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BEHAVIOR OF KAOLINITE PELLETS AT ELEVATED TEMPERATURES

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Abstract—Dimensional changes in kaolinite pellets as a function of temperature show two sharp shrinkage "steps," at about 450–550°C and 900–980°C, which are roughly comparable in magnitude. Isothermal heat-soaking tests confirm that the rates for both are kinetically controlled. Water vapor inhibits shrinkage at low temperature but promotes shrinkage at high temperature. Both the former reaction, related to dehydroxylation, and the latter reaction, related to "mullitization," take place at temperatures well below those observed in DTA, TG, and other measurements, indicating that bond-breaking is a necessary prelude to transitions at higher temperatures.

Bonding energy changes, as measured by X-ray fluorescence shifts, were used in interpreting the phenomena involved. The relative absence of bonding energy changes in the aluminum until the range 950–1100°C, and the presence of such changes in the silicon, suggest that high-temperature energy release is probably related to segregation or crystallization of silica, rather than of an aluminum-containing phase. Caution must be used in interpreting bonding energy changes, and in distinguishing kinetic and thermodynamic contributions to dynamic phenomena.

Key Words—Dehydration, Dehydroxylation, Dilatometry, Kaolinite, Mullite, Spinel.

INTRODUCTION

The behavior of kaolinite as a function of temperature has been examined with some unconventional techniques. Linear dilatometry was applied to pelleted kaolinite using a duPont high-temperature thermomechanical analysis system operated in several different modes, and the results are compared with DTA, TG, and X-ray intensity data. Earlier work (Flank and Skeels, 1977) related expansion-contraction phenomena observed by X-ray powder diffraction and dilatometry, and showed that pelleted crystallite composites reflected single-crystal behavior. When different kinds of measurements are put on a comparable basis, reasonably good agreement between them is obtained, indicating that we are looking at different aspects of the same phenomenon.

Bonding energy changes were measured in heated samples by use of X-ray fluorescence wavelength shifts and peak intensities, to help interpret the nature of the observed phenomena. Recently developed techniques for the analysis of the X-ray spectra (Dowell et al., 1977; Flank and Skeels, 1977) have been used for this purpose. Interpretations of the data are discussed in terms of conventional mechanistic considerations.

EXPERIMENTAL PROCEDURES

Kaolinite pellets were subjected to thermomechanical analysis (TMA) under negligible load in a duPont Model 943 TMA system to study dimensional changes both isothermally at a series of temperatures, and with a linearly programmed rate of temperature increase of 10°C per minute. Experiments were carried out in both dried air and ambient temperature-saturated (20 torr) moist air purges, using a flow rate through the cell of 38 cm^3 per minute.

A calibration check of the temperature scale was performed with a quartz crystal in the TMA cell. Using a programmed temperature rate of 10°C per minute with a dried air purge, the α–β transition was measured in both the heating and cooling modes. As shown in Figure 1, the measured transition temperature is within a few degrees of the commonly accepted value of 572°C.

Isothermal curves were obtained in a time-based mode, with the temperature in the vicinity of the pelleted samples monitored via a second channel. The percent shrinkage from the original micrometer-measured pellet length was measured from the curves at 10-min intervals except in regions of rapidly changing slope, where appropriately shorter intervals were used.

X-ray powder diffraction intensity data were obtained with a Norelco diffractometer equipped with a pulse height analyzer and fitted with an MRC hot stage. Ni-filtered Cu-K_α radiation was used, with a scanning rate of 1° 2θ/min. The peaks used for measurement were those recommended by Carroll (1970) and are noted in Table 2.

X-ray fluorescence wavelength shifts in the Al-K_β and Si-K_β lines were measured using a Siemens SRS-1 instrument. The basic instrumental technique and computational procedure was described by Dowell et al. (1977). An improved version of this (Flank and Skeels, 1977), with about a fivefold improvement in RMS deviation, was used to resolve the asymmetric fluorescence peak into high-energy and low-energy components so that intensity ratios as well as energy shifts could be determined. The bonding energy shifts for Al and Si are measured relative to corundum and quartz standards, respectively.

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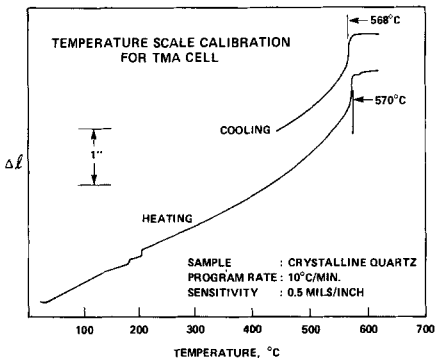


Fig. 1. Temperature scale calibration for TMA cell.

