a defect crystal structure (Burnham, 1964) consisting of chains of slightly distorted Al-O octahedra which run parallel to the c -axis of the orthorhombic unit cell. These chains are linked by discontinuous double chains of Al-O and Si-O tetrahedra with randomly distributed aluminium and silicon atoms. The discontinuities in the latter chains are caused by the movement of some of the aluminium (and possibly silicon) ions into normally unfilled tetrahedral positions because of insufficient oxygen atoms present to bond to them in the normal positions. The occupation of these new sites also increases the coordination of the remaining oxygen atoms and forces them into new positions that are slightly different from their original locations. The connection of octahedra and tetrahedra chains produces relatively wide structural channels that also run parallel to the c -axis.

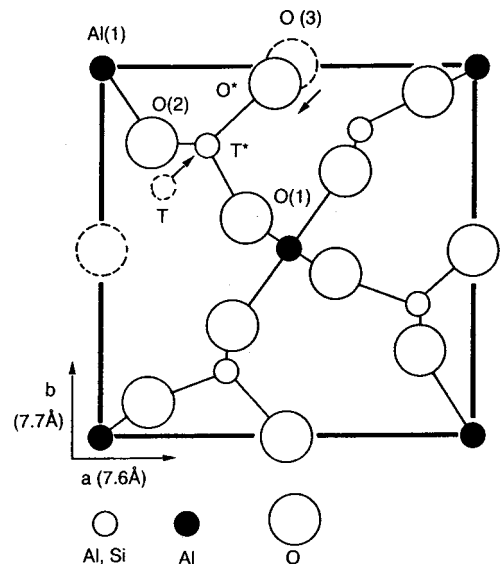
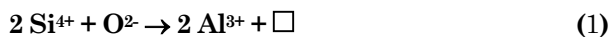


Figure 2. Projection of the ideal orthorhombic mullite unit cell along the [001] direction showing T to T* transition of the cations (indicated by an arrow) which is associated with the formation of an oxygen vacancy and readjustment of oxygen in the O(3) positions. (Aksay, Dabbs *et al.*, 1991)

This defect structure accommodates non-stoichiometry and the average composition of mullite may range from close to $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ to $3\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ (commonly denoted as 3:2 and 3:1). The compositional variation in mullite (an increase in Al^{3+} solubility) is achieved by substitution of an Si^{4+} and removal of an oxygen (O^{2-}) ion from an $(\text{Al},\text{Si})\text{O}_4$ tetrahedron leaving an oxygen vacancy, and by a change in position of the cations in partially occupied columns as shown by moving T to T* in Fig. 2. The cation shift is approximately 0.12 nm and results in the loss of the tetrahedral coordination of these cations. The overall change may be summarised as:



where \square represents the oxygen vacancies. However, the octahedral AlO_6 units remain unaltered by solubility changes. It is common therefore, to write the structure as:



where IV and VI represent the four- and six-fold coordination of aluminium cations respectively and x denotes the number of missing oxygen atoms per average unit cell. The value of x can vary between 0.17 and 0.59 (70.5–83.6 wt.%) and so mullite can exist with a wide range of Al:Si ratios. (Cameron, 1977b) For $x=0$ the above formula represents the composition of the three polymorphic modifications: sillimanite, andalusite, and kyanite (Al_2SiO_5), which are at least partially related to mullite in terms of their structure, whereas $x=1$ represents the chemical composition of the assumed Al_2O_3 phase. (Saalfeld, 1962) However, the more common range for mullites formed by solid-state reaction sintering is $x=0.25$ (3:2) to $x=0.4$ (2:1). The change in composition is associated with a change in the lattice constants.

3.2 Chemistry of Mullite

The composition of mullite is commonly denoted as $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (71.83 wt.% Al_2O_3). However, commercially available mullite which is a solid solution generally consists of 71–76 wt.% Al_2O_3 , 23–24 wt.% SiO_2 , and small quantities of TiO_2 , Fe_2O_3 , CaO and MgO . Stoichiometric ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) mullite can be produced without a glassy grain boundary phase which results in high strength being maintained to high temperatures. As the composition moves away from stoichiometry a glassy grain boundary phase forms, reducing the material's strength, and lowering the maximum use temperatures.

