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CHARACTERISTICS OF $CuAl_2$–Cu_9Al_4/Al_2O_3 NANOCOMPOSITES SYNTHESIZED BY MECHANICAL TREATMENT

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Reactive milling of Cu-hydroxycarbonate – powder aluminium mixture brings many complex chemical reactions such as decomposition, aluminothermic reduction and mechanical alloying resulting in the formation of nanometer size composites that contain intermetallic phases, γ-Cu_9Al_4 and θ-$CuAl_2$, with aluminium oxide.

Keywords: *aluminium, aluminium oxide, composite, Cu-hydroxycarbonate, electron microscopy, high-energy ball milling, intermetallics, thermal analysis, X-ray diffractometry*

Introduction

Intermetallics represent a special group of materials which exhibit a wide spectrum of physical, chemical and mechanical properties. As such they are extensively studied by a host of scientists and engineers. These compounds, as their name suggests, have properties characteristic of both metallic and non-metallic materials. Intermetallics used in material engineering especially as high-temperature structural materials, magnetic materials and hydrogen storage materials are of great world-wide interest [1, 2].

One of the ways of a direct synthesis of intermetallic phases is mechanical alloying (MA) of metals by means of a high-energy ball milling process. The advantage of this method is that the mechanical treatment takes place at room temperature while the disadvantages are the contamination of the products by the milling media and milling atmosphere and a low yield of the materials possibly caused by the cold-welding of the powder to the milling vials and milling balls. Comparing the mechanical alloying with other methods, e.g. rapid solidification processing (RSP) or sputter deposition, it is worth noticing that MA is a non-equlibrium method of a relatively low cost of alloy production and that the materials obtained in this way have a nanometric grain size. In recent years, the production of nanocrystalline materials is of great interest because they possess unique features different from the properties of coarse-grained products [2–4]. As mentioned above the intermetallic phases can be mechanochemically synthesized by milling different powdered metals in appropriate proportions. For instance, copper with zinc forms β'-, γ- and *c*-brasses known as Hume–Rothery's electron phases. Nickel aluminide intermetallics used as high-temperature shape memory alloys, corrosion resistant coating materials and materials for potential high-temperature structural applications are also obtained by ball milling [1, 5]. Another example of promising materials synthesized by mechanical alloying are alloys in the copper-aluminium system. Metallurgically welded Al with Cu is widely used as a transition piece in high direct-current bus systems for transmitting electricity. The literature data show examples of Cu–Al alloys obtained either by reactive milling of pure metals, Cu and Al, or by milling copper oxides with aluminium (CuO/Cu_2O and Al) [6–10].

Our study focuses on the mechanically activated Cu-hydroxycarbonate–Al system in which formation, processing, and structural tailoring of nanocrystalline copper aluminides intermetallics with Al_2O_3 occur [11–15]. The paper is a part of this research.

Experimental

Materials and apparatus

Cu-hydroxycarbonate ($Cu_2(OH)_2CO_3$) (precipitated) and aluminium in a powdered form (99.9% purity) as commercial reagents were used. The two-component (salt–metal) system, $Cu_2(OH)_2CO_3$–Al^0, was prepared as a physical mixture of Cu with Al at a ratio that would yield the Cu_9Al_4 phase.

For mechanical alloying a laboratory planetary mill with balls and milling container made of hardened steel was used. The mass proportion of balls to the sample (BPR) was 14:1. The two milling vials were rotated

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at 1130 rpm. Alloying was carried out in air for several minutes at room temperature and atmospheric pressure.

Equipment and methods of phase identification

X-ray powder diffraction patterns were obtained using a Philips PW 1830 Diffractometer (CoK_{α}) in the 2θ range of 20–130°.

The differential thermal analysis was made in helium up to 1000°C by using a Universal V2.5H SDT 2960 TA Instrument. The sample size was about 40 mg and the heating rate 24 K min^{-1}.

A Philips CM 20 transmission electron microscope (TEM) equipped with an EDAX system was used. The samples were resin mounted and then thin foils were cut using a Reichert microtom.