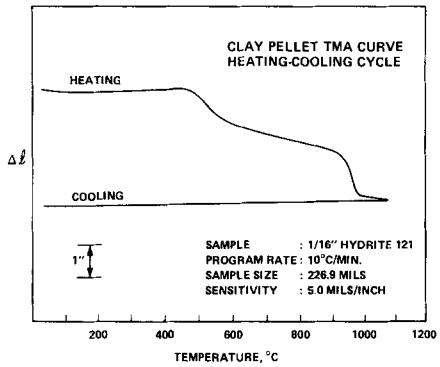


Fig. 2. Clay pellet TMA curve—heating-cooling cycle.

RESULTS AND DISCUSSION

A typical curve for a complete programmed TMA heating and cooling cycle is shown in Figure 2, using a $^1/_{16}$-inch diameter auger-extruded pellet made from an intermediate particle size kaolinite.[1] The moisture content for this extrusion was 44%, and the pellets were air-dried. Figure 3 shows an essentially identical curve for a $^3/_{32}$-inch diameter pellet made from a fine particle size kaolinite[2] which was extruded with a 34% moisture content and then air-dried. Two fairly sharp shrinkage "steps" of roughly comparable magnitude are seen at about 450–550°C and 900–980°C. The first step appears to be related to dehydroxylation and the second to "mullitization," but the temperatures at which they occur are somewhat below those commonly observed for such transitions in DTA, TG, and other measurements. Similar data obtained with other materials show the same relationship, i.e., different techniques show different temperatures for the same changes (Flank and Skeels, 1977). This can be interpreted as suggesting that bond-breaking is a necessary prelude to phase changes and other types of transitions that occur at higher temperatures.

It is still possible to observe the above-noted shrinkage "steps" when clay is incorporated as a bonding agent with a material such as a 4A molecular sieve, as illustrated in Figure 4. A small step can be consistently noted in the 450–550°C region, as well as the further shrinkage that occurs above 900°C after collapse of the molecular sieve structure (Flank, 1974; Flank and Skeels, 1977). It is thus unlikely that the steps are artifacts of the pelleted clay form.

Low-temperature dilatometric data

The kinetic nature of the low-temperature shrinkage step was examined in a series of isothermal experiments conducted at several temperatures. An example of such a run is shown in Figure 5. The mass-action effect of water vapor was investigated by repeating these experiments with a moist air purge instead of a dried air purge. The results, shown in Figure 6, strongly support the conclusion that the low-temperature shrinkage step is related to dehydroxylation of the clay. The inhibition of shrinkage rate by water vapor is quite pronounced, and is analogous to the rate retardation found earlier in DTA measurements by, for example, Stone (1952). It is also clear that shrinkage, and by implication dehydroxylation, can occur at finite rates at modest temperatures. Grim (1968) notes that studies have been reported of complete dehydration of kaolinite at temperatures as low as 350°C, with use of very long heating times.

Shrinkage rates can be estimated from the initial linear portion (which can be taken to approximate first-order kinetics) of the curves shown in Figure 6, or by use of the first-order relation $k = \ln 2/t_{0.5}$ where $t_{0.5}$ is the time required for half of the total shrinkage to occur. Using these rates, Arrhenius temperature coefficients can be calculated and compared. True activation energies cannot be derived in this system because of significant, but indeterminate, entropy contributions. The ratio of the temperature coefficient for the moist air rates to that for the dried air rates was found to be 1.60 using the initial linear portions of the rate curves, and 1.52 using the half-time relation.

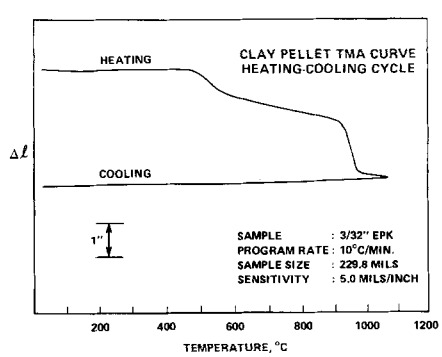


Fig. 3. Clay pellet TMA curve—heating-cooling cycle.

