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Mechanosynthesis and process characterization of some nanostructured intermetallics–ceramics composites

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Abstract

In situ formation of nanostructured composite materials consisting of intermetallic phases and ceramic oxide starting from two different mixtures of $Cu_2(OH)_2CO_3$ or CuO with Al was performed. Composites were synthesized by high-energy ball milling in a laboratory planetary mill. Formation of Cu(Al) solid solution and Al_2O_3 composite was followed by X-ray diffraction and thermal analysis of milling products.

Keywords: Mechanochemical processing; Metal matrix composites; Oxide materials; Thermal analysis; X-ray diffraction

1. Introduction

Large number of mechanically driven SHS reactions occurs in anhydrous metal oxide and active metal systems [1–3]. The literature data show some examples of Cu–Al alloy formation either by reactive milling of Cu and Al or copper oxide with aluminium [4–6]. Thus, Ying and Zhang [5] have observed that in Cu and Al mixture with low aluminium concentration, the first phase formed by the reaction is γ-Cu_9Al_4, while with higher Al concentration it is θ-$CuAl_2$. Milling of the CuO and Al mixture realized by Wu and Li [6] involved the formation of metastable Cu_9Al_4 phase, while $CuAl_2$ phase was observed only after subsequent thermal treatment of mechanically synthesized composite.

It is obvious that oxide materials are important in many fields of technology but a low level of reactivity due to its thermodynamic stability characterise them. Therefore it seems that their use in mechanosyntheses is not necessary efficient. The alternative method is application of compounds containing groups of atoms with oxygen or hydrogen. Such substances are, for example, acidic and basic salts, crystal hydrates, etc. Their certain feature in common is the fact that they react to each other simultaneously evolving water and/or other volatile compounds. These compounds are characterized by 3–4-fold lower hardness than their anhydrous oxides. It probably provides the mechanochemical process with lower mechanical loading. Processes taking place with such type of substances are known as *soft mechanochemical reactions* [7].

In our previous study successful attempts were made applying the hydroxycarbonate of transition metals as “a source” of metal to provide *in situ* SHS reactions that resulted in intermetallics–ceramic oxide composites [8–10].

In this study *in situ* formation of intermetallic phase and ceramic oxide from systems containing aluminium and Cu hydroxycarbonate or Cu anhydrous oxide is compared.

2. Experimental

2.1. Materials

Cu-hydroxycarbonate ($Cu_2(OH)_2CO_3$), CuO and Al in a powdered form (99.9% purity) were used as commercial reagents. Two-component systems, $Cu_2(OH)_2CO_3$–Al and CuO–Al, were prepared as physical mixtures in which the amount of aluminium was calculated assuming the Cu_9Al_4 and Al_2O_3 formation as components of the milling products.

2.2. Instrumentation and milling procedure

For mechanochemical syntheses laboratory planetary mills *Pulverisette 5* and *6* GmbH Fritsch with vials and balls made of hardened steel were used. The

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milling processes were performed under protective atmosphere of argon. The total mass of powders was 5 g and BPR equals 10:1.

In the case of $Cu_2(OH)_2CO_3$–Al system the gas pressure and temperature in the milling vial were monitored using GTM system with radio transmission of data to receiver remote from the mill.

3. Results and discussion

The solid products identification of reactive ball milling of both tested systems, i.e. $Cu_2(OH)_2CO_3$–Al and CuO–Al, reveals the formation of materials which are composed of Cu(Al)/Al_2O_3 phases. This is a consequence of complex chemical reactions occurring during milling process described in details below.

3.1. The effects of mechanosynthesis in the $Cu_2(OH)_2CO_3$–Al system

The XRD patterns (Philips X'Pert diffractometer-Cu Kα) of the $Cu_2(OH)_2CO_3$–Al system mechanically treated at different time intervals are presented in Fig. 1. Results indicate that the initial components of the studied mixture still exist in the system up to 10 h of mechanical treatment. However, their intensities decreased significantly in comparison to the untreated mixture. Peaks of CuO as well as Cu_2O phases appeared in products in the fourth hour of milling. This indicates that $Cu_2(OH)_2CO_3$ started to decompose and metallothermic reduction of CuO by Al proceeded gradually with formation of Cu. Furthermore, the broad diffraction peak appeared in the range of $2\theta = 42–45^\circ$ after 10 h of milling. Its intensity increases significantly with elongation of milling time. The shape of this X-ray reflex indicates its complexity and the deconvolution confirmed the presence of copper beside Al_2O_3 phase. After 15 h and 20 h of milling the position of Cu(1 1 1) peak shifted from $2\theta = 43.32^\circ$ to 43.25°, respectively, while Al peaks completely disappeared. This may suggest that solid solution of Cu(Al) has formed as a result of mechanical alloying of two metals, Cu and Al. Confirmation is done by the increasing the lattice parameter of metallic copper from 3.615 Å to 3.620 Å [11]. According to Vegard's law which states that the lattice parameter of the solid solution is a function of the amount of solute and using parameters of pure Cu and Al, the contents of Al solute in Cu matrix for the mechanically treated $Cu_2(OH)_2CO_3$–Al system can be estimated on the level of about 5%.