A Hitachi S-4700 instrument (SEM) equipped with an energy dispersive X-ray spectrometer was used for the microstructural examination and elemental microanalysis. The atomic number contrast was observed in polished cross-sectioned samples. The specimens were carbon-coated to make them electrically conductive. The BSE imaging and EDX elemental analyses were carried out at an electron beam voltage of 20 kV.

Results and discussion

Reactions during mechanical alloying

On the basis of XRD and DTA measurements, microstructural examinations by scanning and transmission electron microscopy (SEM and TEM), one can postulate that mechanical alloying in the $Cu_2(OH)_2CO_3$–Al system occurs during several minutes of high-energy ball milling. The results are presented below.

As to the alloying process between copper and aluminium itself, these two metals are compatible because they have a high affinity to each other at the temperatures above 120°C. The equilibrium diagram of this system shown in Fig. 1 indicates numerous intermetallic phases in Al concentration range 30–50%. Table 1 contains the short characteristics of some of these compounds [16–18].

Mechanical alloying of salt-aluminium mixtures caused the formation of two intermetallic phases, i.e. $CuAl_2$ and Cu_9Al_4. It is obvious that to this purpose the presence of two metals is required. One of them, i.e., Al, was the initial component. The other one, i.e., copper was formed during the mechanical decomposition of Cu-hydroxycarbonate to copper oxide, which was then metallothermally reduced by Al. The chemical reactions and their enthalpy are listed in Table 2.

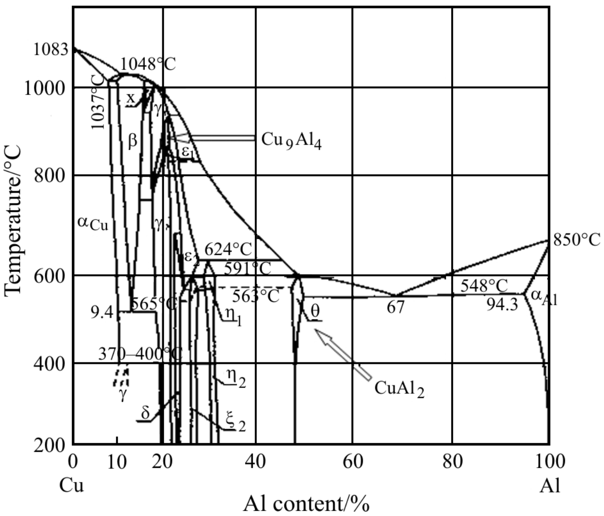

Fig. 1 Phase diagram of the Cu–Al binary system [16]

Table 1 Some intermetallics phases present in the Cu–Al system [16]

Phase	Characteristics
α_{Cu}	Cu solid solution
β	Cu_3Al, high-temperature phase melting at a maximum in the solidus at 1045°C, cubic
χ	high-temperature phase formed peritectically at 1035°C
γ_2	Cu_9Al_4, Hume–Rothery phase, formed peritectoidally at 870°C, cubic
δ	Cu_3Al_2, formed peritectoidally at 686°C, cubic
η_1	CuAl, formed peritectically at 624°C, orthorhombic
θ	$CuAl_2$, formed peritectically at 591°C, tetragonal
α_{Al}	Al solid solution

Table 2 Main chemical reactions occurring in the system of $Cu_2(OH)_2CO_3$–Al during milling

Type of reaction	Equation	ΔH_{298}/kJ mol^{-1} [18]
mechanical decomposition	$Cu_2(OH)_2CO_3 \rightarrow 2CuO+H_2O+CO_2$	+82
aluminothermic reduction	$3CuO+2Al \rightarrow 3Cu+Al_2O_3$	–1179
mechanical alloying	$Cu+Al \rightarrow Cu–Al$	–8(Cu_9Al_4) –4($CuAl_2$)

