

Mechanical Activation of the Decomposition and Sintering of Kyanite

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The influence of attrition milling on the thermal decomposition of kyanite (Al₂O₃·SiO₂) to mullite (3Al₂O₃·2SiO₂) and SiO₂, and its subsequent sintering, was studied. A commercial kyanite was attrition-milled for times up to 12 h. Dilatometry confirmed that as-received unmilled kyanite decomposes between 1300° and 1435°C. The decomposition reaction is slow initially and accelerates during the later stages until about one-half of the decomposition occurs in the last 35°C. For the attrition-milled kyanite, the onset decomposition temperature decreases, the transformation temperature interval is reduced, and both the decomposition reaction and subsequent sintering are accelerated. A dense microstructure of fine equiaxed mullite grains in the 1 µm size range, evenly dispersed in a glassy matrix, is obtained by sintering the attrition-milled kyanites. These results are explained in terms of the energy accumulated during attrition milling, a reduction of the milled kyanite particle size, and the presence of a liquid phase during sintering.

I. Introduction

HIGH-ENERGY, high-intensity mechanical milling has been applied to numerous materials for a variety of reasons, including the alloying of metallic and ceramic powders,¹ the synthesis of compounds,^{2,3} activation of chemical reactions, and phase trans-formations.⁴ Mechanically alloyed powders are usually characterized by the development of supersaturated solid solutions, metastable crystalline or amorphous phases, and nanocrystalline grains and particles. During mechanical synthesis a chemical reaction is often completed in situ or is activated by the input mechanical energy. For example, TiN powder can be produced by milling metallic titanium powder in a nitrogen-containing atmosphere⁵ and the chemical reactions between BaCO₃ and TiO₂ can be accelerated by milling.⁶ Attrition milling has been documented to activate thermal processes.⁴

Recently, the thermal decomposition of attrition-milled andalusite (Al₂O₃·SiO₂) was reported.⁷ It was observed that the mechanical energy input activates the thermal decomposition of

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andalusite to yield mullite and silica. That investigation revealed that attrition milling accelerates the decomposition rate of andalusite and reduces the decomposition temperature by nearly 200°C. The silica is expelled as crystalline quartz. Together with kyanite and sillimanite, and alusite forms a group of minerals, which share the same chemical formula (Al2O3·SiO2), but differ in their crystalline structures (Table I).8 None of the sillimanite compounds are present in the Al₂O₃-SiO₂ equilibrium phase diagram,⁹ although all three occur in nature and decompose on heating to yield a mixture of mullite (3Al₂O₃·2SiO₂) and SiO₂. The mullite content produced by the sillimanite minerals during decomposition is large (\sim 80%). For this reason they are used as an important source of mullite in commercial applications.¹⁰

The decomposition characteristics are quite different for the three sillimanite minerals. Sillimanite decomposes at the highest temperature, while kyanite does so at the lowest temperature. During their decomposition, the three minerals display a volume expansion ($\Delta V/V$) that is very large for kyanite (~20%), relatively small for andalusite (\sim 4%), and intermediate for sillimanite (~8%). Finally, while the SiO_2 expelled by kyanite during the decomposition is in the form of cristobalite, it is usually amorphous silica for the other two group members.¹¹ Both Wilson¹² and Jain et al.¹³ have documented that reducing the particle size accelerates the decomposition of kyanite.

Schneider and Majdic¹⁴ have suggested that the mullite produced by the decomposition initiates at preferential nucleation sites such as grain surfaces, grain boundaries, and defects and then proceeds into the grains. Jain et al.13 and Ildefonse and coworkers¹⁵ confirmed these hypotheses for kyanite and andalusite, respectively. The mullite crystals grow in a direction perpendicular to the elongated direction of the host grains, maintaining a close relation with the *c*-axes of the minerals.¹⁶ However, the morphologies of the resulting mullite crystals which are grown from the different minerals vary. Tomba and co-workers found that elongated mullite crystals are produced during the thermal decomposition of sillimanite.¹⁷ In kyanite, elongated, fibrous mullite grains are developed at low temperatures, but their morphology changes to a tabular one with rounded edges at elevated temperatures.¹⁸ During the thermal decomposition of andalusite single crystals, mullite single crystals develop in the interior of the andalusite parent grains, leaving an interconnected capillary network filled with a silica-rich glass.¹⁵

