EFFECT OF BALL MILLING ON THE KINETICS OF THERMAL DECOMPOSITION OF LEAD CARBONATE AS OBSERVED BY THE DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

The effect of the intensive milling in a planetary ball mill on the kinetics of thermal decomposition of lead carbonate $PbCO_3$ has been studied. It has been found, that the ball milling diminishes the heat effect accompanying the early stage of the thermal decomposition of investigated material. This suggests, that intensive ball milling causes at least partial decomposition of $PbCO_3$ into PbO and CO_2. The qualitative observations of the mass loss of the milling products during the DSC experiments support this supposition.

INTRODUCTION

Mechanochemical (ball milling) treatment of materials in producing new thermodynamically stable and metastable materials, non achievable by other, conventional, methods, is well established and received industrial exploatation after the pioneering works of Benjamin in seventies of the last century. While the method is progressing at the industrial level, basis knowledge about the physical mechanisms operating during the ball milling process is still very limited due to inherent difficulties in quantifying this complex phenomenon [1, 2].

A survey of the recent literature indicates that mechanochemistry is mainly devoted nowadays to forming metallic and hydrogenated alloys. In the field of nonmetallic inorganic compounds the mechanically induced polymorphic phase transitions in PbO_2, SnO_2, TiO_2, WO_3 and heavy rare earth sesquioxides were reported [3, 4]. Gaffet and coworkers [5] carried out various suboxide syntheses by adding some metal to higher oxides. Recently, our team performed a successful, fast (~10 min) synthesis of silver telluride from pure elemental powders of Ag and Te under relatively mild milling conditions [6].

The purpose of the present study was to observe the effect of ball milling on the kinetics of thermal decomposition of the lead carbonate $PbCO_3$.

EXPERIMENTAL CONDITIONS

Lead carbonate powder, pure for analysis, supplied by POCh was used in the experiments. The starting material was milled in a planetary ball mill Pulverisette 7, produced by the firm FRITSCH, in air. Milling was carried in the grinding vials of 25 ccm volume, each containing 5 balls with diameter of 12 mm. Both the vials and the balls were made of stainless CrNi steel. Each vial was filled with 2 g of investigated lead carbonate. The plate supporting the vials was rotated at a rotation speed of 510 rpm. The rotation speed of the vials was 1070 rpm.
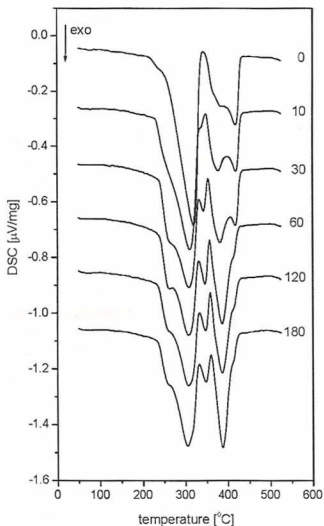

Figure 1. DSC traces for unmilled lead carbonate and for products of milling of different durations. Parameter – milling time in minutes. For the sake of clarity the DSC curves for milling products are systematycally shifted down along the vertical axis by 0.2 μV/mg.
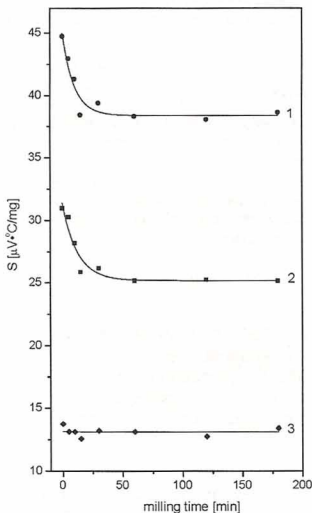
Figure 2. Effect of the ball milling on the area (heat effect) under the whole DSC curve (1) and under the first (2) and second (3) group of peaks on it.
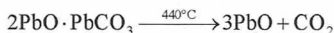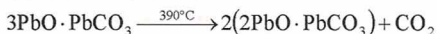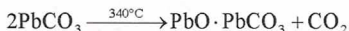
Thermal decomposition of the products of the milling procedure with 7 different milling times (5, 10, 15, 30, 60, 120 and 180 minutes) was investigated by differential scanning calorimetry. DSC measurements were performed using the NETZSCH DSC 404/3/F microcalorimeter with Pt-PtRh measuring head and

standard sample pans made of platinum. An empty pan was used as the reference. The DSC traces were recorded at a constant heating rate of 10 K/min. The masses of the samples in each DSC experiment were nearly the same (53,95 – 54,94 mg).