[1] Hydrite 121, produced by Georgia Kaolin Co.

[2] Edgar Plastic Kaolin, produced by NL Industries.

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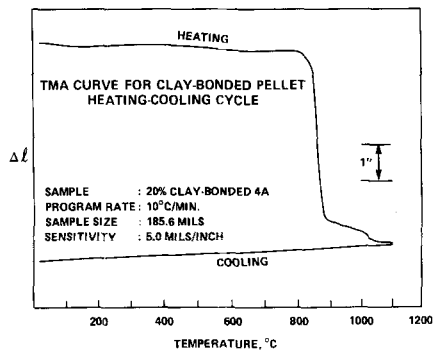


Fig. 4. TMA curve for clay-bonded pellet—heating-cooling cycle.

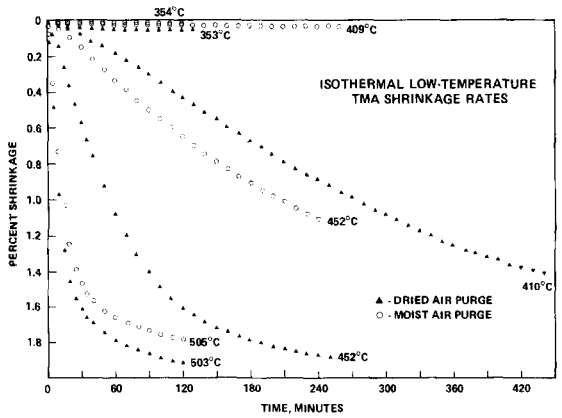


Fig. 6. Isothermal low-temperature TMA shrinkage rates.

The shrinkage rate also can be expressed in terms of the percentage of the total step shrinkage occurring per minute at the point of maximum slope. The rate of weight loss in a TG experiment can be similarly expressed in terms of the percentage of the total weight loss occurring per minute. A comparison of such data is shown in Table 1. Reasonably good agreement can be seen, suggesting that we are looking at different manifestations of the same phenomenon.

X-ray data

Some X-ray powder diffraction intensity measurements were made on a sample of the Hydrite 121 clay after heating at successively more severe conditions, to compare the loss in ordering with the TMA data. As shown in Table 2, structural ordering is lost at a modest rate at the milder conditions, but the loss becomes precipitous at about 500°C. Taking the time factors into consideration, these X-ray powder data are found to be in excellent correspondence with the TMA rate data shown in Figure 6.

High-temperature dilatometric data

The high-temperature shrinkage step also was studied in a series of isothermal TMA experiments with moist and dried air purges. An example of one of these curves is shown in Figure 7. Measurements were taken from the generally fairly distinct inflection point as the cell approached isothermal conditions, and were referred to the original micrometer-measured pellet length. The contribution from the "tail" of the low-temperature step was not taken into account, since the degree of shrinkage occurring prior to the inflection point agreed fairly well with similar measurements made in temperature-programmed runs, indicating that such contribution was not large.

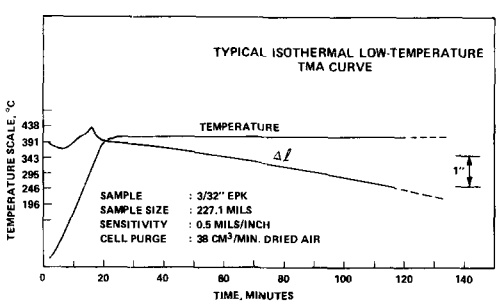


Fig. 5. Typical isothermal low-temperature TMA curve.

The results from the high-temperature shrinkage studies are shown in Figure 8. They indicate that the activation energy for the "mullitization" reaction is comparatively modest and that the reaction proceeds at a measurable rate even at 100° below the sharp 980°C initiation temperature commonly observed in DTA curves. There seems to be a small but distinct promotion effect attributable to the presence of moisture in the purge gas. Mechanistic interpretations for this include the possible provision of a hydrolytic degradation pathway and the promotion of high-temperature silica migration by water vapor. Similar explanations for high-temperature steaming effects have been used for other materials, such as silicas and aluminosilicates (Flank, 1974).

Arrhenius temperature coefficients were also calculated from the moist air and dried air-purged shrinkage rates, using the half-time relation noted earlier. The ratio of the moist air to dried air temperature coefficient is 0.78, about half that found for the moisture-retarded dehydroxylation process.

