

Nano-milling of the sillimanite mineral, kyanite, and its reactions with alumina to form mullite

Richard C. Bradt^{a,*}, Joaquin Aguilar-Santillan^{a,b} and Heberto Balmori-Ramirez^b

^aDepartment of Metallurgical and Materials Engineering, The University of Alabama, Tuscaloosa, AL 35487-0202 USA

^bDepartment of Metallurgical Engineering, ESIQUE, Instituto Politecnico Nacional - UPALM, AP 75-872, Mexico DF, 07300, Mexico

The sillimanite group of minerals, kyanite, andalusite and sillimanite, the three polymorphs of Al_2SiO_4 , is a natural raw material for the production of mullite in many traditional ceramics. However, the sillimanites form at high pressures and are alumina-deficient relative to mullite. This paper addresses the effects of attrition milling kyanite, the most common of the three to the nanoscale. Additions of aluminum metal, that is then oxidized to alumina and an independent addition of pure alumina to yield a phase-pure mullite after firing, are also described. The attrition milling size reduction of natural kyanite to the nanoscale has several pronounced beneficial effects. It reduces the phase decomposition temperature, it eliminates the large volume expansion of the decomposition and it produces a highly reactive form of the rejected silica. When fired with alumina additions adjusted to the mullite stoichiometry, the resulting phase-pure mullite is a high density, fine grain size ceramic body.

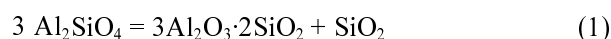
Key words: attrition milling, kyanite, mullite, nanosize, sillimanite.

Introduction

Interest in producing and processing nanoscale ceramics to attain outstanding properties has never been at a higher intensity than it is at the present. The prefix "nano" has been applied, often indiscriminately, to many different materials and their production processes in such a wide fashion that the fundamental parameters of many aspects of the "nanoscale" have hardly been identified. Nevertheless, computer modeling or simulation has already been incorporated into the field, even though the important controlling features of the nanoscale have hardly been identified [1]. This paper considers the production of nanosize mineral powders through the attrition milling of kyanite, the most common of the sillimanite group of minerals [2]. As such it combines the benefits of nanosize in ceramic powders with two other factors, including: (i) the effects of high intensity milling and its attendant stored elastic strain energy and (ii) the decomposition reaction of kyanite, the high pressure polymorph of the sillimanite group. It concludes that nanosize powders can be coupled with other structural phenomena to produce extraordinary results.

The three sillimanite minerals, including kyanite, all have the same chemical formula Al_2SiO_4 , but none of them appear on the familiar binary silica-alumina

equilibrium phase diagram at one atmosphere pressure. This is because the three compounds are high pressure forms of the 1:1 compound that were originally formed at elevated temperatures and high pressures in the earth [3]. The sillimanites are not stable when heated at one atmosphere, and will decompose according to the reaction:



where the 3:2 compound of alumina and silica is known as mullite. Note that additional silica is rejected from the original sillimanite [4]. Mullite is the single most important phase in many traditional ceramics and refractories [5, 6]. Mullite constitutes a major portion of the structure of many products in the 70% alumina class of refractories and in those ceramics it is often derived directly by the above reaction. The decomposition details of all of the sillimanite minerals are summarized in Table 1 which follows.

A major factor which restricts the use of uncalcined sillimanite minerals in their natural state is that upon

Table 1. Several aspects of the sillimanite minerals experiencing reaction (1) above.

Characteristic	Kyanite	Andalusite	Sillimanite
Crystal Structure	triclinic	orthorhombic	orthorhombic
Density (g/cc)	3.53-3.65	3.13-3.16	3.23-3.27
Decomposition T	1410 °C	1500 °C	1625 °C
+ΔV%	~15	~4	~8
Form of Silica	crystalite	amorphous	amorphous

*Corresponding author:
Tel : +1-205-348-0663
Fax: +1-205-348-2164
E-mail: Rbradt@coe.eng.ua.edu

heating there is a substantial increase in volume during the decomposition process. That this type of volume increase should occur is not surprising for the sillimanites were originally formed at high pressures and are generally denser than the 3:2 mullite at 3.16 g/cc. This is especially the case for kyanite which is nearly 15% denser than mullite. It might be added, however, that the three sillimanite minerals and their decomposition product mullite have close structural similarities.

