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Thermal Transformation of Fired Clay Ceramics by Dilatometric Analysis

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In the present study the mechanism and kinetic parameters of allotropic transformation ($\alpha \rightarrow \beta$) of the quartz of Algerian clay from Al-maathed was studied by dilatometric analysis technique. The activation energies measured by both isothermal (Johnson-Mehl-Avrami theory using Ligerio method) and non-isothermal (Kissinger methods) treatments were 980 and 1050 kJmol⁻¹, respectively. The growth morphology parameters n (Avrami parameter) which indicates the crystallization mode were found to be almost equal to 1.5, using non-isothermal treatments, and equal to 1.4 using isothermal (Ligerio method). The numerical factor which depends on the dimensionality of crystal growth m obtained by Matusita et al. equation was 1.50. Analysis of the results shows that the bulk nucleation is the dominant mechanism in β -quartz crystallization and the three-dimensional growth of β -quartz crystals with polyhedron-like morphology occurs, controlled by diffusion from a constant number of nuclei.

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1. Introduction

Clays and clay minerals are very important raw materials in process industries, agriculture, engineering, construction, geology, environmental, and for other miscellaneous applications. They have been widely used as the main raw materials in the fabrication of diversified ceramic products for construction materials such as bricks and tiles due to their specific properties before and after firing [1, 2].

Clays are formed by many processes such as hydrothermal, weathering, sedimenting, etc. They have generally buff, gray, brown, or rusty colors due to the content of clay minerals and due to iron oxides/hydroxides. The clay raw material which was used in this project was obtained from the brickyard area of Al-maathed in the central area of Algeria. This Algerian clay was chosen for its wide applications in the pottery and brick making industries.

The experiments of this study were conducted similar to the traditional practices of potters, to understand the thermal transformation of fired clay ceramics by dilatometric analysis of these materials. Therefore the clays were manually shaped and pressed into a mould, then dried and after that fired.

Densification behavior of clays fired at various temperatures under different heating rates was evaluated. It is expected that the present investigation will collect the knowledge on optimization of the clay ceramics processing.

This study is devoted to the investigation of the thermal transformation of Algerian clay under different firing conditions in order to obtain the non-isothermal and isothermal activation energies of crystallized β -quartz, and the values of the growth morphology parameters n and m .

2. Materials and experimental procedure

Clay materials were taken from a brick-manufacturing factory located at M'sila site in Algeria. The chemical composition of this mineral was determined by X-ray fluorescence (XRF), as shown in Table I.

Chemical composition (wt.%) of clay mineral TABLE I
(calcined at $T = 700^\circ\text{C}$).

Al ₂ O ₃	SiO ₂	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	Fe ₂ O ₃
15.27	68.18	6.86	3.30	1.22	1.77	0.69	2.69

Clay was fired in a furnace at 200, 600, 950 and 1050 °C for one hour with heating rate of 10 °Cmin⁻¹. X-ray diffraction (XRD) was used to identify the phases formed in the heated clay powders. XRD measurements were carried out on powder using a focalization Bragg-Brentano X-ray diffractometer, with Cu-K α radiation with the wavelength of 1.5418 Å and operating at 40 kV and 40 mA. The diffraction angle range was $15^\circ \leq 2\theta \leq 40^\circ$.

The dilatometry measurements were carried out on the clay with a dilatometer (NETZSCH DIL 402C). The samples were fired from room temperature to 1000 °C, at heating rates of 4, 8, 10, 12, 16 and 20 °Cmin⁻¹.