A comparison can be made between the shrinkage profiles at high temperature for a pellet subjected to an abrupt temperature jump and one subjected to slow

Table 1. Comparison of TMA and TG data.

Edgar plastic kaolin	Percent of total change at ~500°C	
	Shrinkage by TMA	Weight loss by TG
Dried air purge	3.7%/min	4.4%/min
Moist air purge	3.5%/min	

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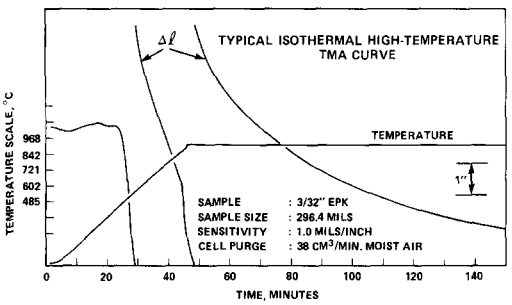


Fig. 7. Typical isothermal high-temperature TMA curve.

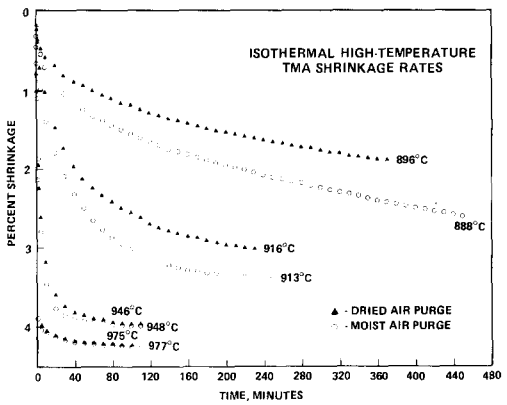


Fig. 8. Isothermal high-temperature TMA shrinkage rates.

stepwise temperature increments. As shown in Figure 9, after establishing a reasonably steady state at 740°C, an abrupt temperature jump gives rise to a precipitous rate of shrinkage. Raising the temperature in increments, however, demonstrates the kinetically controlled nature of the process and the fact that it is occurring at relatively low temperatures.

Figure 9 shows that, with each temperature increment, a progressively larger and more rapid shrinkage occurs, up to the point where the major portion of the transition has already taken place. Comparatively little more occurs above 935°C, but by this time the sample has been heated for more than 7 hr. A gross estimate of the shrinkage rates at the temperature steps shows reasonable agreement with rate data calculated via the half-time relation from the isothermal curves in Figure 8, at least up to the increment to 935°C.

Bonding energy data

The nature of the bonding in Hydrite 121 clay samples, which were muffle-calcined for 1 hr at a series of temperatures, was investigated via measurement of the X-ray fluorescence wavelength shifts and peak intensities for the Al-K_β and Si-K_β lines. These changes reflect bonding energy changes resulting from variations in coordination, bond angle and bond length, and the concentration of structural defects and interstitial atoms, induced by the thermal treatments. For example, it has been shown that, in octahedral oxides, the two components of the Al-K_β peak are of roughly similar intensity, but that if tetrahedral Al is present the high-energy ΔE_1 component becomes a weak shoulder (Flank and Skeels, 1977). The components of the Si-K_β line show a similar kind of relationship when perturbation of the Si–O bonds results in less efficient bonding orbital overlap.

While bonding energy changes cannot easily be directly related to a specific structure, they can be used to indicate the energetic direction and nature of the structural changes that occur. In Figure 10 the higher-energy ΔE_1 component of the Si-K_β band shifts toward lower or more stable bonding energies as calcination temperature increases to the dehydroxylation range. A lower bonding energy implies that the electron involved occupies a lower energy level with respect to the nucleus. This shift might thus be interpreted as an annealing of disorder present in the layer structure of the clay.

In the dehydroxylation temperature range, the ΔE_1 component increases sharply in bonding energy and then levels out, suggesting defect formation, structural disorder, and possibly an increase in bond length or incipient phase segregation. The lower-energy ΔE_2 component remains at the same bonding energy level until about 850°C and then drops to lower energies, which

Table 2. Kaolinite X-ray diffraction intensity after heating.