From the reaction in equation (1) it is evident that when the sillimanite minerals decompose they reject free silica. It is an obvious step to add additional alumina to the sillimanite mineral to react with the rejected silica and fire to form a phase-pure mullite. This has in fact been done commercially with many mullite refractories based on the andalusite member of the sillimanite group [7]. It produces higher density ceramic bodies than can normally be achieved by simply mixing alumina and silica in the 3:2 ratio and often yields a microstructure with superior chemical and physical properties.

This paper summarizes the effects of attrition milling kyanite to nanosize ceramic powders, first just kyanite alone, then kyanite with alumina added to achieve the 3:2 mullite stoichiometry and then finally with aluminum metal added in an amount to oxidize to produce the 3:2 mullite. It concludes that there are several synergistic effects that can be exploited by applying high energy milling techniques to achieve nanosize particles of materials with phase transitions or decompositions.

Attrition Milling of Kyanite

Aguilar-Santillan et al. [8] have attrition milled kyanite to the nanosize regime and studied its subsequent decomposition and sintering. As both Wilson [4] and Jain et al. [9] have previously documented the point that reducing the particle size of kyanite also reduces the decomposition temperature, it is not surprising that high intensity milling to the nanosize regime should have a major effect on the decomposition temperature according to reaction (1). Aguilar-Santillan et al. [8] followed the decomposition by dilatometry during heating as-received and attrition-milled specimens. Figure 1 illustrates the dilatometric traces for the as-received kyanite and the same material after attrition milling for 1 h and for 12 h. Two critical effects of particle size reduction are evident in these dilatometer traces. First, the large ΔV expansion of the decomposition for the as-received kyanite is large and occurs between about 1350 °C and 1435 °C. Attrition milling, only for 1 h has a drastic effect on that decomposition. Not only is the temperature of the initiation of the decomposition reduced to only about 1300 °C, but the magnitude of the ΔV expansion is decreased to only about 6.5%, less than one third of the original expansion.

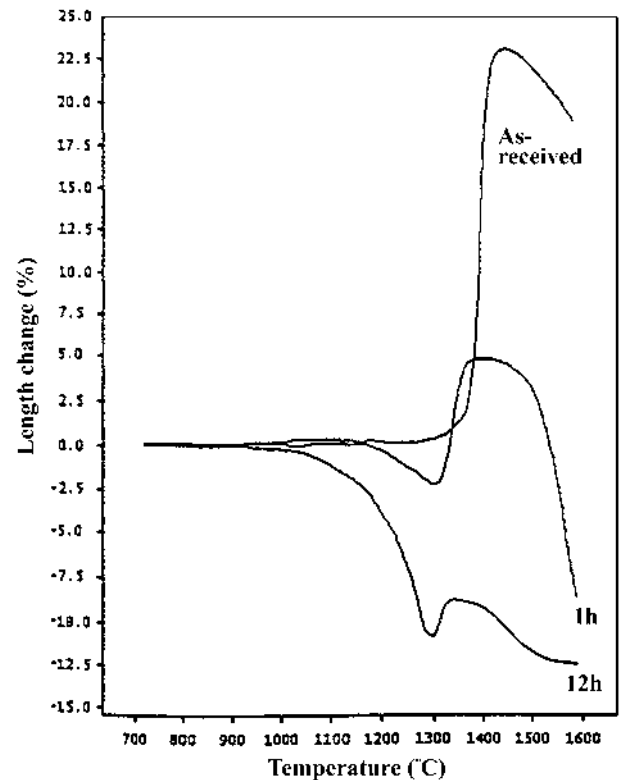


Fig. 1. Dilatometric traces of as-received kyanite and after attrition milling for one hour and twelve hours.

sion. Also of note is a slight contraction from sintering prior to the decomposition expansion. The effect of attrition milling for 12 h further amplifies the initiation temperature decrease, the decrease of the ΔV expansion and the initiation of sintering, as well. After 12 h of attrition milling, the ΔV expansion is only about 2%. One might speculate that addition milling will further reduce and totally eliminate the ΔV expansion of the decomposition reaction. Although detailed particle size analyses were not reported, SEM micrographs clearly illustrated that the original large prismatic shapes of kyanite were reduced to spherical particles on the scale of $< 0.1 \mu\text{m}$ that were in the form of numerous agglomerates.