RESULTS AND DISCUSSION

The experimentally determined DSC traces of unmilled lead carbonate and the products of its milling obtained after various milling times, are presented in Fig. 1. For the sake of clarity, the temperature dependences of the DSC signal shown in Fig. 1 are systematically shifted down along the vertical axis by 0.2 μCV/mg.

In general, the observed kinetics of the thermal decomposition of lead carbonate and of the products of its milling, qualitatively agrees with that reported by Ponnetier et al [7] and by Warne et al [8]. According to these authors, the thermal decomposition of $PbCO_3$ occurs in there main stages, which may be represented as three subsequent reactions:

$$2PbCO_3 \xrightarrow{340°C} PbO \cdot PbCO_3 + CO_2$$

$$3PbO \cdot PbCO_3 \xrightarrow{390°C} 2(2PbO \cdot PbCO_3) + CO_2$$

$$2PbO \cdot PbCO_3 \xrightarrow{440°C} 3PbO + CO_2$$

The DSC curves registered in the present study display the peaks corresponding to the reaction temperatures proposed in [7] and [8]. The differences are due to the fact that our DSC traces were registered in the atmosphere of air, whereas in [7] and [8] the DTA traces were determined in the CO_2 atmosphere. Additionally, the measuring apparatuses used in cited works were much less sensitive than our microcalorimeter and were unable to reveal the subtle structure of the registered traces.

An inspection of Fig. 1 shows clearly, that the thermal decomposition of lead carbonate, as well as products of its milling, occurs in more than three stages. In general, two groups of peaks are observed on the DSC curves – one in the temperature interval ranging from 220 to 350 ºC and the second extended over the temperature interval 350 – 450 ºC. The first group of peaks consists of at least three thermal effects with different temperatures and intensities of heat absorption, whereas the second group represent a sum of at least two different effects of heat consumption. Unfortunately due to the close overlapping of the components our efforts to resolve these peaks failed giving no unambiguous values of both the temperatures and areas (values of reaction heats) of the components of both the groups of peaks.

With increasing the milling time, the structure of both the groups of the peaks on the registered DSC traces changes. The intensity of the low temperature shoulder and the high temperature branch of the first group of increases, whereas the intensity of the main, central component decreases.

In the second group of peaks the low temperature component, peaking at ~390 °C, increases whereas that with a peak of ~410 °C systematically decreases.

It is well know that the area under the DSC peaks corresponds to the heat effect of the corresponding reaction. We determined the total area of the first and the second group of peaks as a function of the milling time. The results of this analysis are shown in Fig. 2. As it is seen from Fig. 2, the total area (total heat effect of thermal decomposition) under the whole DSC curve initially decreases with the milling time, and for milling duration longer than 30 min. stabilises at the level of ~38 µV/mg i.e. is by ~15,5 % lower than that for unmilled sample. However, the diminution of the heat effect is not extended uniformly over the whole   temperature   range.

A comparison of the dependencies of the areas under the first and the second group of the peaks on the milling time reveals that the area of the second group of the peaks on the DSC traces does not depend on the milling time, and the change in the whole heat effect of thermal decomposition of lead carbonate results from the decrease of the area of the first group of the peaks.

The results of our study indicate that ball milling causes partial decomposition of the lead carbonate with evolution of weekly bonded CO which is able to evolve from the sample subjected to thermal decomposition at lower temperatures. This conclusion is supported by observations of the relative differences in the mass of samples at the start and after finishing the total thermal decomposition of the products of milling during the DSC measurements.

The detailed analysis of the kinetics of all the revealed stages of the thermal decomposition of lead carbonate and especially of the effect of mechanochemical treatment on this process, deserves further studies. They are in progress.

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