

Dense mullite from attrition milled kyanite and α -alumina

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Effects of attrition milling on the decomposition of kyanite (Al_2SiO_5) and its reaction with α -alumina (Al_2O_3) to form stoichiometric mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) are reported. Kyanite-alumina mixes were attrition milled for times from 1 h to 12 h. With increasing milling time, the kyanite decomposition was accelerated and secondary mullite formation from the reaction between the rejected silica and the added alumina was enhanced. Milling reduced the decomposition expansion from +15.0% to +0.1% and the final contraction or densification from +2.5% to -13.7%. During firing complete mullite formation occurred after firing at only 1623 K/1h (1350°C/1 h) to produce a dense mullite ceramic with a fine grain size ($\sim 1 \mu\text{m}$).

Key words: Kyanite, alumina, mullite, sinterization and attrition milling.

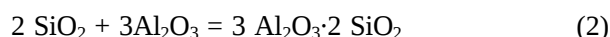
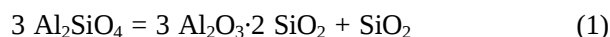
Introduction

Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is the only stable compound ($T_{\text{mp}} \sim 1890^\circ\text{C}$) in the Al_2O_3 - SiO_2 binary system at 1 atm pressure. It is an important phase in many traditional ceramics such as refractories and also in high technology applications for optical, electronic and structural components. Although controversy persists over its melting, this has not inhibited recent research for alternative processing techniques to produce monolithic mullite bodies with high densities and strengths for both structural and non-structural applications [1-4].

Mullite has been produced by a variety of high-tech processing methods, including sol-gel technology [5], chemical syntheses, coprecipitation [6] and hydrolysis [7]. Applying syntheses based on natural minerals such as kaolinite, or the sillimanite group (kyanite, sillimanite and andalusite), and simple alumina-silica mixtures, it is possible to produce a high quality mullite ceramic by conventional processing-sintering methods [8-34].

Mullite derived from aluminosilicate minerals has been studied for many different reasons including phase equilibria [9, 14-15], microstructural development [13, 16-18], its structure [19, 20], methods of synthesis [21], thermal evolution and the mechanical properties [2, 8, 15-34]. The three minerals of the sillimanite group (kyanite, andalusite and sillimanite) have the same chemical formula ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), containing 63.2 wt % Al_2O_3 . They decompose to produce a 3:2 mullite compound, simultaneously rejecting silica over the temperature range from about 1400 to 1600 °C (see Equation

1). The details of the decomposition reaction depend on the specific mineral. Schneider and Majdic [12] have reported that the decomposition reaction temperatures increase in the order: kyanite-andalusite-sillimanite as summarized in Table 1. However, the mullite, which is obtained from the decomposition of those minerals, is normally associated with a rejected silica phase, because of the excess silica in the minerals. By using these three minerals alone, is impossible to produce a phase pure mullite [24]. A source of alumina must be added to achieve a phase pure mullite as described by Equation 2.



Our previous research has demonstrated that reducing the particle size to the nano range through attrition milling also reduces the decomposition temperature of kyanite from 1500 °C to about 1200 °C. Attrition milling also reduces the original decomposition expansion from +18% to a firing shrinkage of -12.5%. This produce at 1600 °C 3:2 mullite grains of 1 mm finely distributed in a silica glass phase with a high density of 3.15 g/cc [4]. It suggests that the extent or degree of attrition milling of the original kyanite can control the decomposition and sintering of kyanite.

Mullite production from the use of the sillimanite mineral group is a common method. Their decompositions produce a mixture of the mullite 3:2 plus free silica. During this transformation there exists a volume expansion for each of the three minerals (see Table 1). The high-pressure phase kyanite has the largest decomposition expansion, > 18%. It is followed by the sillimanite (8%) and the andalusite (4%) volume changes. However, kyanite decomposes at a lower temperature

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Table 1. Several properties of the sillimanite minerals and the 3:2 mullite

PROPERTY	Kyanite	Andalusite	Silimanite	Mullite 3:2
Chemical formula	$\text{Al}_2\text{O}_3\text{-SiO}_2$	$\text{Al}_2\text{O}_3\text{-SiO}_2$	$\text{Al}_2\text{O}_3\text{-SiO}_2$	$3\text{Al}_2\text{O}_3\text{-2SiO}_2$
Hardness (Mohs)	5.5-7	6.5-7.5	6.5-7.5	6-7
Density ($\text{g}\cdot\text{cm}^{-3}$)	3.53-3.65	3.13-3.16	3.23-3.27	3.16
Decomposition ($^{\circ}\text{C}$)	1683 K (1410 $^{\circ}\text{C}$)	1773 K (1500 $^{\circ}\text{C}$)	1898 K (1625 $^{\circ}\text{C}$)	—
Expansion %	18	4	8	—
Silica form	Cristobalite	Amorphous	Amorphous	—
Crystal Structure	Triclinic	Orthorhombic	Orthorhombic	Orthorhombic

(1410 $^{\circ}\text{C}$) than either andalusite (1500 $^{\circ}\text{C}$) or sillimanite (1600 $^{\circ}\text{C}$). The type of silica obtained from the decomposition also depends on the mineral type. For kyanite, the silica is rejected as cristobalite, but for andalusite and sillimanite an amorphous silica phase results [3, 12-14].

An apparent disadvantage of using these natural materials is the level of impurities. They may be critical for the decomposition and the mechanical properties. It is well known that this occurs when the impurities become segregated at the grain boundaries, because of the rejected silica phase. However, it is logical to believe that incorporating alumina to react with the rejected silica to form a single-phase mullite structure can minimize this disadvantage.

The objective of the present research is to apply the decomposition and the reaction processes of attrition milled kyanite with an addition of alumina to produce a phase pure mullite. In this case, mullite formation is expected to originate from two sources: (i) a primary mullite from the initial kyanite decomposition and (ii) a secondary mullite from the reaction of the rejected silica and the alumina addition.

Experimental Procedures

Kyanite and α -alumina were combined to prepare specimens with the 3:2 mullite stoichiometry. The industrial kyanite was received in the form of large prismatic grains, about 250 μm in thickness and 500 μm in length. The 0.2 μm particle size of α -alumina was spherical. Batches of 100 g each were prepared with 27.5 wt % α -alumina and 72.5 wt % of the kyanite to yield the 3:2 mullite. Separate 100-g batches were milled in a steel attrition mill for 1, 3, 6, and 12 h. The attrition milling was performed in a stainless steel vertical attritor with a container 23 cm in diameter and 31 cm in height. Low carbon steel balls, 3 mm in diameter were used. The media-to-mineral weight ratio was 100:1. The milling fluid was isopropanol. The mill rotational speed was 400 rpm. The powders are identified by their individual milling times of 1, 3, 6 and 12 h. A control specimen for comparison was prepared by dry mixing in an alumina ball mill at low intensity. The media-to-mineral weight ratio was 10:1 and the mill rotational speed was 100 rpm.

