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Mechanism of mechanochemical reactions in malachite-active metal systems

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Abstract

Mechanically activated mixtures of some hydroxocarbonates with powder, metallic aluminium caused chemical reactions, which result in alloy formation. The identification of phases formed during milling was successfully achieved by thermal analysis methods supplemented by X-ray diffraction measurement.

Keywords: Hydroxocarbonate; Mechanical alloying; Mechanochemistry; Thermal analysis methods; Transition metals

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1. Introduction

Mechanical impulse operating in the solid–solid system can initiate or intensify chemical reactions. This action is defined as a mechanical activation. To accomplish indispensable high energy milling devices such as planetary or vibrational mills are used [1]. Simultaneously, actions of stroke and friction cause, besides comminution, changes of physicochemical properties of ground materials. It involves the excess energy accumulation in solids. As a consequence, favourable conditions are formed to proceed chemical reactions between components of the milling system. Thus, processes that require high temperature can occur without externally applied heat [2–9].

Nowadays, reactive milling can be used to produce various alloys [10–13]. Mechanical alloying describes the process when mixtures of powders (different metals or other compounds) are milled together. Moreover, mechanical activation is a perspective way for catalyst synthesis [14].

Because of a lot of interesting features of the mechanochemical reactions the main thing is estimating the phase composition of products of milling. The aim of this research is the recognition of types of chemical reactions and physical transformations that occur during activation of the system of copper hydroxocarbonate with powder aluminium in a planetary mill.

2. Experimental

2.1. Materials

Copper hydroxocarbonate (malachite) was obtained by precipitation from aqueous solution [15]. Aluminium was a commercial reagent (99 wt.% pure) in a powder nanocrystalline form. Two systems of salt

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with metal, $Cu_2(OH)_2CO_3$–Al^0, have been prepared as physical mixtures with 20 and 3% of aluminium by weight, respectively.

2.2. Mechanical activation of samples

A laboratory planetary mill with steel balls was used. Ball to powder weight ratio was of 14:1. The velocity of the ball was of $3.20\,m\,s^{-1}$. The two vials were rotated at 1130 rpm. Grinding was carried out in the range 3–15 min in air, at ambient temperature and atmospheric pressure [16].

2.3. Apparatus and procedure

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 up to 950 °C in air at a rate of $24\,°C\,min^{-1}$, in an open platinum crucible. The sample size was about 20 mg.

Differential thermal analysis was made in helium (under the same conditions as thermogravimetric measurements) using a Universal V2.5H TA instrument. X-ray powder diffraction patterns were obtained using a Philips X'Pert diffractometer (Cu Kα) in the 2θ range 10–60°.

3. Results and discussion

In the system $Cu_2(OH)_2CO_3$–Al^0 with 20% of aluminium the mechanical impulse creates a larger difference in physical effects and chemical reactions than in the system with a smaller amount of aluminium (3%). It has been proved by the identification of the solid state products of milling. For phase analyses the X-ray diffraction method was used. Although thermal analyses are more universal because they offer the possibility of identifying highly defected or amorphous phases, which often appear during mechanical activation.

The X-ray diffraction patterns of mixtures with 20% amount of Al^0 after 3 and 15 min of milling are shown in Fig. 1a and b, respectively. After 3 min, the presence of crystalline alloy phases—Cu_xAl_y, besides of aluminium and hydroxocarbonate (initial components of the milled system) is observable. Activation for 15 min shows only alloy phases in crystalline forms.

