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THE CHARACTERISTICS OF MECHANICALLY ACTIVATED MIXTURES OF COPPER HYDROXOCARBONATE WITH ALUMINIUM

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Abstract

The chemical and physical processes occurring during grinding of copper hydroxocarbonates mixtures with aluminium were studied. A planetary ball mill was used. A thermogravimetry and X-ray powder diffraction method allowed to determine the composition of solid products after mechanical activation. The amount of the $Cu_2(OH)_2CO_3$ undecomposed and $Al_2O_3{\cdot}3H_2O$, CuO, Al_2O_3, Cu^0, Cu_xAl_y alloys and remained Al^0 in the systems is strongly dependent on the duration of grinding and on the proportion of components. The comparative results are presented.

Keywords: aluminium, catalysts, CuAl-alloys, grinding, malachite, mechanical activation, phase analysis, thermogravimetry, transition metals

Introduction

Solids need to be prepared into their active state for a variety of practical purposes. This can be done e.g. by heating or grinding. These treatments often lead to structural, physical and/or chemical changes in materials and new substances may be formed.

The physical mixtures of hydroxocarbonates of some transition metals with metals or metal oxides after grinding become catalysts and this method of synthesis could be environmentally friendly, with a low energy consumption [1–6].

A reliable identification of solids present in mechanically activated products is essential to elucidate the processes occurring during grinding [7].

The aim of this research was to show the physical and chemical effects of dry grinding of $Cu_2(OH)_2CO_3$ (malachite) with Al^0 powder at different proportions and different time [8].

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Experimental

Materials

Copper hydroxocarbonate, $Cu_2(OH)_2CO_3$, (malachite), to be activated by grinding was obtained by precipitation from aqueous solution [9]. The systems of salt and aluminium were prepared as physical mixtures at a molar ratio of CuO:Al=1:1 and 9:1, respectively [8].

Mechanical grinding was carried out from 0 to 15 min in air at ambient temperature. A planetary ball mill was used [9, 10].

Equipment and methods of measurement

Thermogravimetric analyses (TG/DTG curves) 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°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 10–60°.

Results and discussion

The compiled TG curves for untreated malachite and after grinding during 3 and 15 min are shown in Fig. 1. The thermal decomposition of all samples corresponds to the evolution of water (from the OH groups bound in the malachite lattice) and CO_2 in one step yielding CuO as a final solid product according to the reaction (1):

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

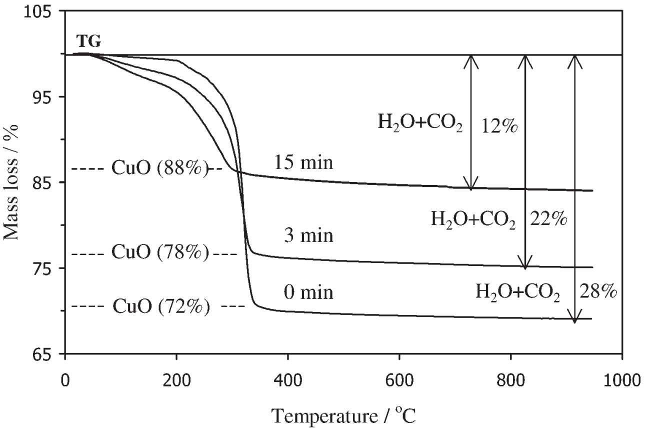

Fig. 1 The compiled TG curves for malachite samples: untreated and after grinding for 3 and 15 min

Theoretical malachite composition (%) is: CuO – 72.0 and sum of H_2O and CO_2 – 28%.

The influence of the grinding time on the amount of undecomposed malachite during mechanical treatment is evident. The proportion of the malachite decomposed during thermal analysis to the malachite decomposed during grinding could be calculated. Thus, the degrees of $Cu_2(OH)_2CO_3$ decomposition were calculated and are equal to 28 and 65%, for samples ground during 3 and 15 min respectively. An increase in the amount of CuO and a decrease in the remaining malachite after treatment (observed in Fig. 1) are confirmed by the X-ray data shown in Fig. 2. Moreover, it is evident that CuO is crystalline and the remaining malachite is amorphous (even its amount is over 40%).