Because of the iron contamination during the attrition milling, the milled powders were leached with a 4 N of HCl solution to remove the iron. Suspensions of 100-g powder batches were prepared with one liter of the leaching solution. A stirring propeller container at 70 $^{\circ}\text{C}$ was used to leach the iron for 30 minutes. After leaching, the powder appeared white. Further washing using distilled water was applied for five exchanges to eliminate the HCl and achieve a neutral condition. The process was monitored by a pH-meter. Finally, the washed powder was dried in air in a furnace at 70 $^{\circ}\text{C}$ for 72 h. These procedures eliminated the iron contamination from the steel attrition mill as corroborated by an atomic absorption test ** (see Table 2).

The dried powder cake was then manually crushed in an agate mortar and pestle to break up the larger agglomerates and finally passed through a -325 sieve. Then 2 g-specimens were uniaxially pressed at 300 MPa into cylindrical pellets, 10 mm in diameter and 5 mm in height. The pressed pellets were then sintered in stagnant air for one hour at temperatures from 1000 to 1600 $^{\circ}\text{C}$ with a rate of 278 K s^{-1} (5 $^{\circ}\text{C s}^{-1}$) in intervals of 373 K (100 $^{\circ}\text{C}$). A dilatometer⁺⁺ was used to monitor the dimensional changes of the pellets during firing from 1023 to 1873 K (750 to 1600 $^{\circ}\text{C}$) in an Argon atmosphere. The heating rate used was 275 K s^{-1} (2 $^{\circ}\text{C s}^{-1}$).

After firing, density measurements were completed by the Archimedes method. The sintered specimens

Table 2. Chemical analysis of the kyanite-alumina specimens (wt %). The weight ratio of $\text{Al}_2\text{O}_3/\text{SiO}_2$ is constant for all the millings at the theoretical ratio of pure mullite

Compound	Specimens (wt %)				
	0-h	1-h	3-h	6-h	12-h
Fe_2O_3	1.62	Trace			
SiO_2	27.32	27.71	27.75	27.74	27.73
Al_2O_3	69.49	70.57	70.62	70.61	70.62
TiO_2	0.88	0.97	0.92	0.90	0.93
Na_2O	0.53	0.58	0.56	0.57	0.56
K_2O	0.15	0.18	0.15	0.18	0.16
$\text{Al}_2\text{O}_3/\text{SiO}_2$	2.54	2.54	2.54	2.54	2.54

**PE 3100 AA Spectrometer

++Setaram TMA-92

were characterized with X-ray diffraction (XRD) at 35 kV, 25 mA and a scanning rate of $2^\circ \text{ minute}^{-1}$. Analysis of the phase content used a quantitative analysis based on D-QUANT software*. This analyzed the kyanite, mullite, cristobalite and alumina phases of the specimens. A scanning electron microscope (SEM)⁺ was used to study the microstructures of the mullites at 15 kV and a spot size of 3.0. The areas observed were the transverse sections of the specimens. They were polished with diamond paste (0.5 μm) and etched in air at 1273 K (1000 °C) for 1h as well as coated with carbon. The SEM micrographs of the microstructures were analyzed in the image analysis Matlab 7.0 to determine the grain size.

Results

Chemical compositions of the kyanite-alumina attrition milled batches are presented in Table 2. The leaching with the 4 N HCl solution not only removes the Fe contamination from the attrition milling, it also eliminates the original Fe in the as-received kyanite. There

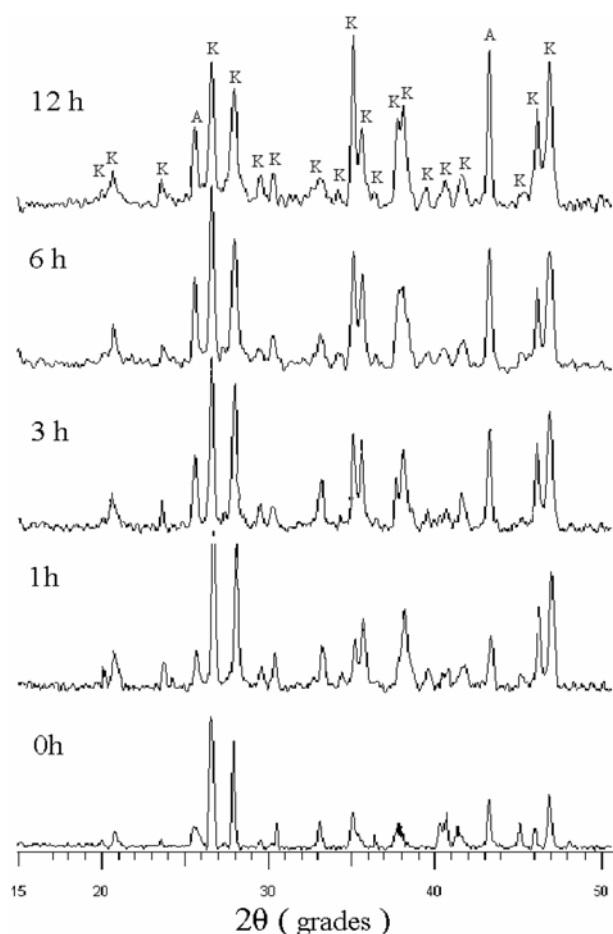


Fig. 1. XRD patterns of the kyanite-alumina specimens for different attrition milling times. Where the K indicates kyanite and the A indicates alumina.

*Siemens Diffractometer D-5000' Software

+Jeol Scanning Microscope 6480

is a homogeneous chemical composition of the milled samples. The $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio for all the milled specimens is the same at 2.546 as the theoretical 3:2 mullite with 71.8% Al_2O_3 and 28.2% SiO_2 .

The X-ray diffraction patterns (XRD) for the original kyanite/alumina mixture and the attrition milled specimens are illustrated in Fig. 1. The characteristic diffraction peaks of kyanite and α -alumina are evident. By observation, the widths of the diffraction peaks increase with increasing milling time (h), indicating the size reduction of the particles. For the as-mixed control specimen without milling (0-h) the diffraction patterns are characteristic of large kyanite crystals containing textural effects.