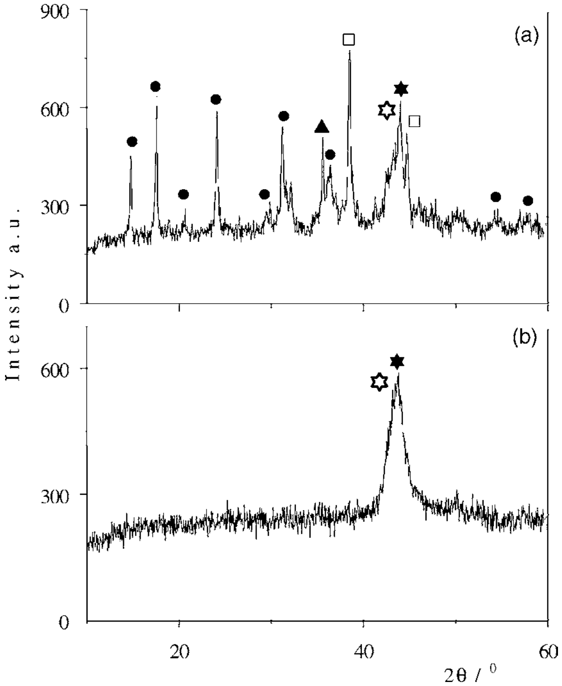

Fig. 1. X-ray diffraction patterns of $Cu_2(OH)_2CO_3$–Al^0 (20 wt.% Al) mixture after mechanical activation for different times: (a) 3 min and (b) 15 min. (●) $Cu_2(OH)_2CO_3$, (▲) CuO, (☐) Al, (✱) Cu_9Al_4, (✡) $CuAl_2$.

The presence of alloys after mechanical activation of $Cu_2(OH)_2CO_3$–Al^0 system requires to elucidate the mechanism of their formation

$$xCu^0 + yAl^0 \rightarrow Cu_xAl_y \qquad (1)$$

(e.g. for Cu_9Al_4 [10]: $\Delta H_{298} = -8\,kJ\,mol^{-1}$). For this synthesis, besides Al^0 (initial component of the system), the presence of metallic copper is necessary. Cu^0 forms in the aluminothermic reduction of copper(II) oxide

$$3CuO + 2Al^0 \rightarrow 3Cu^0 + Al_2O_3$$
$$\Delta H_{298} = -1179\,kJ\,mol^{-1} \qquad (2)$$

The presence of copper oxide is a result of decomposition of copper hydroxocarbonate caused by mechanical treatment

$$Cu_2(OH)_2CO_3 \rightarrow 2CuO + H_2O + CO_2$$
$$\Delta H_{298} = -82\,kJ\,mol^{-1} \qquad (3)$$

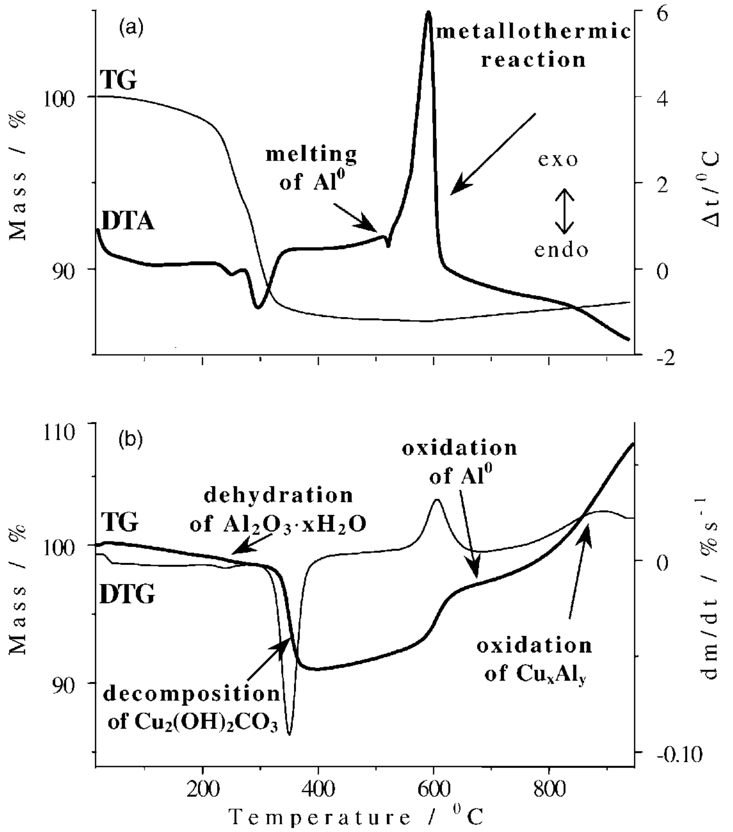

Fig. 2. Two sets of thermoanalytical curves of mixture $Cu_2(OH)_2CO_3$–Al^0 (20 wt.% Al) after mechanical activation for 3 min in (a) helium and (b) air.

The complexity of these processes is induced by the chemical activity of nanocrystalline aluminium. Their occurrence is possible because of the heat emission during oxidation of parts of aluminium in air atmosphere according to the reaction:

$$4Al^0 + 6O_2 \rightarrow 2Al_2O_3 \quad \Delta H_{298} = -1675\,kJ\,mol^{-1} \tag{4}$$

It might be recognised that the high heat accelerates the decomposition of hydroxocarbonate, initiates the metallothermic reduction of copper(II) oxide and facilitates the mechanical alloying process.