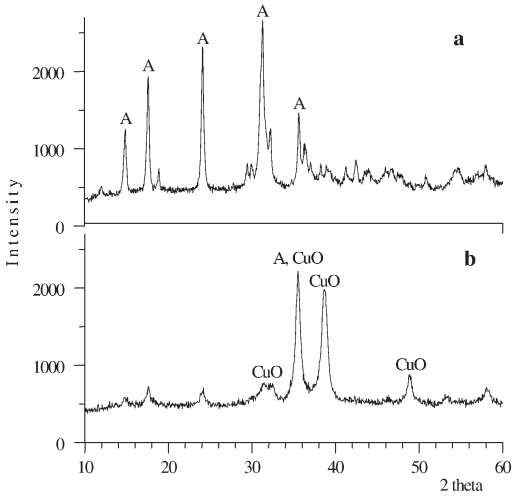

Fig. 2 X-ray diffraction patterns for malachite samples: a – untreated, b – after grinding for 15 min, A – malachite, $Cu_2(OH)_2CO_3$

The identification of solid phases of activated two-component systems, e.g. malachite with Al^0 becomes more complicated. Therefore, exemplary TG/DTG curves are shown in Fig. 3. These mass changes are generally accomplished in four steps:

I – a mass loss due to the dehydroxylation of hydrated aluminium oxide,

II – the mass loss of H_2O and CO_2 strongly dependent on the malachite content,

III – the mass increase (between 400 and 660°C) owing to rapid Al^0 oxidation pointing to a presence of this metal in the activated products,

IV – the final mass increase (above 660°C) is attributed to the oxidation of Al–Cu alloy, if they were formed during grinding,

V – residue (oxides, metals, alloys).

Figures 4 and 5 present the results of thermoanalytical curves and X-ray diffraction patterns, respectively, for samples of malachite-aluminium mixtures AG in molar ratio of 1:1 after grinding for 3 and 15 min. The TG/DTG curves in Figs 4a and b

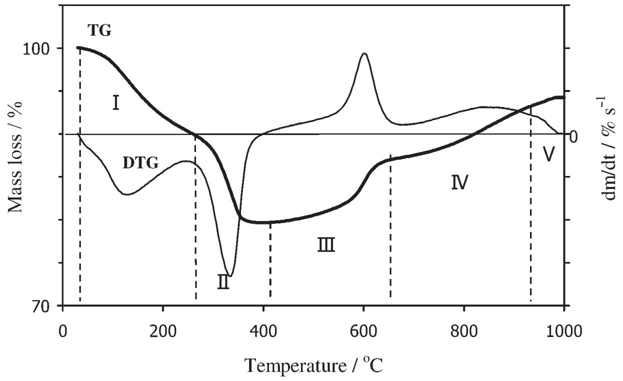

Fig. 3 Exemplary TG/DTG curves for malachite – Al^0 mixture after grinding

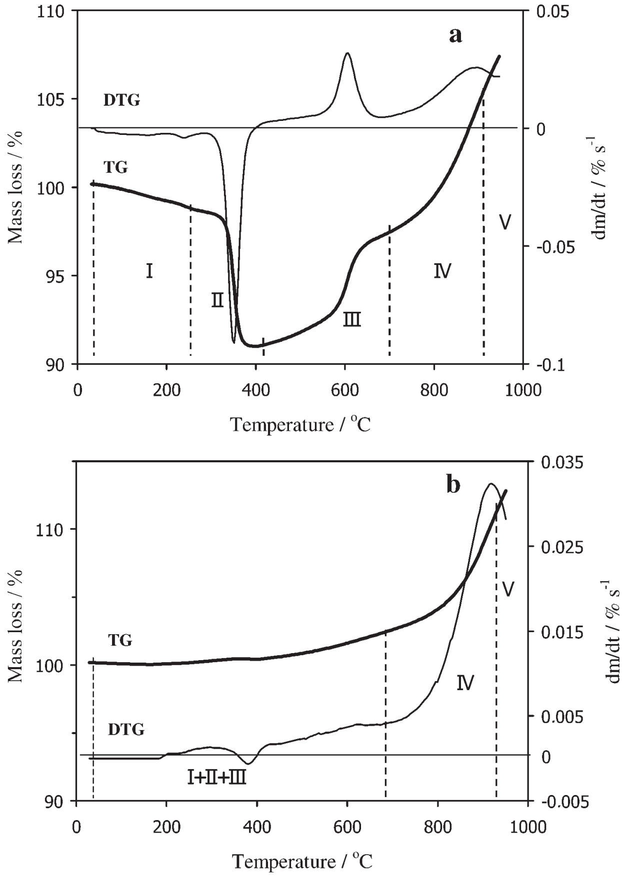

Fig. 4 Two sets of TG/DTG curves for mixture of $Cu_2(OH)_2CO_3$ and Al^0 (CuO:Al=1:1) samples after grinding: a – for 3 min, b – for 15 min