The attrition-milled powders were monitored by SEM and are illustrated in Fig. 2. The original large prismatic particles of kyanite mixed with alumina are presented in the photograph marked "as-mixed". The powders of kyanite and alumina after only 1-h of attrition milling exhibit a significant reduction of the original kyanite grains ranging from 1 to 10 μm . Some of the prismatic geometry forms of the kyanite persist. After attrition milling for 3-h, the particles are about 1 μm and the original prismatic kyanite particles are eliminated.

The 6-h attrition milling produced more homogeneity and a particle size of less than 1 μm . Finally, the attrition milling for 12-h produced spherical agglomerates of small particles less than 1 μm in size.

X-ray diffraction

X-ray diffraction patterns were obtained for each of the sintered kyanite-alumina specimens at different sintering temperatures. These are illustrated in Fig. 3. Without any milling of the kyanite-alumina, the diffraction peaks of kyanite are still observed until a temperature of 1773 K (1500 °C) on heating. Cristobalite is observed to be stable until 1773 K (1500 °C), suggesting that the decomposition of kyanite promotes the bi-formation of mullite and cristobalite upon heating. Increasing the sintering temperature, the cristobalite decreases from the reaction with alumina. These peaks of the alumina addition remain stable until 1873 K (1600 °C). The intensities of the alumina peaks gradually decrease over the temperature interval from 1373 K to 1873 K (1100 °C to 1600 °C).

The 6-h specimen diffraction patterns show that the decomposition of kyanite and the secondary mullite formation occurs between 1573 K (1300 °C) and 1773 K (1500 °C). It can be observed that after firing at 1573 K (1300 °C), the 6-h specimen has partially transformed to mullite from the decomposition of kyanite. At 1673 K (1400 °C) the intensity peaks of cristobalite and alumina decrease because of the secondary mullite formation. The cristobalite disappears between 1673 K (1400 °C) and 1773 K (1500 °C). Above 1773 K (1500 °C) the mullite is the major phase present in the specimen with traces of alumina. After firing at 1873 K

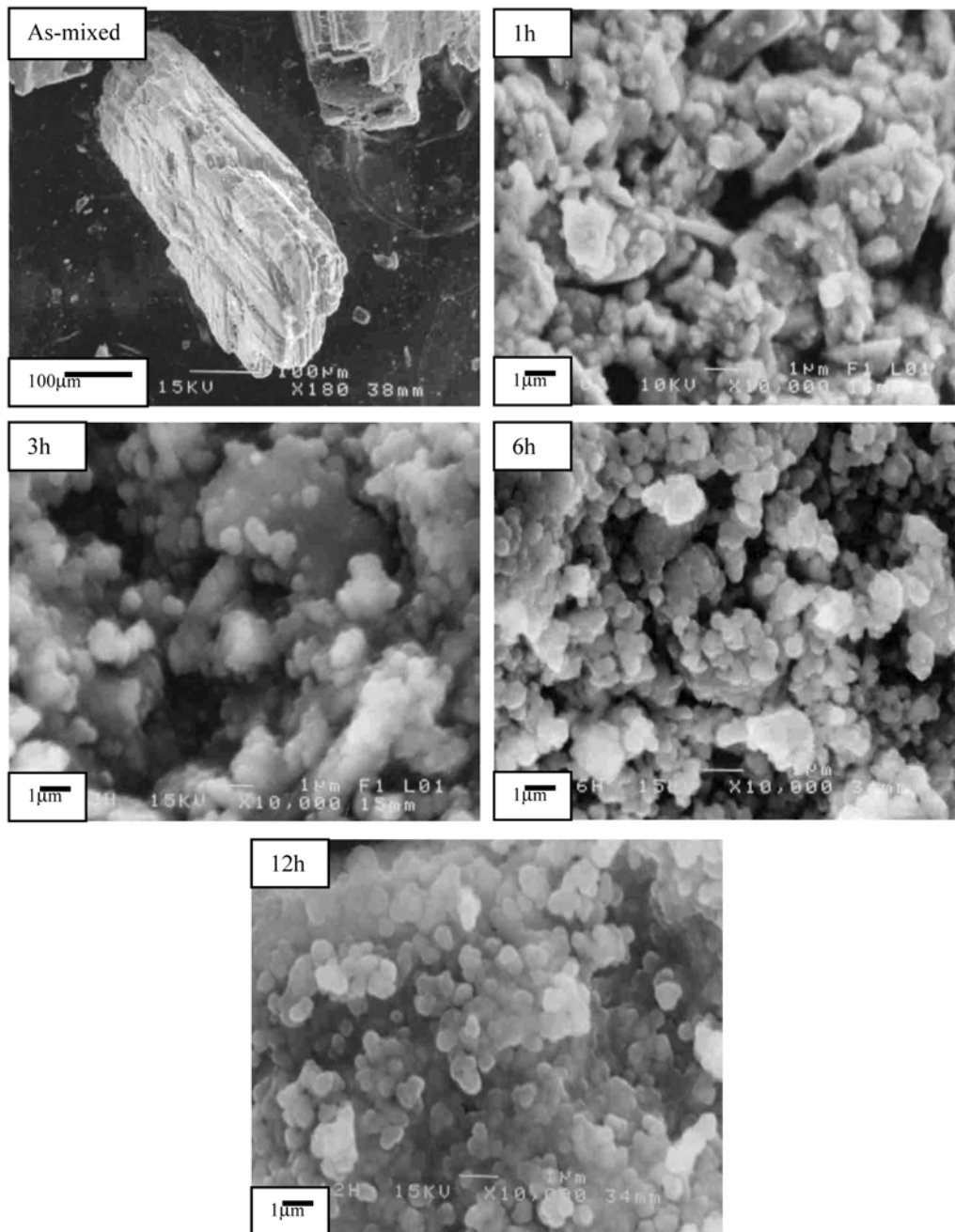


Fig. 2. SEM photomicrographs of the kyanite-alumina mixture specimens after different attrition milling times.

(1600 °C) the major phase present is mullite with remaining alumina unreacted.

The diffraction patterns of the 12-h specimens show that the decomposition of kyanite and the secondary mullite formation occur between 1573 K (1300 °C) and 1773 K (1500 °C). Contrary to the 6-h specimen, it can be observed that after firing at 1573 K (1300 °C), the 12-h specimen has transformed to mullite from the decomposition of kyanite. At 1673 K (1400 °C) the intensity peaks of cristobalite and alumina decrease because of the secondary mullite formation. After firing at 1773 K (1500 °C) the major phase present is mullite with small traces of alumina unreacted. However, after

firing at 1873 K (1600 °C) the only phase present is mullite. Attrition milling clearly enhances the decomposition of kyanite and the reaction from alumina and the cristobalite to form mullite.