The heat emission in reaction 2 is an additional factor which favours the mechanical alloying. The proof of our thesis was provided by a strong exothermic peak in the temperature range 550–650 °C observed

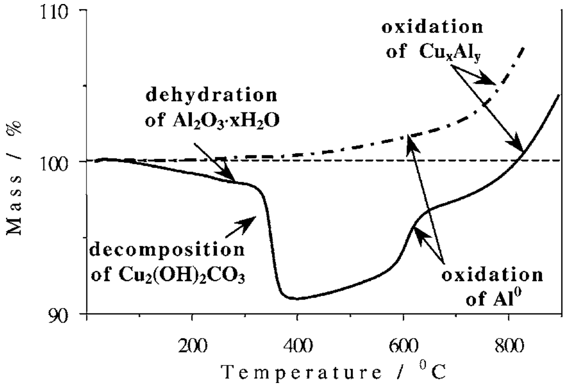

Fig. 3. TG curves of $Cu_2(OH)_2CO_3$–Al^0 (20 wt.% Al) mixture after mechanical activation for different times: (—) 3 min and (- - -) 15 min.

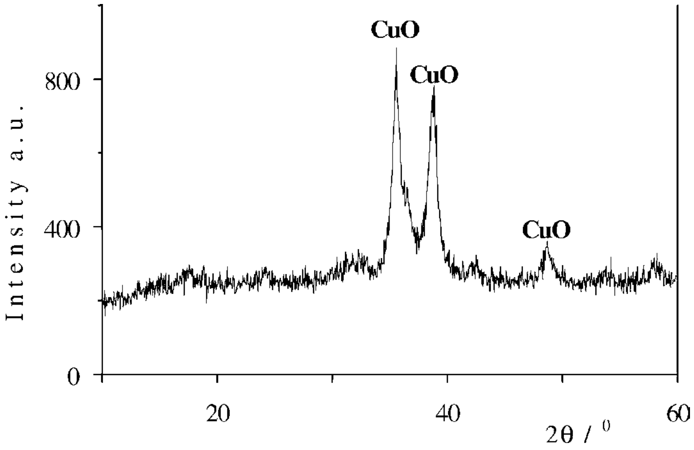

Fig. 4. X-ray diffraction patterns of $Cu_2(OH)_2CO_3$–Al^0 (3 wt.% Al) mixture after mechanical activation for 15 min.

in the DTA curve (Fig. 2a) of mixture containing $Cu_2(OH)_2CO_3$ and Al^0. The measurement was carried out in helium in order to avoid the exothermic oxidation of aluminium. The oxidation of aluminium in air is confirmed by the increase of mass at about 600 °C shown in the TG/DTG curves (Fig. 2b).

The content of alloy in the tested systems increase with the time of milling. Therefore, the TG curves for the mixture of $Cu_2(OH)_2CO_3$ with 20% Al^0 after 3 and 15 min of milling are compared in Fig. 3. Thus, the thermogravimetric curve of mixture for 3 min activation shows besides of alloy oxidation at about 800 °C, the dehydration of aluminium oxide in the

Table 1
Phase composition of ground mixture $Cu_2(OH)_2CO_3$–Al^0 (20 wt.% Al) after mechanical activation for different times

Phase	Composition (wt.%)	
	3 min	15 min
$Cu_2(OH)_2CO_3$	41	0
$Al_2O_3{\cdot}3H_2O$	4	0
CuO + Cu (in alloy)	27	61
Al_2O_3 + Al (in alloy)	21	39
Al^0	7	0

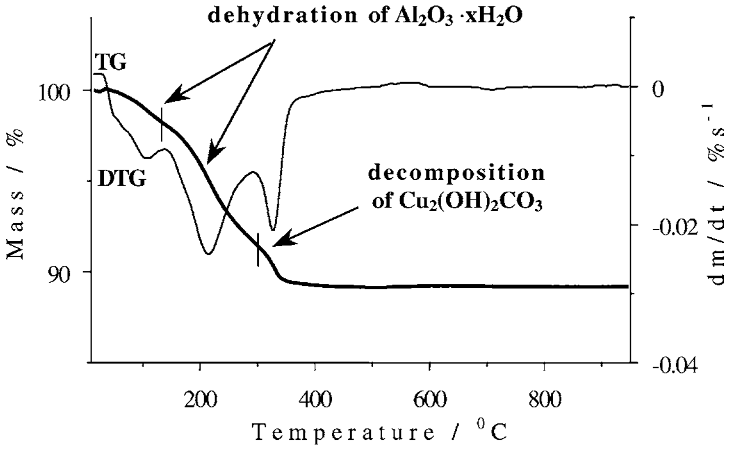

Fig. 5. TG/DTG curves of $Cu_2(OH)_2CO_3$–Al^0 (3 wt.% Al) mixture after mechanical activation for 15 min.

range 100–200 °C, thermal decomposition of hydroxocarbonate at 350 °C and the aluminium oxidation at about 600 °C. After 15 min activation, only the alloy oxidation effect is observed. Complete phase compositions of the investigated system are presented in Table 1.