3.3 Mullite Microstructure

The final phase constitution depends strongly on the processing conditions and substantial differences in behaviour have been identified between mixing on the atomic scale compared with the 10–30 nm range. (Pask, Zhang *et al.*, 1987) These include differences in transient phases and final phase, the presence or not of a grain boundary silica phase and the morphology of the mullite grains. The presence of a liquid silicate phase is associated with the development of microstructures having prismatic mullite grains. High aspect ratio mullite grains are typical of mullites with a residual glassy phase while equiaxed structures are associated with the absence of a grain boundary glassy phase (Fig. 3).

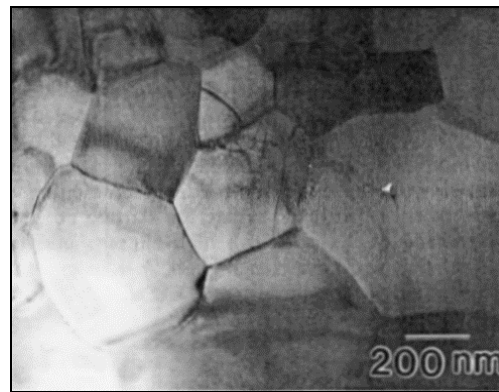


Figure 3. TEM micrograph of mullite with an equiaxed microstructure and grain boundaries free from glassy phase. (Lee and Rainforth, 1994)

Figure 4 demonstrates that high sintering temperatures (1730°C for 48 hours in this case) can give two-phase (diphasic) alumina-mullite microstructures, which may be single-phase mullite when sintered at lower temperatures.

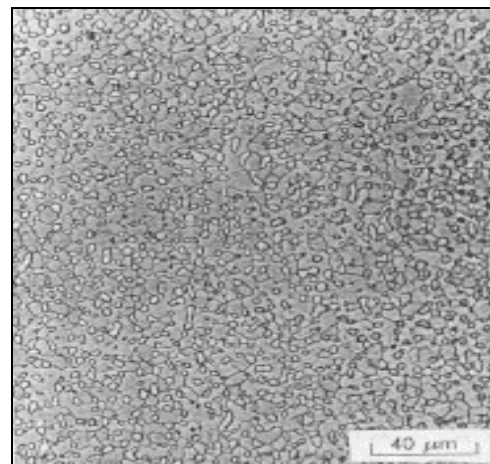


Figure 4. Nomarski micrograph of a 76.5 wt.% alumina mullite after 48 h at 1730°C; the sample was etched to show the alumina particles (light) in a mullite matrix (darker). (Klug, Prochazka *et al.*, 1987)

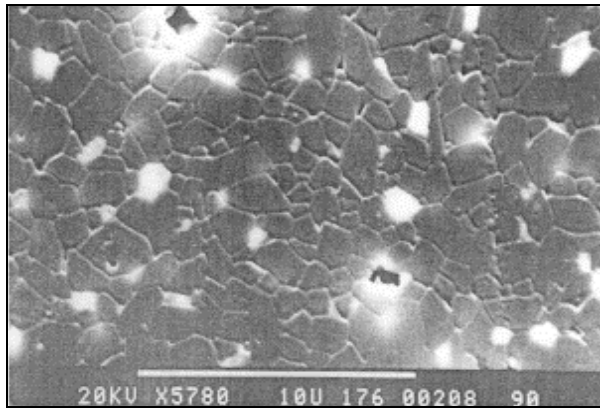


Figure 5. Microstructure of reaction-bonded mullite contains predominantly mullite and traces of tetragonal zirconia. (Wu and Claussen, 1991)

Reaction-bonded mullite ceramics consisting of mullite and traces of tetragonal ZrO_2 (Fig. 5) which is introduced by wear of the TZP (tetragonal zirconia polycrystal) balls during milling. Alumina is no longer detectable after the 1550°C hold. These ceramics have outstanding mechanical bending strength (290 MPa) at high sintering densities (>97 % of theoretical density). (Wu and Claussen, 1991) The sample shown in Fig. 5 was produced by oxidising Al and SiC at 1200°C to form $\alpha-Al_2O_3$ and SiO_2 . On further heating to 1550°C sintering occurred.