The kinetic trends of mullite formation from these kyanite-alumina specimens are presented in Fig. 4. Figure 4 illustrates both the primary mullite from the kyanite decomposition and the secondary mullite from the alumina–cristobalite reaction. There exists an initial mullite formation stage from about 1373 K (1100 °C) to about 1623 K (1350 °C). It increases with increasing attrition milling time. Attrition milling enhances mullite formation at lower temperatures by encouraging the

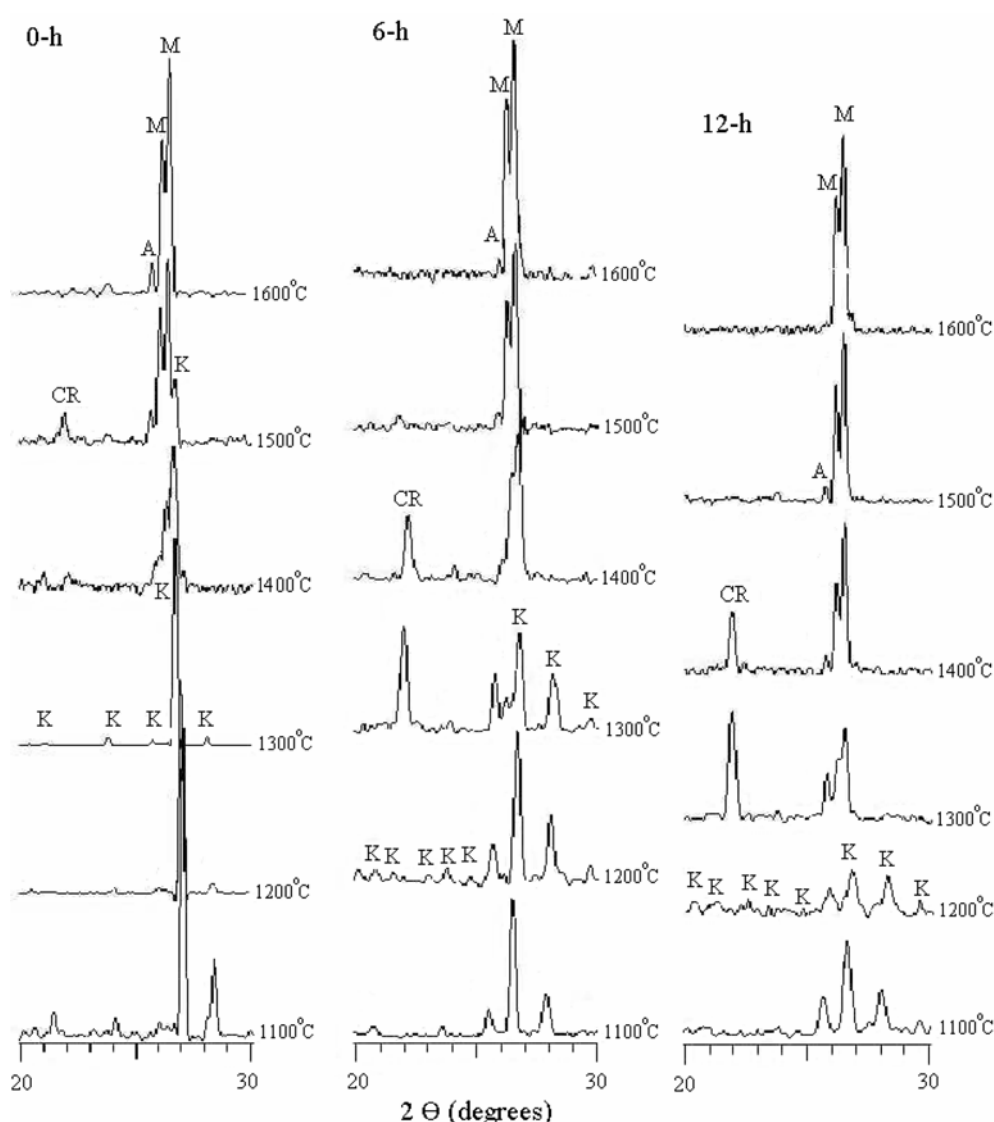


Fig. 3. Diffraction patterns of 0-h, 6-h and 12-h specimens sintered at different temperatures. Where: kyanite (k), cristobalite (CR), alumina (A) and mullite (M).

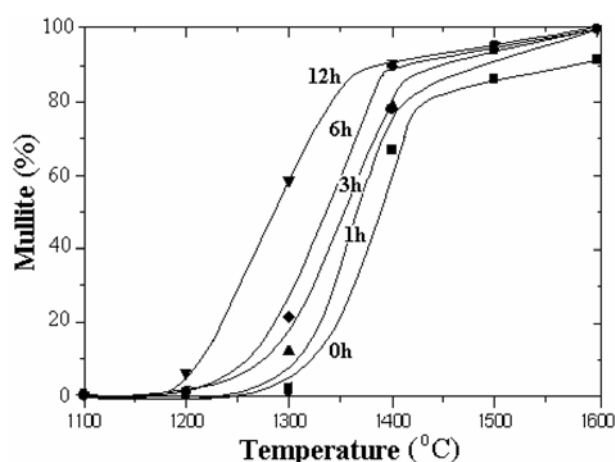


Fig. 4. Kyanite-alumina specimens decomposition and reaction to form mullite as a function of firing temperature for different attrition milling times.

kyanite decomposition. For secondary mullite formation, the 12-h specimen begins more easily than the others as its kyanite decomposition is completed at ~ 1558 K (1285 °C). The reaction between the alumina and the rejected silica to form secondary mullite occurs mostly at and above 1673 K (1400 °C) for all the specimens.

Dilatometry

The dilatometric traces of the specimens during heating without any attrition milling for the as-received kyanite and the as-mixed kyanite-alumina are illustrated in Fig. 5. Analysis of the present data shows differences in expansion from 1573 K (1300 °C) to 1693 K (1420 °C). The as-mixed kyanite-alumina mixture has a slightly smaller expansion of $\sim 15\%$ than the as-received kyanite of $\sim 22\%$ [4]. This is a result of the presence of the 27.5 wt % alumina added to react with the kyanite. It is evident in Fig. 5 that the decrease in expansion is an amount about that of the alumina addi-

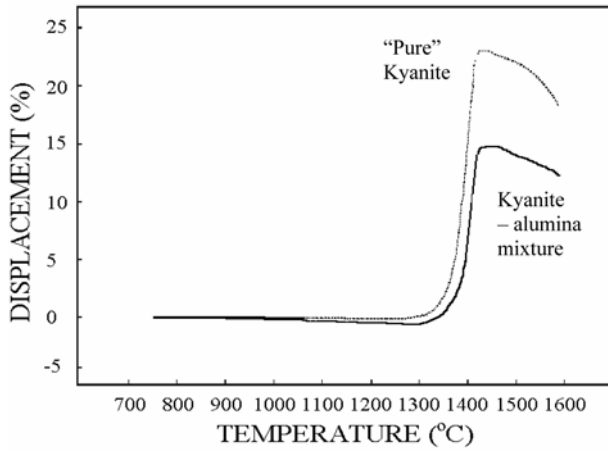


Fig. 5. Dilatometric analysis of the as-received kyanite and the as-mixed kyanite-alumina specimen in the mullite ratio prior to attrition milling.

tion reacting with kyanite particles especially on their surfaces. After the expansion of the kyanite decomposition a final contraction occurs for both specimens. The as-received kyanite contracts 3.0% while the as-mixed alumina-kyanite contracts 2.5%.