Conditions	Intensity of peak at: 12.4° 2θ	24.9° 2θ
—	31	42
0.5 hr at 400°C	33	40
2 hr at 400°C	26	31
0.5 hr at 444°C	23	30
0.5 hr at 500°C	6	6
0.25 hr at 600°C	3	3

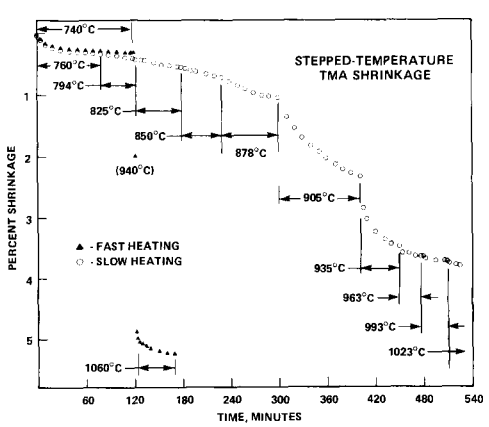


Fig. 9. Stepped-temperature TMA shrinkage.

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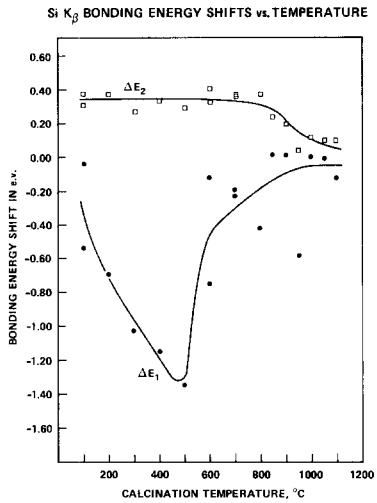


Fig. 10. Si-K_β bonding energy shifts vs. temperature.

would be consistent with the formation of a more stable coherent structure like β-quartz and eventually cristobalite and mullite.

In Figure 11 the higher-energy ΔE_1 Al component remains stable up to the dehydroxylation temperature range, then gradually shifts to higher energies at high temperature. The lower-energy ΔE_2 Al component is unchanged until dehydroxylation, then jumps sharply to much higher energies, falling off slightly beyond about 950°C. This last change is suggestive of incorporation into the more stable mullite structure.

The $\Delta E_1/\Delta E_2$ intensity ratios, shown in Figure 12, indicate a sharp change for the Al atoms at dehydroxylation from higher-energy band predominance to approximately equal contributions, then increasing slightly beyond about 950°C to favor the higher-energy band again. The intensity ratios for the Si atoms show

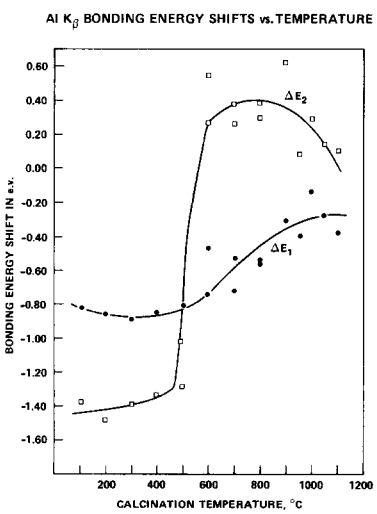


Fig. 11. Al-K_β bonding energy shifts vs. temperature.

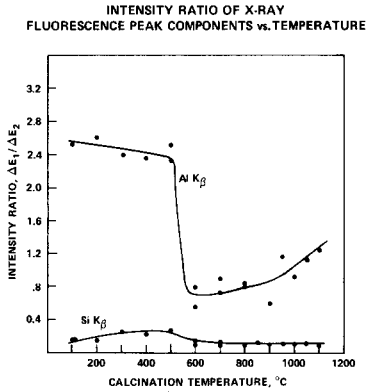


Fig. 12. Intensity ratio of X-ray fluorescence peak components vs. temperature.

that the higher-energy band contribution is small, increasing very slightly to about 500°C, then dropping and remaining quite low thereafter. The lower-energy band is thus the major contributor to the overall Si-K_β peak.

The bonding energy changes for Al suggest that, during dehydroxylation, coordination disorder and structural defects arise, involving changes in bond angles and bond lengths, all of which are related to higher energy states. Eventually, at much higher temperatures (beyond about 950°C), lower bonding energies are achieved by formation of a stable structure such as mullite. The absence of lower bonding energies below 950°C, and the absence of a substantial decrease in the high-energy band intensity, support the view that an intermediate phase involving tetrahedral Al is not formed in the system. Since there should be at least some dependence on coordination, some change might have been expected if tetrahedral Al were formed. While this is not observed, the converse is not as clear-cut, i.e., factors other than coordination change could contribute to observed bonding energy shifts.

