

THE INFLUENCE OF ALUMINIUM AND ALUMINIUM OXIDE ON THE EFFECTS OF MECHANICAL ACTIVATION OF NICKEL HYDROXOCARBONATE

K. Wieczorek-Ciurowa^{1}, K. Gamrat¹, M. Paryło¹ and Ju. G. Shirokov²*

¹Cracow University of Technology, Institute of Inorganic Chemistry and Technology,
Warszawska 24, 31-155 Cracow, Poland

²Ivanovo State Academy of Chemistry and Technology, Engels Prospect 7, 153-260 Ivanovo,
Russia

Abstract

The chemical and physical processes occurring during the grinding of nickel hydroxocarbonate and mixtures of nickel hydroxocarbonate with aluminium and aluminium oxide were discussed. For mechanical treatment a planetary ball mill was used. The phase analyses of ground products were carried out using thermogravimetry and X-ray diffraction methods. The amount of $\text{Ni}_2(\text{OH})_2\text{CO}_3$ undecomposed and $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, $x\text{NiO}$, Ni^0 , Ni_xAl_y alloys and remained Al^0 in the systems strongly depends on the proportion of components and on the duration of grinding in a mill which was used in the study. The comparative results are presented.

Keywords: aluminium, aluminium oxide, grinding, hydroxocarbonates, mechanical activation, NiAl-alloys, phase analysis, thermogravimetry, X-ray diffractometry

Introduction

Reactive milling has opened new ways for the solid state reactions and the alloy syntheses. Mechanical activation is usually carried out in high-energy devices such as vibratory, planetary or attritor mills. The energy transfer to the particles in these mills takes place by shearing action and impact of the high velocity balls with the powdered reagents. Therefore, the mechanical treatment can cause physical and/or chemical changes in materials [1–4], which can be identified by analysis of the solids formed during milling.

An important application of mechanical activation can be obtaining of a catalyst. For example, the ground mixtures of hydroxocarbonate of Ni with powdered aluminium are a catalytic agent in some organic syntheses. Literature data [5] confirmed by our preliminary investigations indicate that such type of catalysts can be used instead of Raney's catalyst in the reactions of hydrogenation of some unsaturated organic compounds.

* Author for correspondence: E-mail: kwc@usk.pk.edu.pl

Elucidation of the mechanism of reactions occurring during grinding is not a simple task. Phase transformations, changes in crystalline structure and formation of new solid phases in mechanically activated mixtures can be examined by thermal analysis and X-ray diffraction methods [6–9]. However thermonalytical techniques are only very useful in this case because of their simplicity in qualitative and quantitative phase analysis.

The aim of this research was to show the influence of aluminium and aluminium oxide in powder form on mechanical activation of nickel hydroxocarbonate.

Experimental

Materials

Ni-hydroxocarbonate ($\text{Ni}_2(\text{OH})_2\text{CO}_3$) was obtained by precipitation from aqueous solution [7]. The aluminium powder and aluminium oxide was nominally >99% Al^0 and $\alpha\text{-Al}_2\text{O}_3$, respectively.

The systems of $\text{Ni}_2(\text{OH})_2\text{CO}_3$ with Al^0 were prepared as physical mixtures at (%) proportions of 80:20, 90:10 and 20:80, respectively and the system of $\text{Ni}_2(\text{OH})_2\text{CO}_3$ with Al_2O_3 at a (%) proportion of 50:50.

A planetary laboratory mill with balls made of W–Co alloy was used for mechanical activation. The two vials were rotated at $1130 \text{ rev min}^{-1}$. The velocity of the ball was of 3.20 m s^{-1} . The mass proportion of balls to sample mass was of 14:1.

Mechanical grinding was carried out in the range of 5–15 min in air at ambient temperature and under atmospheric pressure.

Methods and instruments

Thermogravimetric analyses of the samples were carried out on a Mettler thermobalance TG-50 in a Mettler TA-4000 System. Records were obtained with samples heated at a rate of $24^\circ\text{C min}^{-1}$, up to 950°C , in an open platinum crucible. The sample size was about 20 mg.

X-ray powder diffraction patterns were obtained using a Philips X' Pert Diffractometer (CuK_α) in the 2θ range of $10\text{--}60^\circ$.

Results and discussion

The results of our preliminary investigations indicated that hydroxocarbonate of nickel remains almost undecomposed after 15 min of mechanical treatment, unlike $\text{Cu}_2(\text{OH})_2\text{CO}_3$, which decomposes in over 60% under the same treatment [6]. The reason for this is probably a difference in crystalline state of these two mentioned compounds. It is evident from the previous study that $\text{Cu}_2(\text{OH})_2\text{CO}_3$ is crystalline and whereas $\text{Ni}_2(\text{OH})_2\text{CO}_3$ is amorphous as can be seen in Fig. 1a.

