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Effect of Mechanical Activation on the Kinetics of Kyanite Mullitization

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Abstract

The kinetics of mullitization of kyanite samples, both initial and mechanically activated in high-energy grinding devices within temperature range 1273–1573 K was investigated. It was shown that the kinetics of kyanite mullitization formally corresponds to the equation of monomolecular decomposition. The activation energy of this transformation is (630±10) kJ/mol. It was established that mechanical activation of kyanite accelerates mullitization processes during subsequent thermal treatment. The yield of mullite per unit surface area is almost two times higher for mechanically activated sample than for non-activated one. Possible mechanism of mullitization process and technological aspects of the implementation of this process in industry are discussed.

Key words: aluminosilicates, kyanite, mullitization, thermal treatment, mechanical activation

INTRODUCTION

In view of the use of minerals as the raw material for obtaining the necessary ceramic materials, it appears interesting to study the processes involving the changes of structure and properties of these minerals under the action of mechanical treatment followed by thermal one. In the course of high-energy mechanical activation, high dynamic local pressure is generated; it can lead to the accumulation of structural defects and to the changes of the structure of the matter under treatment. It has been established that mechanical activation is not reduced to simple disintegration of a solid [1]. Substantial part of input mechanical energy turns out to be accumulated in the substance volume.

One of the minerals of significant practical importance is kyanite. It belongs to the minerals of sillimanite group (andalusite, sillimanite, kyanite) with the general formula Al_2SiO_5 (62.9 mass % Al_2O_3, 37.1 % SiO_2). These minerals are characterized by high melting point, they do not soften under heating, are stable against acids, possess good fire-proof properties. They are used as the basis for high-alumina refractory materials, ceramics, glaze, enamel, porcelain *etc*. [5]. The leading position in the pattern of consumption by metallurgical industry in developed countries is occupied by high alumina refractory materials. An excellent raw material for obtaining these materials is burnt kyanite concentrate.

For our country, this kind of raw material is of strategic importance because it is possible

to establish a large-scale production of alumina, silumin and aluminium on the basis of this material [2]. Several large deposits of kyanite are situated in Sverdlovsk and Chelyabinsk Regions [3].

The present study deals with the investigation of phase transformations in natural kyanite during high-energy mechanical activation.

EXPERIMENTAL

Monomineral fraction of kyanite from the Karabash deposit (the Urals) was chosen for investigation. According to the data of X-ray spectral electron probe analysis, the material contains insignificant amount of admixtures (%): MnO 0.10, CaO 0.03, K_2O 0.06. The initial kyanite sample was thoroughly comminuted in a mortar. Mechanical activation of kyanite was carried out using the AGO-2 mill [4] for 10 min with ball acceleration 40*g*. The mass ratio of powder to the balls 8 mm in diameter was 1 : 20. Experiments on the kinetics of kyanite mullitization were carried out at a temperature of 1273, 1423, 1473 and 1573 K using a Thermo Scientific ARL X'tra powder diffractometer equipped with a high-temperature attachment Anton Paar HTK 2000 (silicon-lithium detector with Peltier cooling, CuK_α radiation, the parallel beam geometry, tube more 40 kV, 40 mA). Kyanite sample was deposited as a thin layer on directly on the platinum heater and heated in the air to the necessary temperature at a rate of 50 °C/min. The diffraction profile was accumulated after given time intervals over points (step $2\theta = 0.02^\circ$ with the time of signal accumulation in point 2 s) in the ranges containing the most intensive reflections of kyanite and mullite, 2θ°: 25–26.7, 27.2–28.2, 30.3–31.2. The diffraction data were treated using the WinXRD (Thermo Scientific) software package and the powder diffractometric database PDF-4.

