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ALLOY FORMATION IN MECHANICALLY ACTIVATED MIXTURES

Hydroxocarbonates with Al^0

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Abstract

The physical mixtures of hydroxocarbonates of Cu and Ni with aluminium were activated using a laboratory planetary mill. The chemical reactions and alloy formations as the effects of grinding were followed by the phase analysis of solid products based on the thermogravimetry and X-ray diffractometry. Experimental evidence indicates that the nature of reactions and products of mechanical activation was dependent on the amount of aluminium and time of grinding.

Keywords: activation, alloy, aluminium, aluminium oxide, grinding, hydroxocarbonates of Cu and Ni, mechanical treatment, milling, phase analysis, thermal analysis

Introduction

Many high melting intermetallics difficult to prepare by conventional processing methods could be synthesized by mechanical activation. Mechanical activation is a high-energy milling technique, in which elemental components are ground to form a variety of materials. The activation of crystalline solids in such mills results in structural and textural changes. Moreover, it accelerates the kinetics of chemical reactions through repeated creation of new interfaces between reacting phases by dynamic deformation, fracturing and cold welding of solid particles [1–8].

One of the most interesting applications of mechanical activation is the synthesis of alloy materials. This method is very important especially for metastable alloy obtaining; since their production by metallurgical method is very difficult or even impossible. The Fe–Cu alloy was successfully obtained from Cu and Fe powders in a planetary mill in argon atmosphere [9].

Thus, mechanical alloying by milling is usually carried out in planetary, vibrational or attritor mills. The kinetics of alloying and the phase transformations during

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mechanical alloying depend on the energy transferred from the balls to the materials. The energy transfer is governed by many parameters such as milling speed, ball size and ball size distribution. It is obvious, that the high kinetic energy of the balls is favourable for the mechanical alloying processes [3, 10]. To intensify alloying process, it is necessary to apply the mass excess of balls in comparison to the milling materials. For example, someone [11] synthesized $TiAl_3$ alloy using mass proportion of balls:milling materials equal 47:1.

Moreover, the atmosphere has a strong influence on the phenomena generated during alloying processes. Most researches state that the oxygen in air can be a source of impurities in alloys. For that reason, neutral atmosphere is recommended for mechanical alloying.

The third important factor for mechanical alloying is milling time. The duration of milling is strongly differentiated. The literature data [9, 11] show that a necessary milling time for Fe–Cu metastable alloy which is about 70 h, whilst $TiAl_3$ alloy formation requires 5 h. Our preliminary studies [12] show that alloy formation during hardly several minutes of milling is possible.

Different solid products such as: salts, oxides, hydrated oxides, metals besides of alloys, can be formed during mechanical activation. Their structure as well as phase transformations, chemical reactions can be examined by thermal analysis, X-ray powder diffraction and other physicochemical methods. But only thermoanalytical techniques are universal because they offer the possibility of identifying highly defected or amorphous phases which often occur in these products [12, 13].

The aim of the research was to elucidate the reduction-oxidation reactions that involve alloy formation during mechanical activation in air atmosphere using a planetary mill.

Experimental

Materials

Cu and Ni hydroxocarbonates ($Cu_2(OH)_2CO_3$ and $Ni_2(OH)_2CO_3$) were obtained by precipitation from aqueous solutions [14].

The two-component systems of salts with metal, i.e. $Cu_2(OH)_2CO_3$–Al^0 and $Ni_2(OH)_2CO_3$–Al^0, were prepared as physical mixtures at ratios (%) of about 80:20, 95:5 and 97:3.

Aluminium (99.9% pure) was a commercial reagent in a powdered nanocrystalline form.

A laboratory planetary mill with balls of W–Co alloy was used [15]. The mass proportion of balls to sample was of 14:1.

Mechanical grinding was carried out in an oxidizing atmosphere (air) for several minutes at ambient temperature and atmospheric pressure.

Equipment and methods of phase identification

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 in air at a rate of 24°C min^{-1}, up to 950°C, in an open platinum crucible.

The sample size was about 20 mg.

Quadrupole mass spectrometer QMS ThermoStar by Balzers was used for the characterisation of volatile thermal decomposition products of hydroxocarbonates under study. The QMS was operated with electron energy of 70 eV.

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 experimental results showed that in mixtures of hydroxocarbonates of Cu and Ni with Al^0 under defined conditions metallic alloys were formed. The mass proportions of components, i.e. salt : aluminium, is a crucial factor of mechanical alloying.