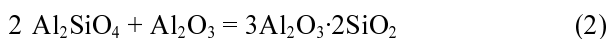
There is clearly an effect of the milling size reduction on the decomposition temperature of kyanite. Similar effects on the andalusite decomposition have been reported by Balmori-Ramirez et al. [10] and also for the α -transformation of aluminum hydroxide by Kano et al. [11]. It is evident that the reduction of particle size to the nanoscale by attrition milling also reduces the temperature of phase transitions, if the materials also experience a phase transition or a decomposition reaction. 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.

When Aguilar-Santillan et al. [8] sintered the attrition

milled kyanite, the presence of the rejected excess silica resulted in a liquid phase sintering process dominating the firing event. In spite of this situation, the bulk densities were ~ 3 g/cc and the open porosity was reduced to $\sim 2\%$ after attrition milling for 12 h. Systematic increases with increasing milling times were reported.

Adjusting the Sillimanites to the Phase-Pure Mullite Composition

The general decomposition reaction of the sillimanites, Equation (1), suggests that any of the three sillimanite polymorphs can be chemically adjusted to form a phase-pure mullite by the addition of alumina to the sillimanite according to:



This alumina addition can be accomplished in at least two different ways: (i) simply by adding the correct amount of alumina, Al_2O_3 , as indicated by reaction (2), or (ii) by adding aluminum metal and the oxidizing it to alumina during the firing of the attrition milled materials. The second approach is just a simple variant of the techniques employed by Claussen and co-workers [12, 13] in the reaction bonded aluminum oxide (RBAO) process, only in this instance it involves the reaction of the oxidized metal to form another compound, namely mullite. Obviously, it is, in principle, possible to introduce the extra alumina for reaction with the rejected silica and formation of a phase-pure mullite by a combination of the two methods. Although it should not change the end result of the formation of a phase-pure mullite, it may provide for additional dimension control during the manufacturing process. This type of combination of alumina adjustments offers intriguing possibilities for close dimensional control of mullite ceramics formed by the combined process and subsequently the manufacture of technical mullite ceramics.

Addition of Alumina to Achieve Phase-Pure Mullite

Alumina has been added to kyanite prior to attrition milling so that the as-received kyanite and the alumina addition are thoroughly mixed prior to firing [14]. Figure 2 illustrates this mixture after attrition milling for 6 h. It is evident that the individual particles are less than one micrometer in diameter and that many agglomerates exist. It is not visually possible to distinguish the original kyanite from the alumina additions as they have been intimately mixed and milled for 6 h.

Firing a series of different milling times at different temperatures results in a distinguishable difference in mullite formation. There is the primary mullite from the decomposition of the kyanite and a secondary

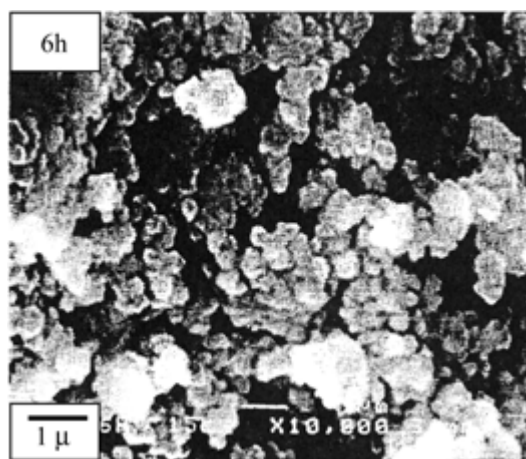


Fig. 2. Micrograph of kyanite alumina mixture after attrition milling for six hours.

