Chapter 2

Literature review

2.1 Crystal chemistry of mullite

The crystal structure of mullite is a modified defect structure of the three polymorphic sillimanite,andalusite and kyanite ($Al_2O_3SiO_2$). The chemical composition is $Al_2(Al_{2+2x}Si_{2-2x})O_{10-x}$. X is denoting the number of missing oxygen atoms per average unit cell varying between 0.17-0.59. For x=0 represents the composition of the polymorphic sillimanite, whereas x=1 represents the composition of Al_2O_3. (2)

Basically, mullite has a stable form under normal condition in two compositions, for x=0.25 and x=0.4. When x=0.25 the average structure is $3Al_2O_32SiO_2$ and x=0.4 the crystal structure is $2Al_2O_3SiO_2$.

Both structures (2/1- and 3/2-mullite) differ only in terms of the occupancies of certain atomic site. The mullite structure consists of chains of edge-sharing AlO_6 octahedral running parallel to the c–axis. These chains are crosslinked by $(Si,Al)O_4$ tetrahedral forming double chains, which also run parallel to the c-axis.

3/2-mullite ($3Al_2O_32SiO_2$) has Al_2O_3 contents with a frequency maximum at 72 wt% (60 mol%) Al_2O_3. This mullite is the stoichiometric mullite and normally called sintered mullite. The term sintered mullite describes a mullite which has been produced from the starting materials by solid-state reactions. The Al_2O_3 content of sintered mullites affects their sintering temperatures, bulk density, grain size and physical properties.

2/1-mullite ($2Al_2O_3SiO_2$) has Al_2O_3 content maximum at 78% (66 mol %) Al_2O_3. This composition can be called fused mullite. The term fused mullite describes mullites which have been produced by melting the raw materials in an electric arc furnace above 2000 ° C with crystallization of mullite during the cooling of the bath.

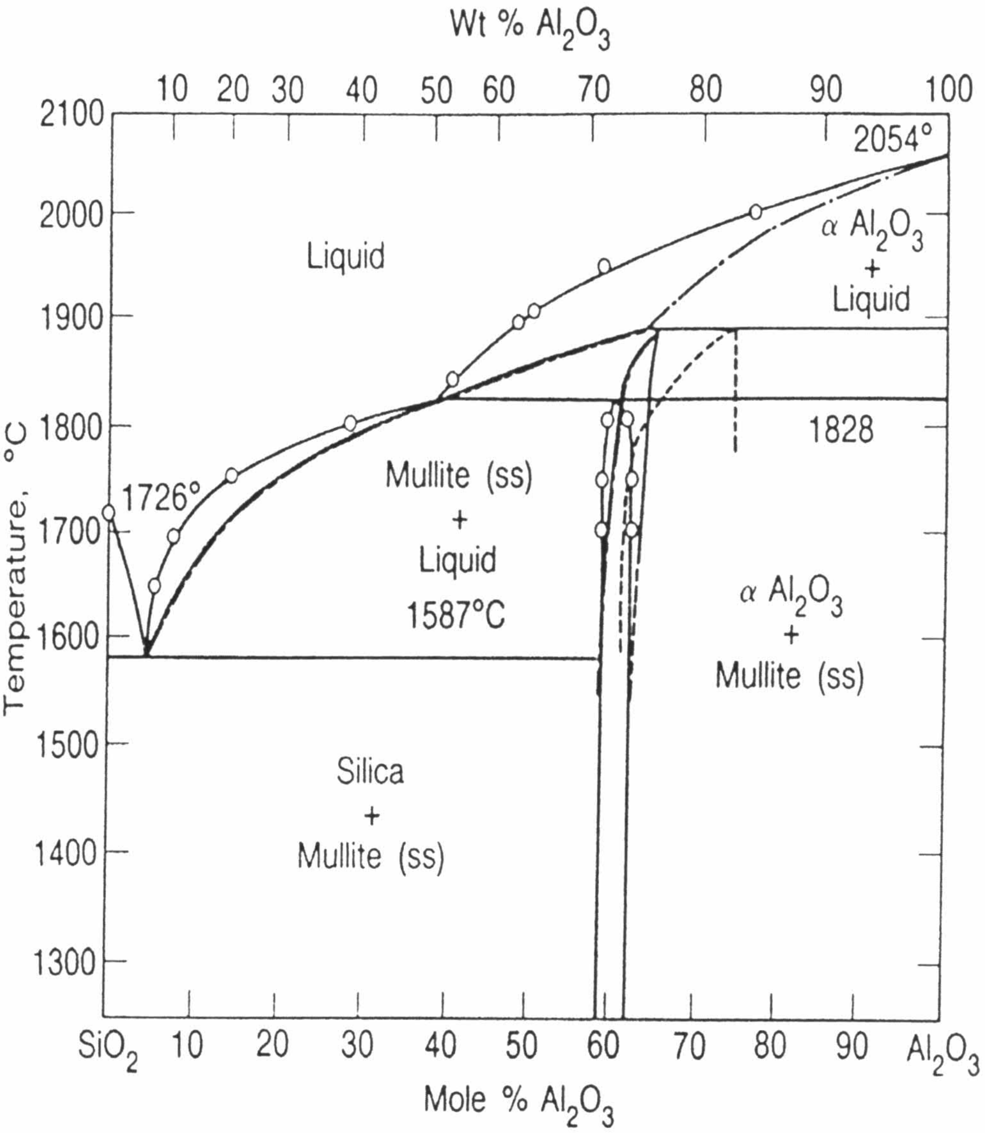


Figure2.1 Phase equilibrium of SiO_2-Al_2O_3 system (2)

The crystal structure of mullite is orthorhombic, unit-cell dimensions depending on chemical composition, for example, for x=0.25 the composition becomes $3Al_2O_32SiO_2$ and unit-cell dimensions are a=7.54 A, b=7.680 A and c=2.850 A (3). Furthermore, unit-cell dimensions of crystal structure and also aspect ratio of mullite crystal structure depend on impurities of the starting materials, soaking time, cooling rate and forming process of mullite ceramics.