In the case of the non-isothermal method the activation energy E_A of crystallization is calculated using Ozawa [3, 4], Boswell [5] and Kissinger [6] methods. The

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theoretical basis for the dilatometry results is provided under the isothermal condition using the Johnson-Mehl-Avrami (JMA) theory. This method describes with the time, t , the evolution of the crystallization fraction, x , during a phase transformation:

$$x = 1 - \exp[(-kt)^n]. \quad (1)$$

Here x is the volume fraction crystallized after time t . It was obtained from the dilatometry results as follows:

$$x = \frac{A_T}{A_0}, \quad (2)$$

where A_T is the area of the peak in the dilatometer curve at temperature T and A_0 is the total area of the peak.

$$k = k_0 \exp\left(-\frac{E_A}{RT}\right). \quad (3)$$

Here k_0 is the frequency factor, T is the temperature in Kelvin, E_A is the activation energy and R is the ideal gas constant.

Through the non-isothermal techniques Ligeró et al. [7, 8] suggested a mathematical method in which the activation energy can be obtained from the slope of the Eq. (4) if we select the same value of x in every experiment with the useful heating rate. There must be a linear relationship between $\ln(dx/dt)$ and $1/T$, the slope of which provides the activation energy.

$$\ln\left(\frac{dx}{dt}\right) = \ln(k_0 n) + \frac{n-1}{n} \ln(-\ln(1-x)) - \frac{E_A}{RT} =$$

$$\ln(k_0 n f(x)) - \frac{E_A}{RT}. \quad (4)$$

Then, it is probable to calculate the value of crystallized fraction x at various heating rates. Hence, the Avrami parameter n was calculated from the plot $\ln(k_0 n f(x))$ vs $1/T$. We can select many pairs of x_1 and x_2 that satisfy the condition $\ln(k_0 n f(x_1)) = \ln(k_0 n f(x_2))$.

$$n = \frac{\ln(\ln(1-x_2)/\ln(1-x_1))}{\ln((1-x_2)\ln(1-x_2)/(1-x_1)\ln(1-x_1))}. \quad (5)$$

3. Results and discussion

Figure 1 shows the typical shrinkage curves for clay powder at different heating rates (Fig. 1a) and first derivative of shrinkage curves for transformation of quartz from phase α to phase β (Fig. 1b).

Figure 1a shows a linear shrinkage of the clay heated at different heating rates $2.5^\circ\text{Cmin}^{-1}$ to 10°Cmin^{-1} . Relative expansions at temperatures lower than 100°C are due to the evaporation of the adsorbed water. Relative shrinkage which starts at 100°C and ends at 200°C is due to the dehydration of the clay powder [9].

The second expansion appearing at about 578°C results in an allotropic transformation of quartz ($\alpha \rightarrow \beta$). This transformation is very fast and causes a sudden increase in volume (1.3% for the quartzite) corresponding to a linear elongation of 0.45% [9, 10].

The third relative shrinkage between 860°C and 940°C corresponds to sintering steps. Figure 1b depicts the first derivative of shrinkage curves for transformation of

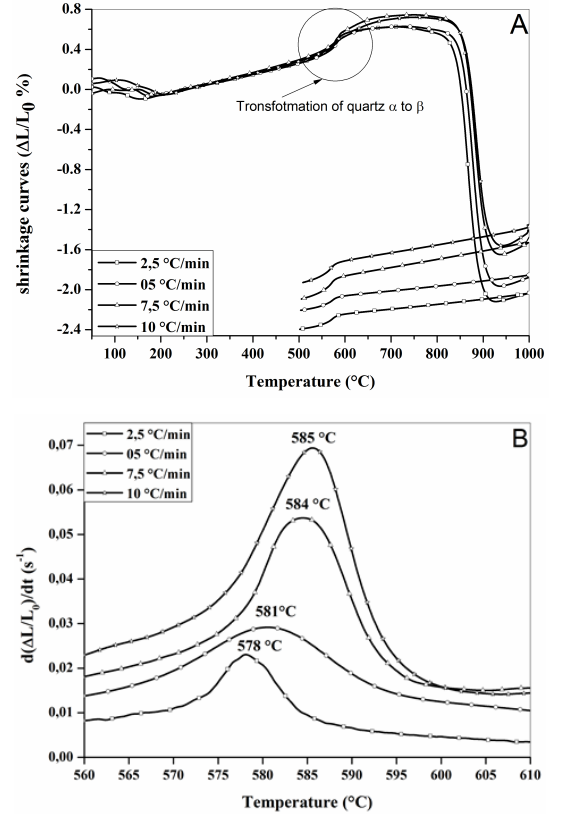


Fig. 1. Shrinkage curves of clay powder at different heating rates (a) and the first derivative of shrinkage curves for transformation of quartz $\alpha \rightarrow \beta$ (b).