The dilatometric traces during firing of the attrition milled kyanite-alumina specimens are illustrated in Fig. 6 and summarized in Table 3. Both contractions and expansions are observed to occur at elevated temperatures. The 1-h attrition milled specimen exhibits four different stages or intervals with increasing temperature. An initial contraction of ~2.5% occurs between the range of 1323 K (1050°C) and 1523 K (1250°C). The second change is the kyanite decomposition giving an expansion of ~5.0% between 1573 K (1300°C) and 1693 K (1420°C). Then a final contraction between 1653 K (1380°C) and 1883 K (1600°C) occurs of ~5.6%. During this final contraction, there is a step of dimensional control over a short temperature range. This occurs, as corroborated by the X-ray diffraction (XRD), from the secondary mullite formation from the reaction of the added alumina and the silica rejected of the decomposition of kyanite.

The specimens that were attrition milled for 3, 6 and 12-h (Fig. 6) exhibit similar sequences of dilatometric change as for 1-h specimen, but with several distinct differences in the magnitudes of the dimensional changes (Table 3). Those differences are described as follows:

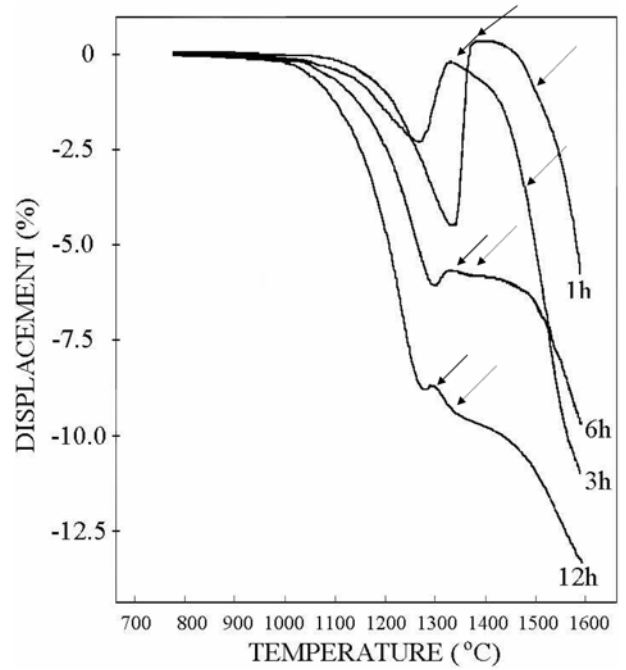


Fig. 6. Dilatometric analysis of the kyanite-alumina specimens after different attrition milling times (h).

i) As the attrition milling time increases, the magnitude of the initial contraction decreases substantially from -4.75% to -11.0% for 1 h and 12 h of attrition milling time, respectively. The initial temperature of this contraction begins for all the milled specimens at 1323 K (1050°C), however the final temperature of the contraction is reduced proportionally with the attrition milling from 1593 K (1320°C) to 1558 K (1285°C) for 1 h and 12 h, respectively.

ii) Attrition milling reduces the range of temperature and the expansion of the kyanite decomposition. The range of temperature changes from 1593 K (1320°C) and 1653 K (1380°C) to 1568 K (1295°C) and 1558 K (1285°C) for 1 h and 12 h of attrition milling, respectively. The decreases of expansion change with attrition milling from +5.0% to +0.1% for 1 h and 12 h, respectively. The largest milling times of 6-h and 12-h have only small decomposition expansions of kyanite of +0.3% and +0.1%, respectively.

iii) The initial temperature and the final contraction or densification also decrease proportionally with the

Table 3. Summary of the dilatometric events of the kyanite-alumina specimens fired from 1023 K (750°C) to 1873 K (1600°C)

Specimen	Initial Contraction		Expansion		Final Contraction		Secondary Mullite	
	Range (°C)	Contraction (%)	Range (°C)	Expansion (%)	Range (°C)	Contraction (%)	Range (°C)	ΔT (°C)
0 h	—	—	1300-1420	15.0	1420-1600	2.5	—	—
1 h	1050-1320	4.8	1320-1380	5.0	1380-1600	5.6	1380-1600	220
3 h	1050-1250	2.5	1250-1320	2.5	1320-1600	11.0	1320-1600	280
6 h	1050-1300	5.8	1300-1315	0.3	1315-1600	9.0	1315-1600	285
12 h	1050-1285	11.5	1285-1295	0.1	1295-1600	13.8	1295-1500	205

increasing attrition milling time. The initial temperature of this contraction begins at 1380 °C for 1-h and reduces to 1295 °C for 12-h, respectively. The final contraction or densification changes from -5.6% to -13.8% for 1-h and 12-h, respectively. The reductions are 125 °C and -8.2% by increasing the attrition milling time.

iv) The secondary mullite formation begins after the decomposition of the kyanite, which reject silica that further reacts with the added alumina to form extra mullite. It is clearly by the dilatometric traces that the initial secondary mullite formation moves to lower temperatures as the attrition milling time increases. The initial temperature of this formation is 1653 K (1380 °C) for 1-h and 1568 K (1295 °C) for 12-h, respectively. The difference is around 373 K (100 °C) between these two specimens. The final temperature of the secondary mullite formation as corroborated with the X-ray diffraction (XRD) lasts until 1600 °C at which a small amount of alumina remains in all the specimens.

The dilatometric trends illustrated in Fig. 6 and Table 3 show that the initial contraction is greatly reduced as the attrition milling time increases. This initial event is responsible for an initial densification process mainly from the mechanical accommodation of the particles into the pressed body. The magnitude of the second expansion event, the decomposition of kyanite, also decreases with increasing milling time. The third event of contraction or final sintering is also favored by increased attrition milling however the secondary mullite formation reduces the rate of sintering as the temperature increases.