2.2 Synthesis of mullite

Synthesis of mullite has been researched for many years. Various preparation methods with various starting raw materials have been reported. They are classified according to three different preparation routes as follows:

(1) Sintered mullite

(2) Fused mullite

(3) Chemical mullite (high purity mullite)

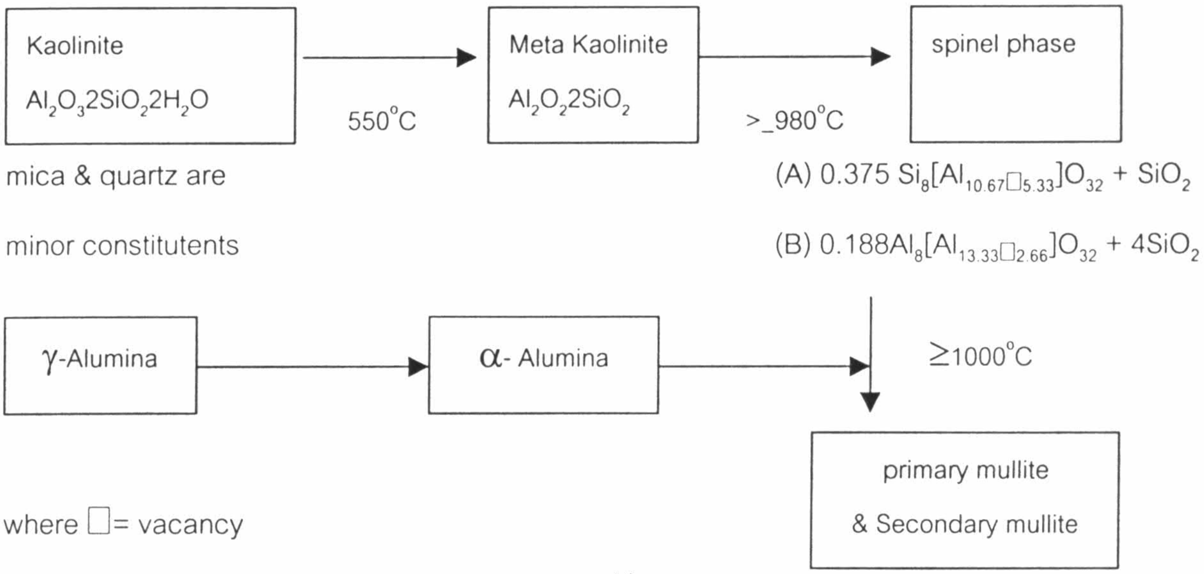
Mullitization temperatures have been reported to different ranges of temperature depending on the synthesis methods, starting material, impurities, particle size of raw material and also specific surface area of particle.

(1) Sintered mullite

Mullite is systhesized by a conventional process started from the mixing of powders of raw materials. Oxides, hydroxides, salts and silicates are used as starting materials. Mullitization takes place by solid-solid or transient liquid phase reactions of the starting materials by aluminum, silicon and oxygen atoms interdiffusion. Hence, the mullitization temperature is controlled by the particle size of the starting powders. The starting materials of sintered mullite are usually of micrometer size, nevertheless, they are not small enough to achieve mullitization at low firing temperature.

Sintered mullite is usually synthesized from the mixture of clay minerals such as kaolinite, halloysite, pyrophyllite, the polymorphic aluminum silicate minerals, kyanite, andalusite and sillimanite ($Al_2O_3SiO_2$), bauxite, aluminum hydroxide, alumina and silica such as quartz, sand, flint, fused silica and amorphous silica.

When kaolinite and alumina is heated, the transformation occurs according to reaction in the following schematic diagram :



where □= vacancy

(A) and (B) are althernative spinel - type phases (4)

For pyrophyllite, Heller(6) studied the thermal decomposition and found that it decomposed to an anhydrous phase and converted into mullite and SiO_2 at around 1000°C. No intermediate phase such as γ-spinel was detected prior to mullitization in this case.

Polymorphic alumino silicate minerals, kyanite, andalusite and sillimanite (all of the composition $Al_2O_3SiO_2$) transformed into 3/2 mullite plus SiO_2 on heating at high temperature under oxidiziing conditions according to the following reaction:

$$3\,Al_2O_3SiO_2 \longrightarrow 3Al_2O_32SiO_2 + SiO_2$$

Kyanite, Andalusite mullite amorphous silica,
Sillimanite cristobalite

In the transformation temperature on going from kyanite to andalusite and sillimanite, the width of the transformation interval increased as shown in Table 2.1

Table 2.1 Data for the high-temperature transformation of kyanite, andalusite and sillimanite powders to mullite plus silica$^{(2)}$

Temperature	**Kyanite**	**Andalusite**	**Sillimanite**
Beginning of transformation (C^o)	1150	1250	1300
Completion of transformation (C^o)	1300	1500	1700
Width of transformation interval (C^o)	150	250	400

Mullite, which was produced by sintered mullite process, was powder or lump. The mullite was mainly used for refractory industry, such as crucible, kiln furniture, thermocouple tube and ceramic roller. The term "old mullite" had sometimes been applied to this type of mullite in comparison with the term "new mullite" , which represented high-purity mullite (chemical mullite)

Sintered mullite mostly contained considerable amounts of impurities, such as Na_2O, K_2O, CaO, TiO_2 and Fe_2O_3. These impurities were the cause of liquid phase at the grain boundary of mullite

Hamano(7) tried to reduce impurities in sintered mullite by using high-purity kaolin in which the impurity level was only less than 1000 ppm and also tried to grind raw material to obtain submicron particle size. Mullite ceramic produced in that way had bending strength between 300 - 400 MPa. This was the same level with high purity mullite that was produced by chemical mullite process and much higher than those reported for conventional sintered mullite (100 MPa). Low impurity contents of the starting materials corresponded to a lowering of glassy phase content at the grain boundary of mullite ceramics, whereas prolonged grinding developed a uniform and fine-grained microstructure so these were the reason for the enhancement of bending strength.

Fe_2O_3 as the impurities in mullite reduced a little amount of density above 1500°C because at that temperature, Fe_3O_4 formed from Fe_2O_3 generated oxygen as shown in the equation, $3\ Fe_2O_3 \ \text{--->}\ 2\ Fe_3O_4 + 1/2\ O_2$.

