Study of Thermal Decomposition of Kyanite Using Density Measurements

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KYANITE, Al_2SiO_5, is one of the few commercially available minerals that is a source of relatively pure alumina and silica but does not contain significant amounts of interfering oxides (e.g. water, alkali and alkaline earth oxides, etc.).[1] Upon heating to high temperatures, kyanite decomposes to mullite plus small amounts of cristobalite according to the following reaction:[1,2]

$$3(Al_2O_3 \cdot SiO_2) \rightarrow 3Al_2O_3 \cdot 2SiO_2 + SiO_2$$

Reaction begins near 1200°C and becomes more and more rapid as temperature increases.[2-9] The rate of decomposition is also a function of kyanite particle size.[5,6,8,9] Decomposition is accompanied by a characteristic volume expansion (reduction of density) which can be as large as 15 to 17%.[5,6,9] As a result, kyanite is frequently used to counterbalance the shrinkage of other batch components in many refractory bodies.

For solid state reactions such as the kyanite decomposition in which there are sizable density changes, precision density measurements provide a useful way to 1) measure the extent of conversion, and 2) gain some insight into the kinetics of the reaction. The primary objective of the present study is to develop a procedure using pycnometric density measurements that is a quick, accurate and inexpensive method of measuring the degree of conversion of kyanite in commercial calcining processes. In addition, the kinetics of the thermal decomposition of two size fractions of kyanite are discussed and interpreted as far as possible in view of the density data presented.

Raw Materials

Commercial grade "35 mesh" kyanite* was used exclusively throughout this investigation. A typical chemical analysis of this material is listed in Table I. Of the two size fractions of kyanite used in this study, one, −35, +50 mesh, was obtained by selecting that material which passed a standard 35 mesh screen but was retained on a 50 mesh screen. A −200, +270 mesh fraction was obtained by wet grinding and screening "35 mesh" kyanite. Because kyanite particles have long thin blade-like shapes, many particles will or will not pass a certain size screen depending upon their orientation with respect to the screen surface. To more completely characterize the two size fractions, their particle size distributions were measured† (Fig. 1). According to these data (which actually reflect

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The thermal decomposition of kyanite to mullite and free silica is accompanied by a density reduction of 15 to 17%. Using pycnometric density measurements, this relatively large density differential was used to measure the degree of decomposition in two typical size fractions of commercial kyanite (−35, +50 and −200, +270 mesh) when heat treated for different lengths of time over the 1200° to 1400°C range. In addition to being a quick, accurate and inexpensive method of measuring the extent of decomposition, the density measurements provided results that indicated 1) there is no appreciable nucleation period in the decomposition of kyanite, and 2) there are two distinct stages in the decomposition with the first being very fast and apparently interface controlled and the second being much slower and probably dominated by the growth rate of mullite. The coarse size fraction obeys a linear reaction rate expression whereas the fine fraction fits a first order expression better. The activation energy for the former was calculated as 225 kcal/mole and for the latter, 132 kcal/mole.

Table I. Typical Chemical Analysis of Kyanite Used in This Investigation (wt%)

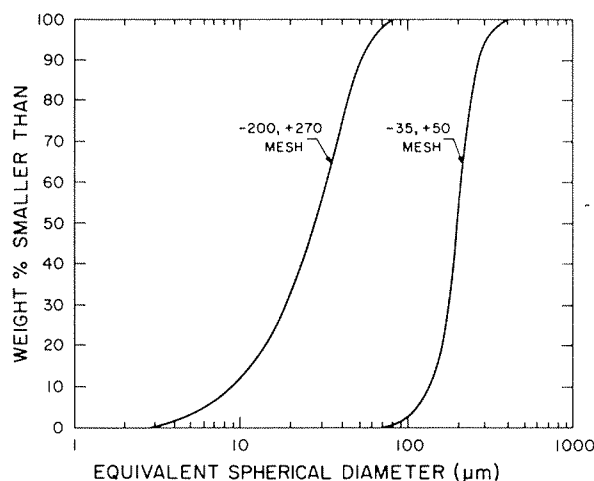|	
Alumina	59.06 to 61.80
Silica	38.65
Iron oxide	0.16 to 0.94
Titania	0.67
Lime	0.03
Magnesia	0.01
Alkalies	0.42
Ignition loss	0.21

Fig. 1. Particle size distribution of two size fractions of kyanite used for study.

the equivalent spherical diameters of the particles), the particles are appreciably smaller than the screen mesh designations suggest.