4. Mullite Synthesis

The preparation methods can be classified into three different preparation routes as follows: (1) sinter-mullite, (2) fused-mullite (3) chemical-mullite (high-purity mullite). In terms of starting materials, they can be grouped into the following six categories: (1) a mixture of solids such as oxides, hydroxides, salts and clay minerals (2) a mixture of sols (3) a mixture of sols and salts (4) a mixture of Si-alkoxide and Al-salt (5) a mixture of Al-alkoxide and Si-alkoxide, and (6) a mixture of other materials. Homogeneity of raw materials depends largely on the processing and synthesis method used, i.e. how to mix, precipitate, hydrolyse, or react SiO_2 and Al_2O_3 components. The mechanism of mullite formation depends upon the method of combining the alumina- and silica-containing reactants. It is also related to the temperature at which the reaction leads to the formation of mullite (mullitisation temperature). Mullitisation temperatures have been reported to differ by up to several hundred degrees Celsius depending on the synthesis method used. The three synthesis methods used to prepare mullite are discussed in the following sections.

4.1 Sinter-Mullite

In conventional processing methods, mullite powders are shape formed and sintered. This mullite is designated 'sinter-mullite'. The term sinter mullite describes a mullite which has been produced from its starting materials essentially by solid-state diffusion controlled reactions. Oxides, hydroxides, salts, and silicates can be used as the starting materials. The Al_2O_3 content of sinter-mullites is influenced by the sintering temperature, the duration of heat treatment, the initial bulk composition, by the nature, grain size and efficiency of mixing of the starting materials, and also whether $\alpha-Al_2O_3$ nucleates. Mullitisation takes place by solid-solid or transient liquid-phase reactions of the starting materials by aluminium, silicon, and oxygen atom interdiffusion. Since this formation reaction is considered to occur by the diffusion of two components, the mullitisation temperature can be lowered by using finer powders and also by better mixing. The starting materials of SiO_2 and Al_2O_3 components are usually of micrometre size, and are not small enough to accomplish complete mullitisation at relatively low firing temperatures within a reasonable duration of time. Another reason why sintering of mullite powders to high densities normally requires relatively high temperatures, is because of the low bulk and grain boundary diffusion coefficients for mullite. For example, the mullitisation temperature was reported to be higher than 1400°C when quartz particles below 2 μm in size and $\alpha-Al_2O_3$ particles with the average particle size of 0.3-0.5 μm were used. (Hamano, Sato *et al.*, 1986) Extensive mullitisation needs very high temperatures in the 1600 to 1700°C range (Sacks and Pask, 1982a), which is too high to produce raw materials for sintering purposes. In order to lower the mullitisation temperatures it is advantageous to use systems in which the aluminium and silicon components are atomically mixed. Aluminium silicate minerals, well known as mullite raw materials, are clay minerals such as kaolinite ($2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$) and pyrophyllite ($4SiO_2 \cdot Al_2O_3 \cdot H_2O$), and also the Al_2SiO_5 polymorphs silimanite, kyanite, and andalusite. Admixtures of boehmite, diaspore both with the composition $AlO(OH)$, and gibbsite [$Al(OH)_3$] and of refractory-grade bauxite with silica have also been used. (Schneider, Seifert-Kraus *et al.*, 1982; Schneider, Wang *et al.*, 1986; Schneider, Wang *et al.*, 1987) In the classical method of mullite preparation, kaolinite and related materials are thermally decomposed to mixed oxides and these transform to mullite by several steps at high temperature according to the reaction shown in Fig. 6.