Large pores were formed, consequently, in the sintered specimen. Thus the density of specimen decreased considerably above 1500 °C(8)

Sintered mullite process produced not only mullite powder but also dense mullite ceramic. The very famous process was the reaction bonding of mullite (RBM). RBM was a novel synthesis route for manufacturing dense mullite ceramic, however, RBM process had a disadvantage about the shrinkage. The shrinkage of RBM was very large comparing with mullite ceramic which was fabricated from mullite powder. (9)

(2) Fused Mullite

Fused mullite was produced by melting the raw material in an electric arc furnace above about 2000°C. Raw materials for fused-mullite ceramics were quartz, sand, fused silica, kaolin, alumina and aluminum hydroxide. After melting liquid mullite was cast into ingot moulds and cooled to room temperature. The chemical composition of fused mullite depended on the crystallization temperature and the cooling speed and also the chemical composition of the starting material.

Fused - mullite usually had Al_2O_3 composition in the range of 2/1 - mullite while sintered mullite had the 3/2 - mullite.

Iron content in raw material might effect crystallization of α-Al_2O_3 , the formation of pores and voids and the formation of a large amount of residual glass phase, then raw material for producing fused mullite should have small amount of Fe_2O_3 (less than 1%)

Normally, fused mullite was used as refractory brick for blast furnace because the low porosity of fused mullite showed excellent resistance, for slag corrosion.

(3) Chemical mullite

It was refered to mullite which was prepared by advanced processing. For the last ten years many authors published about chemical mullite synthesis by different ways. Usually it can be categorized into 6 routes

1. Sol-gel method
2. Hydrolysis
3. Precipitation
4. Spray pyrolysis(15)
5. Chemical vapor deposition (CVD)
6. Other process

Sol-Gel method

Sol-Gel method is started from admixtures of sols and also admixture of sols and salt. The particle size of sols is about nanometers (nm), which is much smaller than those used in the conventional method (sintered mullite and fused mullite).

SiO_2 sol and Al_2O_3 sol are prepared from various methods and are mixed to prepare the starting materials. SiO_2 sol can be prepared from dispersion of ultra-fine particles such as fumed silica, and colloidal silica, and also from the hydrolysis of silicon alkoxides. Al_2O_3 sol can be prepared from dispersion of ultra-fine particles of γ-Al_2O_3 and from dispersion of pseudo - boehmite [γ-AlO(OH)].(10)

The stability of sols changes with the pH of the solution as shown in Figure2.2

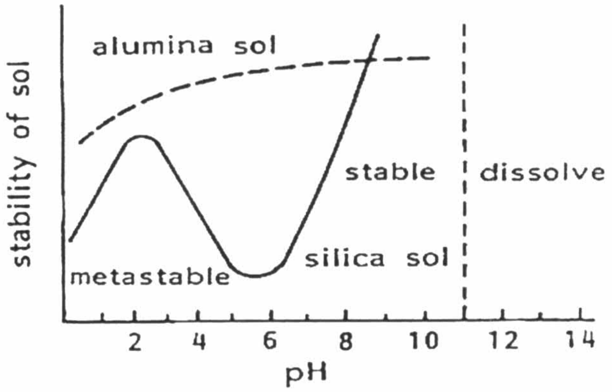


Figure 2.2 Stability of silica and alumina sols plotted versus pH. (10)

From figure 2.2, alumina sol is stable over a wide pH range except for strong acidic condition. The stability range of silica sol is complex, it shows a maximum value at about pH 2 and decreases with the increasing pH of the solution. At pH 5 - 6 a minimum is achieved and flocculated very easily. The stability of the silica sol increases again at higher pH values (>7), and SiO_2 dissolves easily under strong basic conditions above pH 12.

Ghate et al (11) prepared aluminum sol by dispersing γ-Al_2O_3 particle in hydrochloric acid solution. Silica sol was added slowly to this suspension and adjusted to pH 6-7. In this pH range the surfaces of aluminum particles were positively charged where as those of silica particles were negative. Therefore, heteroflocculation, which caused intimate mixing of two sol particles, occurred.

Sack et al (12) proposed a preparation method for the synthesis of low temperature mullite by using amorphous silica coated on α-Al_2O_3 particle. The step started from preparation of α-Al_2O_3 particles in the size of 0.2 μm by elutriation and suspended in ethanol. This suspension was mixed with ethanol solution containing dissolved tetraethoxysilane (TEOS).(13) The TEOS solution was then hydrolyzed by adding ammonia solution and the silica component precipitated on the surface of α-Al_2O_3 particles. When the powder was sintered until 1500 °C for 2h, the Al_2O_3 / SiO_2 composite converted to mullite

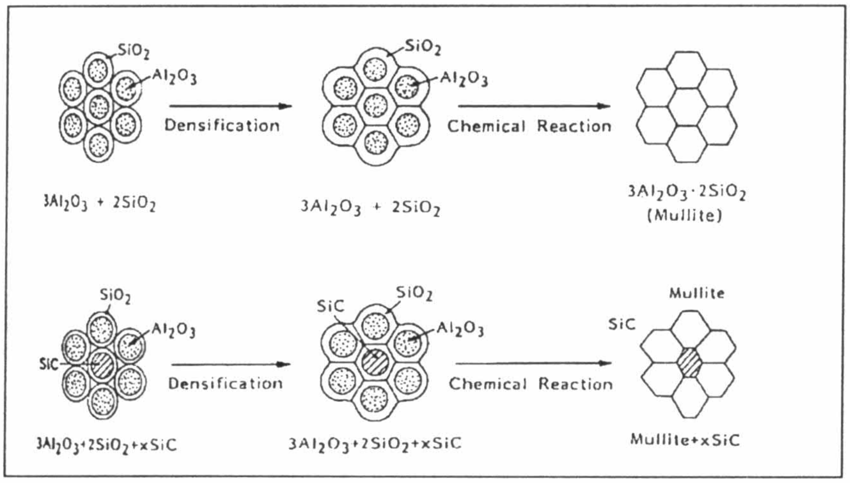


Figure 2.3.The concept of composite particle formation and sintering mechanism of mullite. (13)

There are two admixture system of sol and salt were reported. One was the combination of SiO_2 sol and solutions dissolving various kinds of aluminum salt such as sulfate, nitrate and chloride. The other was a combination of $Al(OH)_3$ sol and monosilisic solution. The $Al(OH)_3$ sol was prepared by adding aqueous ammonia into an aluminium chloride solution until pH 8. The monosilisic solution was prepared by dissolving a silica gel in boiling water which was adjusted to pH 9 by aqueous ammonia.

