Investigation of the effect of intensive milling in a planetary ball mill on the thermal decomposition of basic nickel carbonate

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Abstract: The kinetics of thermal decomposition of basic nickel carbonate NiCO₃·Ni(OH)₂·nH₂O and the effect of intensive milling in a planetary ball mill on its parameters, have been investigated. The values of the reaction heat and of the activation energy of thermal decomposition have been determined. Investigations of the thermal decomposition of the products of ball milling of investigated compound revealed a distinct effect of milling on the reaction temperature and heat consumed during the thermal decomposition of investigated compound.

1. Introduction

Studies of the effect of mechanical deformation on the chemical reactivity of solids, called mechanochemistry, are nowadays an important research area in the field of physical chemistry and chemistry of solids [1,2]. Mechanochemistry offers the possibility to conduct various reactions, including the synthesis of substances in the nanocrystalline and amorphous states, at low temperatures without dissolution or fusion of the reactants.

Mechanochemical treatment of substrates in producing new thermodynamically stable and metastable materials, often non achievable by traditional methods, is well established and received industrial applications. While the method is progressing at the industrial level, knowledge about the physical mechanisms operating during the mechanochemical treatment (eg. ball milling) is still very limited due to serious difficulties in quantifying this complex process [3].

A survey of the recent literature indicated that nowadays the research effort in mechanochemistry is mainly devoted to preparation of new metastable and stable metallic materials. In the field of nonmetallic inorganic compounds the mechanically induced polymorphic phase transition in many oxides were reported. Successful syntheses of many compounds, eg. copper and silver chalcogenides, have been described, too [3-6].

In our previous studies [7,8] a distinct effect of ball milling on the thermal decomposition of lead and cadmium carbonates, as well as of the basic zinc carbonate, has been observed. The purpose of the present study was to observe the eventual effect of ball milling on the thermolysis of basic nickel carbonate NiCO₃·Ni(OH)₂·nH₂O. The thermal decomposition of basic nickel carbonates is of...
particular interest, since pure nickel and several nickel catalysts are prepared by decomposition of these carbonates and reduction of the decomposition product. The activity and service life time are dependent on the prehistory of parent materials, calcinations conditions, doping with foreign oxides, etc. Despite of intensive research effort (see e.g. [9-12]), including even the action of ionizing radiation, there is still not quantitatively substantiated model of thermal decomposition of basic nickel carbonate. Till now the effect of ball milling on the thermal decomposition on the kinetics of thermal decomposition has not been investigated.

2. Experimental conditions
Chemically pure basic nickel carbonate NiCO$_3$·Ni(OH)$_2$·nH$_2$O, supplied by POCh Gliwice, was used in the experiments. Thermal decomposition of starting material, as well as of products obtained by intensive ball milling, was investigated by differential thermal analysis, performed using the NETZSCH DSC 404/3F differential scanning calorimeter with the S-type Pt-PtRh measuring head and standard platinum sample pans. An empty sample pan was used as the reference. The masses of the samples in each DSC experiment series were nearly the same ~19 mg.

The investigated compound was milled in a planetary ball mill Pulverisette 7 produced by FRITSCH. Milling was carried out in the two grinding vials of 25 ccm volume containing 5 balls with diameter of 12 mm. Both the vials and balls were made of stainless CrNi steel. Each of the two milling vials containing 5 balls were charged with 2 g of the investigated basic nickel carbonate. The rotation speed of the plate supporting the milling device was 370 turns per minute. The milling conditions were changed only by changing the milling time.

All the milling procedures and DTA experiments were performed in atmospheric air under normal pressure.

3. Results and discussion
The DSC traces for unmilled NiCO$_3$·Ni(OH)$_2$·nH$_2$O as well as of the product of ball milling lasting 2 hours, all registered at the same heating/cooling rate of 10 K/min, are shown on Fig.1. In the first heating run distinct endotherms, revealing the two main stages of thermal decomposition of investigated compound, were observed. On the DSC traces registered in the cooling run as well as during the second heating run (with the same sample) no thermal effects were observed. This means that the investigated carbonate samples have been completely decomposed in the first heating run.