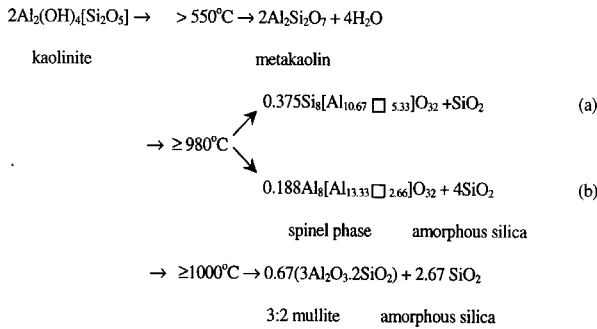


Figure 6. Series of reactions which make kaolinite transforms into 3:2 mullite during heating. (Schneider, Okada *et al.*, 1994)

Where \square = vacancy and (a) and (b) are alternative spinel-type phases which their composition can be seen in the work of Bulens *et al.* (Bulens, Leonard *et al.*, 1978)

The reaction between bulk samples of alumina and silica occurs at relative high temperatures (>1550°C) by nucleation and growth at the interface between the two phases.

4.2 Fused-Mullite

The term fused-mullite describes mullites which have been produced either by melting the raw materials in an electric furnace above 2000°C with subsequent crystallisation of mullite during cooling of the bath, or by Czochralski crystal growth techniques. (Guse and Mateika, 1974) The aluminium silicate melt obtained is then cast into ingot molds and cooled to room temperature. Raw materials for fused-mullite ceramics and refractories are Bayer alumina, quartz sand, rock crystals and fused silica. The impurity level of the raw materials is relatively low. For fused-mullite of lower quality, bauxites or mixtures of Al₂O₃ and kaolinite have also been used. Higher Al₂O₃ contents can be achieved by rapid quenching and lower Al₂O₃ bulk composition or, alternatively, by a very slow cooling process. The composition of mullite crystallised from liquids is primarily a function of temperature and, to a lesser degree, of the initial composition.

4.3 Chemical-Mullite

Mullite powders prepared by advanced processing, e.g. sol-gel, precipitation, hydrolysis, spray pyrolysis, chemical vapour deposition (CVD) techniques are designated 'chemical-mullite.' The general approach to powder processing is summarised in Fig. 7 (Okada and Otsuka, 1990), which represents mixing of the Al³⁺ and Si⁴⁺ on scales ranging from the atomic to the micron level. Each processing method to produce 'chemical-mullite' will be discussed in the next section.

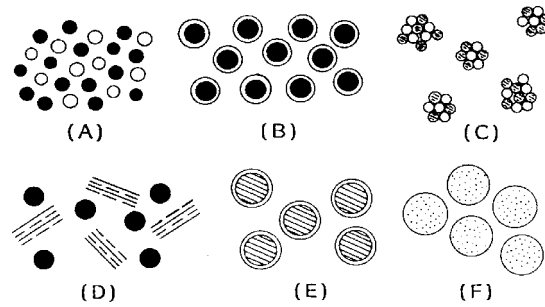


Figure 7. Schematic microstructural models of mullite starting materials prepared by the various approaches (A) sol mixing; (B) composite particles; (C) hydrolysis of alkoxides; (D) conventional mixing of clay minerals and alumina; (E) coprecipitation; (F) spray pyrolysis. (Okada and Otsuka, 1990)