The amount of aluminium in the mixtures of $Cu_2(OH)_2CO_3$–Al^0 was a crucial factor which decides what occurs in the mechanical alloying process. In the system with 3% aluminium the alloys were not observed. The X-ray analysis (Fig. 4) of mixture after 15 min of activation showed only the presence of copper oxide. However, the TG/DTG curves shown in Fig. 5 reveal the presence of undecomposed hydroxocarbonate and hydrated aluminium oxide. $Cu_2(OH)_2CO_3$ became amorphous by the mechanical impulse action. Therefore, one cannot observe the peaks of malachite in the X-ray diffraction patterns in Fig. 4.

4. Conclusions

Investigations of the mechanical activation effects in the system $Cu_2(OH)_2CO_3$–Al^0 performed on the basis of the solid product identification reveals the universality the thermoanalytical methods complemented by X-ray diffractometry. The phase analyses of ground products enable to elucidate the mechanism of the alloy formation in the mixtures of copper hydroxocarbonate with aluminium.

The mechanical alloying in an oxidising atmosphere is a consequence of the following reactions:

- decomposition of hydroxocarbonate,
- oxidation of aluminium,
- aluminothermic reduction of CuO.

The alloy formation depends mainly on three factors: the “sufficient” content of aluminium in the system, the duration of mechanical treatment (the longer milling time increases the amount of alloys) and the atmosphere. It can be stated that the oxygen present during activation seems to be determining reasonable time for mechanical alloying in our study. Some literature data concerning the mechanical alloying point to the possibility of alloy formation in an inert gas atmosphere after very long time of milling, e.g. TiZrCuNi for 100 h [17] and Ni_3Al for 3 h [10].

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References

[1] J. Schilz, Mater. Trans. JIM 39 (1998) 1152.
[2] I.J. Lin, J. Therm. Anal. Calorim. 52 (1998) 453.
[3] K. Tkačova, Mechanical Activation of Minerals, Elsevier, Amsterdam, 1989.
[4] C. Surynarayana, Prog. Mater. Sci. 46 (2001) 1.
[5] N.J. Welham, Mater. Sci. Eng. A 255 (1999) 81.
[6] J.A. Pfaendtner, R.C. Muthiah, C.T. Liu, C.J. McMahon Jr., Mater. Sci. Eng. A 260 (1999) 1.
[7] M. Senna, Intern. J. Miner. Process. 44–45 (1996) 187.
[8] P.M. Botta, E.F. Aglietti, J.M. Porto-Lopez, Thermochim. Acta 363 (2000) 143.
[9] P. Butyagin, J. Mater. Synth. Process. 8 (2000) 205.
[10] B.S. Murty, S. Ranganathan, Intern. Mater. Rev. 43 (1998) 101.
[11] N.S. Cohen, M. Odlyha, D.H. Ucko, Q.A. Pankhurst, J. Therm. Anal. Calorim. 56 (1999) 239.
[12] M. Guomin, F. Saito, Mater. Trans. JIM 39 (1998) 810.
[13] F. Cardellini, V. Contini, G. Mazzone, Phil. Mag. A 78 (1998) 1021.
[14] V.A. Zazhigalov, J. Haber, J. Stoch, L.V. Bogutskaya, I.V. Bacherikova, Catal. Appl. A 135 (1996) 155.
[15] K. Wieczorek-Ciurowa, Ju.G. Shirokov, M. Paryło, J. Therm. Anal. Calorim. 60 (2000) 59.
[16] K. Wieczorek-Ciurowa, M. Paryło, Ju.G. Shirokow, Czasopismo Techn., Ed. Polit. Krak., Z.3-Ch/(1999) 67. (in Polish).
[17] X.D. Liu, M. Nagumo, M. Umemoto, Mater. Sci. Eng. A 252 (1998) 179.