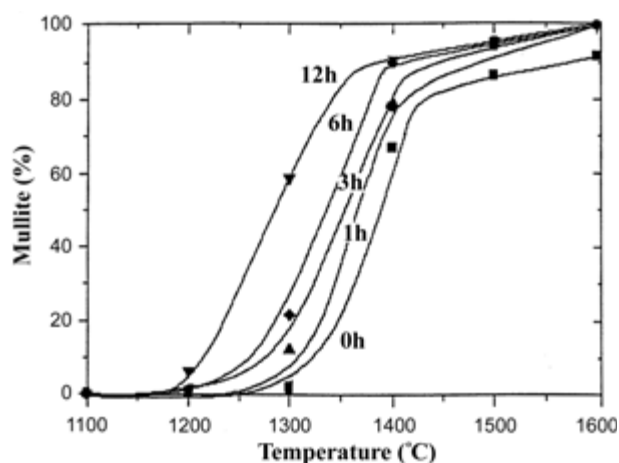


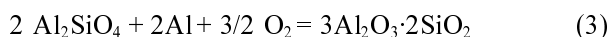
Fig. 3. Mullite formation after firing attrition milled kyanite alumina mixture for different milling times and at temperatures.

mullite from reaction of the rejected silica and the additional alumina. This is illustrated in Figure 3. The result is a phase-pure mullite after firing at only 1600 °C whenever the milling time exceeded just 1 h. The 12 h attrition milled ceramics achieved densities of 3.03 g/cc after firing for one hour at 1600 °C in air and had a microstructure that consisted of a mix of equiaxed grains and lath-like forms about 1 μm in dimension. Obviously, this is an excellent technique to produce mullite technical ceramics for without optimization of the processing, a density of $> 97\%$ was achieved with a fine grain size microstructure.

Addition of Aluminum Metal to Achieve a Phase-Pure Mullite

Balmori-Ramirez et al. [15] have applied a variation of the RBAO process to attrition-milled kyanite plus attrition-milled aluminum metal, then fired them in a multi-step process to produce a phase-pure mullite. This process requires the minimization of the oxidation

of the aluminum metal during the attrition milling [16] so that the aluminum was initially attrition milled separately in isopropyl alcohol before milling with the kyanite. It also requires the formation of mullite through a reaction process involving oxygen from the furnace atmosphere, the kyanite and the aluminum metal, which may be summarized as:



Although this approach seems quite simple, it in fact can have numerous variations relative to the oxidation of the aluminum metal below and above the melting point of aluminum, ~660 °C, which is considerably below the firing temperatures for typical mullite technical ceramics. The reader is referred to the original RBAO literature on this point, for it can be quite involved.

When specimens consisting of the attrition-milled mixture of oxidized aluminum metal and kyanite were subsequently fired in air, extensive mullite formation was observed after firing at only 1100 °C, again indicative of increased reactivity of the rejected silica and the alumina. It is quite evident that the nanosized attrition-milled kyanite plus alumina has a substantially higher reactivity than conventionally-milled kyanite.

Similar to the phase-pure mullite from simply an alumina addition, those with an addition of aluminum metal which was subsequently oxidized and reacted with the rejected silica from the kyanite, the resulting mullite density after firing at 1600 °C in air for 1 h, was high, 3.08 g/cc, also > 97% dense. The microstructure was also that of a fine equiaxed microstructure about 1 μm in average grain size, but without evidence of the classical mullite lath-like grain growth. This is suggestive that incorporating the RBAO process with attrition-milling to the nanoscale may have distinct advantages in microstructural control during subsequent firing of mullite ceramics. Similar to the simple alumina addition, this process was not optimized either, so it is probable that the technique can result in even more superior mullite technical ceramics than just described.

