

The non-isothermal kinetics of mullite formation in mechanically activated kaolinite–alumina ceramic system

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Abstract The non-isothermal kinetics of mullite formation from both non-activated and mechanically activated kaolinite + alumina ceramic system have been studied by differential thermal analysis (DTA). The mixture of kaolinite and alumina was activated mechanically in a planetary mill, while amorphization in the kaolinite and alumina structure was studied by X-ray diffraction analysis. The activation energies depending on the conversion for mullite formation have been calculated from the DTA curves by using the non-isothermal method of Coats and Redfern at heating rates of 5, 10, 15, and 20 °C min⁻¹. The mechanical activation of the kaolinite and alumina mixture resulted in the decrease in activation energy values for mullite formation.

Keywords Kaolinite · Alumina · Mullite · Mechanical activation · Non-isothermal kinetics

Introduction

Mullite (3Al₂O₃·2SiO₂) is known for its several important properties such as good chemical inertness, low thermal conductivity, high creep resistance, high refractoriness, and low thermal expansion coefficient. It is an important phase in conventional ceramics (such as tableware, construction ceramics, and refractories), advanced high-temperature structural materials, heat exchangers, catalysator converters, filters, optical devices, and electronic packaging materials. For most applications, mullite is synthetically

made with predominance of reaction sintering from alumina and silica precursors [1, 2].

Mullite can be prepared from a variety of starting materials, all of which follow more or less different mullitization routes on heating [3]. These pathways fall into two broad categories, i.e., (1) mullite formation above 1200 °C via an γ -Al₂O₃ precursor, and (2) direct formation of Al-rich mullite at about 900–1000 °C [3, 4]. Liu et al. [5] studied the primary and secondary mullite formation in high kaolinite- α -alumina and reported that monosized primary mullite was formed in plate-like kaolinite at 1300 °C or below. Sahnoune et al. [6] synthesized mullite through reaction sintering of Algerian kaolinite and high purity alumina. In their study, ball-milled kaolinite and alumina samples were maintained at different temperatures, complete transformation of kaolinite took place at 700 °C and the primary mullite phase started to form from the interaction of amorphous SiO₂ either with alumina of the kaolinite or the spinel phase from metakaolinite at 1150 °C. Temujin et al. [7] investigated the phase evolution behavior of kaolinite–gibbsite mixtures by mechanochemical treatment and they reported that grinding mixtures of kaolinite and gibbsite produced a poorly homogeneous mullite precursor which behaved on thermal treatment more like a mixture of kaolinite- α -alumina. Viswabaskaran et al. [8] prepared the stoichiometric mullite by reacting sintering, using the clay and reactive alumina as the starting materials and reported that clay and reactive alumina completely reacted at 1600 °C and formed mullite phase. Liu and Thomas [9] investigated the time–temperature–transformation curves for kaolinite- α -alumina and they stated that there was very little difference in the thermal behavior of kaolinite- α -alumina and kaolinite and α -alumina has no any effect on primer mullite formation up to 1150 °C.

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Many researchers have investigated the kinetics of mullitization, all reporting that mullitization occurs by nucleation-growth mechanisms. Okada [3] summarized the activation energy values for mullitization from various starting materials (such as diphasic gel, monophasic gel, hybrid gel, coprecipitated gel, sol mix, glass fiber, glass, kaolinite + alumina), and discussed the reasons for the unusually large activation energy values. Chen et al. [10, 11] reported that the unreacted alumina powder dispersed in the kaolinite–alumina ceramics reduces homogeneity and makes difficult the mullite transformation in the first stage.

Milling an inorganic materials causes the disintegration of particles and the consequent formation of new active surfaces in addition to changes in its physicochemical properties that decrease its crystallinity (though amorphization) and increase its surface reactivity. These mechanochemical effects are observed mainly when the material is milled using equipment involving friction and impact forces on particles (e.g., vibratory, oscillating, or planetary milled) [12]. Mechanical activation, which results in reduced crystalline size and induces residual stress to the particles, is responsible for such a phenomenon. In some cases, chemical reactions may further take place during milling in some others, the reaction temperature may be lowered, depend on the amount of energy stored in the particles [13]. Mechanical treatment in a high energy mill generates a stress field within the solids. Stress relaxation can occur via several channels: (1) heat release (2) development of surface area as a result of brittle fracture of the particles (3) generation of various sorts of structural defects and (4) stimulation of chemical reactions within the solids. All of the relaxation channels cause changes in the reactivity of the solid substance that is under treatment, which is why the resulting action is called mechanical activation [14]. The concentration of the mechanically induced defects and their spatial distribution depend upon the condition of the energy transfer in the mill. The creation of defects enhances the stored energy in the solids and consequently causes a decrease in the activation barrier for the process and/or subsequent processes [15].