Although most of the alumina and silica indicated in Table I is tied up on the mineral kyanite, some free silica (quartz) is present as inclusions in the kyanite grains. In an effort to determine the amount of free silica present in the starting materials, 50 g samples of both size fractions were wet ground until they completely passed a 325 mesh screen. The −325 mesh material was then mixed thoroughly in a beaker with S-tetrabromoethane which has a density of 2.965 g/cm³, between that of quartz ($\rho \approx 2.65$ g/cm³) and kyanite ($\rho \approx 3.55$ g/cm³). The quartz content was determined by weighing the material that floated.

Density Measurements

Density was measured by using 50 ml capacity pycnometers.* The bottles were cleaned before each set of measurements with a solvent which consisted of a mixture of 37 ml saturated potassium dichromate or sodium dichromate with 1000 ml concentrated sulfuric acid. The pycnometers were completely immersed in the solution and heated to 140°C. After removal, each bottle was rinsed thoroughly with water followed by a final alcohol rinse.

The actual density measurements were conducted by weighing on an analytical balance to ±0.1 mg first the empty pycnometer bottle (W_p), and then the pycnometer filled with about 10 g of dry sample (W_{ps}). Next, the pycnometer bottle, still containing the sample, was filled $\approx \frac{2}{3}$ full of water and placed in a vacuum chamber until all entrapped air was removed. After the air was removed, the pycnometer was completely filled with water and weighed (W_{pst}). Finally, the pycnometer filled with water only was weighed (W_{pt}). All measurements were made at 25°C. The density of the sample was then calculated using the formula

$$d_s = \frac{(W_{ps} - W_p)\, \rho_w}{(W_{ps} - W_p) - (W_{pst} - W_{pt})}$$

where ρ_w = specific gravity of water at 25°C. The density of each sample was measured three times and the average value was used. The measurements were reproduced to ±1%.

Experimental Procedure

Approximately 100 g of both the −35, +50 and −200, +270 size fractions of kyanite were completely converted to mullite (and silica) by heating at 1450°C for two hours in an SiC furnace. To insure complete conversion, each sample was mixed thoroughly and reheated at the same temperature for two more hours. Complete conversion was verified by X-ray diffraction analysis and observations under the petrographic microscope. The densities of the starting kyanite and of the converted material for both size fractions were measured by the pycnometric method. Mechanical mixtures of kyanite and mullite (plus silica) for both size fractions were prepared at 10 wt% intervals between kyanite and mullite. Each preparation was thoroughly mixed and its density carefully measured. These data were used to establish a curve of density as a function of degree of conversion for both size fractions of kyanite.

A series of kyanite samples (≈ 35 g each) for both size fractions were heated in vitreous silica crucibles for different lengths of time at 1200°, 1250°, 1300°, 1350° and 1400°C. Temperature was controlled to ±15°C and time to within 1%. At the higher temperatures when the duration of the heat treatment was short, special care was taken to standardize the heat up conditions. Immediately prior to the insertion of the sample, the temperature of the furnace was increased slightly (the actual amount determined by trial and error) to compensate for the temperature drop that resulted from opening the small door when a sample was inserted. Three minutes were allowed for heat up of the samples before the actual time counting began. Each sample was kept relatively small and mass was kept as constant as possible from sample to sample. These procedures minimized, but did not totally eliminate, heat up effects. At the

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completion of the heat treatment, the samples were removed from the furnace and allowed to cool in air. After heat treatment, the density of each sample was carefully measured and the degree of conversion was determined from the density vs conversion curves for that particular size fraction of kyanite starting material. By successive increases in the time of heat treatment at each temperature, a plot of per cent conversion vs time was generated.

