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MORPHOLOGICAL OBSERVATIONS ON THE THERMAL DECOMPOSITION OF CALCIUM CARBONATE

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ABSTRACT

Morphological observations of sintering and decomposition processes of polycrystalline $CaCO_3$ have been carried out as function of temperature, pressure and atmosphere. The investigations prove,that the properties of the solid products formed are strongly influenced by phenomena occurring before and during the decomposition and which, in turn, are governed by the actual experimental conditions.

INTRODUCTION

It is well known that properties of solid products obtained in the thermal decomposition process depend on the conditions of the reaction (see e.g. for calcium carbonate ref.1-3). On the other hand a lot of parameters of the thermal decomposition reaction strongly influence its kinetics and mechanism. Describing mathematically this very complicated process it is necessary to make some simplifying assumptions, which are often not checked and compared with the real course of the investigated reaction. The real phenomena occurring during decomposition are not introduced to the kinetic models and the best fit of the experimental results by some kinetic equation is often not sufficient proof for the proposed mechanism of the decomposition. In the present paper the morphology of the solids in the thermal decomposition of $CaCO_3$ is investigated. These observations provide the possibility for drawing the conclusions about properties of the product and macromechanism of the reaction.

EXPERIMENTAL PROCEDURE AND RESULTS

Sintering and decomposition experiments were carried out on a Mettler 2000 C thermoanalyzer. For each sintering process about 20 mg of polycrystalline calcite (Merck p.a.) was heated under CO_2 and dynamic conditions (heating rate: 3.5 $Kmin^{-1}$) from room temperature to the required temperatures. In order to prevent the decomposition,

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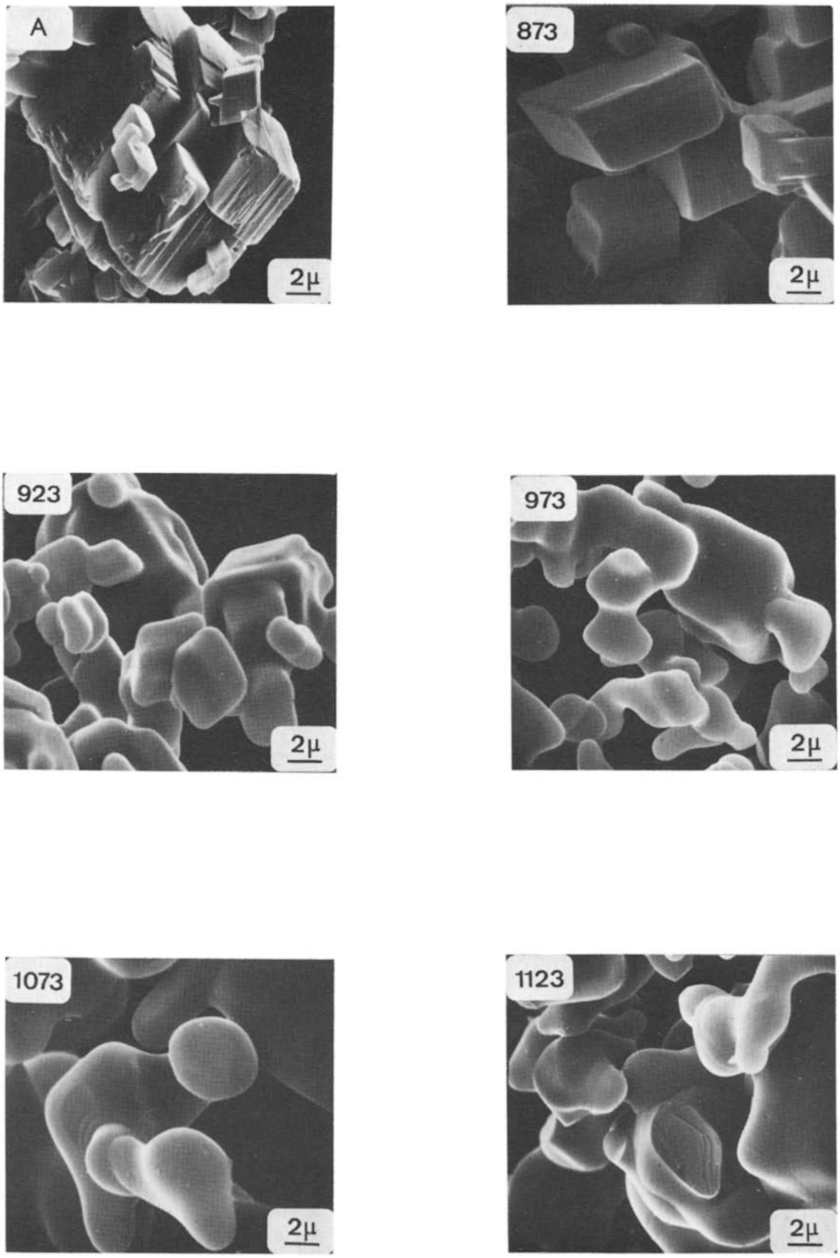

Fig. 1. Sintering of calcite heated with the rate 3.5 Kmin^{-1} till the temperatures marked on micrographs (in K). Sample A - unheated calcite.