quartz ($\alpha \rightarrow \beta$). The temperature of the maximum of the exothermic peak, T_p , shifts to a higher temperature as the heating rate increases from 2.5 to 10°Cmin^{-1} . The calculated energy of phase transformation of quartz ($\alpha \rightarrow \beta$) obtained by various methods is shown in Fig. 2 and its values are shown in Table II.

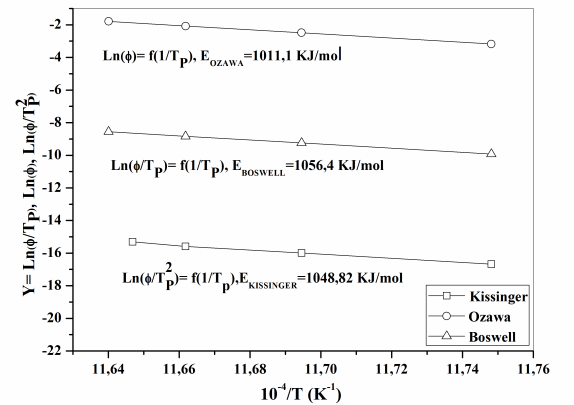


Fig. 2. Plots of Y versus $10^4/T_p$ for phase transformation of quartz ($\alpha \rightarrow \beta$).

TABLE II

Values of E_A and R^2 obtained using Kissinger, Ozawa and Boswell methods.

Method	Kissinger	Ozawa	Boswell
E_A [kJ mol ⁻¹]	1049	1011	1056
R^2	0.995	0.994	0.997

Figure 3a shows the variation of the crystallized fraction of β -quartz formation with temperature under different heating rates. The crystallized fraction x was determined from the dilatometry results (Fig. 1a).

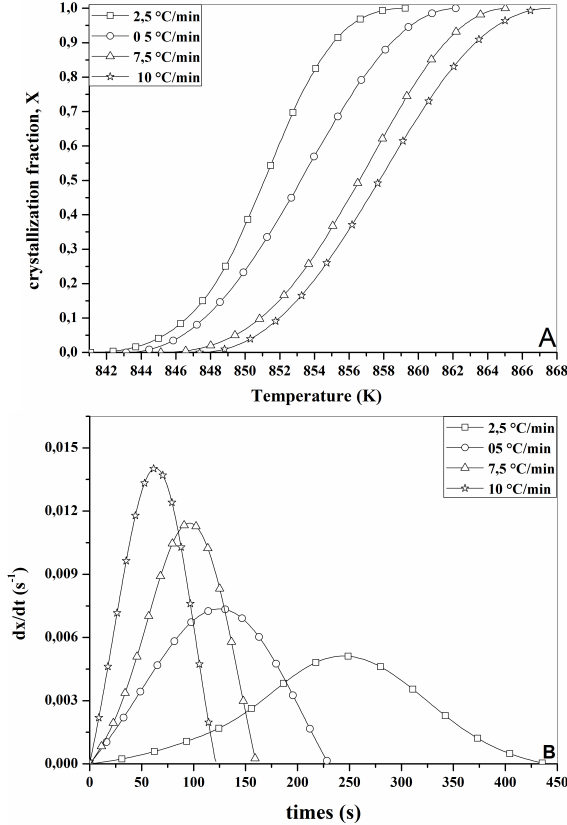


Fig. 3. Crystallized fraction (a) and the rate (b) of β -quartz growth with time, under different heating rates.