Experimental Results and Discussion

1). Construction of density vs per cent conversion curve - Using the sink-float method, the quartz contents of the −35, +50 and −200, +270 mesh size fractions of kyanite were found to be 0.4 and 0.6 wt%, respectively. This fact is reflected in Fig. 2 where the densities of the kyanite/mullite mechanical mixtures are plotted as a function of mullite content. The densities of the smaller size fraction are consistently slightly lower than those of the larger size fraction. It should be noted that although the abscissa indicates weight percent mullite, there is, in fact, an increasing amount of free silica present as the mullite content increases. The amount of mullite
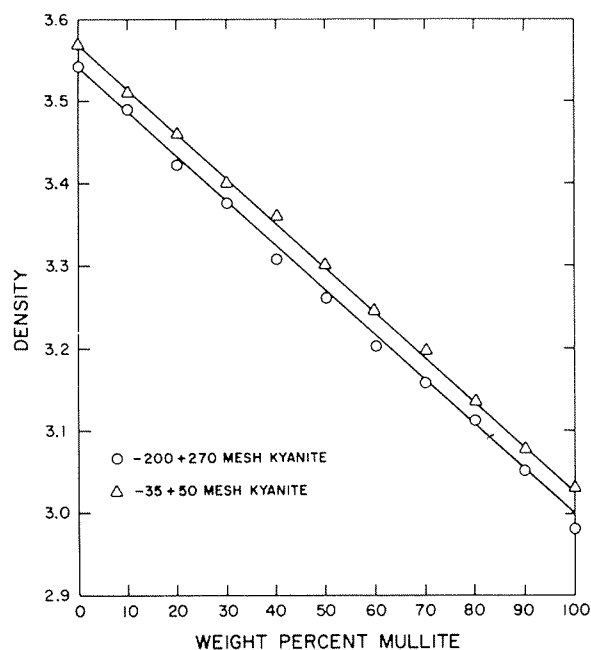

Fig. 2. Variation of density as a function of kyanite/mullite ratio for −35, +50 and −200, +270 mesh kyanite.

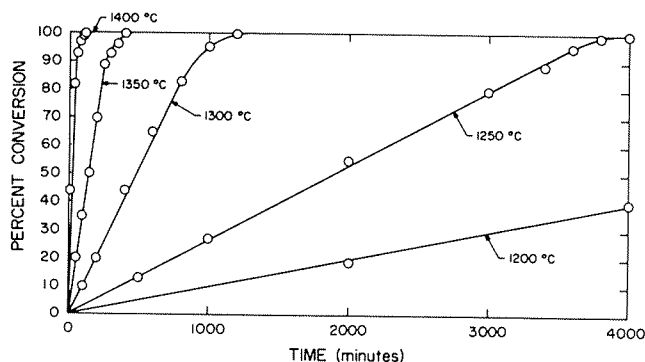*Distributed by Fisher Scientific Co., Pittsburgh, Pa.

Fig. 3. Variation of degree of conversion of kyanite to mullite as a function of time and temperature for −35, +270 mesh kyanite starting material.

Fig. 5. Effect of temperature on rate of conversion of kyanite to mullite.

present in the sample never reaches 100% even after complete conversion has taken place.

2). Decomposition of kyanite - Although the density technique described here appears to be extremely useful in measuring the extent of kyanite to mullite conversion, it is probably not the best method to study the kinetics of the reaction. Moreover, it must be noted that the starting materials used were commercial grade kyanite and that significant impurities were present. Nevertheless, it is instructive to extract as much kinetics information as possible from the data.

It was shown[10] that solid state reactions of the decomposition and transformation type are generally characterized by a period of nucleation of a new phase followed by a period when the new phase propagates in the old phase. These reactions generally provide a sigmoid percent transformation vs time curve, with the acceleratory period being dominated by the nucleation rate of the new phase and the deceleratory period by its growth rate. A long acceleratory period results if the activation energy for the nucleation process is considerably larger than that for growth.