The mullitization reactions from these two types of starting materials were largely different. The former showed spinel phase formation at around 1000°C and converted to mullite above 1200°C

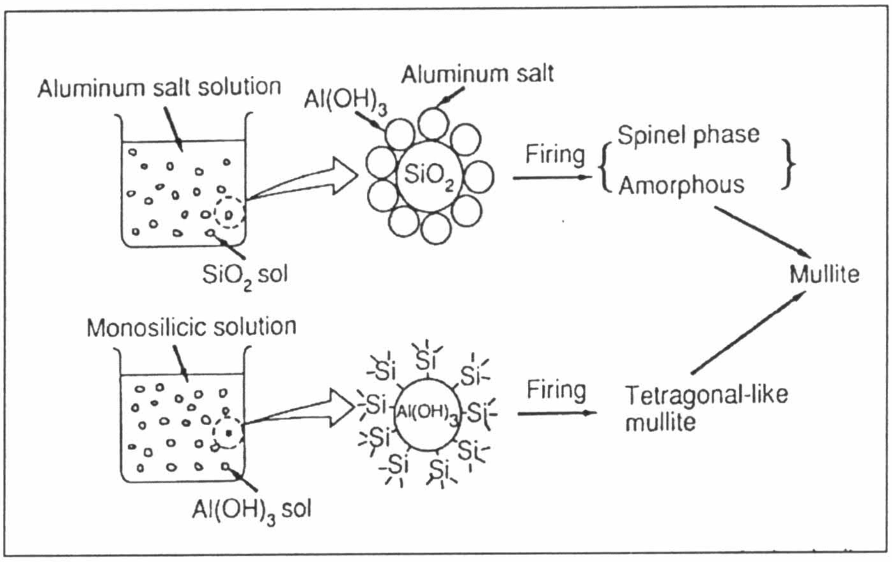


Figure 2.4 Schematic models for the two types of starting material for a mixture of Sol and Salt.

Hydrolysis method [(16)]

A combination of silicon alkoxides and Aluminum salt and a mixture of silicon alkoxides and aluminum alkoxides were hydrosized. Hydrolysis occurred by addition of water. An acid or base was sometimes added as a catalyst for hydrolysis of the alkoxides.

Mixture of silicon alkoxide and aluminum salt.

Combinations of TEOS and various aluminum salts such as nitrate, sulfate and chloride dissolved in an alcohol were used for the starting solution. The combination of

TEOS and aluminum nitrate had been examined by many groups. Hydrolytic and polymeric reactions of TEOS spontaneously proceeded and were very complexed. These reactions were mainly affected by the pH of the solution and also the amount of H_2O. (14)

Mixture of silicon alkoxide and aluminum alkoxide

A combination of TEOS and TMOS (tetramethoxysilane) was used for silicon alkoxide, and aluminum isopropoxide was used for aluminum alkoxide. These alkoxides were hydrolyzed under the various pH conditions and H_2O amounts. This method had many factors effecting the structure of starting materials such as pH value, aging time in solution, solubility of aluminum salt and amount of H_2O.

Precipitation method

Starting materials such as nitrates, sulfates, chlorides, alkoxides, etc had been used as aluminum sources for the precipitation method. For the silicon components were from silicon alkoxide, silicate, silicon chloride and silicon acetate.

Mechanical properties of mullite ceramics

Mechanical strength and Fracture toughness

Because densification of mullite is very difficult to achieve so liquid phase sintering by additives or impurities that are present in the raw material can enhance densification rate.

The densification of high purity mullite is very difficult, but the pure mullite has a very good creep resistance. Distinct development of mullite ceramics having excellent mechanical properties was reported by Kanzaki et al.(15) They prepared fine, high-purity and chemically homogeneous mullite powder by the spray pyrolysis method. The relative density of mullite was accomplished to 95 % by firing at 1650°C for 4 h. The bending strength of these mullite ceramics was 360 MPa and the fracture toughness was 2.8 $MPam^{-1/2}$. (16) These values were much higher than those reported by Mah and Mazdiyasni (150 MPa and 1.8 $MPam^{-1/2}$). The high-temperature mechanical strength of mullite was much higher than that of alumina, TZP and magnesia. Therefore, mullite had become a candidate material for high-temperature engineering ceramic application. (17, 18)

The good mechanical properties were considered to be achived as a result of three major improvements, that were, less glassy phase at the grain boundaries, smaller pore size and uniform grain size. The development of a fine and uniform microstructure was induced by grinding of the starting raw materials for more time. Yamade (2) examined the relationship between the bending strength and fracture toughness on the one hand, and porosity and grain size of mullite ceramics on the other, and gave the following equations :

$$\text{Bending Strength (MPa)} = ad^{-0.433} \exp(-0.036p) \qquad (A)$$

$$\text{Fracture toughness (MPa.m}^{-1/2}\text{)} = bd^{0.182} \exp(-0.036p) \qquad (B)$$

Where a and b were constants, d was the grain size (μm), and p was the porosity (%) From equation A and B shown, the fracture toughness increased with increasing grain size, while the bending strength decreased.

The mechanical properties of mullite ceramics at room temperature prepared by pressureless sintering could be summarized that the bending strength was about 150-300 MPa and fracture toughness was about 2-3 MPa.m$^{-1/2}$. The bending strength of mullite ceramics prepared by hot pressing was slightly higher and ranged from 300 to 400 MPa, however, these value were still low in comparison with other structural ceramics.