Exemplary TG/DTG curves illustrate the way of the phase identification which are formed during mechanical activation of the mixtures of hydroxocarbonates with Al^0 are shown in Fig. 1. The first step corresponds to a mass loss due to dehydroxylation of hydrated aluminium oxide – $Al_2O_3{\cdot}xH_2O$. This behaviour of hydrated aluminium oxide is confirmed by literature data [16]. The next stage (II) strongly depends on the malachite content. So, calculation of the amount of malachite undecomposed during milling is possible from the mass loss of H_2O and CO_2 simultaneously. This is illustrated in Fig. 2 by the mass spectra of water and carbon dioxide. The third (III) stage characterized by mass increase results from an oxidation of aluminium. The final stage (IV) is attributed to the oxidation of metallic alloys formed during mechanical treatment.

The univocal influence of aluminium for mechanical alloying is presented in Fig. 3. Index a, b and c refers to 20, 5 and 3% of Al^0 content, respectively in the mixture of malachite–aluminium. The mass increase (IV) appears only in Fig. 3a, that indicates existence of Cu–Al alloys. The presence of these alloys was confirmed by the results of X-ray powder diffraction, as is shown in Fig. 4.

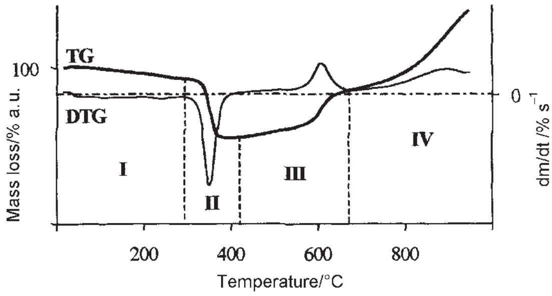

Fig. 1 Exemplary TG/DTG curves for $Cu_2(OH)_2CO_3$–Al^0 after mechanical activation

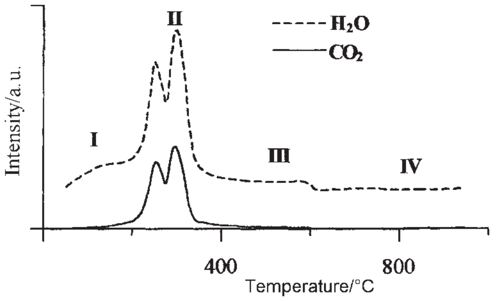

Fig. 2 Evolved H_2O and CO_2 curves for the decomposition of $Cu_2(OH)_2CO_3$–Al^0 system

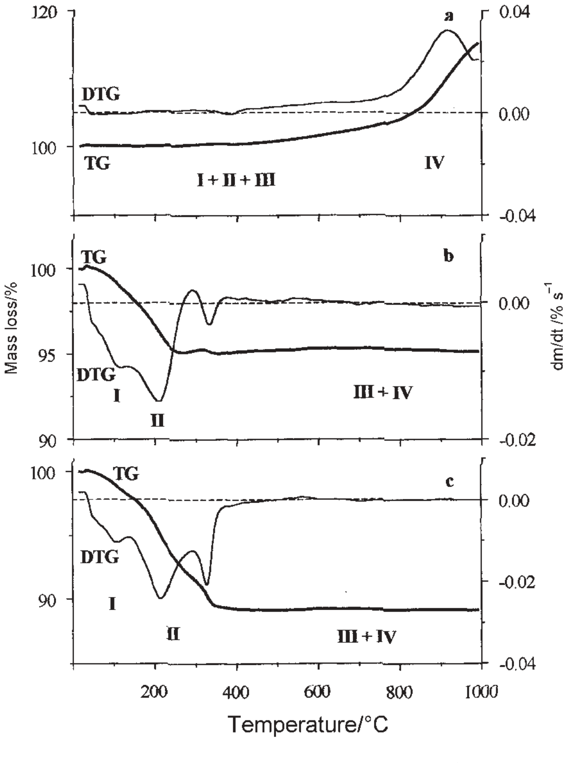

Fig. 3 Three sets of TG/DTG curves for $Cu_2(OH)_2CO_3$ and Al^0 mixtures after 15 min of grinding: a – $Cu_2(OH)_2CO_3$ and Al^0 (80:20); b – $Cu_2(OH)_2CO_3$ and Al^0 (95:5); c – $Cu_2(OH)_2CO_3$ and Al^0 (97:3)

The attempt of elucidation of chemical mechanism of the alloy formation, during milling in an oxidizing atmosphere at ambient temperature was undertaken. For this purpose, the phase analysis of the mechanical activation systems $Cu_2(OH)_2CO_3$–Al^0 and