For the quantitative determination of phases that are present in burning products, we used the integral intensities of strong non-overlapping (or slightly overlapping) reflections of kyanite and mullite, determined with the help of PROFIT programme. Their concentrations were estimated on the basis of the ratio of intensities of diffraction peaks at a given profile and the intensities of corresponding peaks at the profile of the sample containing the maximal amount of one or another phase. It should be noted that kyanite possesses perfect cleavability over (100). The content of each phase was determined on the basis of three intensive resolved (non-overlapping or slightly overlapping) peaks. The calculated values were averaged, and the sum of phases was normalized for the theoretical sum taking into account SiO_2 formed in the reaction. The specific surface of powders was determined with the help of Katakon instrument by means of the thermal desorption of nitrogen.

RESULTS AND DISCUSSION

Thermal mullitization of initial kyanite

According to the data of gas adsorption study, the specific surface of kyanite comminuted in a mortar is (1.3±0.1) m^2/g. High-temperature thermal treatment involves kyanite disproportionation into mullite and quartz according to equation

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

Gibbs' energy for this reaction at room temperature is 18.8 kJ/mol, while at a temperature of 1473 K it is −11.9 kJ/mol.

The data of X-ray phase analysis of kyanite samples subjected to thermal treatment for 3 h at a temperature of 1623 K are shown in Fig. 1. One can see that mullite and quartz are present in the products of thermal treatment. For mullite, a complete correspondence with the data from PDF-4 database (card No. 1-618) is observed. Reflections in the angle range $2\theta =$ 28, 36, 53° correspond to silicon dioxide.

In the kyanite lattice, aluminium ions have the coordination number equal to 6, while in the product of its decomposition – mullite – half of aluminium ions is present in the octahedral surrounding and another half is in the tetrahedral surrounding. In kyanite, Al atoms having octahedral coordination are incorporated into chains; SiO_4 tetrahedra are situated in the gaps between them, intermittent with AlO_6 octahedra. In mullite, the chains are conserved but the chains composed of alternating tetrahedral groups AlO_4 and SiO_4 go in parallel to

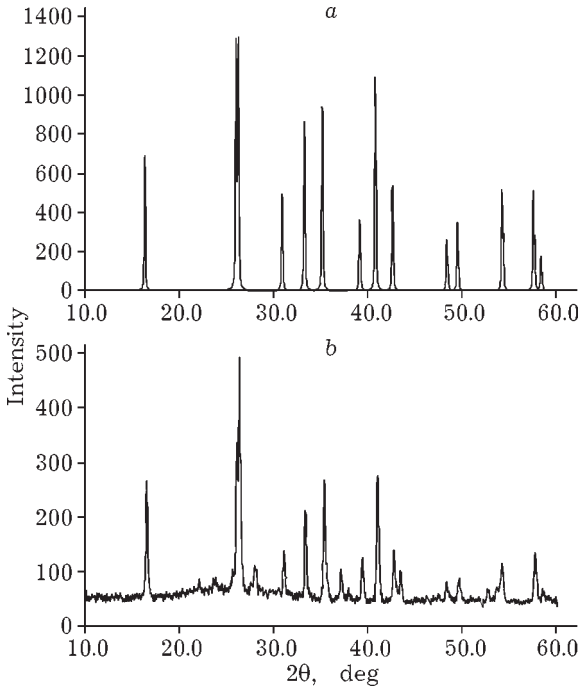

Fig. 1. Diffraction profiles of mullite from the ASTM database (*a*) and mullite obtained through thermal treatment of kyanite (*b*).

the octahedral chains. So, the initial stage of kyanite mullitization during thermal treatment can be the formation of the nuclei of the new phase due to thermally activated transition of aluminium cation from the octahedral to tetrahedral coordination. It may be assumed that the rate of transformation will be determined by the rate of nuclei formation, while their subsequent growth will not be the limiting stage. Then we may use the following equation for transformation degree (α):

$$\alpha = 1 - \exp(-k_0 t) \quad (1)$$

where $\alpha = N_t/N_0$ (N_0 is the initial reagent content; N_t is the amount of product after time interval t; k_0 is the constant equal to the fraction of molecules decomposing during the unit time. Or

$$\ln(1 - \alpha) = -k_0 t \quad (2)$$

The data on mullitization degree for kyanite after thermal treatment at temperatures 1373, 1423 and 1473 K depending on exposure are presented in Fig. 2, *a*. The results of data processing in the coordinates of equation (2) are shown in Fig. 2, *b*. One can see that the experimental data are in good agreement with the indicated equation. The activation energy of kyanite mullitization was determined to be equal to (630±10) kJ/mol.