Figure 6 illustrates arrows of the thermal steps of the secondary mullite formation. The solid arrow shows the initial temperature at which the secondary mullite formation occurs. The dashed arrows show a small contraction, which varies with the dilatometric curves. This is a result of volumetric changes from the reaction of cristobalite and alumina to form secondary mullite. Details of this reaction can be corroborated with the X-ray diffraction (XRD).

Bulk densities

Bulk densities of the kyanite-alumina specimens after firing are summarized in Table 4. The trends are illustrated in Fig. 7. The bulk densities of the kyanite-

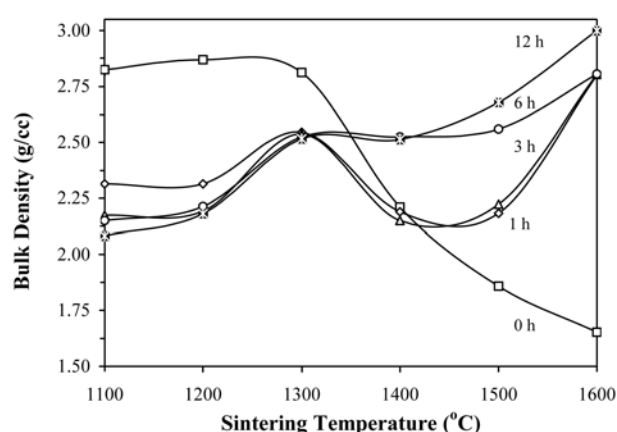


Fig. 7. Variation of kyanite-alumina bulk density with the sintering temperature.

alumina specimens exhibit similar trends as previously reported for pure kyanite [4], although pure kyanite becomes less dense upon firing. Specimens increase in bulk density when the temperature reaches ~1573 K (1300 °C) on heating. From 1573 K (1300 °C) to 1773 K (1500 °C) there is a decrease in bulk density because of the kyanite decomposition expansion. This latter expansion effect is almost eliminated for 6-h and 12-h milled specimens. Bulk density increases slowly after firing at 1773 K (1500 °C) and above. This is the region at which the secondary mullite grows and because of its nature of formation, the diffusion process slows the final densification. The 12-h milled specimen clearly shows the effects of the alumina addition on the densification process.

The 6-h and 12-h specimen bulk densities increase similarly for the firing temperature interval from 1573 K (1300 °C) to 1673 K (1400 °C). This is because of a similar secondary mullite formation between the reaction of the added alumina and the rejected silica. A balance occurs between the secondary mullite formation and the sintering processes. The 12-h milled specimen achieves the highest final density with 97% of the theoretical density of the 3:2 mullite (3.16 g cc⁻¹).

Microstructures

The surface of an unmilled kyanite-alumina specimen after firing at 1873 K (1600 °C) is illustrated in Fig. 8. It shows a fine alumina covering the expansion of the transformed kyanite grains. Many cracks are visible because of the large volume change of 15% that accompanies the kyanite decomposition.

Microstructures of the mullite specimens after 6-h and 12-h of attrition milling and after firing at 1873 K (1600 °C) are shown in Figs. 9 and 10. The 6-h milling specimen has a fine, equiaxed grain size with a few lath-like grains and porosity. The mullite grains are ~1 µm in size. Some lath-like mullite grains are beginning to emerge. The microstructure of the 12-h attrition milled specimen is illustrated in Fig. 10. It has less

Table 4. Kyanite-alumina densities (g cc⁻¹) from each milled specimen. These results can be compared with the theoretical density of mullite of 3.16 g cc⁻¹

Milling times	Firing temperatures (°C)					
	1100	1200	1300	1400	1500	1600
0-h	2.83	2.87	2.81	2.21	1.86	1.65
1-h	2.31	2.31	2.54	2.19	2.18	2.80
3-h	2.18	2.19	2.54	2.15	2.22	2.80
6-h	2.15	2.21	2.52	2.52	2.56	2.80
12-h	2.08	2.18	2.52	2.51	2.68	3.03

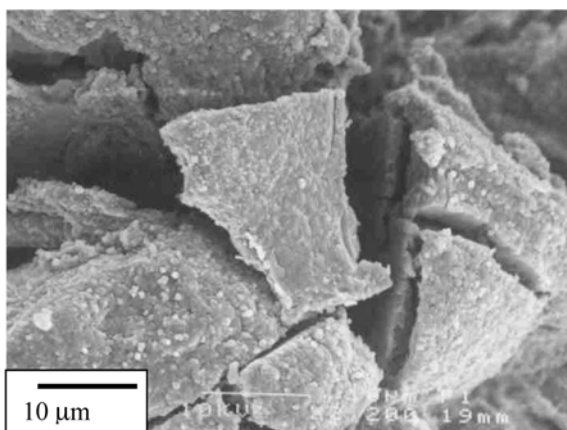


Fig. 8. Fracture surface of the un-milled specimen of the kyanite-alumina fired at 1873 K (1600°C).

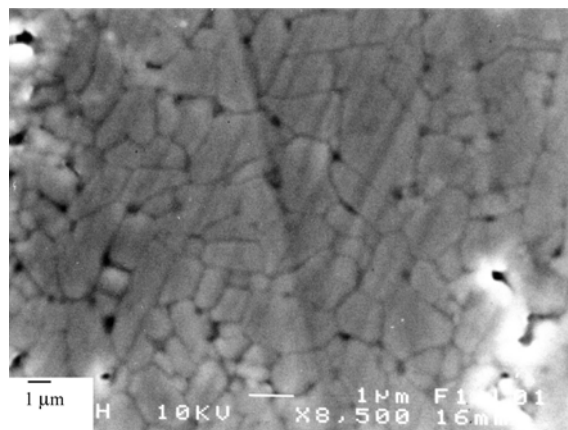


Fig. 10. Microstructure of the kyanite-alumina specimen ($\rho = 3.03 \text{ g cc}^{-1}$) fired for 1 h at 1873 K (1600°C), after 12-h attrition milling.

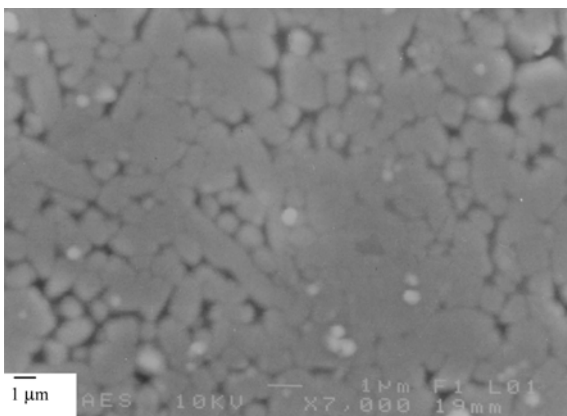


Fig. 9. Microstructure of the kyanite-alumina specimen ($\rho = 2.80 \text{ g cc}^{-1}$) fired for 1 h at 1873 K (1600°C), after 6-h of attrition milling.

porosity and retains a fine grain size. A number of the familiar and larger lath-like mullite grains are visible in the form of rectangles $> 2 \mu\text{m}$. These are in the early stages of evolving into the characteristic mullite lath-like grain morphology.