As estimated, the crystallization fraction, x , at a temperature T differs at different heating rates and hence the curves dx/dt versus time are also different as is shown in Fig. 3b, which depicts the rate of β -quartz growth with time for different heating rates.

The rate of crystallization increases with the heating rate. Figure 4a shows the plot of the $\ln(dx/dt)$ versus $1/T$ at the same value of x . The values of the activation energy, E_A , for different crystallized fraction, which were calculated by the average of the slopes of the lines, are listed in Table III.

The average activation energy of phase transformation of quartz ($\alpha \rightarrow \beta$) in clay mineral is 858 kJmol⁻¹. Figure 4b shows the plot of $\ln(k_0 f(x))$ versus x for phase

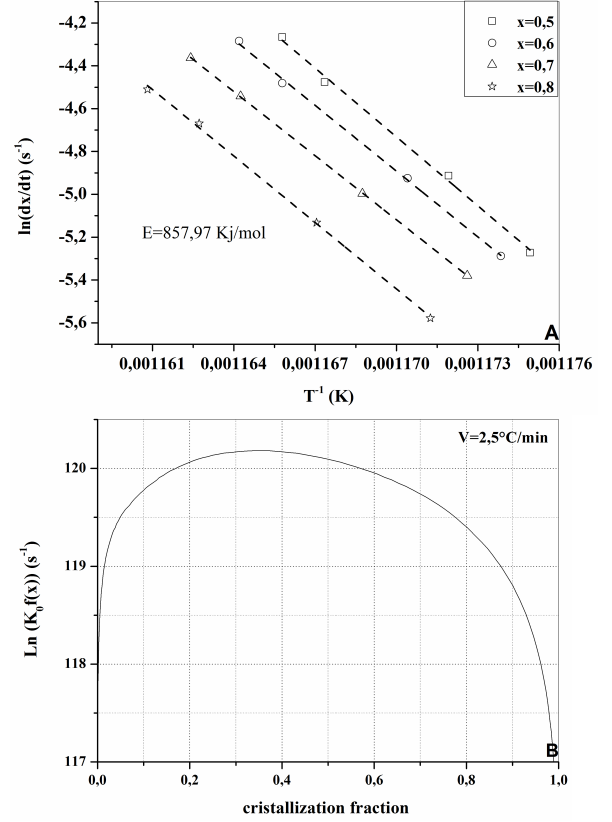


Fig. 4. Plot of $\ln(dx/dt)$ vs $1/T$ for the same value of crystallized fraction x (a). Plot of $\ln(k_0 f(x))$ vs crystallization fraction x for clay powder heated at a heating rate of 2.5 °Cmin⁻¹ (b).

TABLE III

Values of the activation energy, E_A , for different values of crystallized fraction.

Crystallized fraction	R^2	E_A [kJ mol ⁻¹]
0.3	0.9553	1001.87
0.4	0.8480	1139.61
0.5	0.995	890.696
0.6	0.998	850.671
0.7	0.999	830.180

transformation of quartz ($\alpha \rightarrow \beta$) heated at a heating rate of 2.5 °C min⁻¹. Similar curves were obtained for the other heating rates. The Avrami parameter, n , was determined. The average value of Avrami parameter was 1.5, thus showing that the crystallization process of β -quartz in clay mineral should be controlled by the diffusion growth.

4. Conclusions

The dilatometric analysis conducted at heating rates of 2.5, 5, 7.5 and 10 °Cmin⁻¹ shows an expansion around 570 °C associated with the transformation of quartz ($\alpha \rightarrow \beta$). The non-isothermal and isothermal activation

energies of crystallized β -quartz for clay, calculated using Kissinger, Ozawa and Boswell methods were (1049, 1011 and 1056 kJmol⁻¹) and 858 kJmol⁻¹, respectively. The values of the growth morphology parameters $n = 1.5$ indicate that bulk nucleation is the dominant mechanism in β -quartz crystallization.

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