In this study, the effects of mechanical activation on structural disordering (amorphization) in kaolinite–alumina ceramics system were analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM), and differential

thermal analyses (DTA). Also, the crystallization kinetics of mullite for non-activated and activated kaolinite–alumina ceramic system was investigated using DTA.

Experimental

Kaolinite and alumina were supplied from Çelvit Company, Turkey. The chemical compositions of the raw materials are given in Table 1. Kaolinite and alumina were mixed corresponding to stoichiometric according to chemical formula of mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) in ashless rubber-lined ceramic jars for 2 h using zirconia balls and distilled water as the milling media. After drying, the mixture was carried out a high-energy planetary ball mill (Fristch) with a rotation speed 600 rpm. Ball-to-powder weight ratio was adjusted to 20. The precursor milling was carried out for 2 h.

X-ray diffraction analysis was performed using a Rigaku Ultima X-ray diffractometer and $\text{CuK}\alpha$ radiation. A Joel 6060 LV scanning electron microscope was used for morphological analysis of non-activated and activated mixed powders. The degree of amorphization (%A) mechanical activated was calculated from Eq. 1 [16, 17],

$$\%A = \left[1 - \frac{B_o \cdot I_x}{B_x \cdot I_o} \right] \cdot 100 \quad (1)$$

where I_o is the integral intensity of the diffraction peak for non-activated mixture, B_o is the background of the diffraction peak for non-activated mixture and I_x and B_x are equivalent values for mechanically activated mixture.

The activation energies depending on the conversion (α) for mullitization were calculated with the Coats & Redfern equation (see Eq. 2) [18] by using the data in the Differential Thermal Analysis (TA Instruments SDTQ 600) at heating rates of 5, 10, 15, and 20 $^\circ\text{C min}^{-1}$ under an air atmosphere;

$$\ln(\beta_i/T_{\alpha,i}^2) = \text{Cons.} - (E_\alpha/R \cdot T_{\alpha,i}) \quad (2)$$

where β_i is the heating rate, $T_{\alpha,i}$ is the temperature at a given conversion (α), E_α is the activation energy, and R is the gas constant. A plot of $\ln(\beta_i/T_{\alpha,i}^2)$ versus $(1000/T_{\alpha,i})$ corresponding to different conversions α can be obtained by a linear regress of least-square method. The activation energies E_α can be calculated from the slopes of every line.

Table 1 Chemical composition of raw materials

	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	Na_2O	MgO	TiO_2	L.O.I ^a
Kaolinite [Ref. 2]	52.12	33.83	0.55	0.15	0.13	0.01	0.05	0.45	12.45
Alumina	0.52	99.425	–	–	–	0.055	–	–	–

^a Loss on ignition

Results and discussions

Structural changes in activated kaolinite–alumina mixture powders

The X-ray diffraction analysis of non-activated and activated mixture powders is given Fig. 1. Comparing the peak in the two diffraction patterns shows that all diffraction peaks get shorter after mechanical activation. This reflects the partial amorphization and structural disordering in kaolinite and alumina. Mechanical activation has already reported to amorphize materials [17]. Tromans and Meech