From the microstructures of these mullites it can be observed that the lath-like morphology grains may be from the initial decomposition of kyanite and the equiaxial grains from the secondary formation of mullite from the reaction of the added alumina and the rejected silica. The reason of this understanding is that the grains of mullite from the decomposition of kyanite have more resiliency time and temperature to coarsen the grains than the equiaxed ones present in the microstructure which are from the secondary mullite formation.

Discussion

The X-ray diffraction (XRD) and fired density results, coupled with the dilatometry confirm that the kyanite decomposition and the subsequent rejected silica reaction with the alumina are both substantially enhanced by the attrition milling. The thermal events are discussed separately as follows:

Decomposition of kyanite

The dilatometry of all the kyanite-alumina specimens during firing reveals an expansion in a range of temperature from 1523 K (1250 °C) to 1693 K (1420 °C) which is directly related to the kyanite decomposition. This decomposition temperature range and the expansion from the kyanite decomposition are reduced, as the attrition milling time is increased (see Table 3). For example, after 12-h of attrition milling, the decomposition occurs from 1558 K (1285 °C) to 1568 K (1295 °C) and its compared expansion of only about 0.1%. This is clearly reduced from the as-mixed specimen, for which the decomposition occurs from 1573 K (1300 °C) to 1693 K (1420 °C) and its expansion is about 15%. This indicates that attrition milling enhances the decomposition of kyanite.

The above also indicates that by reducing the particle size by attrition milling, the surface areas as well as defects created on the particle surface and within the particles are increased. It is not clear, however, just how important the particle size reduction is relative to the introduction of deformation, strain and defects into the crystal structure. Additional study is required to be more definitive on that issue.

Secondary mullite formation

The second event is a reaction step, which initiates at 1653 K (1380 °C) and at 1568 K (1295 °C) for 1-h and 12-h specimens, respectively. It is related to the secondary mullite formation as confirmed by X-ray diffraction studies (XRD). However, it is clear that for the 6-h and 12-h specimens, there is a complete formation of secondary mullite at about 1763 K (1490 °C) and 1723 K (1450 °C), respectively. This is not the case for the specimens of 0-h, 1-h and 3-h, which retain an alumina amount at 1873 K (1600 °C). Therefore, a larger attrition milling time enhances the secondary mullite formation by promoting the reaction between the added alumina and the rejected silica from the decomposition of kyanite.

The formation of secondary mullite affects the final

densification of the specimens however this effect is reduced by increasing the attrition milling time. The bulk densities were 3.03 g cc^{-1} and the open porosity was reduced to 4% after the attrition milling for 12-h for a pure mullite phase. The secondary mullite effect can be easily observed from our previous study at Aguilar-Santillan et al. [4], where the sintered attrition-milled kyanite present rejected silica in a liquid phase. This dominated the sintering process of attrition-milled kyanite specimens. The bulk densities were 3 g cc^{-1} and the open porosity was reduced to 2% after the attrition milling for 12-h. The resultant microstructure was in the form of mullite grains dispersed in a silica matrix.

Final densification process and microstructure

The third dilatometric event is a final contraction, or densification, where the slope is altered by the secondary mullite formation during the reaction of the added alumina and the rejected silica. Fired densities increase as the attrition milling time increases to achieve a higher final density of the resulting mullite bodies, i.e., 3.03 g cc^{-1} for 12-h of attrition milling (see Table 4).

After firing, the bulk density of the kyanite-alumina specimens follows a similar densification path to that reported for pure kyanite [4]. Both specimens increased their bulk density with increasing milling time. However, one critical feature that differentiates these two materials is the secondary mullite formation. It actually appears to decrease the densification rate slightly from that of pure kyanite [4]. Two reasons are that the liquid silica presented in the pure kyanite is decreased from the reaction with the alumina to form mullite in the kyanite-alumina specimens. The densification is also inhibited by the lath-like grain contact between the primary and the secondary mullite. The resulting density of the mullite is $\sim 96\%$ of its theoretical value (3.16 g cc^{-1}) after firing at 1873 K (1600°C).

Microstructures of the 0-h, 6-h and 12-h fired specimens are similar to those previously reported by others [8, 15-17, 30]. The unmilled kyanite specimen showed transformed kyanite grains covered by the fine alumina additions. However, the attrition milled specimens have a microstructure of mullite grains with a distinct equiaxed tendency, but with some lath-like extended grains. The 6-h attrition milled specimen has both types of grains, some equiaxed and some lath-like. The microstructure appears homogeneous overall. The microstructure of the specimen milled for 12-h at 1873 K (1600°C) consisted of a mixture of equiaxial grains and lath-like grains with a final open porosity of 4.0%.

The fired densities in Table 4 and illustrated in Fig. 5 both suggest that additional densification is possible for firing at temperature above 1873 K (1600°C). Firing times larger than just one hour may also slightly increase the density. Application of longer attrition milling to produce higher fired densities is also a distinct possi-

bility. Certainly the expansion of the 12-h milled specimen from the 6-h milling for firing above 1673 K (1400°C) suggests the benefit of addition milling for further densification.

However, for the case of mullite, which has a lath-like grain shape, the bridging and steric hindrance that are created have a tendency to leave entrapped porosity between the grains and inhibit complete densification as has been noted by Abe and Bradt for silicon carbide [27]. Additional process modifications may be necessary to achieve a low porosity and high density because of the steric hindrance.

Comparison with other technical mullite ceramics

Table 5 summarizes several different mullite-processing methods to achieve high-density technical ceramic mullite bodies. For example, Huang and et al. [28] used a commercial mullite powder to achieve a high mullite density of 3.09 g cc^{-1} by using a sintering process under pressure of 30-35 MPa at 1823 K (1550°C) for one hour. The grain size of this mullite was $< 1 \mu\text{m}$.

Balmori-Ramirez et al. [28] used kyanite mixed with aluminum metal. The two were previously attrition milled separately and then milled together to form a pure mullite at 1873 K (1600°C) after one hour of firing in air. The density achieved was 3.08 g cc^{-1} . This is similar to the results reported by Lee et al. [30]. Although, that mullite was dense; the grain size was not equiaxed and shows two different sizes and forms of $\sim 1 \mu\text{m}$ and other of $\sim 3 \mu\text{m}$. This may related to the secondary mullite formation.