• Sol-Gel Method

There has been considerable interest in the preparation of mullite from chemically synthesised precursors. In particular, sol-gel methods have been used extensively to produce mullite powders, fibres and bulk samples at relatively low processing temperatures. (Sacks, Lee *et al.*, 1990), (Aksay, Dabbs *et al.*, 1991), (Okada, Otsuka *et al.*, 1991a) In sol-gel processing, colloidal particles or molecules in suspension, a sol, are subject to a chemical change (e.g. pH change) which causes them to join together into a continuous network, called a gel. The sol-gel method allows the preparation of a homogeneous and reactive gel which can be sintered at low temperature and consequently a homogeneous submicronic microstructure can be achieved. This term covers preparation techniques using starting materials of admixtures of sols and also admixtures of sols and salts. In many cases, the reaction by this method is essentially the same as that which occurs by a mixed solid (conventional method using oxides or silicates as discussed in section 4a in 'Sinter-Mullite'), if the materials are mixed under wet conditions. However, the particle size differs significantly for the two preparation methods. The particle size of sols is in the range of ten to several tens of nanometres (nm) and is therefore much smaller than those used in the conventional method (several microns (μm)). Mullitisation, therefore, occurs at lower temperatures than with mixed solids, e.g. 1200 to 1300°C. (Hamano, Sato *et al.*, 1986)

Ghate *et al.* (1973) cleverly utilised the properties of silica and alumina sols for mullite synthesis. (Ghate, Hasselman *et al.*, 1973) They prepared an alumina sol by dispersing γ-alumina particles in HCl solution. Silica sol was added slowly to this suspension and adjusted to pH 6-7. In this pH range the surfaces of the alumina particles are positively charged whereas those of silica particles are negative. Therefore, heteroflocculation, which causes intimate mixing of two sol particles, can be expected.

Many studies have been reported using admixtures of sols and salts as starting materials for mullite synthesis. Fumed SiO_2 with a particle size of less than several tens of nanometres is usually used for the raw material of the SiO_2 sol. Aluminium salts used are sulphate, nitrate and chloride. These preparation methods were considered to be advantageous compared with that of admixtures of sols, because composite particles and not only mixed particles were expected to form under certain conditions. Even if this is not the case, precipitation of the salt component is expected on the surface of the sol particles, which act as heterogeneous nucleation sites. Composite particles can be prepared by adsorption, hydrolysis and precipitation reactions of a salt component on the surface of sol particles. As shown in Fig. 8, the mullitisation reactions from these two types of starting materials are largely different.

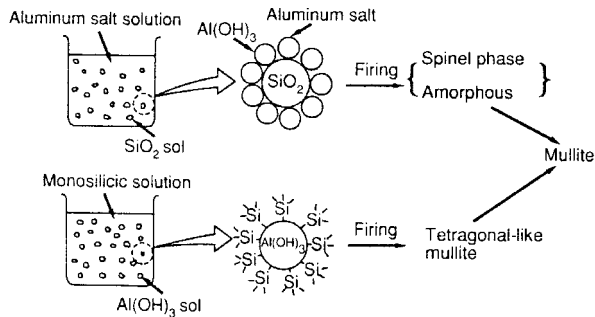


Figure 8. Schematic model for the two types of starting material for a mixture of sol and salt (Okada, Otsuka *et al.*, 1991b)

The former shows spinel phase formation at around 1000°C and transforms to mullite by further firing at higher temperatures (above 1200°C). On the other hand, the latter shows direct mullitisation by firing at 980°C . Sacks *et al.* (1991) proposed a new preparation method for composite particles with $\alpha\text{-Al}_2\text{O}_3$ coated by amorphous SiO_2 layers. (Sacks, 1991) The concept is shown schematically in Fig. 9.

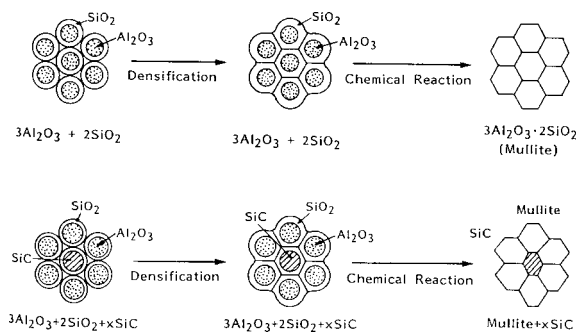


Figure 9. The concept of composite particles formation and sintering mechanisms of mullite and SiC-mullite composites developed by Sacks *et al.* (1991), making use of transient viscous sintering. (Sacks, 1991)