Sintering of the sillimanite group of minerals has never been investigated in detail. It is believed that the thermal expansion that accompanies the mullitization is detrimental to densification. However, the large thermal expansion displayed by the decomposition of kyanite has been used to counteract the sintering shrinkage of some refractories.¹⁹ Dilatometric studies of large crystals of sillimanite,¹⁷ kyanite,¹⁸ and andalusite⁷ suggest that these species may possess rather poor sintering characteristics. However, pressed compacts of attrition-milled andalusite do attain very high

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rubic in Characteristics of the Similarite Oroup minerub	Table I.	Characteristics	of	the	Sillimanite-Group	Minerals
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	Kyanite	Andalusite	Sillimanite	Mullite
Chemical formula	Al_2O_3 ·SiO ₂	Al ₂ O ₃ ·SiO ₂	Al ₂ O ₃ ·SiO ₂	3Al ₂ O ₃ ·2SiO ₂
Hardness	5.5–7	6.5–7.5	6.5–7.5	6–7
Specific gravity (g/cm ³)	3.53–3.65	3.13–3.16	3.23–3.27	3.15
Final decomposition temperature (°C)	1410	1500	1625	
% expansion	>20	~4	~8	
Crystalline structure	Triclinic	Orthorhombic	Orthorhombic	Orthorhombic

densities after sintering at 1500°C.⁷ The resulting microstructures consist of fine interconnected mullite ($\sim 1 \ \mu m \ cross \ section$) platelets.

Studies of the formation of mullite in mixtures of the sillimanite minerals combined with alumina are rare. Ildefonse *et al.*¹⁵ obtained a mullite with ~5% retained glass by the reactive sintering of micronized andalusite (0.4–10 μ m) and alumina at 1600°C. There were larger amounts of residual glass when larger andalusite particles were used. Mullite and mullite–corundum aggregates have been produced from mixtures of beach sand sillimanite and corundum fired at 1550°C with additions of 4 wt% TiO₂²⁰ or 2 wt% Fe₂O₃.²¹ These additives improve the sinterability of the aggregates through liquid-phase sintering, but their effects on the sillimanite decomposition are unknown. No publications of the mullitization of kyanite–alumina mixtures have been reported.

The present investigation addresses the influence of attrition milling on the thermal decomposition of a commercial kyanite. These experiments are part of a larger investigation to understand the thermal changes and mullitization processes of the attritionmilled sillimanite group of minerals.

II. Experimental Procedure

(1) Attrition Milling of Kyanite

A commercial kyanite with the chemical composition (wt%) 58.30% Al_2O_3 , 38.6% SiO_2 , 0.40% Fe_2O_3 , 1.78% TiO_2 , 0.82% Na_2O , and 0.10% K_2O was used as the starting material. It is slightly richer in silica than stoichiometric kyanite (62.92% Al_2O_3 and 37.08% SiO_2), and also contains minor impurities.

Batches of kyanite (100 g) were attrition-milled (Union Process) in a 304 stainless steel container (3.5 L) employing 3 kg of stainless steel milling media (3 mm diameter) at a rotational speed of 400 rpm. The kyanite was milled for 1, 6, and 12 h in distilled water, recovered by filtration, and then leached in a HCl solution to remove any iron contamination from the mill and media. The milled kyanite was then washed in distilled water and recovered by filtration, dried at 70°C, and sieved through a 325-mesh sieve. The residual iron content of the leached, attrition-milled kyanite powders was measured by atomic absorption spectroscopy. These attrition-milled powders were then uniaxially die-pressed into disks of 10 mm diameter \times 5 mm thickness at 200 MPa and then cold isostatically pressed at 400 MPa. Sintering was done between 1200° and 1600°C for 1 h in air. A heating rate of 5°C/min was used.

(2) Characterization

The attrition-milled powders were characterized by X-ray diffraction (XRD, Cu $K\alpha$ radiation, Model D-5000, Siemens), scanning electron microscopy (SEM, Model 6300, JEOL), and specific surface area. Chemical composition was analyzed by atomic absorption spectroscopy.

Dilatometry (Model TMA92, Setaram) was conducted on small samples (5 mm height) cut from the pressed disks. Heating was to 1600°C at 5°C/min. The samples were placed on a high-alumina plate and linear dimensional changes were monitored with a high-alumina probe. Platinum foils separated the sample surfaces from the alumina fixtures. Phase changes after heating were followed by XRD. The microstructures of the samples sintered at 1600°C were observed in a scanning electron microscope (SEM,







Fig. 1. Micrographs of the kyanite attrition-milled for different times: (a) as-received, unground kyanite; (b) kyanite attrition-milled 1 h; and (c) kyanite attrition-milled 12 h.



