Kinetic study of non-isothermal decomposition of a composite diasporic-boehmitic bauxite

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Abstract. In the current study, the kinetic of the thermal decomposition of a composite diasporic-boehmitic bauxite is investigated under non-isothermal heating conditions by means of thermogravimetric analysis. The calculation of activation energy ($E_a$) has been performed by various methods and the attained values range from 185000 to 190000 J∙mol⁻¹ for conversion rate of 0.5. The first-order kinetic model can adequately be used to describe thermal decomposition of bauxite composite, while the pre-exponential factor value was found to be 2.088*10¹¹ min⁻¹. The calculated activation energy value together with pre-exponential factor and the solid state kinetic model factors enable the simulation of the thermal decomposition under various heating conditions by the implementation of an ordinary differential equation. The calculated values are in satisfactory agreement with the experimental ones.

1. Introduction
Bauxite is an aluminum ore which mainly consists of the minerals gibbsite [Al(OH)₃], bayerite [α-AlO(OH)], boehmite [γ-AlO(OH)], diasporic [α-AlO(OH)] and minor phases of iron oxides, kaolinite and anatase. Bauxite consist the major primary source for the alumina (Al₂O₃) and metallic aluminum. Non metallurgical applications of rough bauxite ore include the production of hydraulic fracturing proppants and low cost abrasives [1]. Recently, a heightened interest is presented concerning the production of low cost refractory cements and dense ceramics using a concrete rich in bauxite material [2]. The above applications require the calcination of bauxite which practically equivalents with the dehydroxylation of its aluminum phases. Although the thermal decomposition kinetic of gibbsitic and diasporic bauxites has been examined [3, 4], in the current study, for first time in the literature, the thermal decomposition of composite diasporic-boehmitic bauxite is kinetically studied in detail.

2. Experimental
The diasporic-boehmitic bauxite ore used in the present study originates from an open pit of the Greek aluminum producer “Aluminum of Greece” located in Parnassos Mountain, Greece. Its granulometric distribution is: +80-120 μm (22.4% w/w), +120-160 μm (41.6%) and +160-200 μm (36%). The bulk chemical analysis of the bauxite ore is presented in Table 1, while its mineralogical analysis can see in Figure 1. The thermogravimetric analysis experiments that were used in the current kinetic analysis were carried out on a Labsys DTA/DSC Setaram. Approximately 80 mg of dried bauxite composite samples were placed in platinum crucibles and heated in helium atmosphere with a flow rate of 30
mL·min$^{-1}$. In Figure 2 the TG, DTG and DSC diagrams versus sample temperature are presented at four constant heating rates; 2, 5, 10 and 20°C min.

Table 1. XRF analysis of the bauxite ore

| Species   | Mass (w/w.%) |
|-----------|--------------|
| Al$_2$O$_3$ | 58.68        |
| Fe$_2$O$_3$ | 22.53        |
| SiO$_2$    | 3.36         |
| TiO$_2$    | 2.37         |
| ZrO$_2$    | 0.88         |
| CaO        | 0.43         |
| Cr$_2$O$_3$ | 0.151        |
| Na$_2$O    | 0.056        |
| L.O.I      | 11.04        |

Figure 1. XRD pattern of the rough bauxite ore

Figure 2. (a) TG, (b) DTG and (c) DSC plot of diaspore-boehmite composite bauxite heated under various heating rates

Figure 3. Thermogravimetric analysis of the rough bauxite ore
Figure 3 presents the TG-DTA curves of the bauxite ore in the temperature range between 300 and 1473K with a 10°C/min-1 heating rate. The data curve shows two main endothermic peaks at 778.3 and 805.5 K that correspond to the dehydroxylation of the boehmite and the diaspore respectively and their transformation to $\text{Al}_2\text{O}_3$. The weight loss between 523 and 723K can be attributed to the dehydroxylation of minor amorphous, undetectable by X-ray diffractometry, aluminum phases. The slight weight loss that observed around 1273K can be attributed to the partially decomposition of hematite to magnetite ($\text{Fe}_3\text{O}_4$) and metastable wustite ($\text{FeO}$).