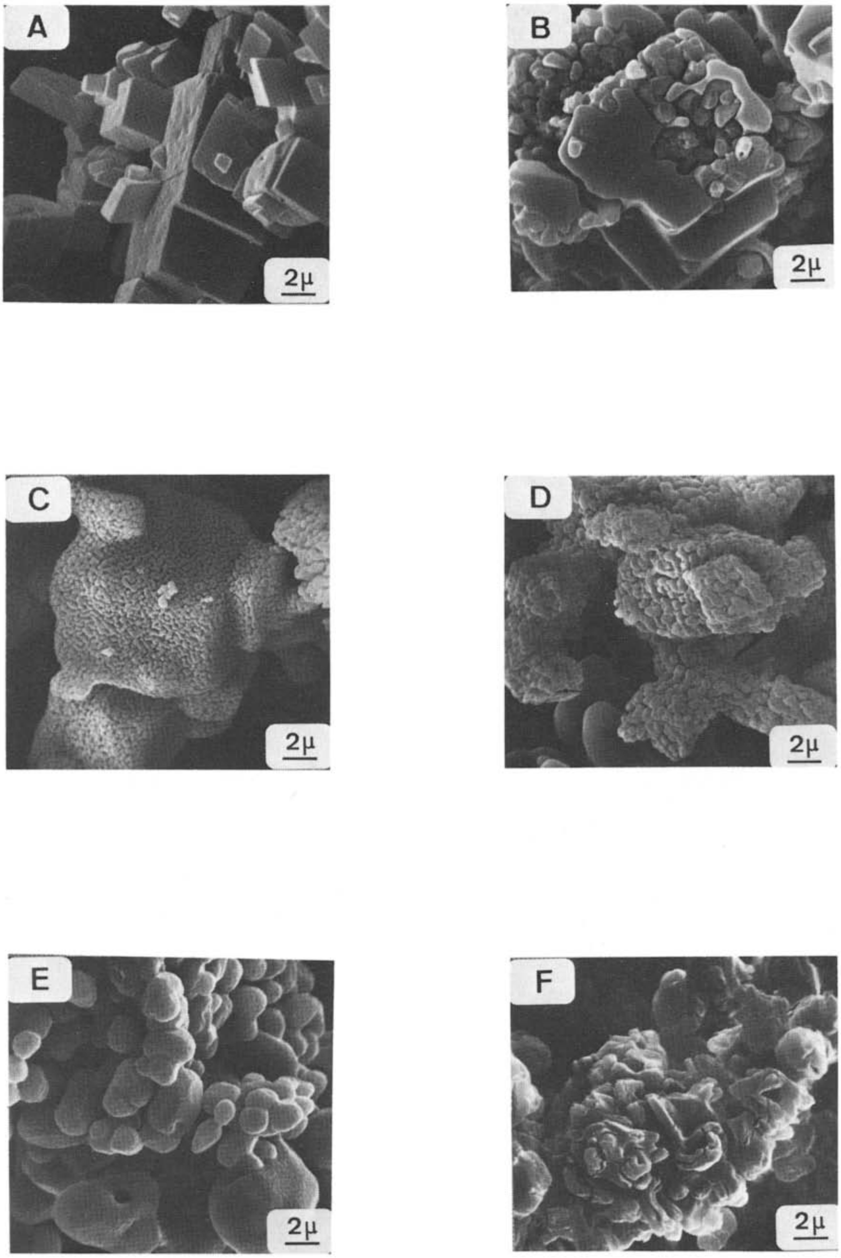

Fig. 2. The morphology of CaO obtained from $CaCO_3$ under different conditions: A - vacuum, B - nitrogen, sample decomposed in 50 % at 893 K, C-E - CO_2 at 1053 K and pressures 20, 50 and 80 Pa respectively, F - CO_2, 1000 Pa.

the CO_2 pressure was slightly higher than the equilibrium pressure at the final temperature of each sintering experiment. Seven products were obtained by stopping the heating at temperatures between 873 and 1173 K in 50 K intervals. Scanning electron micrographs were taken (Stereoscan 1, Cambridge Instruments). The results of these investigations are presented in Fig. 1.

Sintering of calcite is observed at temperatures as low as 873K. This process is more pronounced at temperatures, at which the decomposition is usually investigated. The observed sintering phenomena indicate, that under different experimental conditions - such as differences in partial pressures of CO_2, sample weights, particle sizes, shape of crucibles and ambient atmospheres - the onset temperature of the actual decomposition shifts. Moreover, the surface properties of the solid products show differences.

The big influence of the ambient pressure on the morphology of the product was observed during the decomposition. The samples were decomposed isothermally under vacuum, in nitrogen and under different CO_2 pressures. Fig. 2A - 2F confirm, that under vacuum the reaction starts at a much lower temperature, i.e. at 730 K, and the surface is not affected by sintering: The decomposition is initiated by the formation of a large number of nuclei (Fig. 2A). By increasing the CO_2 pressure (Fig. 2C - 2F) the rate of nuclei formation decreases and the morphology of the product as well as its activity for the back-reaction differ from those of CaO prepared in vacuum.

The investigations of the sintering of CaO obtained under vacuum confirmed that morphology and crystal size do not change in the range of 773-1273 K. This supports the conclusion, that the properties of CaO are mainly a consequence of processes taking place before and during the thermal dissociation. These results clearly show, that the observation of real phenomena occurring during decompositions are an important part of any accurate description of reaction mechanisms, as it allows more realistic conclusions than mechanistic interpretations based solely on kinetic data.

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