• Precipitation Method

Preparation of precipitates from a clear solution using a precipitant is the basis of this method. On the other hand, similar methods with no particular precipitant were designated as hydrolysis. Many studies have been reported and there are two kinds of precipitation methods: coprecipitation and homogeneous precipitation. The former involves adding a precipitant (usually ammonia solution) to a solution to form precipitates. The latter involves first dissolving a precipitant such as urea or hexamethylenetetramine beforehand in the solution, and subsequently forming a precipitate by changing the solution pH through the decomposition of the precipitant in the solution.

Many starting materials have been used as aluminium sources for the precipitation method: nitrates, sulphates, chlorides, alkoxides, etc. On the other hand, the choice of the starting materials for the silicon component is restricted. Silicon alkoxides were commonly used and there have been only a few reports of the use of sodium silicate, silicon chloride and silicon acetate instead. (Ossaka, 1961), (McGee and Wirkus, 1972)

There have been many reports on the preparation methods using a combination of silicon alkoxide and aluminium salts. The starting components of this technique are dissolved in ethanol and precipitates are obtained by addition of ammonia solution. Okada and Otsuka (1986) dissolved TEOS and aluminium nitrate in ethanol, and precipitates were obtained by adding ammonia solution during vigorous stirring of the solution. (Okada and Otsuka, 1986) Mullitisation occurred extensively by firing at 1150°C for 24 hours and spinel phase formation was observed before mullitisation at 980°C . Since the pH of the solution changed from acidic to neutral on the addition of ammonia solution, the precipitation was considered to be initiated by the formation of nuclei of the aluminium component with the accompanying silicon component to result in coprecipitation. The reason for this is that the solubility of the aluminium ion decreased quickly between the different pH conditions whereas that of the silicon ion did not. The particles obtained are very small but some inhomogeneity of the chemical composition exists because of the above-mentioned coprecipitation mechanism. The inner part of a precipitate is considered to have an alumina-rich composition whereas the surface parts are silica rich. Schematic microstructural models for these particles are shown in Fig. 9.

• Hydrolysis Method

Preparation using a combination of silicon alkoxides and aluminium salts and admixtures of aluminium and silicon alkoxides have also been examined. Hydrolysis occurs by addition of water,

and an acid or base is sometimes added as a catalyst for hydrolysis of the alkoxides. A proposed model for the hydrolysis reaction between alkoxide and water in the solution based on the work of Yasumori *et al.* is shown in Fig. 10. (Yasumori, Anma *et al.*, 1989) When a basic catalyst such as ammonia is used, the hydrolytic reaction which results from the nucleophilic reaction of the silicon atom with the OH-radical, is expected to occur. The susceptibility of this reaction is strongly influenced by the degree of steric hindrance of the radicals. The species of $\text{Si}(\text{OR})_3(\text{OH})$ is more susceptible to attack by the OH-radical than those of $\text{Si}(\text{OR})_4$ and hence, easily forms Si-O-Si bonds by aging. Therefore, the polymerisation reaction which occurs is more dominant than the hydrolytic reaction under this condition. On the other hand, the nucleophilic reaction corresponding to the proton is expected to occur by means of an acidic catalyst. In this case, $\text{Si}(\text{OR})_4$ is more susceptible to attack by the OH-radical than $\text{Si}(\text{OR})_3(\text{OH})$ because the former species has a higher electron density around the silicon atom. The hydrolysis reaction to form silanol (Si-OH) is, therefore, more dominant than the polymerisation reaction in this case.