The two-component systems, i.e. $\text{Ni}_2(\text{OH})_2\text{CO}_3$ with Al^0 , become more complicated. The TG/DTG curves for the systems with a different content of Al^0 and after

milling time for 5 and 15 min are shown in Figs 2 and 3, respectively. The mass changes, generally accomplished in four steps, can be attributed to:

- I – a dehydroxylation of hydrated aluminium oxide ($-\Delta m_{\text{H}_2\text{O}}$),
- II – the decomposition of $\text{Ni}_2(\text{OH})_2\text{CO}_3$ ($-\Delta m_{\text{H}_2\text{O}+\text{CO}_2}$),
- III – the rapid Al^0 oxidation ($+\Delta m_{\text{O}_2}$),
- IV – the oxidation of Ni-Al alloys ($+\Delta m_{\text{O}_2}$).

A reliable identification of solids present in ground products made on the basis of results of thermogravimetry and X-ray powder diffractometry (Fig. 4) was essential to elucidate the processes (1–6) occurring during mechanical activation, which is schematically shown in Fig. 5.



It is worth-while to notice that an oxidation of aluminium (process 2) with great heat evolution may initiate further reactions, e.g. the metalothermic reduction [10] of

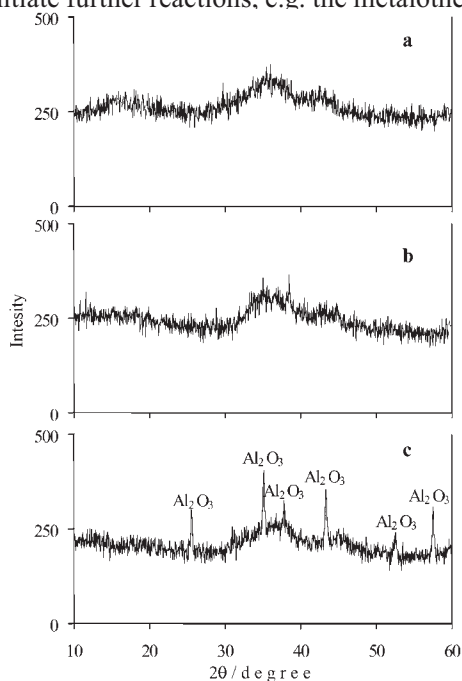


Fig.1 X-ray diffraction patterns for the systems after grinding for 15 min:
 a – $\text{Ni}_2(\text{OH})_2\text{CO}_3$; b – $\text{Ni}_2(\text{OH})_2\text{CO}_3$ and Al^0 (90:10); c – $\text{Ni}_2(\text{OH})_2\text{CO}_3$ and Al_2O_3 (50:50)

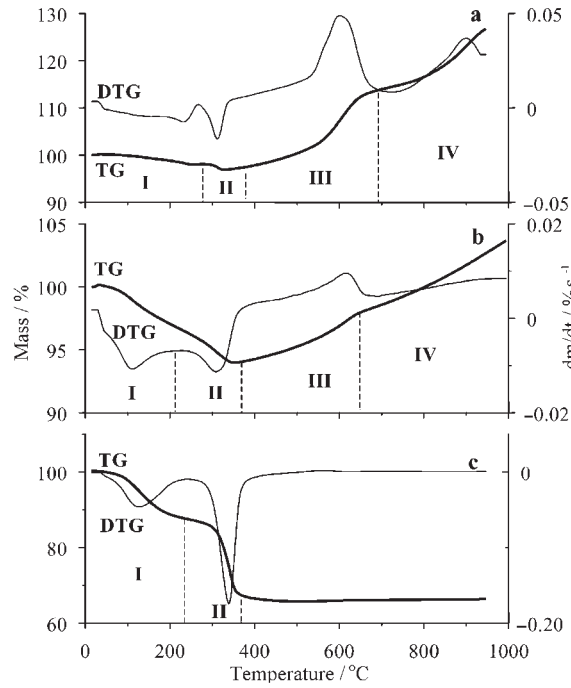


Fig. 2 Three sets of TG/DTG curves for ground (15 min) mixture of $\text{Ni}_2(\text{OH})_2\text{CO}_3$ with Al^0 with different component proportions: a – 20:80, b – 80:20, c – 90:10

