Thermochimica Acta, 92 (1985) 211-214
Elsevier Science Publishers B.V., Amsterdam

# EFFECT OF GRINDING ON THE KINETICS OF THE TRANSFORMATION VATERITE-CALCITE

Cristobalina Barriga, Julian Morales* and Jose L. Tirado
Departamento de Quimica Inorganica, Facultad de Ciencias
Cordoba, Spain

## ABSTRACT

The influence of preliminary grinding on the kinetics of the transformation vaterite-calcite are studied by the analysis of DSC traces recorded under isothermal and dynamic conditions. The transformation proceeds according to a nucleation-growth mechanism and the activation energy increases with the mechanical treatment. This behaviour is attributed to a recrystallization process that occurs simultaneously to the phase transition.

## INTRODUCTION

The phase transition vaterite-calcite is promoted by thermal and mechanical treatment. The kinetics of the thermal transformation has been studied by Rao (1), who finds that a contracting sphere model describes the reported data. Moreover, a change in the activation energy throughout the transformation is associated to the rupture of vaterite particles. However, the data necessary to support this assumption were not reported.

On the other hand, a recent paper (2) showed that prolonged grinding of vaterite alters significantly the thermal behaviour of the samples. Thus, the crystallinity of vaterite may have a direct influence on the kinetics of its transformation to calcite. In this respect, the aim of the present study is to reexamine the kinetics of the thermal transformation vaterite-calcite. These results are complemented by considering the influence of preliminary grinding on the kinetics of the phase transition.

## EXPERIMENTAL

A synthetic vaterite sample of high purity was obtained by the method reported in (1). Grinding was performed in a Fritsch ME 030177 planetary mill equipped with a cylindric agate mortar 80 ml capacity and three balls 10 mm diameter. The starting charge of vaterite was 10 g.

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Proceedings of ICTA 85, Bratislava

Isothermal runs were carried out in a furnace with a Jumo temperature control and Ni-NiCr thermocouple. The degree of conversion was determined by quantitative interpretation of X-ray diffraction patterns by applying the autoflushing theory of binary systems (3).

Differential Scanning Calorimetry traces were recorded under isothermal conditions and with selected heating rates by using a Mettler TA 3000 system. The measurements were carried out in static air atmosphere and sample weights of ca. 25 mg.

The X-ray diffraction patterns were recorded in a Phillips PW 1130 apparatus with $CoK_{\alpha}$ radiation and Fe filter. The analysis of diffraction line profiles recorded at $0.125° 2\theta \min^{-1}$ was carried out by the variance method (4) and making the corrections suggested in (5).

Scanning electron microscopy was performed with a Philips SEM 501 B. Samples were dispersed in acetone by ultrasound placed in Ni holders and covered with electrodeposited gold for observation.

## RESULTS AND DISCUSSION

The isothermal runs followed by X-ray diffraction were performed in the temperature range 445-485°C. For the lower temperature traces, an induction period was observed. The data were analysed by applying various kinetic models, including growth of nuclei ($F_1$,$A_2$, $A_3$), contracting area and contracting sphere models ($R_2$, $R_3$) and diffusion controled processes ($D_1$-$D_4$). A least squares analysis was carried out for the different functions $g(\alpha)$ vs. time plots. The linear regression coefficients were compared by using the statistical t test (6). This analysis allows to discard some kinetic laws ($A_2$ and $A_3$) with a significance level of 99 %. However, a single model cannot be selected.

The Arrhenius plots were obtained for the most significant mechanisms. The activation energy values computed from these plots we comprised between 61 ($A_3$) and 138 ($D_3$) Kcal $mole^{-1}$.

In order to discriminate the kinetic law that describes more accurately the reaction pathways, the reduced time plots were obtained. These plots indicate that the best fit is obtained for $F_1$ , $R_2$ and $R_3$ mechanisms. Additionally, the method proposed by Sharp et al. ( 7 ) was applied to the isothermal data. The mean value of slope was 1.1, in agreement with an $R_2$ or $R_3$ mechanism. The activation energies computed for these kinetic laws were 84 an 86 Kcal mole$^{-1}$ respectively.

The electron micrographs of the original vaterite and partially decomposed samples give additional information. Thus, a "typical peanut-like" shape is observed for the synthetic vaterite. This shape remains unaltered throughout the transformation and no cracks or fisures are developed. These facts show that a three dimensional model of interface displacement may be considered adequate to describe the reaction in such particles.

On the other hand, the values of crystallite size and microstrains were computed for the samples obtained in the isothermal experiment at 460°C after 2, 4 and 6 hours of thermal treatment. These results show that crystallite size reaches a maximum at 4 hours and decreases thereafter, while microstrains decrease continuously. A sintering of vaterite crystallites confined by the development of calcite may explain these observations.

The isothermal measurements performed in the DSC apparatus need higher temperatures (518-530°C) and a change in the slope of the $\ln(-\ln(1-\alpha))$ vs. ln t plots is obtained. The mean value is 2.4 0.3 and suggests that the mechanism of the transformation is governed by a random nucleation process and a rapid growth of nuclei under these conditions. Since the activation energy decreases - 65 Kcal mole$^{-1}$ - the propagation process is associated to a relatively low activation energy as compared with that required for the nucleation process at the surface and the movement of the interface inwards the particles.

The values of the kinetic parameters obtained from DSC traces recorded at 3°min$^{-1}$ by using the Coats and Redfern method (8) are in good agreement with the isothermal results only if a nucleation-growth mechanism is assumed.

The influence of prior mechanical treatment on the kinetics of the transformation was studied by the analysis of isothermal and dynamic DSC curves of a vaterite sample ground for seven hours. The X-ray diffraction pattern of this sample evidenced a small amount of calcite of ca. 10 % and the analysis of line profiles yielded a lower crystallite size and an increase in microstrain content.

The results obtained from the analysis of isothermal curves can be summarized as follows. The mechanical treatment does not alter the mechanism of the transformation, although an increase in the value of activation energy of approximately 10 Kcal mole$^{-1}$ is found.

On the other hand, the range of temperature in which the exothermal peak develops under dynamic conditions decreases for ground vaterite. This phenomenon causes an increase in the slopes of the Coats and Redfern plots and, consequently, in the activation energy. This fact is in agreement with the results obtained from isothermal data.

The changes in activation energy induced by grinding may be explained in the light of the evolution of crystallinity throughout the transformation. As it has been previously discussed, a recrystallization process occurs simultaneously to the formation of calcite. Thus, the activation energy represents a combination of both processes. For the unground sample, the activation energy is mainly associated to the value required for the transformation. In contrast, the contribution of the recrystallization effect becomes notorious in ground vaterite (2) and could act as the agent that increases significantly the activation energy of the overall reaction.

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