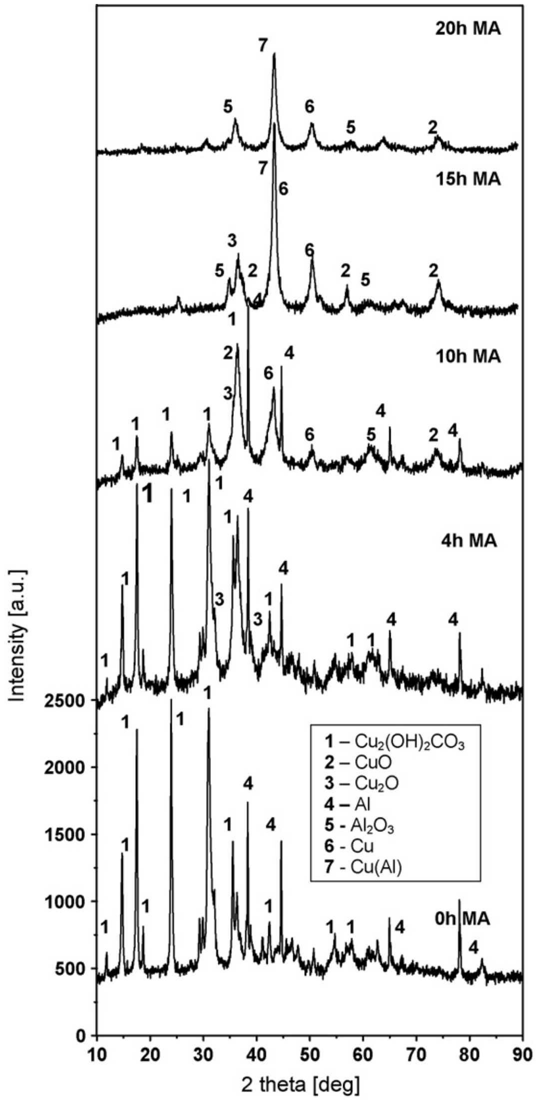

Fig. 1. X-ray diffraction patterns for $Cu_2(OH)_2CO_3$–Al system after different time of mechanical alloying (intensities with the same scale).

From thermodynamic point of view the reactions occurring in the tested system are highly exothermic, e.g. the enthalpy of alu-

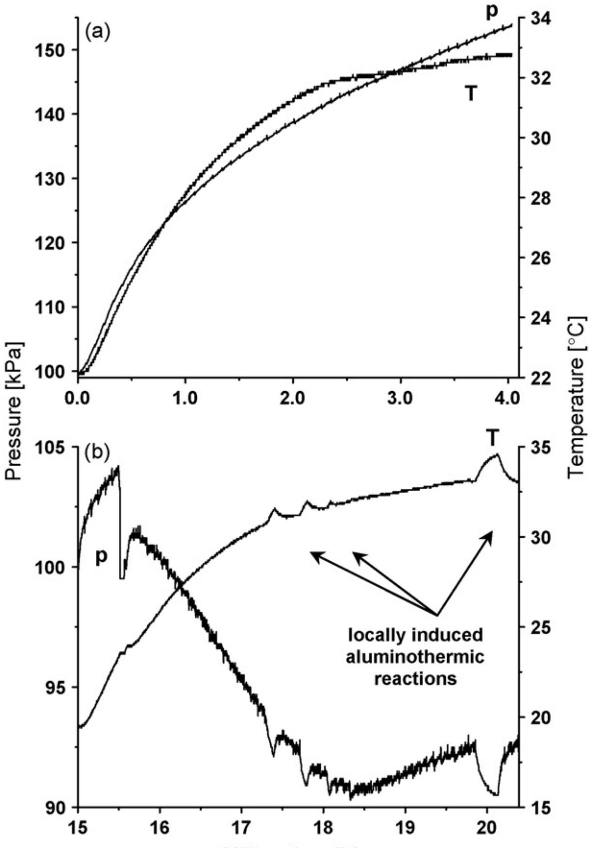

Fig. 2. GTM curves for $Cu_2(OH)_2CO_3$–Al system: (a) beginning of mechanical treatment and (b) final steps of mechanosynthesis.