The bonding energy changes for Si suggest some kind of annealing process up to the temperature of dehydroxylation, followed by a higher-energy disordered state. A more stable structure appears to form at about 850°C and may involve silica segregation and crystallization in the early stages of the overall mullitization process, followed by further crystallization of mullite and cristobalite at somewhat higher temperatures.

DISCUSSION OF EARLIER WORK

These results and conclusions can be compared with earlier discussions in the literature, and a logical starting point is the comprehensive survey of the voluminous earlier studies published by Brindley and coworkers (Brindley and Nakahira, 1959; Brindley and McKinstry, 1961). In this four-part work, single-crystal X-ray diffraction studies provided the basis for concluding that the kaolinite-metakaolin-mullite reaction series is primarily characterized by structural conti-

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nuity and orderly recrystallization processes. Metakaolin retains a considerable degree of structural ordering, albeit mostly short-range and primarily two-dimensional, even though the initial kaolinite three-dimensional regularity has been disrupted. A silicon-containing aluminum spinel-type structure was postulated as being an essential intermediate phase, with mullite being formed from this unstable transition stage along with cristobalite. The mullite phase, it was suggested, undergoes progressive compositional change as the reaction proceeds. It was further concluded, on the basis of Al-K_α wavelength shifts, that the Al atoms in metakaolin are in fourfold coordination and revert to sixfold coordination upon calcination at 1024°C. The data obtained in the present work, however, are inconsistent with the formation of an intermediate phase involving tetrahedral aluminum. As has been noted earlier, bonding energy changes cannot be directly related to specific structures or solely to changes in formal coordination.

The experimental and thermodynamic studies of Schieltz and Soliman (1966) showed that, among the possible high-temperature transformations of metakaolin, that which produced mullite provided the greatest enthalpic energy release. It was further shown that the crystallization energy for mullite at 980°C is about 9 times that for an aluminum spinel at this temperature, the latter's crystallization energy in turn being about 5 times that for crystalline silica. Silica crystallization, while it contributes about 8% of the total mullite energy release, is not, however, central to the thermodynamic argument. It was also observed that coexistence of mullite and an aluminum spinel at 980°C would result in a lower net energy release. While such coexistence is possible as a consequence of kinetic factors, Schieltz and Soliman (1966) found that the crystallization of the aluminum phase was very slow, especially in comparison with mullite. However, it may not be necessary to provide a maximum-enthalpy explanation.

Measurement of the heat released at 980°C by differential thermal calorimetry allowed Nicholson and Fulrath (1970) to compare their experimental value of 9 kcal per mole of kaolinite with a calculated value of 9.1 kcal per mole for the enthalpy of crystallization of amorphous silica to β-quartz. They postulated that, at this stage, 1 mole of the 4/3 moles potentially available had been segregated from the metakaolin, citing evidence presented by Brindley and Nakahira (1959). They then concluded that silica crystallization was primarily responsible for the observed heat release, since the other phases present at 980°C appear at lower temperatures and form continuously. It can be suggested further that kinetically controlled bond-breaking, migration, and phase segregation processes combine to produce a critical concentration for silica crystallization. The results of Nicholson and Fulrath (1970) were supported by a demonstration that metakaolin, from which amorphous silica had been leached by NaOH solution, did not exhibit an exotherm. It is unlikely that these workers affected significant amounts of other components in this latter experiment, since to do so would have produced a crystalline reaction product with the NaOH which would have exhibited a distinctive DTA exotherm (Flank, 1974). This exotherm occurs at about 870°C, and no residual X-ray powder diffraction lines from such a product can be seen in a sample heated to 1000°C (Ambs and Flank, 1969), casting doubt on Chakraborty and Ghosh's reexamination (1977) of the work of Nicholson and Fulrath (1970).

Kinetic studies suggesting a nucleation-controlled reaction to form mullite were reported by Duncan et al. (1969). A comparison of experimental rate data with theoretical rate equations based on various solid-state processes led to the conclusion that the reaction mechanism involved lattice reordering, leading to nucleation of mullite, rather than phase-boundary-controlled crystal growth or long-range diffusional processes.

Kinetic studies on the dehydroxylation of kaolinite by Johnson and Kessler (1969) showed that the rate was proportional to the surface area of the particles, and that the data did not fit either a radial diffusion-controlled or a phase-boundary-controlled reaction, even when the particle size distribution was taken into account. They concluded that the reaction proceeds by a pseudophase-boundary-controlled path in a direction normal to the layer structure, and is mediated by the water partial pressure gradient through the interior of the polycrystalline particle.