XRD analysis

The XRD results of products activated during different times shown in Figs 2 and 3 confirm the pathway of alloy formation mentioned above. On the basis of these data we can assume that Al gradually reduces CuO. This is connected with the degree of salt decomposition. It was observed that after 3 or 5 min of MA (Fig. 2) the patterns still indicate the existence of crystalline Cu-hydroxycarbonate – initial component. This phase is negligible after 10 min of milling (Fig. 3). Although the peaks related to pure aluminium are identified on the X-ray patterns even after 15 min of milling, their positions remain unchanged whereas their intensities decrease gradually with the elongation of the activation time. This indicates that the amount of Cu diffusing into the Al phase is insignificant and that the aluminium is utilized in the aluminothermic reaction and formation of the intermetallics. Thus, the $CuAl_2$ and Cu_9Al_4 phases are observed in the sample activated for barely 3 min. However, the most intensive peak of $CuAl_2$ phase ($2\theta=24.01°$) disappears after 15 min of milling. Simultaneously, the increase of the peak intensity of Cu_9Al_4 phase is observed. The appearance of Cu_2O indicates that a chemical reaction between Al and CuO also takes place. In all patterns the peaks corresponding to α-Al_2O_3 are identified.

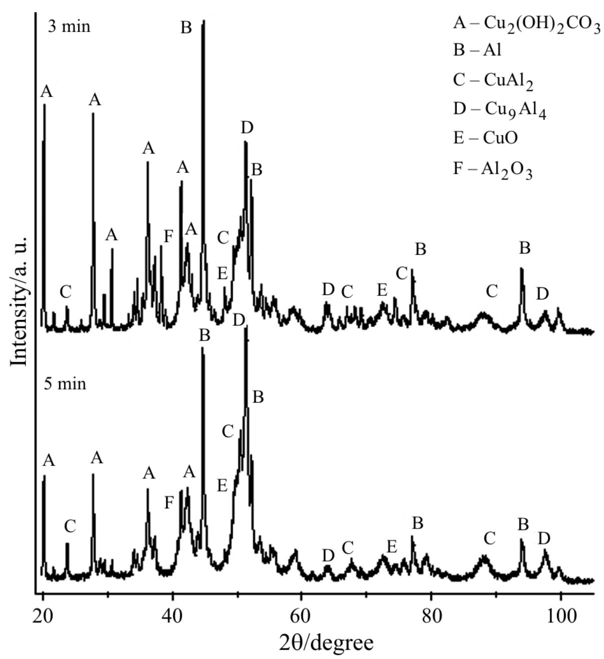

Fig. 2 X-ray diffraction patterns for $Cu_2(OH)_2CO_3$ and Al mixtures after first steps of mechanical alloying (intensities with the same scale)

DTA analysis

A simulation of the metallothermic reaction occurring in the $Cu_2(OH)_2CO_3$–Al system in the mill was performed using a thermoanalytical measurement in non-oxidizing atmosphere (helium). The DTA curve for the product milled for 3 min, which consisted of mechanically undecomposed salt and the remaining

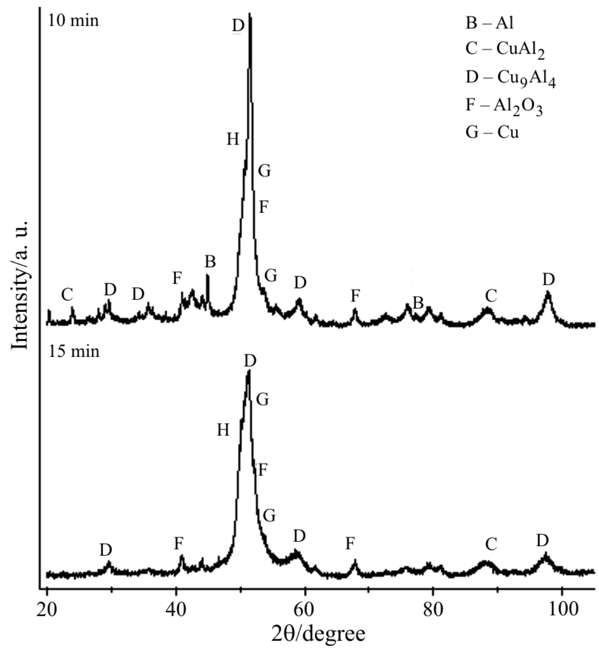

Fig. 3 X-ray diffraction patterns for $Cu_2(OH)_2CO_3$ and Al mixtures after final steps of mechanical alloying (intensities with the same scale)