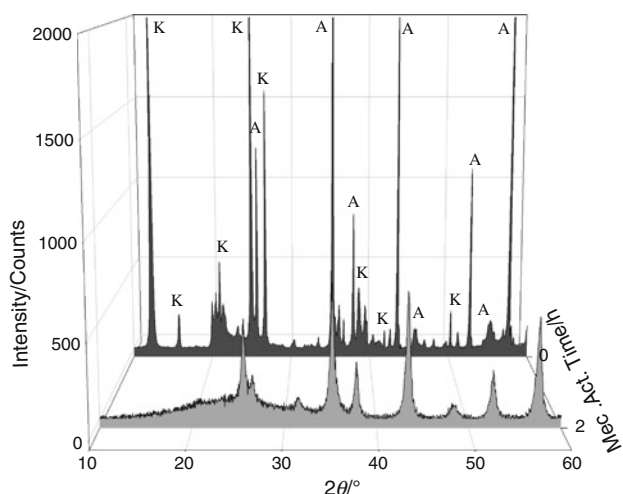
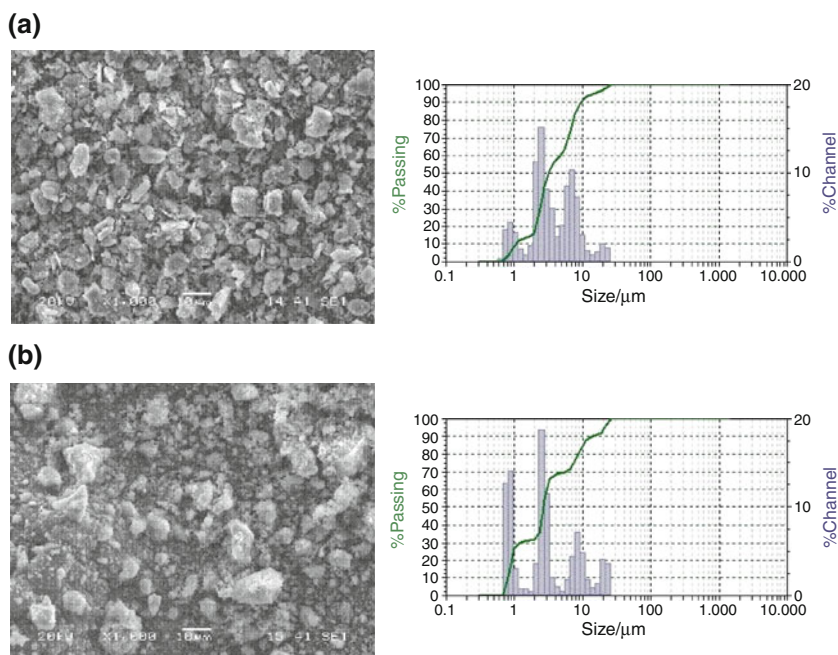


Fig. 1 XRD patterns of non-activated and activated kaolinite–alumina powders [K Kaolinite, A Alumina]

Fig. 2 SEM micrographs and particle size analysis of non-activated (a) and activated (b) kaolinite–alumina powders



[19, 20] found that mechanical activation results in a large number of dislocations and associated strain fields, which may lead to an overall decrease in long-range lattice periodicity. This may be interpreted as the formation of a metastable amorphous phase since extended milling causes X-ray diffraction peaks to show line broadening or to disappear all together.

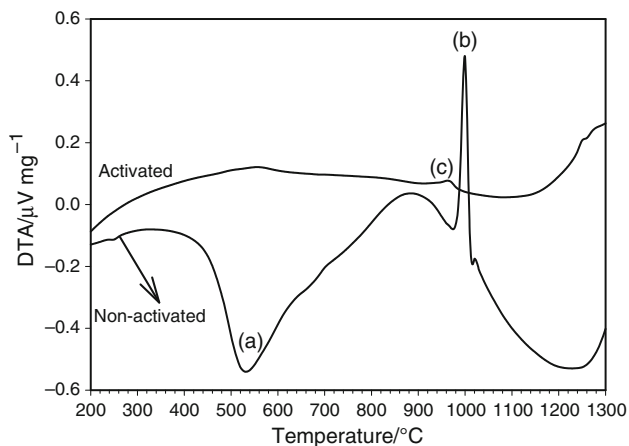
The scanning electron micrographs (SEM) and particle size analysis of the non-activated and activated kaolinite and alumina mixture powders can be observed in Fig. 2a, b. The particle size of non-activated mixture is over 3 μm (Fig. 2a). After mechanical activating, the mixture of powders is agglomerated. D_{10} , D_{50} , and D_{90} sizes corresponding to the particle sizes at the 10, 50, and 90% points on the cumulative distribution for the non-activated and activated samples are shown in Table 2. The degrees of amorphization of alumina and kaolinite after mechanical activating were calculated by Eq. 1. The degrees of amorphization of alumina and kaolinite were founded approximately 75 and 95%, respectively.