Figure 3 shows the sigmoid reaction curves obtained by heating − 35, + 50 mesh kyanite at five different temperatures. The data are less reliable at the higher temperatures because the reaction times become very fast. It can be seen that 1) there is no induction period (nucleation is apparently instantaneous), and 2) there are two distinct stages in the kyanite decomposition. The first part of the curves, rising steeply in a linear fashion, apparently indicates a diffusion controlled growth period. In the second deceleratory period, the curves begin to level off as the conversion nears completion. In this part the conversion proceeds at a much slower rate, apparently dominated by the growth rate of mullite.[11]

Visual examination, under an optical microscope equipped with a hot stage, of kyanite particles undergoing conversion to mullite
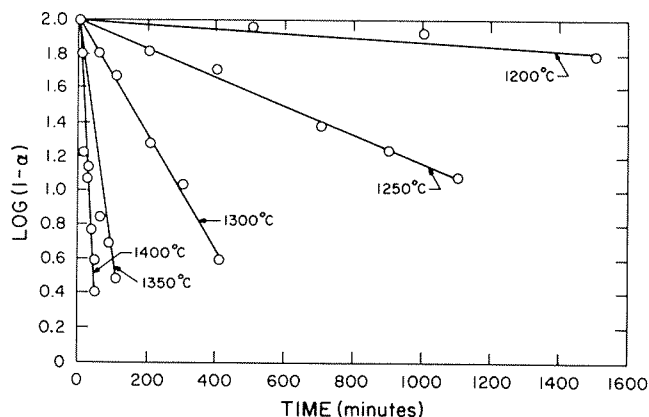

Fig. 4. Variation of degree of conversion of kyanite to mullite as a function of time and temperature for − 200, + 270 mesh kyanite starting material.
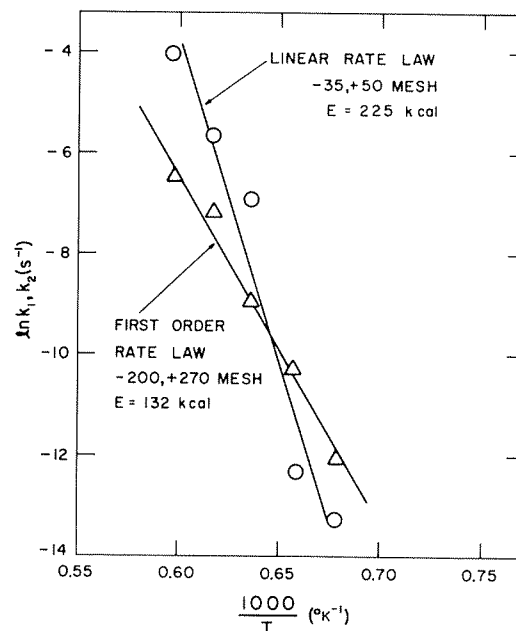
(and silica) showed that the reaction begins at grain boundaries and numerous surface cracks immediately appear. The appearance of these cracks together with the fact that volume decreases as kyanite decomposes to mullite, strongly suggests that the reaction initiates on the surface of the grains and proceeds inward. Individual grains of kyanite, only partially decomposed, showed unreacted cores. These facts, together with the long linear regions of the curves in Fig. 3 suggest that an interface controlled (linear kinetics) model of the type $\alpha = k_1 t + c$ where α is the fraction reacted can be used to describe the decomposition. With this model the rate is proportional to the particle surface area or the number of possible reaction sites per unit area. Because the rate is proportional to the surface area, the geometry of the crystals must be such that the interfacial area can remain constant throughout the reaction. In view of the long, thin blade-like shape of the kyanite particles, it is possible that the reaction could proceed in a face-wise direction in such a fashion that the interfacial area remains substantially constant during the reaction and gives rise to the long linear portion of the curve. A first order expression of the type $\ln(1 - \alpha) = k_2 t + c$ does not fit the data.