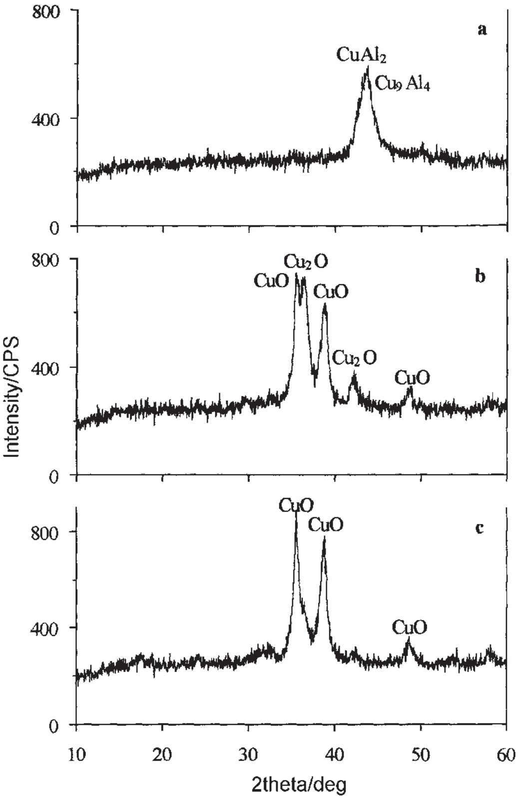

Fig. 4 X-ray diffraction patterns for $Cu_2(OH)_2CO_3$ and Al^0 mixtures after 15 min of grinding :a – $Cu_2(OH)_2CO_3$ and Al^0 (80:20); b – $Cu_2(OH)_2CO_3$ and Al^0 (95:5); – $Cu_2(OH)_2CO_3$ and Al^0 (97:3)

$Ni_2(OH)_2CO_3$–Al^0 was essential. The following products: Cu_xAl_y, CuO, Cu_2O, Al_2O_3, $Al_2O_3{\cdot}xH_2O$ or Ni_xAl_y, NiO, Al_2O_3, $Al_2O_3{\cdot}xH_2O$ and some undecomposed hydroxocarbonates appeared in the activated systems. One can assume, that these results correspond to the reactions presented below:

$$M_2(OH)_2CO_3 \rightarrow 2MO+H_2O+CO_2 \tag{1}$$

$$4Al^0+3O_2 \rightarrow 2Al_2O_3 \tag{2}$$

$$2Al^0+6H_2O \rightarrow Al_2O_3{\cdot}3H_2O+3H_2 \tag{3}$$

$$3MO+2Al^0 \rightarrow 3M^0+Al_2O_3 \tag{4}$$

and/or

$$6MO+2Al^0 \rightarrow 3M_2O+Al_2O_3 \tag{4'}$$

$$xM^0+yAl^0 \rightarrow M_xAl_y \tag{5}$$

where *M*: Cu^0 or Ni^0

Chemical activity of powdered aluminium determines the occurrence of these reactions. The oxidation of aluminium (2) with enthalpy of $\Delta H_{298}= -1675$ kJ mol^{-1} can initiate the aluminothermic reduction of CuO, as well as NiO (4 and/or 4′), which are the products of mechanical decomposition of hydroxocarbonates (1). As the effects of these processes, Cu^0 or Ni^0 appears, and alloys with Al^0 are formed (5). The presence of alloys depends on the amount of aluminium in the system. Thus, if aluminium content reached 20%, alloys do exist in the systems.

It is observed that reduction of CuO to Cu_2O occurs when the system contains 5% of aluminium. If the amount of Al^0 is 3% or less, this type of reaction does not occur. The phase compositions for the mixtures of malachite with Al^0 after mechanical treatment are shown in Table 1.

Table 1 Phase composition of ground mixture of $Cu_2(OH)_2CO_3$ and Al^0 for samples at ratio of 80:20, 95:5, 97:3 after 3 and 15 min mechanical activation and decomposition degree (α) of $Cu_2(OH)_2CO_3$

	Phases						
	$Al_2O_3\cdot 3H_2O$	$Cu_2(OH)_2CO_3$	CuO+ Cu (in alloy)		Al_2O_3+ Al (in alloy	Al^0	α/%
80:20	4	41	27		21	7	56
	0	0	61		39	0	100
	Phases						
	$Al_2O_3\cdot 3H_2O$	$Cu_2(OH)_2CO_3$	CuO	Cu_2O	Al_2O_3	Al^0	α/%
95:5	5	56	13	20	5	1	46
	6	11	48	28	7	0	90
	Phases						
	$Al_2O_3\cdot 3H_2O$	$Cu_2(OH)_2CO_3$	CuO		Al_2O_3	Al^0	α/%
97:3	7	65	28		0	0	38
	8	30	62		0	0	75

Table 2 Some examples of metal alloy formation under different conditions

Alloy	Milling time/h	Atmosphere	Type of mill	Refs
Mg_2Ni	2	nitrogen	planetary	[17]
AlV	30	nitrogen	vibrational	[18]
TiAl	30 100	nitrogen argon	planetary	[3]
TiZrCuNi	100	argon	planetary	[19]
FeCu	70	argon	planetary	[9]
Ni_3Al	3	argon	planetary	[3]

It is worth to underline that such metallic alloys as Cu_xAl_y and Ni_xAl_y are formed after several minutes of milling. This time is considerably shorter than other results from the literature data [3, 9, 17–19] presented in Table 2, where the duration of milling for different kind of alloys takes from 2 to 100 h.