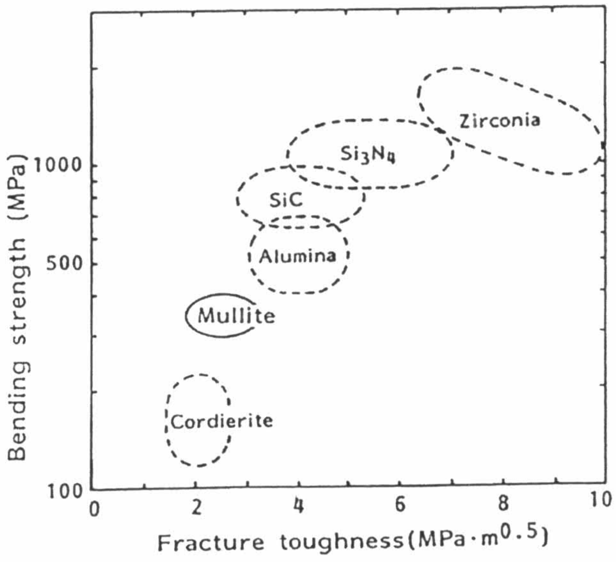


Figure 2.5 Bending strength and fracture toughness of important ceramics

Mechanical properties of mullite ceramic at high temperature reported by Ismail et al. (1987), Kumazawa et al (1988), Ohnishi et al (1990), Hamano et al (1991) and Mizuno (1991) are summarized in figure 2.6$^{(17)}$

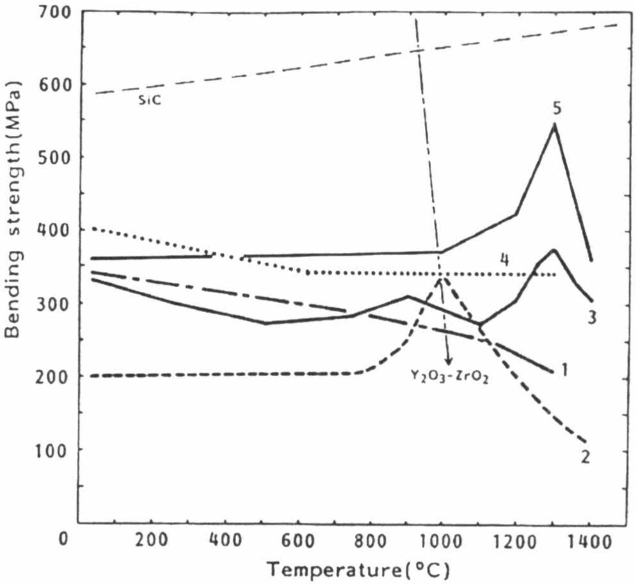


Figure 2.6 Bending strength of mullite ceramic as a function of temperature

1=Hamano et al(1991) ,2-3=Ohnishi et al(1990) ,4=Ismail et al(1987),5=Kumazawa et al (1988

Two typical curves are observed. The first type (curves 2, 3, 5) shows strength maxima at high temperature. The second (curves 1, 4) shows no distinct maximum and decreases monotony with increase in temperature. (19)

Microhardness

The microhardness of mullite is about 10.5 GPa at room temperature and decreases slightly with increase in temperature up to 1000°C. The temperature dependence of microhardness can be expressed by

$$H = Ho/e^{-kT}$$

Where H is the hardness at a given temperature, Ho is the hardness at 0 °C , k is a material constant, and T the temperature.

Figure 2.7 shows the comparison of micro hardness between α-Al_2O_3, SiC (single crystal) and mullite (single crystal). At room temperature the hardnesses of α-Al_2O_3 and

SiC are higher than that of mullite but, the hardnesses of α-Al_2O_3 and SiC dramatically decrease with increasing temperature. This means that the hardness of mullite becomes higher than that of α-Al_2O_3 at above 300°C and higher than SiC above 1000°C

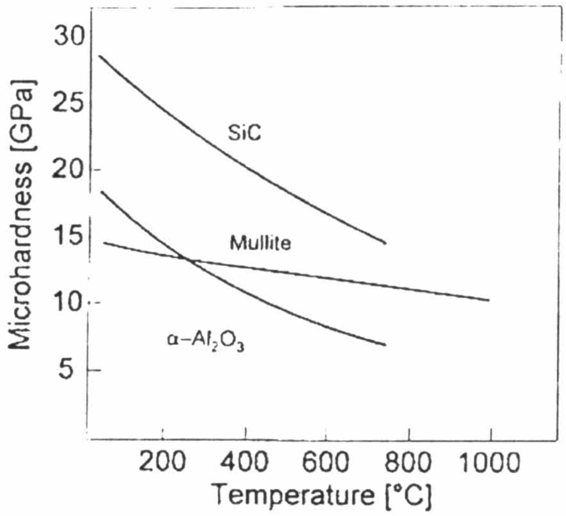


Figure 2.7 Comparison of microhardness for the structural ceramics

Creep resistance

It was reported that mullite ceramics showed high creep resistance and no plastic deformation up to 1500°C.

The creep behavior of mullite was strongly influenced by the microstructure, the chemical composition of the specimens, and the testing method. The microstructure of the specimens with less than 60 mol % Al_2O_3 was composed of rod-like and fine-grained mullite and a glassy phase covering the grain boundaries. Ashizuka et al (20) studied the effect of grain size on creep in mullite ceramics and reported a decrease of strain rate with increasing grain size. The effect of chemical composition on the creep resistance is shown in figure 2.8. From figure 2.8 the strain rate is high up to 60 mol % Al_2O_3 and decreases steeply with increasing mol % of Al_2O_3 and above this composition, the strain rate increases slowly again.