Summary and Conclusions

The effects of attrition milling of kyanite as a prototype of the sillimanite minerals was addressed relative to its formation of mullite, both with and without alumina additions, the latter to yield a phase-pure mullite. It was concluded that attrition milling to the nanoscale affects several aspects of this sillimanite group mineral. It decreases its decomposition temperature significantly, presumably because the very fine particle sizes experience a change in the kinetics of the decomposition reactions. One may also note that because the large volume expansion of the decomposition is eliminated that it also has profound effects on the decomposition reaction itself. Attrition also produces a much more reactive rejected silica that readily combines with

alumina additions to produce a phase-pure mullite. It is evident that combining the process of attrition milling to the nanoscale with that of a phase decomposition, or transition reaction can produce added benefits above and beyond those of just the particle size reduction.

In closing, the authors would be remiss if they did not state that the attrition milling process combined with decompositions and synthesis reactions, as described and summarized in this paper has much wider applications in ceramic science and technology. There is no reason why the principles discussed in this manuscript cannot be applied to minerals other than the sillimanites, such as kaolinite [17] or other clays. Neither must the end product be restricted to mullite, as other familiar high temperature ceramics such as cordierite could be similarly synthesized. Many variations are possible.

Acknowledgements

The authors gratefully acknowledge the assistance and contributions of numerous individuals including J. Marra of Alcoa, E. Anderson of Reynolds, G. Dixon of Virginia Kyanite for the supply of raw materials. One of the authors (J. A-S) is especially thankful to CONACYT for support of his graduate studies at IPN in Mexico and The University of Alabama in the USA.

References

1. L.A. Pozhar, V. F. de Almeida, and M.Z. Hu, *Bull. Am. Cer. Soc.* 83[5] 17 (2004).
2. E.R. Varley, *Sillimanite*, Chem. Pub. Co., New York, NY (1968).
3. M.J. Hibbard, *Mineralogy*, McGraw-Hill, New York, NY (2002).
4. H.H. Wilson, *Bull. Am. Cer. Soc.* 48[8] 796-97 (1969).
5. J. Grofcsik, *Mullite, Its Structure, Formation and Significance*, Hungarian Academy of Sciences, Budapest, Hungary (1961).
6. H. Schneider, K. Okada, and J.A. Pask, *Mullite and Mullite Ceramics*, J.S. Wiley, New York, NY (1994).
7. I. Peretz and R.C. Bradt, pp. 613-633 in *Ceramic Transactions*, 6, Proc. of Mullite and Mullite Composites edit. by S. Somiya, R.F. Davis, and J.A. Pask, Amer. Cer. Soc., Westerville, OH (1990).
8. J. Aguilar-Santillan, R. Cuenca-Alvarez, H. Balmori-Ramirez, and R.C. Bradt, *J. Am. Cer. Soc.* 85[10] (2002) 2425-31.
9. D.C. Jain, J.J. Brown, Jr. and C. Kay, *Bull. Am. Cer. Soc.* 53[9] (1974) 650-653.
10. H. Balmori-Ramirez, E. Torres-Torres, and R.C. Bradt, pp 233-247 in Proc. of Advances in the Met. Ind, III edited by M. Rigaud, TMS, Montreal, Canada (1999).
11. J. Kano, Y. Yoshizawa, and F. Saito, *J. Cer. Soc. Jap.* 34[5] (2000) 294-298.
12. D. Holz, D. Wu, S. Scheppokat, and N. Claussen, *J. Am. Cer. Soc.* 77[10] (1994) 2509-2517.
13. S. Lathabai, D.G. Hay, F. Wagner, and N. Claussen, *J. Am. Cer. Soc.* 79[1] (1996) 248-256.
14. J. Aguilar-Santillan, H. Balmori-Ramirez, and R.C. Bradt

(submitted to J. Am. Cer. Soc.)

15. H. Balmori-Ramirez, E. Rocha-Rangel, E. Refugio-Garcia, and R.C. Bradt, J. Am. Cer. Soc. 87[1] (2004) 144-146.
16. M.J. Watson, H.M. Chan, M.P. Harmer, and H.S. Caram, J. Am. Cer. Soc. 81[8] (1997) 2053-2060.
17. H.R. Rezaie, W.M. Rainforth, and W.E. Lee, Trans. Brit. Cer. Soc. 96[5] (1997) 181-187.