Thermal mullitization of mechanically activated kyanite samples

According to the XPA data, strong amorphization is observed in mechanically activated kyanite samples. The intensity of reflection lines decreases by a factor of 5–7, which is the evidence of the high degree of grinding and disordering of the lattice under the effect of mechanical activation. This is exhibited as weak (at the background level) peak at diffraction angles characteristic of the most intense mullite reflections. For the sample subjected to mechanical activation for 10 min and kept at a temperature of 1573 K for 3 h, complete trans-

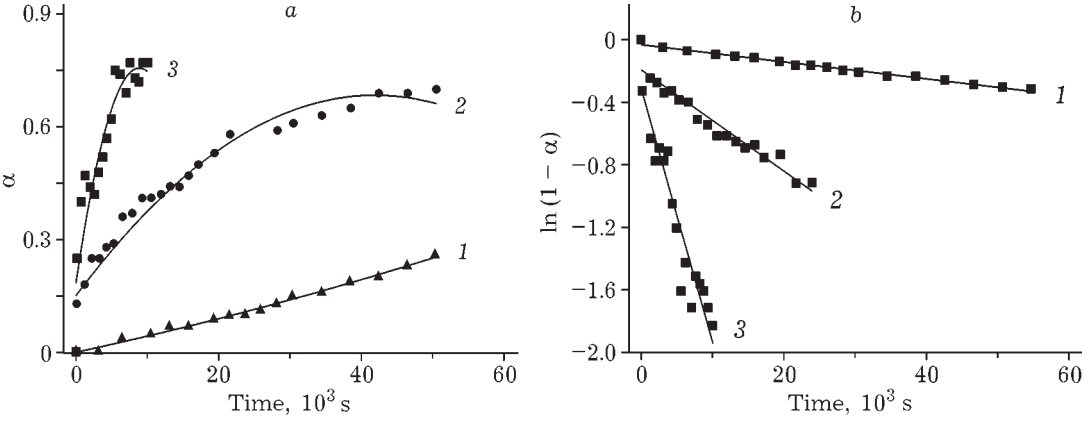

Fig. 2. Kinetics of thermal mullitization of kyanite (*a*) and results of experimental data processing in the coordinates of eq. (2) (*b*). Process temperature, K: 1373 (*1*), 1423 (*2*), 1473 (*3*).

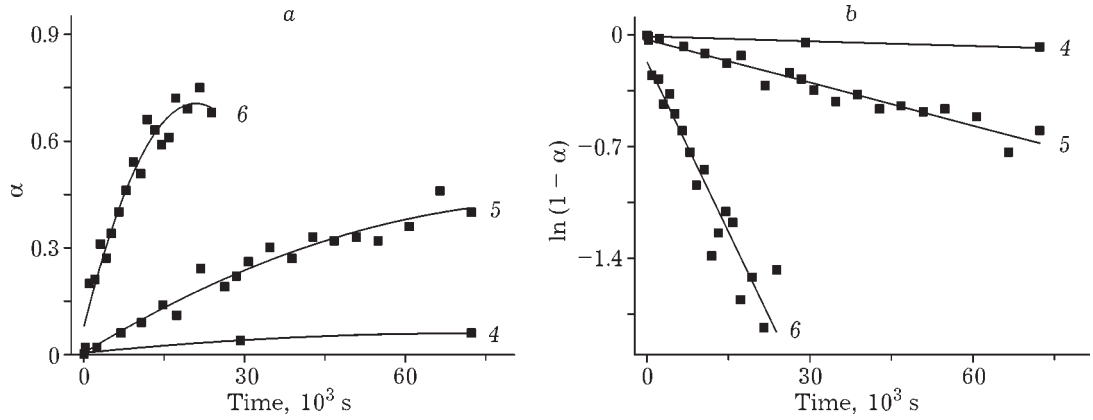

Fig. 3. Kinetics of thermal mullitization of mechanically activated kyanite (*a*) and the results of experimental data processing in the coordinates of eq. (2) (*b*). Process temperature, K: 1273 (*1*), 1323 (*2*), 1373 (*3*).