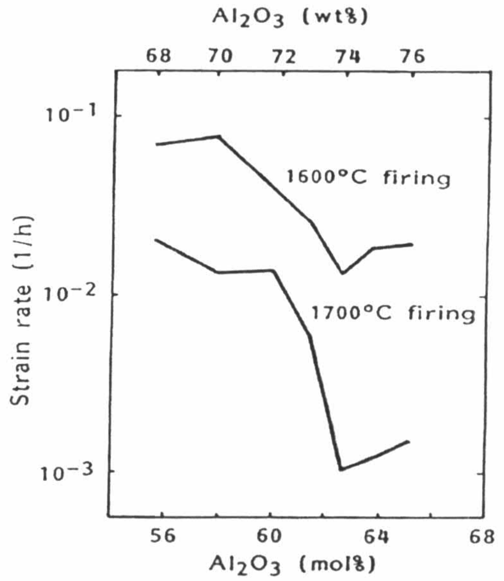


Figure 2.8 Relationship between %alumina and the creep resistance of mullite

Thermal properties of Mullite

Heat capacity and Thermal conductivity

Heat capacity and thermal conductivity control the rate of thermal changes in ceramic and, therefore define temperature gradient in a material. The increase in heat capacity with increase in temperature is depended on bond strength, elastic constant and the melting point of material. The heat capacity curve of mullite increases from 400 $Jmol^{-1}k^{-1}$ at room temperature to 550 $Jmol^{-1}k^{-1}$ at 1700°C as shown in figure 2.8

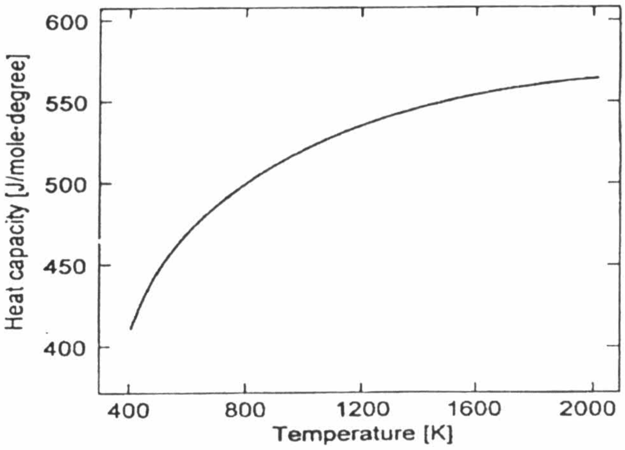


Figure2.9 Heat capacities of mullite at various temperatures.

The thermal conductivity corresponds to the amount of heat conducted through a specimen per unit temperature gradient. Mullite has a low thermal conductivity and from room temperature to 800°C it is almost constant, yet rapidly decreases when temperature rises over 800°C as shown in figure 2.10

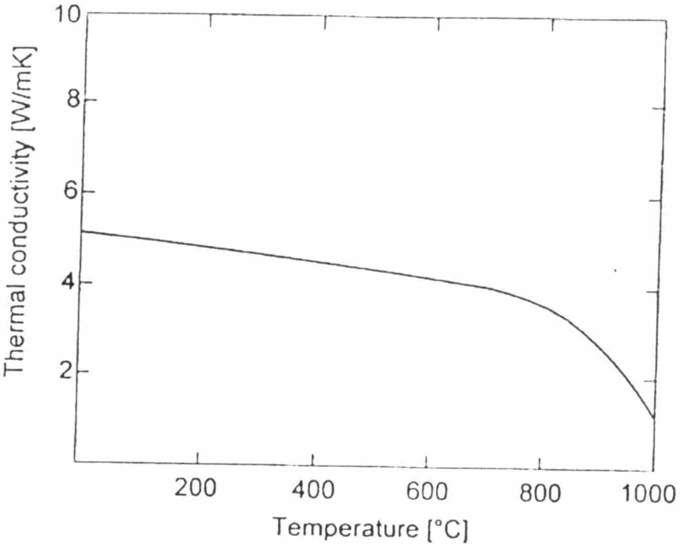


Figure 2.10 Thermal conductivities of mullite at various temperatures

Thermal Expansion

For high temperature ceramic, thermal expansion properties are necessary because they give information on the shape stability of specimens at high temperature and on possible temperature - produced strains in a ceramic body.

Mullite has low thermal expansion coefficient when comparing with other structural ceramic then it is used for refractory application such as kiln furniture, ceramic roller, thermocouple tube and also as the substrate in electronic devices. Mullite shows low and non-linear thermal expansions below 300 °C, but higher and linear expansion above about 300 °C.

At temperatures between 400-500 °C thermal expansion coefficient of mullite change discontinuously as shown in figure 2.11

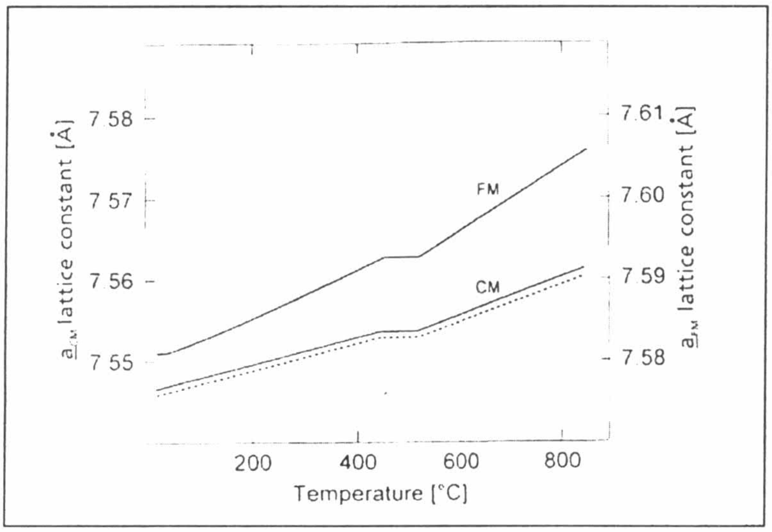


Figure 2.11 Thermal expansion coefficient of mullite

FM is fused mullite CM is conventional mullite

In spite of the weak expansion discontinuities between 400-500 °C, mullite ceramics indicate a good thermal shock resistance (sudden temperature change). The expansion properties of mullite ceramics can be further improved when chromium is doped to pure sintered mullite.

Furthermore, the excellent thermal shock resistance of the pure sintered mullite is thought to be resulted from the needle-like or rod-like interlocking jigsaw grain structure. (21, 22)

2.4 Application of mullite

Normally mullite is a main phase of conventional ceramics after firing; stone ware (floor tile, sanitary ware, dinner ware and etc), porcelain (table ware, insulator, granite tile and etc.), earthen ware (wall tile, terra cotta and etc.) and also refractory materials.