Lee et al. [30] used fumed silica and alumina to produce mullite by high energy milling in a controlled pH. The milled specimens at pH 9.5 achieved a density that was 99.7% of the mullite theoretical density. This is not the case for the milled specimens at a pH 6.5, which were reported to have a high level of agglomeration. The microstructure of that mullite was an equiaxed grain size of 90% $< 1 \mu\text{m}$. The study further confirms the benefit of attrition milling.

Additions of BaO to high purity alumina and quartz were reported by Kong et al. [31]. They suggest that BaO helps to increase the density of mullite resulted from the alumina and quartz reaction. However, it is well known that BaO is quite dense (5.72 g cc^{-1}) relative to mullite (3.16 g cc^{-1}) and 10% addition will result in densities well beyond that for a pure mullite. BaO also reacts with alumina to form Ba-aluminates that may affect the mullite formation and density.

Viswabaskaran et al. [32] used a clay and reactive alumina mixture to produce a phase pure mullite by ball milling for ~ 30 minutes. An addition of 5% boehmite, $\text{Al}_2(\text{OH})_3$, for the reactive alumina increased the density to 3.01 g cc^{-1} . The microstructure of this mullite consisted of lath-like grains $> 5 \mu\text{m}$ in size.

Saruhan et al. [33] studied powder mixtures of SiO_2 glass and cristobalite with a fine Al_2O_3 fired at temper-

Table 5. Comparison of several different technical mullites. The mullite theoretical density is 3.16 g cc⁻¹

Researchers	Processing	Special Conditions	Firing	Density (g cc ⁻¹)
Huangand, et al. [28]	Hot-pressed commercial mullite powder (d ₅₀ =0.7 µm)	Under pressure of 30-35 MPa	1550°C/1h	3.09
Balmori-Ramirez, et al. [29]	Attrition milled kyanite plus aluminum metal	Kyanite milled for 6h and aluminum for 3h and then mixed	1600°C/1h	3.08
Lee, et al. [30]	High energy mixing of fumed alumina and silica powders	pH 9.5	1600°C/2h	3.15
		pH 6.5	1600°C/2h	3.08
Kong, et al. [31]	High energy milling of alumina and quartz	Addition of BaO (10%)	1500°C/4h	3.22
Viswabaskaran, et al. [32]	Milling of clay and reactive alumina	Ball-mixing (30 min) and addition of Bohemite (5 %)	1600°C/3h	3.01
Saruhan, et al. [33]	Mix of cristobalite (1-10 µm) and α-alumina	Ball milling for 5h	1800°C	2.84
	Mix of silica glass powder (2-3 µm) and α-alumina		1800°C	2.69
Ebadzadeh [34]	Mix of boehmite and colloidal silica	pH = 3 and dried gel at 120°C. A ball milling was applied for 16 h	1700°C/2h	3.00
	Mix of aluminum sulfate and colloidal silica		1700°C/2h	2.85
This study	Attrition milled kyanite plus alumina	Milling for 12h	1600°C/1h	3.03

atures to 1973 K (1700 °C). Green samples consisting of SiO₂ glass plus Al₂O₃ (RSS) generally sintered to higher densities than those consisting of cristobalite plus Al₂O₃ (RSC). In the powder compacts (RSS and RSC) different sintering mechanisms were active before and after the onset of mullitization. Before mullite formation begins, densification occurs in the RSS sample through viscous flow sintering and in the RSC sample by solid-state sintering. After the formation of mullite begins, transient liquid-phase sintering occurs for both RSS and RSC specimens. The amount of SiO₂-rich liquid phase, which controls the degree and rate of the second-stage sintering mechanism, depends on the amount of residual SiO₂ which is left unreacted after initial mullitization. This study suggests that andalusite and sillimanite may have advantages for mullite formation.

The temperature-dependent mullite formation process is complex. At 1973 K (1700 °C) sample RSS formed only ~80% mullite, while the mullitization of sample RSC was nearly ~90% complete. Both samples displayed near-total mullitization at 2023 K (1750 °C). Four different temperature stages of mullite formation could be distinguished: (i) mullite nucleation was observed at <1773 K (1500 °C), (ii) a region of high mullitization degree from 1773 K (1500 °C) to 1823 K (1550 °C), (iii) and finally a high mullitization at >1898 K (1625 °C).

The densities of these mixtures were relatively low, only ~90% for (RSS) and ~85% for (RSC) specimens. These densities suggest that the larger portion of the final density for the RSS is because of a liquid-phase assisted the sintering process at the lower temperatures prior to mullitization <1773 K (1500 °C). However, the RSC major sintering mechanism was the solid-state diffusion that only part of the densification occurs prior

mullitization. It was concluded that the reaction sintering of cristobalite and α-alumina often produces a lower reaction rate than for silica glass and α-alumina.

The work presented here can also be compared with the study by Sainz et al. [13] for a kaolinite-alumina mixture. Their results suggest that mullite formation can be achieved above at 1700 °C in the presence of a liquid silica phase. It is clear that mullite formation in their system is slower than that of the present study.

Summary and Conclusions

Attrition milling and firing of a mixture of kyanite and alumina of the 3:2 mullite stoichiometry was investigated. Attrition milling has two beneficial effects on the decomposition of kyanite: (i) the reduction of the decomposition range temperature from 1573 K (1300 °C) to 1693 K (1420 °C) for the as-mixed specimen to the range of 1558 K (1285 °C) to 1568 K (1295 °C) for the 12-h attrition milled specimen, (ii) the ΔV of expansion of the decomposition is reduced from 15% of the as-mixed specimen to 0.1% of the 12-h attrition milled specimen.

Attrition milling of kyanite-alumina mixings has benefits for the formation of secondary mullite and their densification process from the reaction of the added alumina and rejected silica in two forms: (i) the range of temperature ΔT for a complete mullite formation is reduced to 428 K (155 °C) for the 12-h of attrition milling, and (ii) the secondary mullite formation is greater with increasing attrition milling. This enhances the densification process for the larger attrition milled specimens.

Attrition milling reduces the kyanite decomposition temperature and drastically decreases the volumetric

expansion of the kyanite decomposition. It also enhances the reaction of the rejected silica with the alumina addition to form secondary mullite and increase the density of the fired mullite bodies. It yields a refined equiaxed mullite microstructure and a high-density mullite ceramic.

Although milling was only completed for a 12h duration and firing was limited to 1873 K (1600 °C) in this study, property trends suggest that additional milling times and higher firing temperatures will produce even better mullite ceramics.

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