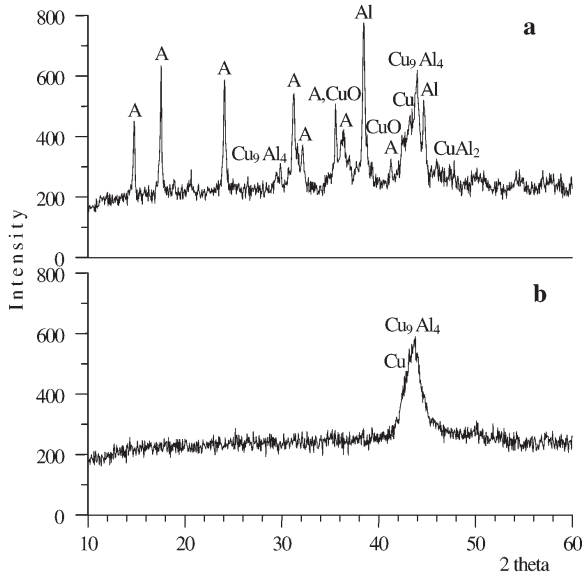

Fig. 5 X-ray diffraction patterns for mixture of $Cu_2(OH)_2CO_3$ and Al^0 (CuO:Al=1:1) samples after grinding: a – for 3 min, b – for 15 min

are quite different. One can see from Fig. 5 that after 3 min activation, malachite is decomposed in 54% but after 15 min – completely. Oxides of copper and aluminium and Al–Cu alloy are present, as the activated products of this mixture. The results of the complete phase analyses are listed in Table 1.

Table 1 Phase composition of mixture of $Cu_2(OH)_2CO_3$ (A) and Al^0 (G) samples after grinding, (CuO:Al=1:1)

Sample AG	Time/ min	Phase composition/%				
		$Al_2O_3 \cdot 3H_2O$	$Cu_2(OH)_2CO_3$	CuO +Cu (in alloy)	Al_2O_3 +Al (in alloy)	Al^0
1:1	3	4	41	27	21	7
	15	0	0	61	39	0

In the system of malachite with metal aluminium but in smaller amount, the molar ratio of 9:1 (Figs 6a and b), the effects III and IV are negligible, it means that oxidation processes of Al^0 and alloy do not occur. In consequence – these products have not form during activation by dry grinding. Malachite was not decomposed completely as in the case with a higher content of Al^0 (Table 2). In this system only crystalline copper oxide is detectable by XRD (Fig. 7) suggesting that present aluminium oxide and malachite are amorphous.

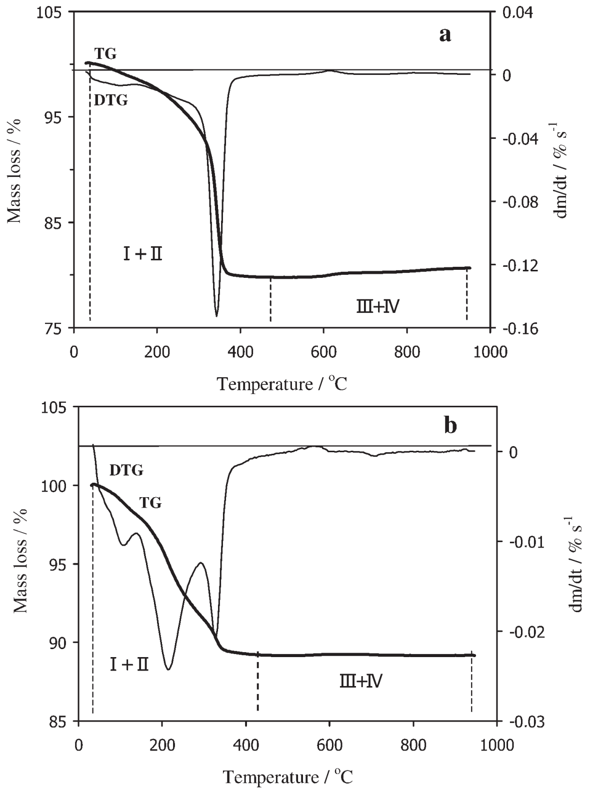

Fig. 6 Two sets of TG/DTG curves for mixture of $Cu_2(OH)_2CO_3$ and Al^0 (CuO:Al=9:1) samples after grinding: a – for 3 min, b – for 15 min