The advantage of mullite for conventional ceramic products is the forming of fiber structure with glassy phase. As a result the mechanical properties of products are improved. Mullite in conventional ceramic products is a secondary phase when products is heated, alumino silicate materials change the composition and crystal structure to mullite.

In addition to the advantage for mechanical properties of conventional products , mullite also has many advantage properties for various kinds of ceramic products such as refractory products, engineering materials, electronic packaging materials, optical materials and miscellaneous materials.

Refractory applications

Mullite has good properties for high temperature applications :

1. high melting point (~ $1890^{o}C$)
2. good creep resistance
3. good corrosion resistance
4. low thermal expansion
5. high shear modulus

Mullite-based materials can be used as refractories in many industrial fields, for example, the steel-making industry (mullite-based bricks are used for the linings in various kilns), furnaces such as conventional ceramic kiln, glass furnace, frit furnace and rotary kiln for cement industry.

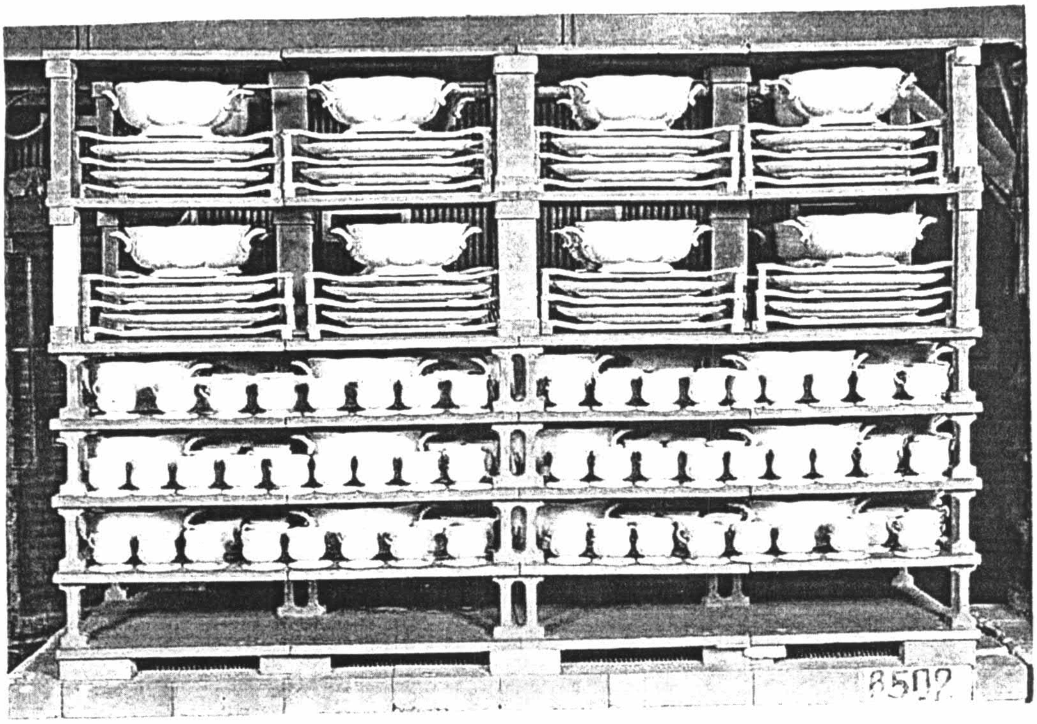


Figure2.12 Mullite ceramic for kiln furniture application

Moreover, mullite and mullite-cordierite composites have been used for kiln furniture; saggers, shelfs and slab. These applications require low thermal expansion, good thermal shock resistance, good corrosion resistance during firing and low creep deformation.

Mullite fibers have also been used as heat-insulating materials for furnaces. (23)

High temperature and engineering application

Mullite ceramics have a good chemical resistance and corrosion resistance, then they are widely used as heat-resisting material for crucibles, protection tube and thermocouple tube.

For molten metals, mullite has a corrosion resistance less than zirconia, but is excellent against gas corrosion.

Recently, technology for firing conventional ceramic has changed dramatically from tunnel kiln to roller kiln because it can save energy consumption and fire faster. Materials for roller are alumina and also mullite.

High-temperature heat exchangers are exposed to high-temperature corrosive gases, so that the properties required for this product are high mechanical strength at high temperature, good thermal shock resistance, good corrosion resistance and good oxidation resistance. Mullite-cordierite composites are good candidate materials for this application

Mullite matrix composite systems were studied to improve fracture toughness and strength of mullite. In the ZrO_2 - mullite system, phase transformation, and microcracking of ZrO_2 caused the increase of mechanical properties. (24)

SiC-whisker - mullite and Si_3N_4-whisker – mullite system increased the density, strength and fracture thoughness of mullite. The maximum strength reached 750 MPa at room temperature.

Electronic packaging materials

Ceramic materials have been used as the packaging and substrate materials since the 1950s due to the following properties:

1. good insulation resistivity
2. good thermal conductivity
3. low dielectric constant
4. good chemical stability
5. good heat resistivity
6. similar thermal expansion to silicon
7. high mechanical strength

Alumina is currently used as the substrate material. However, the speed with which the signals pass through the substrate is controlled by the dielectric constant of the media through which it passes. The signals are measured in terms of the signal transmission delay time (STDT).

$$t_{d} = (£ * S)^{1/2}/C$$

Where t_{d} = STDT

S = the signal path length

C = the velocity of light

£ = the dielectric constant of the material (1)

Table 2.2 Various data important for electronic package substrate materials

Material	Dielectric constant (1 MHz)	Dielectric loss (tan ð)	Thermal expansion ($*10^{-6}$ °C^{-1}	Thermal conductivity ($Wcm^{-1}K^{-1}$)
Mullite	7	0.0003	5.0	0.06
Alumina	9.5	0.0003	8	0.3
AlN	8.9	0.001	4.5	2.6
Zircon	7.8	0.001	4.8	0.05
Cordierite	5.0	0.003	1.8	0.01
SiC	45	-	4	1.5
Si3N4	8.1	0.0007	4	0.3
Glass ceramic	5.8	0.0007	11.5	0.02