Fig. 2. XRD patterns of the kyanite at different attrition-milling times. k = kyanite.

Jeol 6100). Samples for SEM were prepared by cutting the sintered pellets in the transverse direction, grinding and polishing following standard techniques, and thermally etching at 1400°C for 30 min. Surfaces of the SEM specimens were coated with a thin layer of an Au–Pd alloy. The density and porosity of the sintered samples was measured by the Archimedes technique.

III. Results

(1) Characterization of the Attrition-Milled Kyanite

The iron oxide content of the acid-leached kyanite was 0.40% and 0.43% for the powders ground for 1 and 12 h, respectively. These are similar to the initial Fe_2O_3 content of 0.40% and confirm that the acid leaching treatment removed any iron contamination from the milling process.

Figure 1 illustrates the kyanite particles before and after milling. The as-received kyanite had prismatic crystals with nearly equiaxed cross sections (~50 μ m × 100 μ m) and lengths larger than 300 μ m. For the 1 h milling time, many of the broken crystals still retained some evidence of those geometric forms as cleavage dominates the milling process. However, there were also numerous submicrometer-size particles. Distinctive geometric forms were completely eliminated after 12 h of milling, yielding typically equiaxed submicrometer particles with rough surfaces. Particles were agglomerated as a consequence of the acid leaching and drying treatments that followed the attrition milling. The specific surface area of the powders increased from 0.25 m²/g in the as-received powder to 12 m²/g after 1 h, 27 m²/g after 6 h, and 43 m²/g after 12 h of attrition milling, respectively. This reflects the particle size reduction observed in the micrographs.

The X-ray diffraction patterns for the kyanite after the milling are shown in Fig. 2. The as-received kyanite pattern is dominated by a very large peak at 26.6° 20, the (200) planes, while the relative intensities of the remaining reflections are smaller as reported in the JCPDS Card No. 11-46.²² This texture can be explained by the packing of the raw kyanite particles, which lie on either of the prism faces that are parallel to the crystallographic *c*-directions exposing a large quantity of the (200) planes. The attrition-milled particles are more rounded, and therefore, this texture disappears. The XRD line broadening and higher background levels observed in the patterns of the milled powders are caused by the combined milling effects such as the reduced particle size, creation of defects, and lattice strains.

(2) Decomposition of the Attrition-Milled Kyanite

The linear thermal dimensional changes of the as-received kyanite and of the attrition-milled kyanite are reported in Fig. 3. The curve for the kyanite attrition-milled for 6 h is not presented for the sake of clarity. It lies between those of the kyanites attrition-milled for 1 and 12 h. The as-received kyanite exhibits a total linear expansion of 23% that occurs between 1300° and 1435°C. This expansion initiates slowly and then accelerates about 1400°C. Nearly half of the expansion occurs over a narrow temperature interval of only 35°C, from 1400° to 1435°C. These temperatures coincide well with those reported by Sainz *et al.*,¹⁸ but are slightly higher than those of Wilson¹² and Schneider and Majdic.²³ Above this temperature, shrinkage occurs, but it is insufficient to compensate for the large lower temperature expansion.

The dilatometry curves of the kyanite after attrition milling for 1 and 12 h are also presented in Fig. 3. Unlike the as-received kyanite, these two samples do not exhibit the large expansion. Rather, after milling, they contract significantly before they expand. As the milling time increases, the contraction initiates at



Fig. 3. Dilatometry curves of as-received kyanite, kyanite attrition-milled 1 h, and kyanite attrition-milled 12 h.

lower temperatures and a larger amount of shrinkage occurs before the decomposition expansion initiates. The expansions that follow are only 6.5%, 3.2% and 2.1% in the samples milled for 1, 6, and 12 h, respectively, much less than the 23% for the raw mineral. The expansion occurs from 1290° to 1365°C for the sample milled for 1 h and from 1280° to 1320°C for the sample milled for 12 h. Shrinkage reoccurs or continues after the decomposition is completed. The dilatometer curve of the sample milled for 12 h suggests that the sintering process is near completion at temperatures above about 1500°C.

The nature of the expansions observed in the dilatometer curves was determined from the XRD of samples heated at selected temperatures. The results for the as-received, unground kyanite are presented in Fig. 4(a). The XRD pattern of the as-received kyanite fired 1 h at 1300°C is similar to the pattern of the as-received kyanite shown in Fig. 2. Any mullite that might have formed at this temperature is in such a small amount that it is undetectable by X-ray diffraction. For the sample heat-treated at 1400°C, there is a mixture of kyanite and mullite, but the former phase still predominates. The XRD pattern of the sample fired at 1500°C reveals the two main peaks of mullite located at 25.9° and 26.3° 20, although its unsymmetrical shape indicates either that the mullite is poorly crystallized or that there remains a small amount of undecomposed kyanite. This XRD pattern also has a peak of cristobalite that crystallized from the SiO₂ expelled during the kyanite decomposition.