The decomposition data for the fine size fraction of kyanite (− 200, + 270 mesh) yielded sigmoid reaction curves similar to those of the coarse fraction except that 1) the acceleratory period was initially somewhat slower, and 2) the growth periods deviated from linearity. In this case the data fit a first order model (Fig. 4) much better than the linear expression. As was the case for the coarse size fraction, at higher temperatures the reaction times are so fast that the data can be interpreted equally well using either expression.

Assuming that the reaction initiates on the surface of the particles as optical data indicate, the difference in the kinetics of the two size fractions may reflect a difference in particle shape. In view of the long blade-like habit of kyanite, it is quite possible that screening produces proportionately more of the long thin grains in the coarser fractions than in the fine. If this is the case, then it follows that the interfacial area between the reacted and unreacted material can remain approximately constant longer for blade-like particles (coarse) than for the more equidimensional particles (fine). Linear kinetics require this interfacial area to remain nearly constant whereas first order kinetics suggests a "contracting sphere" type of interface.

Numerous other reaction models have been checked unsuccessfully.[12-15] Experimentally it seems impossible to determine positively a correct expression that fits all the data. This situation is an inherent difficulty in studying powder reactions,
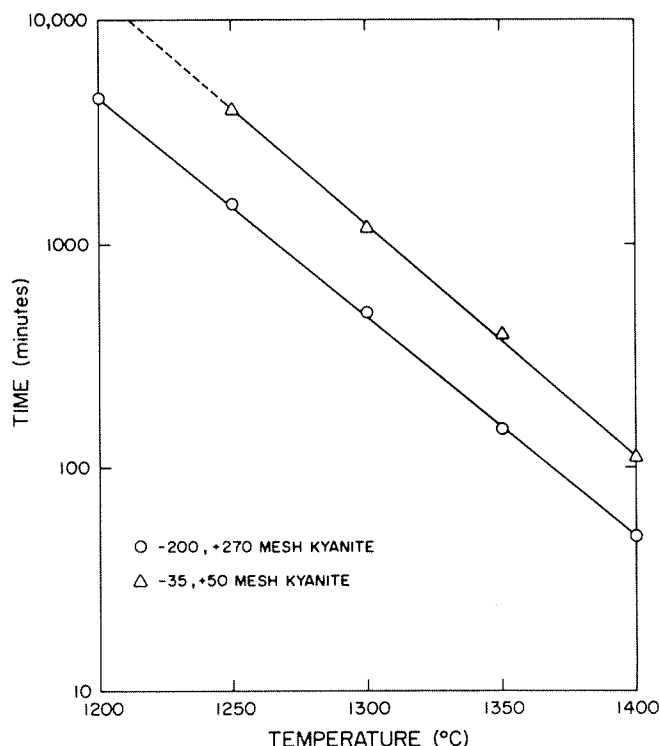
Fig. 6. Time required for complete conversion as a function of temperature.

especially kyanite where the geometry of the crystals is not certain and the particle size varies widely.

Arrhenius plots for the two size fractions are shown in Fig. 5, using the linear expression for the coarse size fraction and the first order expression for the fine fraction. The curves yield an activation energy for the coarse fraction of ≈ 225 kcal/mole and 132 kcal/mole for the fine. Considering the nature of the starting kyanite material, especially the difference in size and shape of the particles, the difference in the two activation energies as determined by different rate expressions is to be expected. Ordinarily activation energy should not change appreciably with changing particle size.

Figure 6 illustrates the time required for essentially complete conversion to take place as a function of temperature. Part of the difference between the two curves is a result of the different initial interfacial areas. In addition, diffusion distances especially in the latter stages of the reaction, may also be related to the particle size.

Summary

Precise density measurements can be easily used to accurately measure the extent of the kyanite decomposition. From a kinetics standpoint, the reaction appears to initiate on the surface of the kyanite grains and proceed inward. For coarse particles, a linear rate expression seems to fit the data best, but as the particle size decreases, a first order expression gives a better fit. Many factors such as impurities, particle size and shape, experimental technique, temperature and others must be carefully considered in using these data.

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