A picture involving phase segregation and crystallization of silica, followed at higher temperature by crystallite growth of silica, and nucleation and growth of mullite crystallites, is compatible with the scanning electron microscopy evidence presented by Segnit and Anderson (1971). These workers showed that little morphological change is evidenced below a 1200°C kaolinite firing temperature, indicating that radical recrystallization to mullite and cristobalite has not yet taken place, but X-ray powder diffraction data for samples fired at or below this temperature establish that mullite nucleation has already occurred. Exothermic mullite crystallization from several amorphous aluminosilicate phases has been observed between 1000–1100°C (Ambs and Flank, 1969), with sharpening of the diffraction lines upon heating for longer times or at higher temperatures. Grim (1968) has noted some of the factors and impurity effects involved in the "mullitization" process, and mineralizer effects have been reported recently by Lemaitre and Delmon (1977).

The importance of distinguishing both kinetic and thermodynamic contributions to dynamic phenomena observed by different techniques is borne out by the work of Jernigan and McAtee (1974). They noted that loss of metakaolin structure is observed at much lower temperature in hot-stage electron microscopy than in

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DTA and X-ray powder diffraction studies. This was attributed to the prolonged heating times employed, in contrast to the relatively short exposure used in DTA and other techniques. They also noted that there is little evidence from electron diffraction data that an aluminum spinel is present at 1000°C, although it may be present at lower temperature, along with mullite.

If the effect of dehydroxylation on the density of heated kaolinite pellets is considered, the density changes indicated by the linear shrinkage found in the present work are in good general agreement with those critically discussed by Freund (1973) who reasonably proposed an entropy driving force for the high-temperature energy release in kaolinite and other layer silicates, postulating that a highly defective structure collapses to a more dense close-anion packing. However, it is claimed that "the relative stability of metakaolin between 600°C to nearly 1000°C is due to the fact that, in the absence of fluxes, the activation energy needed to rupture Si–O bonds is quite high." Since it is evident from the present work that a kinetic factor is involved in this high-temperature reaction, it may be more reasonable to attribute energy release to silica segregation and recrystallization upon attainment of a critical precipitation concentration.

X-ray emission wavelength shifts were also measured by Freund (1973) and interpreted narrowly on the basis of coordination change, although a number of other major contributions to the bonding energy are now recognized. A distorted defect structure need not be force-fit into a regular tetrahedral or octahedral array. Furthermore, the concept of relative stability for metakaolin extending over a range of about 400°C is strongly contradicted by the substantial and nonlinear chemical reactivity changes reported by Nagai (1936) over this temperature range, which the author has been able to repeat and confirm. Grim (1968) also cites several studies related to this same point.

Some of the disparate observations in the literature regarding high-temperature phases may be explainable on the basis of data reported by Korneva and Yusupov (1976). With increasing extent of dry grinding, the kaolinite structure was destroyed and the intensity of the exothermic DTA peak was increased. This, in turn, was related to the amount of mullite detected by X-ray powder diffraction. With wet grinding, the kaolinite structure was only partially destroyed, but the DTA exotherm intensity was reduced and γ-alumina was observed rather than mullite. Bond-breaking and phase segregation of stabilized species can thus be sufficiently enhanced, under some extreme circumstances, to permit the appearance of a γ-alumina or silicon-containing spinel phase prior to mullite formation. What is actually observed in a given experiment may well depend on whether kinetic or thermodynamic effects predominate.

CONCLUSIONS

While a definitive description of the mechanistic steps involved in the transitions of kaolinite at elevated temperatures still cannot be given, several relevant findings can be pointed out. Both dehydroxylation and "mullitization" are kinetically controlled and are affected by water vapor, but not equally. Various types of measurements show fairly good agreement when put on comparable bases, and indicate that bond-breaking, migration, and crystallization processes are normally involved in kaolinite transitions. An unstable tetrahedral aluminum phase does not seem to be formed in the system, and the high-temperature energy release phenomenon is most likely associated with silica crystallization.

Finally, it has been pointed out that bonding energy changes cannot be interpreted strictly on the basis of formal coordination state, but must include substantial defect and disorder contributions. Care must also be taken to distinguish kinetic and thermodynamic contributions, especially when considering a dynamic effect such as a DTA endotherm or exotherm, which may involve a number of factors rolled up together.