The XRD patterns of the samples milled for 1 and 12 h and then heat-treated to 1200° C look similar to those in Fig. 2. The corresponding XRD patterns of the samples fired at 1300° and 1400° C are presented in Figs. 4(b) and (c), respectively. The sample milled for 1 h and heat-treated at 1300° C (Fig. 4(b)) shows one peak at 16.4° 20 and two peaks to the left of the (200) peak of kyanite (26.6° 20). These two are the beginning of the formation of mullite. It also has a cristobalite peak. At 1400° C, the peaks of mullite and cristobalite increased in size.



Fig. 4. XRD patterns of the kyanite heated to different temperatures for 1 h: (a) as-received kyanite, (b) kyanite attrition-milled 1 h, and (c) kyanite attrition-milled 12 h; (K) kyanite, (M) mullite, (CR) cristobalite.

A small peak centered at $26.6^{\circ} 2\theta$ suggests that this sample still contains some undecomposed kyanite. The XRD patterns of the samples milled for 12 h, fired at 1300° and 1400°C, are presented in Fig. 4(c). The XRD patterns obtained after firing at these two temperatures are similar. This sample is completely transformed after heating to 1300°C for 1 h and has large peaks of cristobalite.





Fig. 5. XRD patterns of the as-received kyanite and of the kyanites attrition-milled for 1 and 12 h, after firing them at 1600° C for 1 h. M = mullite.

(3) Sintering of the Attrition-Milled Kyanite

Pellets of kyanite prepared with the as-received mineral, and with powders attrition-milled for 1 and 12 h, were fired at 1600°C for 1 h in air. The XRD patterns of these samples only show peaks of mullite. The cristobalite peak is not present. A characteristic pattern is shown in Fig. 5. The cristobalite is no longer present because the 1600°C sintering temperature is in the biphasic liquid-mullite phase field of the binary Al₂O₃–SiO₂ system. The amorphous silica, which is present in all of the samples, cannot be detected by XRD, and therefore does not appear in the XRD patterns.

A micrograph of the fracture surface of the unground kyanite heat-treated at 1600°C is shown in Fig. 6(a). It illustrates the poor sintering characteristics and the presence of severe cracking that it experienced as a consequence of the large transformation expansion that occurs during the decomposition of kyanite. The preparation of polished samples of this material for observations at higher magnification was not possible. By contrast, the samples milled for 1 and 12 h show a dense microstructure composed of equiaxed grains of mullite dispersed in a matrix rich in SiO₂, similar to those shown in Figs. 6(b) and (c). The mullite grain size in both samples is on the order of about 1 µm. The mullite grains appear slightly larger for the kyanite attrition-milled for 12 h and sintered at 1600°C for 1 h. These mullite microstructures are distinctly different from those that form during the decomposition of large crystals of kyanite,¹⁸ which produce tabular mullite plates with rounded faces. They are also different from the typical microstructures obtained during the decomposition of kaolinite,²⁴ which consist of elongated mullite grains with a very large aspect ratio.







Fig. 6. Microstructures of kyanite fired at 1600°C for 1 h: (a) as-received kyanite, (b) kyanite attrition-milled 1 h, and (c) kyanite attrition-milled 12 h.

The densities and open porosities of the three samples fired at 1600°C for 1 h are reported in Table II. The density increases in proportion to the milling time. Dense samples with less than 2% open porosity are obtained with the kyanite ground for 12 h. On the other hand, the unground kyanite is very porous.

IV. Discussion

These results clearly indicate that attrition milling induces significant changes in the thermal decomposition and sintering characteristics of kyanite. They can be summarized as follows.

Table II. Density and Porosity of Samples Sintered at 1600°C

Milling time (h)	Bulk density (g/cm ³)	Open porosity (%)
As-received, unmilled	1.9	59.3
l 6	2.8	7.3 4.6
12	3.1	1.9

Attrition milling causes (i) a narrowing of the decomposition temperature interval of kyanite, (ii) an acceleration of the decomposition rate of kyanite, (iii) a significant reduction of the volume expansion associated with the decomposition, and (iv) a greatly enhanced sinterability. These effects make it possible to obtain high-density ceramic bodies at relatively low firing temperatures from kyanite.