### 3. Kinetic analysis

The governing equation for kinetic analysis of solid-state decomposition under isobaric conditions is described by the following equation [5]:

$$\frac{da}{dt} = k(T)f(a) \quad (1)$$

Where, $T$ is the temperature, $a$ is the extension of conversion and, $k$ is the reaction rate constant.

Typically, the dependence of the decomposition evolution by the temperature is introduced in Eq. 2 by replacing $k(T)$ with the Arrhenius equation, which gives the following form:

$$\frac{da}{dt} = A \cdot \exp \left( \frac{-E_a}{RT} \right) f(a) \quad (2)$$

Where, $(A)$ denotes the pre-exponential factor, $(E_a)$ is the activation energy and $(R)$ the gas constant. The integral form, with respect to temperature, of the equation (2) can be written as:

$$g(a) = \frac{A}{\beta} \int_{0}^{T} \exp \left( \frac{-E_a}{RT} \right) \text{d}T \quad (3)$$

The objective of the kinetic analysis constitutes the calculation of the three basic parameters, namely, the activation energy, the pre-exponential factor and the kinetic model.

Three model free methods (Table 2) where implemented for the calculation of activation energy distribution throughout the conversion range allowing the estimation of the apparent activation energy at progressive degrees of conversion [6-10].

#### Table 2. Model free methods used for the calculation of the activation energy

| Methods                        | Equation                                                                 | Calculation                      |
|--------------------------------|--------------------------------------------------------------------------|----------------------------------|
| Friedman method                | $\ln \left[ \frac{\beta_i (da/dT)_{a,i}}{a,i} \right] = \ln [A f(a)] - \frac{E_{a,a}}{RT} \right]  \text{versus } l/T_a$ | $ln[\beta_i (da/dT)_{a,i}] \text{versus } l/T_a$ |
| Flynn, Wall, Ozawa method      | $\frac{d\log \beta}{dT_{T_a}} \approx 0.457 \frac{E_a}{R}$             | $\log \beta \text{versus } l/T$ |
| Flynn, Wall, Ozawa method      | $\frac{d\log \beta}{dT_{T_a}} \approx 0.457 \frac{E_a}{R}$             | $\log \beta \text{versus } l/T_{\text{m}} (T_{\text{m}} \text{when DSC max peak})$ |
| Lyon method                    | $E_{a,a} = -R \left[ \frac{\text{dln}\beta}{dT_{T_a}} + 2T_{a} \right]$ | $\ln \beta \text{versus } l/T_a$ |

The determination of the appropriate kinetic model requires the introduction of the function $z(a)$ which is derived by multiplying the integral and the differential form of the reaction kinetic models [20]:

$$z(a) = f(a) \cdot g(a) = \left( \frac{da}{dt} \right) T_a^2 \left[ \frac{\pi(x)}{x} \right] \quad (4)$$

Where $\pi(x)$, is a function and $x=E/RT$. It has been established [11] that the term in the brackets of Eq. 4 has a negligible effect on the shape of $z(a)$ function. Thus, the values of $z(a)$ can be determined by
multiplying the experimental values \((\frac{da}{dt})_a\) and \(T_a\). The resulting experimental values of \(z(a)\) are plotted as a function of \(a\) and compared against theoretical \(z(a)\) master plots of several kinetic models. A suitable model is identified as the best match between the experimental and the theoretical \(z(a)\) master plots using the Criado method [12]. The adequacy of each model to simulate the non-isothermal decomposition of bauxite was tested by two error factors (\(RSS\)) and (\(RSQ\)). Finally, the pre-exponential factor \((A)\) is calculated by the following equation [13]:

\[
A = \frac{-\beta E_a}{RT_{\max} f(a_{\max})} \exp \left( \frac{E_a}{RT_{\max}} \right)
\]

Where, the subscript \(a_{\max}\) in the aforementioned equation denotes the conversion value where the weight loss rate maximizes.