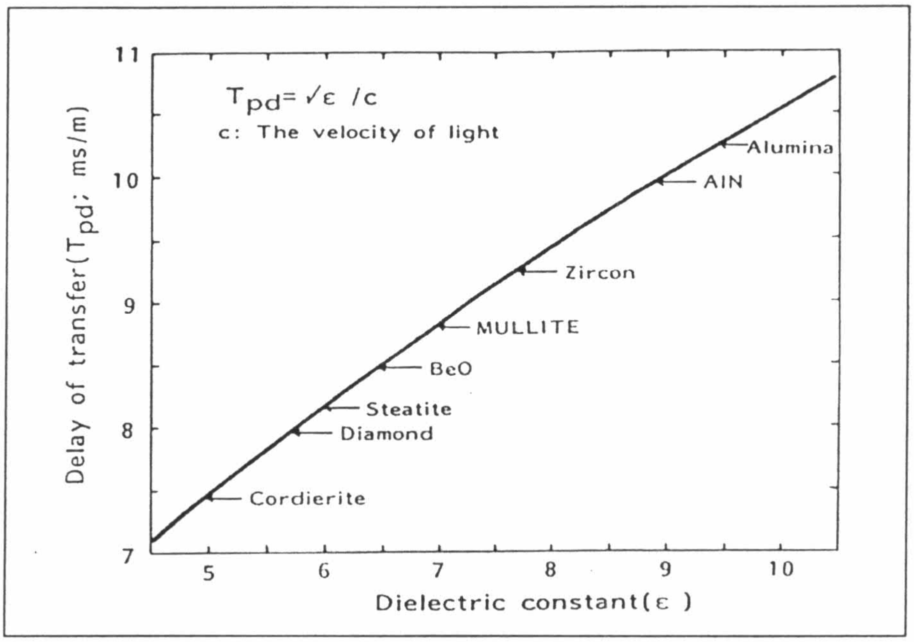


Figure2.13 Relationship between signal transmittance delay times and dielectric constants of mullite in comparison with other ceramic substrate materials

From Table 2.2 and Fig 2.13, mullite, with £ = 7.0 has smaller t_d than alumina, which has £ = 9.5. So mullite is considered as a replacement material for alumina in high frequency (speed) circuit.

There are other properties of mullite that are useful for packaging. The thermal expansion of mullite is close to that of silicon. It is advantage in providing many numbers of connections between silicon chip and substrate. This connection requires a good thermal expansion match between silicon and the substrate. Mullite is a suitable material for this application. However, the matching can be improved by producing composites of mullite and glass or ceramics with lower thermal expansion such as cordierite or spodumene.

Composite with glass or cordierite reduces the sintering temperature. Then it can be cosintered with low-melting metals such as copper.

Optical application

The low thermal conductivity, low density and low thermal expansion of mullite make it useful for optical application, as a window for the mid-infrared wavelength range from 3-5 µm and in the visible light range.

In general, in the preparation of transparent polycrystalline materials, critical requirements are as follows:

1. high chemical purity
2. low porosity
3. phase purity
4. absence of microcracks
5. small-sized residual pores
6. a final grain size less than the wave length of the transmitted radiation

The preparation of translucent mullite ceramics was first reported by Prochazka and Klug (1983). IR-transparent mullite ceramic could be obtained by hot - pressing of homogeneous Al_2O_3 - SiO_2 composition containing 72-76 % Al_2O_3 and controlled grain size less than 0.5 µm. Microcrack was absent in microstructures. (24)

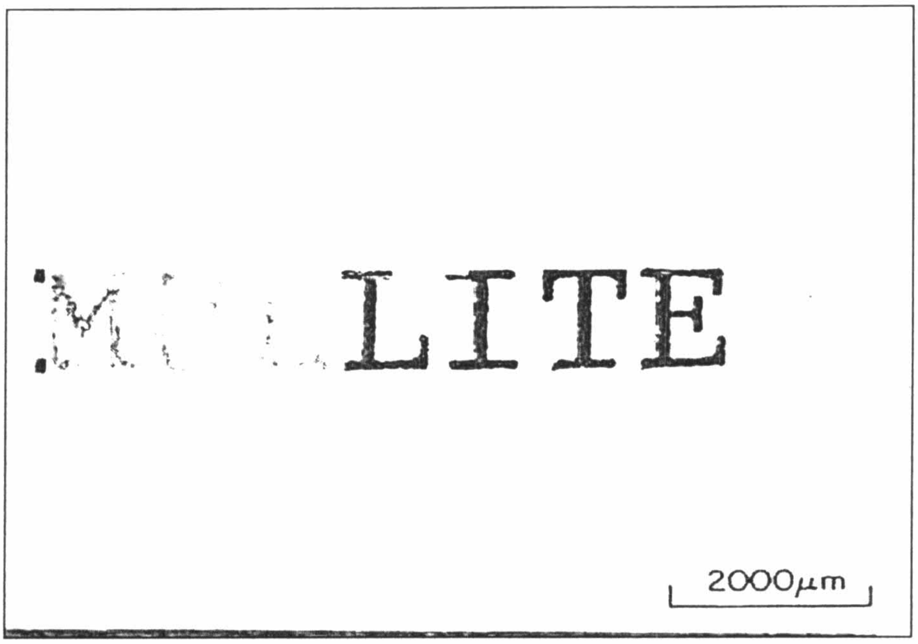


Figure 2.14 Sample of transparent mullite (25)

Miscellaneous application

Brake lining

Cermets containing mullite were used for brake lining materials. These composites could be used as brakes for aircraft and for rapid transit railway systems because they had heat resistance and durability better than conventional brake lining materials that made from asbestos and polymers.

Porous ceramic materials

Porous mullite-based ceramic have been fabricated to a honeycomb by extrusion and corrugation method. The porous ceramic has been used for catalytic convertor in automobile, bioreactors, breweries and waste water disposal plant.

In addition to these applications they are also used as filters and sound - absorbing materials.