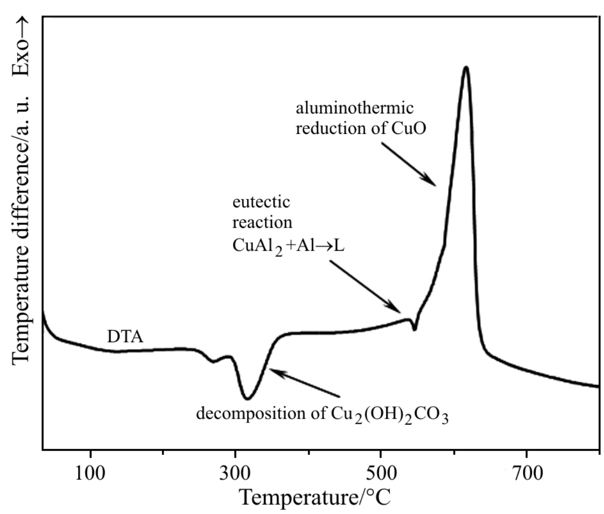

Fig. 4 DTA curve (non-oxidizing atmosphere) of the milling of the $Cu_2(OH)_2CO_3$–Al system after first step of mechanical alloying (the product contains undecomposed $Cu_2(OH)_2CO_3$ and unreacted Al)

amount of aluminium is shown in Fig. 4. The strong exothermic effect at about 600°C corresponds to the thermally initiated SHS – aluminothermic reaction. During milling this process was activated by mechanical energy. Two endothermic effects can be observed. The first at 350°C reveals the thermal decomposition of Cu-hydroxycarbonate. The second one at 520°C is related to the reverse eutectic reaction of $CuAl_2$ with Al→L, typically at 528°C, according to the Al–Cu binary phase diagram (Fig. 1).

TEM observations

TEM measurements were performed to analyse the composition of mechanically alloyed products and to estimate their phase microstructures. Figures 5a–c show in turn the bright, dark and electron image of the sample activated for 15 min. The EDX elemental analysis of a large grain shown in the dark image (Fig. 5b) shows the presence of 53.4Cu, 35.3Al, 9.0O and the contamination with 1.6Fe, 0.3Cr, 0.4Ni (mass%) from the milling medium (hardened steel). From the ratio of copper to aluminium we can assume that in this large grain $CuAl_2$ intermetallic phase is located. The diffraction lines on the electron diffraction image (Fig. 5c) confirm this assumption. The diffusive character of the diffraction rings shows strong comminution of the ground products. From the dark field image (Fig. 5b) we can calculate that the grain size of $CuAl_2$ phase is about 100 nm.

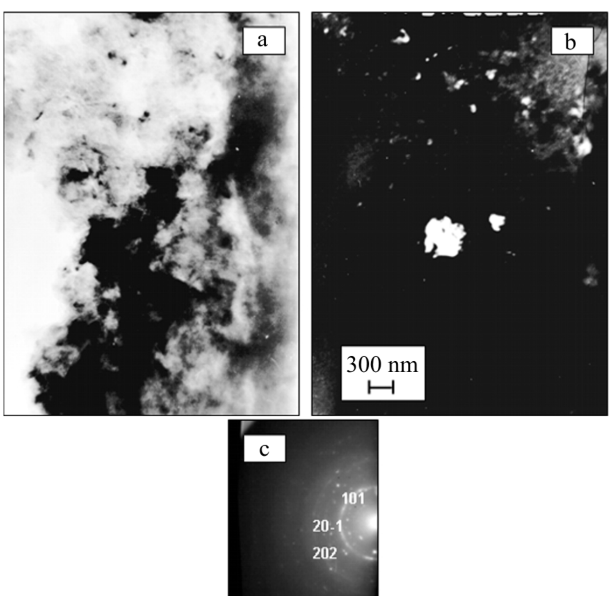

Fig. 5 Set of TEM microphotographs of $Cu_2(OH)_2CO_3$–Al system after mechanical alloying shows $CuAl_2$ intermetallic phase, a – bright field, b – dark field, c – electron diffraction patterns