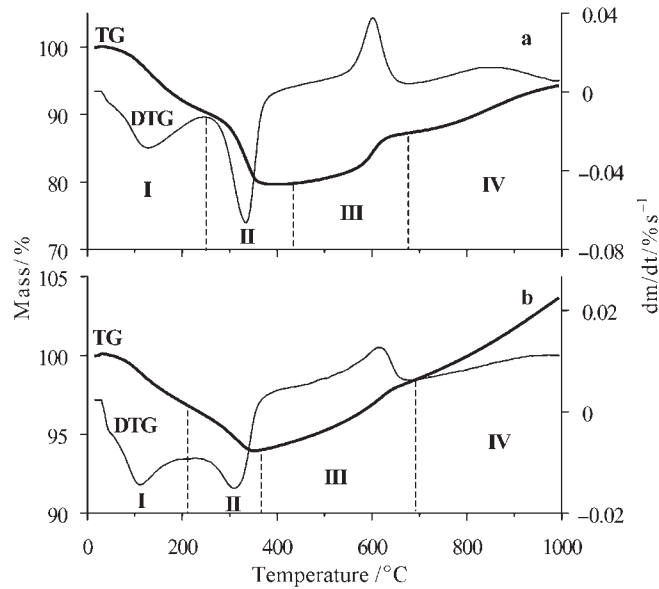


Fig. 3 Two sets of TG/DTG curves for of $\text{Ni}_2(\text{OH})_2\text{CO}_3$ with Al^0 mixture (80:20) after grinding: a – for 5 min, b – for 15 min

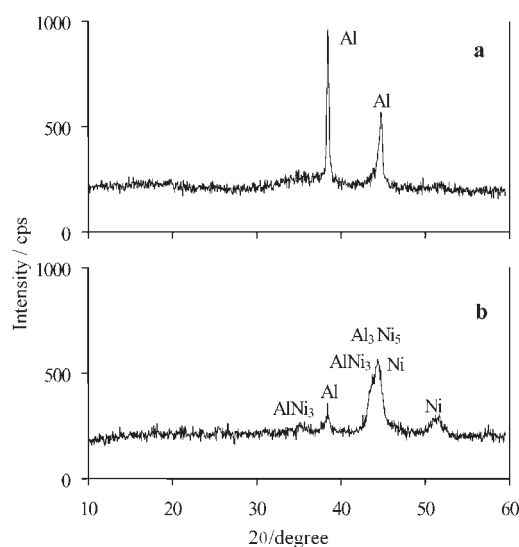


Fig. 4 X-ray diffraction patterns for $\text{Ni}_2(\text{OH})_2\text{CO}_3$ and Al^0 system (80:20) after grinding: a – for 5 min, b – for 15 min

nickel oxide by Al^0 (process 3) and accelerates decomposition of Ni-hydroxocarbonate with water and carbon dioxide evolution (1). The water in turn may react with aluminium producing a certain amount of hydrogen and $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (4). The hydrogen can be an agent for nickel oxide reduction (5), however the aluminothermic reaction (3) is more favourable from the thermodynamic standpoint. The presence of nickel–aluminium alloys in the system suggests an interaction between the solid components, which have formed during mechanical activation. In this system, aluminium and aluminium alloys are only crystalline phases, while aluminium oxide and Ni-hydroxocarbonates are amorphous (Fig. 4). The results of the complete phase analyses of the system of $\text{Ni}_2(\text{OH})_2\text{CO}_3$ and Al^0 (20:80) calculated from thermogravimetric data are listed in Table 1.

Table 1 Phase composition of $\text{Ni}_2(\text{OH})_2\text{CO}_3$ and Al^0 mixture (80:20) during 5 and 15 min of grinding

Time/min	Phase composition/%				
	$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	$\text{Ni}_2(\text{OH})_2\text{CO}_3$	NiO+Ni (in alloy)	Al_2O_3 +Al (in alloy)	Al^0
5	22.5	36	27	6.5	8
15	5	9.5	52	29.5	4

In order to indicate an action of aluminium in $\text{Ni}_2(\text{OH})_2\text{CO}_3$ – Al^0 system during mechanical treatment, different proportions of salt to metal were applied. Thus, in the systems with Al^0 in amount of 80–20%, the oxidation of aluminium and alloy forma-

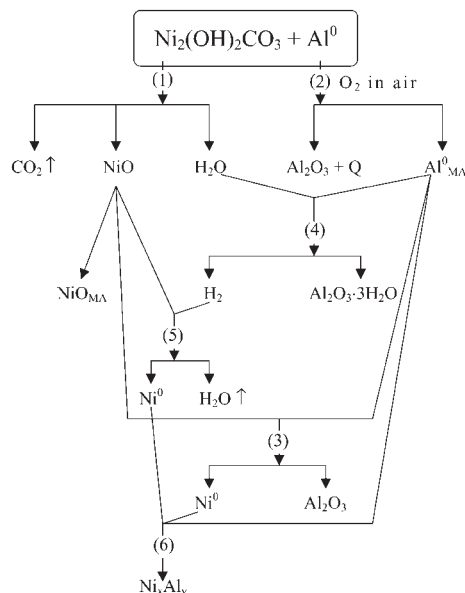


Fig. 5 The scheme of the chemical processes in the system of $\text{Ni}_2(\text{OH})_2\text{CO}_3\text{-Al}^0$ during mechanical treatment