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Резюме- Размерные изменения шариков каолина как функции температуры показывают два резких этапа в сокращении,один при низкой температуре и один при высокой температуре,которые приблизительно сравнимы по величине. Изотермические испытания прогреванием подтверждают,что скорости обоих контролируются кинетически. Водяной пар замедляет скорость сокращения при низкой температуре,но ускоряет сокращение при высокой температуре. Как первая реакция,связанная с дегидроксилированием,так и вторая,связанная с "муллитизацией",имеют место при температурах значительно ниже тех,которые наблюдались при дифференциальном термальном и термо-гравиметрическом анализах и других типах измерений. Это указывает,что разрушение связей является необходимой прелюдией к превращениям при высоких температурах.

Изменения энергии связей,измеренные по рентгеновскому флуоресцентному смещению,использовались в помощь интерпретации природы наблюдавшихся явлений. Относительное отсутствие изменений энергии связей в алюминии до температуры 950-1100°C и наличие таких изменений в кремнии позволяют предположить,что высокотемпературное высвобождение энергии возможно связано с сегрегацией или кристаллизацией двуокиси кремния скорее,чем содержащей алюминий фазы. Следует проявлять осторожность при интерпретации изменений энергии связей и при определении кинетической и термодинамической составляющих в динамических явлениях.

Kurzreferat- Kaolinitkörnchen,die dreidimensionale Veränderungen als eine Funktion der Temperatur untergehen,zeigen zwei scharfe Schrumpfungsstufen bei etwa 450-550°C und bei 900-980°C,beide von etwa gleicher Größe.Isothermische Hitze-Einweich Versuche bestätigen,daß die Geschwindigkeiten für beide kinetisch kontrolliert werden.Wasserdampf unterdrückt das Schrumpfen bei niedriger Temperatur aber fördert Schrumpfen bei hoher Temperatur.Sowohl die erste Reaktion,die mit Dehydroxylierung verwandt ist,wie auch die letzte Reaktion,die mit "Mullitisation" verwandt ist,nehmen bei Temperaturen statt,die viel niedriger sind als die für DTA,TG und andere Messungen,was andeutet,daß Brechen von Bindungen notwendig ist,um Übergang bei höheren Temperaturen zu erhalten.Änderungen in Bindungsenergien,gemessen mit Röntgenfluoreszenzverschiebungen,werden benutzt,um die Phenomena zu interpretieren.Die relative Abwesenheit von Änderungen in Bindungsenergien bis 950-1100°C im Aluminium und die Anwesenheit dieser Änderungen im Silizium,deutet an,daß Freilassung von Energie bei hohen Temperaturen wahrscheinlich mehr mit Ausscheidung oder Kristallisation der Kieselerde verbunden ist als mit einer Phase,die Aluminium enthält.Vorsicht muß benutzt werden,wenn die Änderungen in Bindungsenergien interpretiert werden,und es ist wichtig,kinetische von thermodynamischen Beitragungen zu dynamischen Phenomena zu unterscheiden.

Résumé-Les changements de dimensions de boulettes de kaolin en fonction de la température montrent deux "étapes" accentuées de retrécissement,l'une à basse température et l'autre à température élevée,et qui sont à peu près d'importance égale.Des tests isothermiques d'échauffement confirment que les vitesses de réaction sont kinétiquement contrôlées pour les deux.La vapeur d'eau réprime la vitesse de retrécissement à basse température,mais l'encourage à haute température.La première réaction,due à la déshydroxylation,et la seconde,due à la "mullitisation",se passent toutes deux à des températures bien au-dessous de celles observées en DTA,TG,et d'autres sortes de mesures.Ceci indique que la brisure de liens est une étape nécéssaire à des transitions à de plus hautes températures.Les changements d'énegie de liaison,mesurés par des décalages de fluorescence de rayons-X,ont été utilisés pour aider à interpréter la nature du phénomène en question. L'absence relative de changements d'énergie de liaison dans l'aluminium jusqu'à 950-1100°C, et la présence de ces changements dans la silice,suggére que la libération d'énergie à température élevée est sans doute apparentée à la ségrégation ou à la cristallisation de silice,plutôt qu'à une phase contenant de l'aluminium.Il faut interpréter les changements d'énergie de liaison,et distinguer les contributions kinétiques et thermodynamiques au phénomène dynamique avec prudence.

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