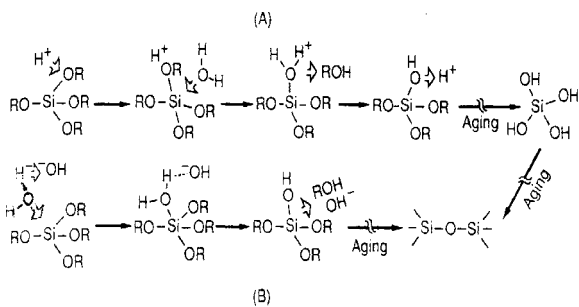


Figure 10. Proposed model for the hydrolysis reaction between alkoxide and water in the solution (A) with an acidic catalyst and (B) with a basic catalyst. (Yasumori, Anma *et al.*, 1989)

• Spray Pyrolysis Method

This preparation method consists of the atomisation of a precursor solution into droplets which are subsequently driven through a furnace in order to dry and calcine them. Reactions such as evaporation of solvents, precipitation of compounds, and thermal decompositions occur instantaneously. Therefore, it is considered to be an appropriate preparation method for the synthesis of multi-component ceramics.

The powders obtained by this process have characteristic spherical shapes with a submicrometre to micrometre size. Scanning electron microscopic (SEM) photographs of the mullite precursor powders prepared by Sakurai *et al.* are shown in Fig. 11. (Sakurai, Mizutani *et al.*, 1988) Droplets were mainly prepared by two different methods, using atomizers and ultrasonicators, respectively.

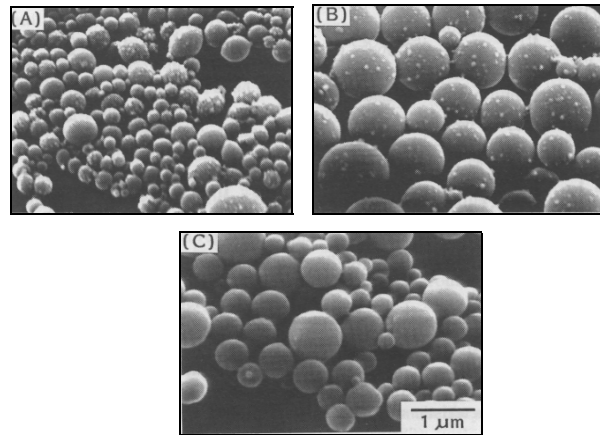


Figure 11. SEM photographs of spray pyrolyzed mullite precursor powders prepared by Sakurai *et al.* (A) B-1, (B) D-1 and (C) D-3 specimen. (Sakurai, Mizutani *et al.*, 1988)

• Chemical Vapor Deposition (CVD) Method

Almost all of the processes described above are syntheses from a solution phase. In contrast, the CVD method utilising vapour-phase processes has also been applied for mullite synthesis. Hori and Kurita used silicon and aluminium chlorides as starting materials. (Hori and Kurita, 1990) The chlorides were separately evaporated and were transported by nitrogen gas to the mixing zone. In the mixing zone they were quickly heated by a hydrogen-oxygen combustion flame in which the temperature was estimated to be 1900°C. The temperature gradually decreased through the reaction zone and was approximately 900°C at the exit. The process time was estimated to be about 65 ms. The obtained powders were of spherical shape and 40-70 nm in size. Small amounts of mullite and a spinel phase were detected in the as-prepared specimens. Extensive mullitisation occurred after firing at 1000°C for 10 min but complete mullitisation required temperatures as high as 1500°C.

5. Summary

In spite of its rareness in natural rocks, mullite is one of the most important phase in the field of conventional ceramics. Mullite can be found as the main constituent in a pottery, porcelains, sanitary ceramic, and structural clay products such as building bricks, pipes and tiles. However, mullite is becoming increasingly important since its outstanding properties were recognised in 1970's. During the last decade, the spectrum of actual application of mullite now includes its use as a matrix material for high-temperature composite development, a substrate in multilayer packaging, protective coatings, turbine engine components, and an infrared-transparent window especially for high-temperature application. This paper also describes all the possible routes of mullite synthesis including the recent innovations using fine-particle synthesis.

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