The high-energy input of attrition milling is directed toward the creation of more particle surface area via particle size reduction. It also creates defects and cracks, as well as extensive deformation of the crystal lattice, as the XRD peak broadening indicates (Fig. 2). Several researchers have shown that the decomposition of the sillimanite minerals starts at the grain surfaces and cracks.^{13–15} Therefore, it is likely that the attrition milling activates the thermal decomposition of kyanite, because there is an increased concentration of nucleation sites (particle surface area and cracks) where mullite formation can initiate. In addition, the growing mullite grains do not have to maintain a restrictive crystallographic relationship with other contiguous mullite grains, as is the case when mullite grows within large grains of kyanite. As a consequence of these factors, the formation rate of mullite is increased by attrition milling.

The formation of a liquid at high temperatures and changes in its distribution within the microstructure are additional factors that help to understand the high mullite formation rate in the attritionmilled kyanite. The dilatometric curves suggest that a liquid is formed near 1000°C in the attrition-milled kyanites, as the shrinkage starts and before the kyanite decomposes. The alkali and the excess of silica present in the raw kyanite can account for the formation of this liquid. This primary liquid does not crystallize during cooling because the XRD patterns of the samples fired below 1300°C do not have peaks of any crystalline silica. The lowest liquid formation temperature in the Al₂O₃-SiO₂-Na₂O system is at 1050°C and can be as low as 985°C in the presence of K₂O. Such a liquid can probably activate the formation of mullite by a solution-precipitation mechanism similar to the one that operates during the transformation of kaolinite to mullite and silica.^{25,26} It is evident that this liquid is more effective in the attrition-milled kyanites because the solubility of solids in liquids increases at smaller particle sizes and the solid-liquid interface reaction area increases.

At higher temperatures, the kyanite decomposes and rejects the excess silica, part of which might dissolve in the liquid. The XRD patterns indicate that some of it crystallizes as cristobalite. This phenomenon is more prevalent when the kyanite particle size is smaller. Two possible mechanisms could account for the greater crystallization of cristobalite in the attrition-milled kyanites. First, a higher density of nucleation sites exists as a result of the smaller particle size and defects created in the attrition-milled minerals. Second, the low-temperature liquid may be enriched in silica as the silica expelled from the kyanite dissolves into it, and this favors the crystallization of cristobalite.²⁶

Although liquid also forms in the unmilled kyanite, both at low temperatures and when the kyanite decomposes, it may be isolated in small regions within the parent kyanite grains, or expelled and segregated at the surface. Large kyanite particles do not dissolve in the liquid as effectively as the small ones. Besides, any isolated liquid may achieve saturation in a short time and will not contribute much to the solution-precipitation mechanism. Therefore, the decomposition of large kyanite grains is slower, because it relies more on a solid-state diffusion mechanism to transfer the aluminum and silicon ions in and out of the transforming regions in the parent grains until the chemical composition of mullite is reached.

The attrition-milled kyanite exhibits a very high sinterability. This is a consequence of the submicrometer particle size of the milled mineral coupled with the liberation of a silica-rich liquid at high temperatures. The latter enhances the densification via liquid-phase sintering. This improved sinterability also contributes to the reduction of the transformation expansion that is observed in the dilatometric curves of the attrition-milled kyanite. The high degree of shrinkage that creates this increased sinterability compensates for the transformation expansion of the kyanite. The intermediate plateau that appears in the dilatometric curves when the decomposition of kyanite is complete can be explained by the formation of mullite and cristobalite as these two phases possess reduced sintering characteristics at low temperatures.²⁷ Also, the low-temperature liquid viscosity might have increased significantly if it dissolved at least part of the SiO₂ expelled during the decomposition of the kyanite. The presence of TiO₂ impurities in the kyanite can account for the resumption of shrinkage at higher temperatures, because this oxide favors the formation of a liquid at a temperature close to 1400°C.²⁰ The consequence is that it is possible to attain relative densities for kyanite-based ceramics in excess of 99% by relatively simple and inexpensive ceramic processing methods based on attrition milling.

V. Conclusions

Attrition milling is an effective process to enhance the thermal decomposition of kyanite to mullite and silica. The decomposition temperature interval of attrition-milled kyanite is reduced nearly 100°C relative to that for the as-received mineral. The large expansion associated with the decomposition of unmilled kyanite is drastically reduced in kyanite that has been attrition-milled. Attrition milling also enhances the sinterability as dense glass–mullite ceramics are formed after firing the attrition-milled kyanite.

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