formation of kyanite into mullite is observed. Mechanical activation of kyanite accelerates mullitization of kyanite almost by a factor of 10. Complete transformation of kyanite into mullite after activation is achieved as a temperature of 1373 K within 5.5 h. For initial kyanite sample (thoroughly ground in a mortar), mullitization degree within the same time does not exceed 20 %. The data on the degree of mullitization for mechanically activated kyanite after thermal treatment at a temperature of 1273, 1323 and 1373 K depending on exposure are shown in Fig. 3, *a*, while the results of data processing in the coordinates of equation (2) are presented in Fig. 3, *b*. The activation energy of mullitization of mechanically activated kyanite turned out to be the same as that for the case of non-activated kyanite sample: (630±10) kJ/mol.

Specific surface increases during treatment in the mill and reaches (4.3±0.2) m^2/g. Mullitization degree per unit surface of the product (Fig. 4) shows that mechanical activation is connected not only with an increase in surface area but also in structural distortions simplifying the transformation of kyanite into mullite.

Structural changes accompanying kyanite mullitization was considered in detail in [8], where it was demonstrated that the transformation of aluminium from the octahedral surroundings to tetrahedral ones is accompanied by the removal of oxygen atom from the structure and the formation of oxygen vacancies in mullite. We suppose that the high activation energy of the process, the same for the initial sample and for non-activated one, is due to the rupture of one of Al–O bonds as a result of the rearrangement of the octahedral surroundings into tetrahedral. The energy of this bond rupture is 480 kJ/mol [9], which is comparable with the value of activation energy obtained by us ((630±10) kJ/mol).

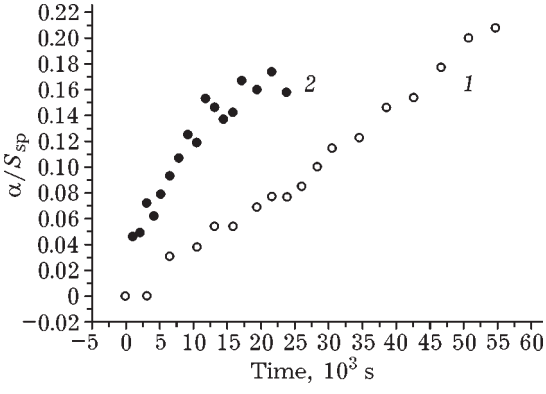

Fig. 4. Kinetics of thermal mullitization (T = 1373 K) of non-activated (*1*) and mechanically activated (*2*) kyanite taking into account the specific surface area.

Technological aspect of the application of research results

A waste-free production of kyanite concentrates (for refractory bricks, ceramics, silumin, aluminium) can be arranged on the basis of the ore from the deposits of the Urals. The results obtained demonstrate that the use of

mechanical activation allows substantial decrease in the temperature of kyanite mullitization. Even at 1373 K mechanically activated kyanite is transformed almost completely into mullite and quartz within 4–5 h. For initial kyanite (thoroughly ground in a mortar) such a result is achieved within the indicated time only at a temperature of 1473 K.

For the implementation of activation process in the continuous mode, we proposed a centrifugal disc mill of flow type. The operation principle, efficiency of activation and other parameters of the mill were described in detail in [17]. Using this mill, we carried out experiments on kyanite activation. These experiments showed that even a single pass of kyanite through the mill provides mullite yield from kyanite at a level of 90 %.

CONCLUSION

Thus, as a result of investigation, the optimal parameters were established for obtaining mullite from kyanite by means of thermal treatment of both the initial and mechanically activated mineral. For the practical realization of the method, we proposed the design of the centrifugal disc mill of flow type providing the necessary level of kyanite activation.

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