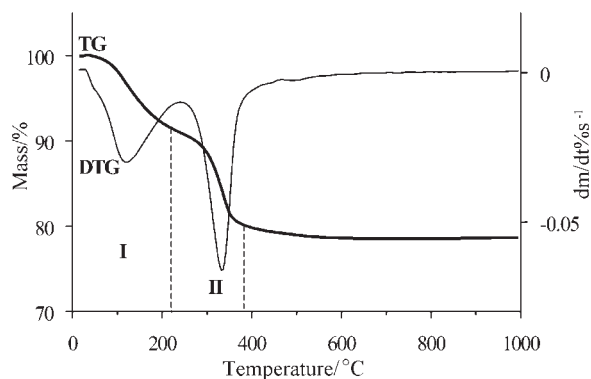


Fig. 6 TG/DTG curves for $\text{Ni}_2(\text{OH})_2\text{CO}_3$ with Al_2O_2 mixture after grinding for 15 min

tion are observed in Fig. 2a–b, effects III and IV, respectively. In the systems which contain smaller amounts of Al^0 (e.g. 10%), alloys do not occur (Fig. 2c). In such cases the effects III and IV are negligible. The final solid products ($\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ and remaining $\text{Ni}_2(\text{OH})_2\text{CO}_3$) are amorphous (Fig. 1b).

Our investigations indicated that the influence of aluminium oxide for mechanical activation on Ni-hydroxocarbonates is not substantial. There is no chemical interaction between Al_2O_3 and $\text{Ni}_2(\text{OH})_2\text{CO}_3$, however, TG/DTG curves in Fig. 6 reveal that a certain amount of water from salt decomposition during milling has combined with aluminium oxide forming the hydrated aluminium oxide [11] so, the step I corre-

sponds to $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ dehydroxylation and effect II – $\text{Ni}_2(\text{OH})_2\text{CO}_3$ decomposition. Al_2O_3 is only crystalline (Fig. 1c).

Conclusions

- The final solid products of mechanical activation of $\text{Ni}_2(\text{OH})_2\text{CO}_3$ -Al strongly depend on the amount of aluminium in the system; if there is more aluminium than about 10%, the Ni_xAl_y alloys appear. The reduction process of Ni(II) by Al^0 is mainly responsible for alloying (aluminothermic reaction).
- There are not specific interactions between Al_2O_3 and $\text{Ni}_2(\text{OH})_2\text{CO}_3$.

* * *

The authors wish to thank Dr. W. Balcerowiak at the Institute of Heavy Organic Synthesis in Kędzierzyn-Koźle (Poland) for his help in the thermoanalytical measurements.

This work was supported by the Polish State Committee for Scientific Research (KBN), grant C-1/138/DS/2000.

References

- 1 B. Murty and S. Ranganathan, *Int. Mater. Rev.*, 43 (1998) 43.
- 2 I. J. Lin, *J. Therm. Anal. Cal.*, 52 (1998) 453.
- 3 K. Tkačová, *Mechanical Activation of Minerals*, Elsevier, Amsterdam 1989.
- 4 P. G. Fox, *J. Mater. Sci.*, 10 (1975) 340.
- 5 G. B. Gołubkova, T. F. Grigoriewa, E. Ju. Iwanow, O. T. Kalinina, S. D. Mihalienko and A. B. Fasman, *Khim. Techn.*, 297 (1987) 1181 (in Russian).
- 6 K. Wieczorek-Ciurowa, Ju. G. Shirokov and M. Paryło, *J. Therm. Anal. Cal.*, 60 (2000) 59.
- 7 K. Wieczorek-Ciurowa, M. Paryło and Ju. G. Shirokov, *Czasopismo Techn.*, Ed. Polit. Krak., Z.3-Ch (2000) 77 (in Polish).
- 8 K. Wieczorek-Ciurowa, M. Paryło Ju. G. Shirokov and K. Gamrat, *J. Therm. Anal. Cal.*, 65 (2001) 359.
- 9 K. Wieczorek-Ciurowa, M. Paryło and Ju. G. Shirokov, *Czasopismo Techn.*, Ed. Polit. Krak., Z.3-Ch (1999) 67 (in Polish).
- 10 P. M. Botta, E. F. Aglietti and J. M. Porto-Lopez, *Thermochim. Acta*, 363 (2000) 143.
- 11 K. J. D. MacKenzie, J. Temuujin, M. E. Smith, P. Angerer and Y. Kameshima, *Thermochim. Acta*, 359 (2000) 87.