As it seen on Fig.1, the thermal decomposition of investigated carbonate occurs in two stages. The low temperature stage consists of evolution of crystalline and hydroxilic water. The solid product of this process is NiO. The DSC endotherm corresponding to this stage is anomalously brood. Most

![Figure 1. DSC traces for NiCO$_3$·Ni(OH)$_2$·nH$_2$O registered at the heating/cooling rate of 10 K/min. 1 – first heating run, 2 - cooling run, 3 – second heating run.](image-url)
probably, the loss of crystalline water occurs at temperature slightly differing from that for the decomposition of Ni(OH)$_2$. These two processes produce two overlapping DSC peaks, and the low temperature endotherm in the registered DSC traces is a result of their superposition.

The high temperature endotherm peaking at about 590 K corresponds to the decomposition of NiCO$_3$ into NiO and gaseous CO$_2$. So, the only solid product of heating of investigated basic nickel carbonate up to ~ 770 K is NiO.

On the DSC traces registered in the first cooling run as well as in subsequent heating and cooling runs a small discontinuity (jump) is observed at temperature of about 510 K. This effect can be ascribed to the antiferromagnet-paramagnet phase transition (Neel point) of NiO, being the final solid product of thermolysis of the investigated carbonate. The Neel temperature for pure stoichiometric NiO is 520 K, and this second order phase transition is accompanied by a well know $\lambda$ - anomaly in the temperature dependence of the heat capacity.

![Exemplary DSC traces for unmilled and milled samples](image)

**Figure 2.** Exemplary DSC traces for unmilled and milled by 3 hours NiCO$_3$·Ni(OH)$_2$·nH$_2$O samples registered at different heating rates. Parameter – heating rate in K/min.

![Ozawa’s plots for reaction temperatures](image)

**Figure 3.** Ozawa’s plots for reaction temperatures of unmilled and milled basic nickel carbonate. Milling time – 2 hours.
With increasing the heating rate in the DSC experiments, the positions of endotherms corresponding to the two stages of thermal decomposition of investigated compound systematically shift towards higher temperatures (Fig. 2). This effect is typical of thermally activated processes, and allows for determination of the value of activation energy.

The activation energies for thermal decomposition of NiCO\textsubscript{3} (high temperature stage) has been determined by the method proposed by Ozawa [13]. For this purpose the so called “Ozawa plots” \( \ln v = f(1/T) \) were constructed (Fig. 3), where \( T \) denotes the reaction temperature determined at the heating rate \( v \). Reaction temperatures \( T \) were determined from the intersection of tangent to the low-temperature (left) side of endotherm with the base line of recorded DSC trace. As it is seen on Fig. 3, the data points for reaction temperatures registered at different heating rates are located along straight lines. The slopes of these lines multiplied by the universal gas constant \( R \) give the value of the activation energies of investigated processes.

The obtained this way value of the activation energy for the high temperature stage of thermal decomposition of unmilled basic nickel carbonate (thermolysis of NiCO\textsubscript{3}) is 142.46 kJ/mole. Activation energy for the same stage of thermolysis of compound submitted to 2 hour ball milling is distinctly higher and amounts 167.29 kJ/mole. This leads to the conclusion that the milling procedure increases the thermal stability of investigated compound.

Determination of the activation energy for the low temperature stage of thermolysis of investigated basic nickel carbonate was impossible, because of the complexity of shape of the low temperature endotherm on the registered DSC traces.

The conclusion about enhancement of the thermal stability of basic nickel carbonate by milling has been confirmed by investigations of the effect of the milling time on the reaction temperatures and on the heat consumed during the two stages of the thermal decomposition of investigated material.

The area under the peaks on the DSC traces is proportional to the heat of observed chemical reaction or structural transformation. Making use of the calibration experiments in which the endotherms corresponding to the melting of high purity tin and zinc were registered, the heat consumed during the thermal decomposition of investigated nickel carbonate has been determined.

![Figure 4](image)

\textbf{Figure 4.} Effect of the milling time on the decomposition temperature (left) and the reaction heat (right) for the two stages of thermolysis of basic nickel carbonate.

Figure 4 represents the experimentally determined dependencies of the temperatures (left) and heats (right) consumed during the two stages of thermolysis of basic nickel carbonate on the milling time. As it is seen, milling causes a distinct increase of temperatures and heat of both the stages of thermolysis. The enhancing effect of milling on the thermal stability of investigated basic nickel
carbonate, documented by the results of the present study, is rather surprising – in our previous studies [7,8] on the lead carbonate and basic zinc carbonate an opposite effect has been observed and no substantial effect of milling on the thermal decomposition of cadmium carbonate has been found. The elucidation of this discrepancy requires further experimental and theoretical studies.

4. References

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