4. Results and discussion

![Figure 4](image_url)

Figure 4. Plotting of diagrams used in the calculation of activation energy through: Friedman (a), Flynn-Wall-Ozawa (b), Flynn-Wall-Ozawa with DSC data (c) and Lyon methods (d)

The methodology of activation energy calculation via various methods is presented in Figure 4, while its values throughout the whole conversion range are presented in the diagram of Figure 5. The results show that the activation energy calculated by the aforementioned methods is almost constant for a wide (a) range from about 0.1 to 0.9.

![Figure 5](image_url)

Figure 5. Activation energy upon conversion rate as calculated by various isoconversional methods
For the determination of the kinetic model that describes the thermal decomposition of bauxite composite, the Criado diagram has been created and presented in Figure 6. For each theoretical model, $Z(a)\cdot Z(0.5)^{-1}$ values throughout the whole conversion range accrued by solving Eq. 4 for $g(a)$ and $f(a)$ values of specific kinetic models. The determination of the deviation of each theoretical model from experimental values that are presented with black and white symbols, was performed by calculating the error factors $RSS$ and $RSQ$. A value of $RSQ$ close to unity implies that the model is consistent with the experimental data, while, as far as the $RSS$ factor is concerned, the lower its value, the lower is the divergence between model and experimental values.

It was found that the models $A_3$ and $F_1$ can adequately describe the decomposition of bauxite composite under non-isothermal, constant heating rate conditions. The mean $RSQ$ value is 0.965 while the mean $RSS$ 0.237 implying adequate accuracy. In order to find which is the most appropriate model between $A_3$ and $F_1$, a new formula is introduced, namely $y(a)$ [14].

$$y(a) = \left(\frac{da}{dT}\right)_a \exp\left(\frac{E_o}{RT_a}\right)$$

The value of the conversion ($a_m$) when maximum value of $y(a)$ occurs is characteristic for each model. As far as the experimental data of bauxite thermal decomposition are concerned and regardless of the heating rate, the maximum $y(a)$ values occur at the initial stage, namely for $a_m= 0$. In case of $A_3$ model, $a_m$ value equals to 0.283, while for the $F_1$ model, the value of $a_m$ equals 0 [14]. It’s thus clear, that the thermal decomposition of bauxite, can be described by $F_1$ model, namely a first order reaction model. The pre-exponential factor calculated by Eq. 5 was found to be $2.088 \times 10^{11} \text{min}^{-1}$. After calculation of the kinetic triplet, namely the activation energy, pre-exponential factor as well as the kinetic model, Eq. 4 takes the following form:

$$\frac{da}{dT} = \frac{2.088 \times 10^{11}}{\beta} \cdot \exp\left(\frac{-183000}{8.314T}\right) \cdot (1 - a)$$

In Figure 7, experimental data from thermogravimetry are compared to the modeling data that have been accrued by Eq. 7. In fact, Eq. 7 fails in calculating the decomposition progress at the initial and final stages, namely at temperature below 550K and above 900 K due to the realization of minor reactions, as already has been mentioned, at these temperature ranges. In order to identify whether Eq. 7 is capable to simulate the weight loss of bauxite composite due to dehydroxylation of boehmite and diaspore, the conversion was assumed to be 0 at 650K while it was considered that the decomposition has been completed at 950 K, where $a=1$. By applying Eq. 7, and under the aforementioned assumption, it can be seen that the theoretically calculated conversion progress is in good agreement with the experimental data.
5. Conclusion
In the current study, the kinetic of thermal decomposition of a diasporic-boehmitic bauxite ore were investigated at the temperature range between 300 and 1273 K. The kinetic study under non isothermal conditions is based on the determination of kinetic triplet values, namely $E_a$, $A$ and $f(a)$. The value of $E_a$ ranges depending on the method used, between 184994 and 190357 J·mol$^{-1}$ for a 0.5 conversion rate. The dependence of decomposition progress by the conversion was found to obey the $F_1$. Although decomposition of diaspore and boehmite occur in slightly different temperature, distinction of reactions is impossible and thus it is inevitable the assumption of a single step reaction. Thus, the decomposition of the composite bauxite ore kinetically follows a single process pathway due to the almost simultaneous decomposition reactions of boehmite and diaspore to $\text{Al}_2\text{O}_3$.

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