The main difference in conditions of alloy formation during mechanical treatment by other authors is just an atmosphere in high energy ball mills. The presence of oxygen from air in our experiments creates a strong exothermic reaction (2). The heat initiates the aluminothermic reaction (4) and/or (4′).

It was observed that the amount of alloy formed in the tested systems increases with the time of milling (results of milling after 3 and 15 min are compared in Table 1). It is caused by the decomposition of hydroxocarbonates to Cu/Ni oxides – illustrated by the decomposition degrees (α) of $Cu_2(OH)_2CO_3$ in Table 1. The amount of CuO/NiO limits an alloy content in solid products of activation because the metal oxides are indispensable for the aluminothermic reaction (4) and/or 4’ as well as for the alloy formation (5).

Conclusions

The mechanical activation has created many complex physical and chemical processes. It has been shown that alloys of copper–aluminium and nickel–aluminium can be formed through high-energy ball milling in air atmosphere.

The alloy formation in the systems of $Cu_2(OH)_2CO_3$ –Al^0 and $Ni_2(OH)_2CO_3$–Al^0 depends on three general factors:

1. Amount of aluminium: alloy formation is observed when Al content reaches 20% in the system of $Cu_2(OH)_2CO_3$–Al^0 and more than 10% of Al is needed in the $Ni_2(OH)_2CO_3$–Al^0 system;

2. Milling time: 3 min is enough to form alloys, however after 15 min, the amount of alloys increases significantly;

3. The oxidizing atmosphere: the oxygen presence determining reasonable time of treatment for mechanical alloying is univocal.

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References

1 I. J. Lin, J. Therm. Anal. Cal., 52 (1998) 453.
2 P. G. Fox, J. Mater. Sci., 10 (1975) 340.
3 B. Murty and S. Ranganathan, Intern. Mater. Rev., 43 (1998) 43.
4 K.Tkačova, Mechanical Activation of Minerals, Elsevier, Amsterdam 1989.
5 P. M. Botta, E. F. Aglietti and J. M. Porto-Lopez, Thermochim. Acta, 363 (2000)143.
6 C. Y. Xie, R. Schaller and C. Jaquerod, Mater. Sci. Eng., A 252 (1998) 78.

7 J. A. Pfaendtner, R. C. Muthiah, C. T. Liu and C. J. McMahon Jr., Mater. Sci. Eng., A 260 (1999) 1.

8 W. Ju. Shirokova and Ju. G. Shirokov, Khim. and Khim. Techn., 40 (1997) 58 (in Russian).

9 N. S. Cohen, M. Odlyha, D. H. Ucko and Q. A. Pankhurst , J. Therm. Anal. Cal., 56 (1999) 239.

10 J. Schilz, Mater. Trans. JIM, 39 (1998) 1152.

11 N. J. Welham, Mater. Sci. Eng., A 255 (1999) 81.

12 K. Wieczorek-Ciurowa, Ju. G. Shirokov, M. Paryło and K. Gamrat, , J. Therm. Anal. Cal., 65 (2001) 359.

13 K. Wieczorek-Ciurowa, Ju.G. Shirokov and M. Paryło, J. Therm. Anal. Cal., 60 (2000) 59.

14 K. Wieczorek-Ciurowa, M. Paryło and Ju. G. Shirokov, Czasopismo Techn., Ed. Polit. Krak., Z.3-Ch/(2000)77 (in Polish).

15 K. Wieczorek-Ciurowa, M. Paryło and Ju. G. Shirokov, Czasopismo Techn., Ed. Polit. Krak., Z.3-Ch/(1999)67 (in Polish).

16 K. J. D. MacKenzie, J. Temuujin, M. E. Smith, P. Angerer and Y. Kameshima, Thermochim. Acta, 359 (2000) 87.

17 M. Guomin and F. Saito, Mater. Trans. JIM, 8 (1998) 810.

18 F. Cardellini, V. Contini and G. Mazzone, Phil. Magaz., A 78 (1998) 1021.

19 X. D. Liu, M. Nagumo and M. Umemoto, Mater. Sci. Eng., A 252 (1998) 179.