Thermal behavior of non-activated and activated kaolinite–alumina

The DTA curves of non-activated and activated mixture powders are given in Fig. 3. In the non-activated mixture powders, an endothermic peak (a) at around 530 $^{\circ}\text{C}$ corresponds to the dehydration of kaolinite. This peak is disappeared in the activated kaolinite + alumina sample, due to the occurrence of dehydration of kaolinite during mechanical activation. Miller and Oulton [21] investigated

Table 2 D_{10} , D_{50} , and D_{90} particle sizes for the non-activated and activated samples

Samples	$D_{10}/\mu\text{m}$	$D_{50}/\mu\text{m}$	$D_{90}/\mu\text{m}$
Non-activated kaolinite + alumina	1.04	3.22	9.27
Activated kaolinite + alumina/2 h	0.79	2.64	13.43

**Fig. 3** DTA analyses of non-activated and activated kaolinite-alumina powders

the effect of grinding on thermal behavior of kaolinite and stated that the grinding provided dehydroxylation reaction to actualize at lower temperatures. Frost et al. [22] pointed out that the mechanochemical treatment of kaolinite resulted in the dehydroxylation of the kaolinite and this dehydroxylation occurred through a homogenous process involving proton transfer. They also stated that the amount of dehydroxylation increased with grinding time.

Alumina is inert to the formation of primary mullite. In the temperature ranges from 1300 to 1500 °C, the amount of mullite increases rapidly, the amount of alumina decreases rapidly instead [10]. This inert behavior of alumina in the

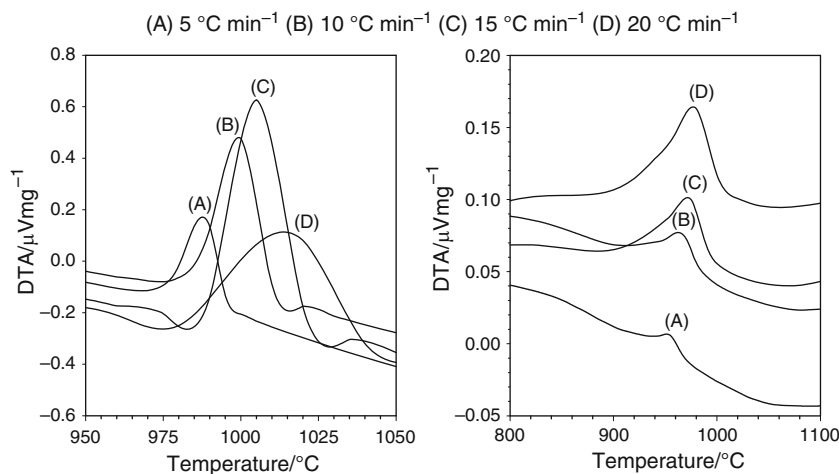
kaolinite–alumina system up to 1150 °C was reported in the study of Liu and Thomas [9]. Chen et al. [11] stated that the mullitization process of kaolinite–alumina ceramics was described by two stages: the primary mullite transformation at temperatures from 1000 to 1300 °C, and the secondary mullite forming at temperatures from 1200 to 1600 °C.

An exothermic peak (b) at around 1010 °C could be due to the mullite phase formation. The mullite formation (c) is lowered to 960 after 2 h of mechanical activation. The transformation of kaolinite to crystalline of the Al–Si spinel phase, weakly crystalline mullite, amorphous silicate phase, and amorphous silica has been reported by Chakraborty [23], Sakizci et al. [24], and Kamseu et al. [25]. The bulk nucleation is dominant in mullite crystallization and the crystal growth is controlled by diffusion. When sintering temperature is at 1000 °C the transformation from kaolinite to mullite occurs [11, 26]. The transformation from non-activated and activated kaolinite to mullite was studied by our group [2] and we stated that the exothermic peak at about 1000 °C in the non-activated kaolinite was related to the appearance of mullite crystallization. When the unreacted alumina was added to kaolinite, the transformation temperature raised to 1010 °C.

Mullitization kinetics

The DTA curves of non-activated and activated kaolinite–alumina mixture powders determined at various heating rates are showed in Fig. 4a, b. The top temperatures of these exothermic peaks increase with increasing heating rate, from 988 to 1014 °C. Also, the top temperatures of the exothermic peaks in the DTA of the activated kaolinite increased as the heating rate increased from 953 to 978 °C. Precursor activating decreases mullitization temperature significantly.