SEM analysis

The scanning electron microscopy (SEM) with the backscattered electron (BSE) imaging and the quantitative energy dispersive X-ray microanalysis (EDS) of Cu, Al, O and C provided more information about the composition and microstructure of the composite. Since the BSE signal is sensitive to the changes in the average atomic number of the specimen and thus it gives variations in grey levels associated with different phases, it was possible to obtain direct information regarding the composition and localisation of the products [19, 20].

The microstructure of the products of the mechanical activation of the mixture of $Cu_2(OH)_2CO_3$ with Al is shown in Fig. 6. It can be seen that the material reveals a lamellar structure. On the basis of EDX analyses (Table 3) it is possible to estimate that the mechanically alloyed composite consists of aluminium oxide and intermetallic phases. The darker the network, the higher the amount of Al_2O_3. The brighter the network, the higher the amount of the intermetallic phases.

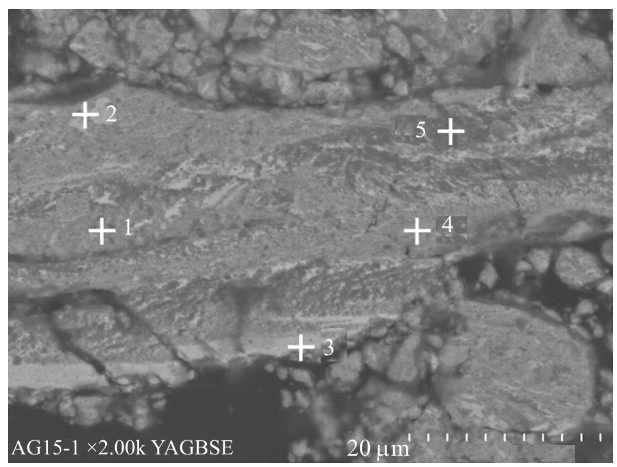

Fig. 6 SEM microphotographs of $Cu_2(OH)_2CO_3$–Al mixture after mechanical alloying shows the lamellar structure of $CuAl_2/Cu_9Al_4$–Al_2O_3 nanocomposite. The darker network corresponds to higher amount of Al_2O_3, the brighter one – to higher content of intermetallics

Table 3 Results of the EDX microanalysis of the $Cu_2(OH)_2CO_3$–Al system after 15 min of milling

Point	Concentration/mass%			BSE image
	Cu	O	Al	
1	32.7	30.1	37.2	dark grey
2	39.0	25.5	35.5	grey
3	47.2	22.2	30.6	grey
4	38.4	25.3	35.5	grey
5	23.3	32.6	44.1	dark grey

Conclusions

During mechanical alloying of the salt–aluminium mixture, the $CuAl_2$–Cu_9Al_4–Al_2O_3 composite powders of nanometer-sized grains are obtained.

The XRD and TEM analyses unquestionably confirm the formation of two intermetallic phases, i.e. $CuAl_2$ and Cu_9Al_4 by mechanical alloying in $Cu_2(OH)_2CO_3$–Al system for several minutes. Although the system tested contains the amount of Al which favours the formation of Cu_9Al_4, the $CuAl_2$ phase appears in the activated products especially after the very beginning of milling. This means that the nucleation of $CuAl_2$ proceeds easier than that of Cu_9Al_4 due to structural factors. Thus, $CuAl_2$ crystallizes in tetragonal symmetry and Cu_9Al_4 in cubic symmetry (Table 1). Cu_9Al_4 Hume–Rothery phase is characterized by high parameters of the unit cell [16] and possibly for that reason it is difficult to nucleate.

The results of high energy ball milling of the salt-reactive metal system reveal the possibilities of metal matrix nanocomposites (MMCs) formation during only several minutes of milling in air atmosphere at room temperature.

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