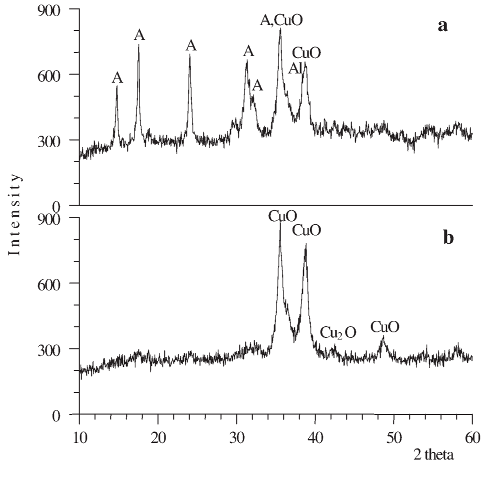

Fig. 7 X-ray diffraction patterns for mixture of $Cu_2(OH)_2CO_3$ and Al^0 (CuO:Al=9:1) samples after grinding: a – for 3 min, b – for 15 min

Table 2 Phase composition of mixture of $Cu_2(OH)_2CO_3$ (A) and Al^0 (G) samples after grinding, (CuO:Al=9:1)

Sample AG	Time/ min	Phase composition/%				
		$Al_2O_3{\cdot}3H_2O$	$Cu_2(OH)_2CO_3$	CuO	Al_2O_3	Al^0
9:1	3	7	65	28	0	0
	15	8	30	62	0	0

Considering the effects of mechanical activation of the copper hydroxocarbonate with aluminium system, it can be stated that reactions (1) to (6) may be responsible for numerous different phase formations:

$$4Al^0+3O_2 \rightarrow 2Al_2O_3 \qquad \Delta H=-1675 \quad \Delta G=-1581 \tag{2}$$

$$2Al^0+6H_2O \rightarrow Al_2O_3{\cdot}3H_2O+3H_2 \qquad \Delta H=-949 \quad \Delta G=-895 \tag{3}$$

$$CuO+H_2 \rightarrow Cu^0+H_2O \qquad \Delta H=-120 \quad \Delta G=-135 \tag{4}$$

$$3CuO+2Al^0 \rightarrow 3Cu^0(Cu_2O)+Al_2O_3 \qquad \Delta H=-1179 \quad \Delta G=-1169 \tag{5}$$

$$xCu^0+yAl^0 \rightarrow Cu_xAl_y \tag{6}$$

where ΔH_{298}, ΔG_{298} (kJ mol^{-1}).

As we can see in the scheme in Fig. 8, grinding brings about many chemical processes. Thus, an oxidation of aluminium with great heat evolution (2) may initiate another reactions, e.g. the decomposition of hydroxocarbonates with water evolution (1). This water in turn may react with Al^0 producing certain amount of hydrogen (3). Simultaneously, H_2 can be an agent for copper oxide reduction (4). Moreover, the

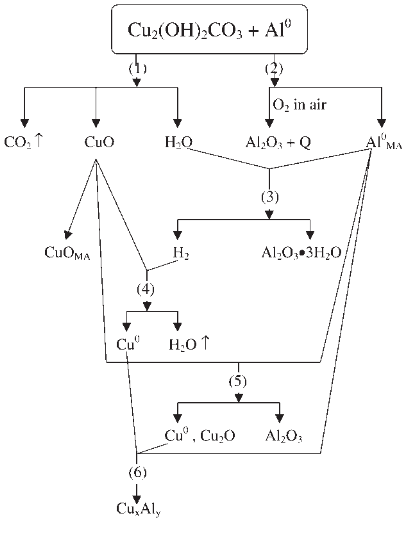

Fig. 8 The scheme of the chemical processes which can occur in the system of malachite – aluminium during mechanical treatment

presence of copper-aluminium alloy in the system suggests an interaction between the solid components, i.e. – two metals. It is worth noticing that the reaction (5) for producing copper is more favourable from the thermodynamic point of view than reaction (4). Additional data are required to fully understand the nature of the phenomena of mechanochemical activation of solids.

Conclusions

With regard to the identification of solids in mechanically activated products of malachite with aluminium:

– the copper-aluminium alloy formation is dependent on the amount of Al^0 in the system. If aluminium is more than about 5%, the aluminium-copper alloys appear. The reduction reaction of copper oxide by Al^0 is mainly responsible for alloy formation. This is known as aluminothermic reaction. It can be initiated by local overheating during oxidation of Al^0 powder,

– the $Cu_2(OH)_2CO_3$ decomposition is caused, above all, by the duration of mechanical treatment independently of the presence or absence of metal,

– the $Cu_2(OH)_2CO_3$ decomposition is promoted by the bigger amount of Al^0 during the same grinding time. Even small amount (about 3%) of Al influence substantially the activation.

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