According to Eq. 2, the plots of $\ln(\beta/T_x^2)$ versus $1000/T$ corresponding to different conversions (α) was obtained

Fig. 4 DTA curves of non-activated (a) and activated (b) kaolinite–alumina measured at different heating rates

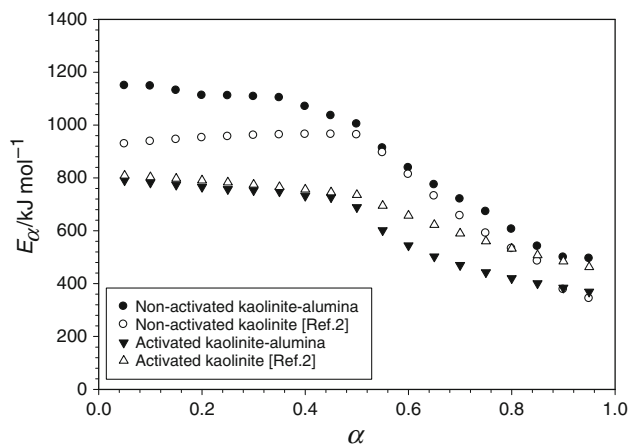


Fig. 5 Variation of activation energy with conversion for mullite formation in the non-activated and activated kaolinite–alumina powders

for non-activated and activated kaolinite–alumina mixture powders. The activation energies (E_x) were calculated from the slopes of every line. The α -dependence of the apparent value of E_x is shown in Fig. 5. From these data, a Kissinger plot [$\ln(T_p^2/\beta)$ vs. T^{-1}] was obtained for non-activated mixture powders as seen Fig. 5. And also, in figure the activation energy of mullite formation for non-activated and activated kaolinite were compared with non-activated and activated kaolinite–alumina mixture powders. As seen from Fig. 5, there double-step kinetics in the formation of mullite form kaolinite. With kaolinite in the 950–1050 °C temperature range, nucleation, and crystal growth processes occur simultaneously [26]. The bulk nucleation is dominant in mullite crystallization and the crystal growth is controlled by diffusion in kaolinite [11]. In the first study of our groups [2], the activation energy values of the bulk nucleation and crystal growth in mullite crystallization for non-activated kaolinite were reported 928–962 and 895–343 kJ/mol, respectively. In this study, the activation energy values of the bulk nucleation in mullite crystallization for the non-activated kaolinite–alumina mixture were calculated between 1148 and 1003 kJ/mol. Also the activation energy values for crystal growth step were calculated between 913 and 495 kJ/mol. Chen et al. [11] reported that unreacted alumina is inert the crystallization mullite in alumina–kaolin ceramic system until 1200 °C. They also pointed out that the reaction between alumina and glass phase to mullite starts from 1300 °C. Chen et al. [11] also stated that the unreacted alumina powders in kaolinite–alumina mixture increased the activation energy of mullite formation. After mechanical activation, the activation energy values of bulk nucleation and crystal growth decreased 790–688 and 602–369 kJ/mol, respectively. These values are lower than activated kaolinite. The application of high energy milling allows a dramatic

change in the structure and surface properties of solids to be induced [17, 27].

Conclusions

The effects of mechanical activation on the thermal behavior of kaolinite – alumina ceramic system and the non-isothermal kinetics of mullite formation were investigated and the following results were obtained.

- In the kaolinite–alumina ceramic system, the mechanical activation caused 95% and 75% of amorphization degree for kaolinite and alumina, respectively, after 2 h of mechanical activation.
- In the DTA curve of non-activated kaolinite–alumina ceramic system, dehydroxylation reaction in kaolinite was seen at 530 °C but this endothermic peak disappeared in the activated system and this reaction occurred during milling.
- Alumina behaves as inert material to the formation of primary mullite in the non-activated kaolinite–alumina system. When alumina was added to kaolinite, the transformation temperature raised to 1010 °C.
- The exothermic peak in the non-activated system decreased from about 1010 to 960 °C after 2 h of mechanical activation, due to the structural disordering and amorphization in the structure of kaolinite and alumina after mechanical activation.
- There is the bulk nucleation and crystal growth steps in mullite crystallization. Alumina addition to kaolinite increased the activation energy for the bulk nucleation step in the non-activated system but has no important effect on the crystal growth step. Mechanical activation of kaolinite or kaolinite–alumina system decreased the activation energies for these two steps. Alumina addition to kaolinite in the activated system has no effect on the bulk nucleation but has an effect on the crystal growth in mullite crystallization.

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