minothermic reduction of CuO with Al is equal—1179 kJ/mol. However, in the studied system of hydroxysalt–active metal the processes in mill occur in a control manner. From Fig. 2a and b illustrating the changes of temperature and pressure in vial during milling process one can see that in the first hours of milling the temperature and pressure increase simultaneously. The rise in pressure is due to the decomposition of $Cu_2(OH)_2CO_3$ with evolving of H_2O and CO_2, while the temperature increase is involved (caused) by the friction and impact of balls. But when Cu-hydroxycarbonate is decomposed completely to CuO any rise of pressure is observed. Instead one can see the transitory rise in temperature (Fig. 2b). The duration of this temperature rise corresponds to locally induced aluminothermic reduction. Based on these data one can postulate that in our case mechanosynthesis takes place in a controlled way, i.e. CuO is reduced by Al in many steps proceeding locally, in isolated part of treated powders. Such run of aluminothermic reduction may be explained by the fact that the occurrence of a highly exothermic reaction in combustive way depends not only thermodynamic but on other factors such as mechanical properties of reactants, their crystalline structures, stability during milling [7,12]. In our case reaction does not proceed in an explosive manner probably due to ductility of Al. Ductile materials tend to form large particles which cover the surface of the milling tools, and therefore decreases the efficiency of treatment.

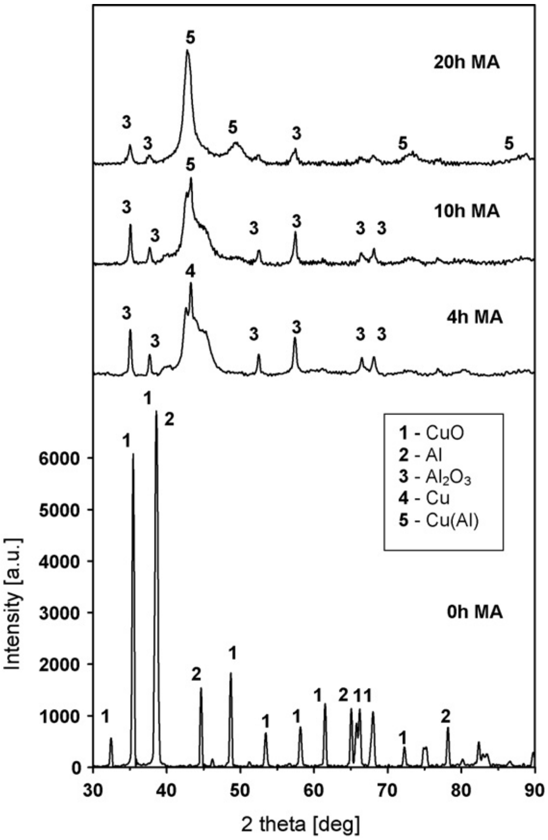

Fig. 3. X-ray diffraction patterns for CuO–Al system after different time of mechanical alloying (intensities with the same scale).

3.2. The effects of mechanosynthesis in the CuO–Al system

Fig. 3 shows X-ray diffraction patterns for mechanically treated mixture of CuO with Al during different time intervals. It can be observed that initial components disappeared completely within 4 h of milling. This time is considerably shorter than in the case of the $Cu_2(OH)_2CO_3$–Al system, where they still exist until 10 h of milling. It may suggest that the kinetics of mechanochemical reactions in the CuO–Al system is higher than in the $Cu_2(OH)_2CO_3$–Al one. The presence of reflexes from Al_2O_3 confirmed that the aluminothermic reduction in CuO–Al system occurred within 4 h of milling. After this time a broad peak, similar to the system of $Cu_2(OH)_2CO_3$–Al after 10 h of milling, is detected in the range of $2\theta = 42–45°$. The shape of this peak indicates its multiphase character. However, the strongest line located inside this reflex is related to copper. The calculated lattice parameter of this phase is equal to 3.656 Å. Comparison of this parameter with its value of pure Cu suggests the expansion of the copper lattice by aluminium forming the solid solution of Al into Cu matrix. It is indirectly confirmed by the lack of Al peaks on X-ray diffraction patterns. In fact the content of Al solute was estimated on the level near to 10%. Conventionally Al dissolves in Cu at the temperature of eutectoidal transformation (565 °C) in 9.4%.

4. Conclusions

Mechanosynthesis in both systems, the copper hydroxycarbonate–Al and copper oxide–Al, brings about the formation of composite material consisting of Al_2O_3, Cu(Al) solid solution and Cu. The amount of Al dissolved into Cu matrix is considerably higher for the CuO–Al system than for $Cu_2(OH)_2CO_3$–Al one. This is probably caused by the different kinetics of mechanochemical reactions in these two systems.

It is worth to notice that the expected Cu_9Al_4 phase formation is not observable although in both systems the stoichiometric amounts of components were prepared. Deficiency of Al is probably due to its sticking onto milling tools. It is typical for ductile substances such as aluminium which easily adheres to the milling media [12].

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