# Mechanochemical Synthesis of Cu–Al/$Al_2O_3$ Composite in CuO–Al System Under Different Conditions

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## Abstract

The objective of the present work was to show the beneficial effects of mechanochemical treatment of CuO–Al system for fabrication of composites consisting of Cu(Al) solid solution and $Al_2O_3$ ceramic with ultrafine grain microstructures. In particular, our research focused on explanation of the mechanism and kinetics of mechanochemically induced reactions in metal oxide–active metal system.

## INTRODUCTION

Composites are materials consisting of two or more components with different properties and distinct boundaries between them. Intensive research over the last two decades has led to the emergence of composites as a new class of engineering materials that provide enhanced combination of high temperature strength and acceptable levels of ductility, toughness, fatigue resistance required for a variety of applications. Metal matrix composites (MMCs) are one of the groups of such type of materials [1–3].

Cu–Al/$Al_2O_3$ is a metal matrix composite (MMC) that has interesting properties from practical point of view. This kind of material is widely used as resistance welding electrodes, lead frames and electrical connectors. This is due to the fact that $Al_2O_3$ in this MMC possesses favourable physical and chemical properties such as high strength, hardness, high elastic modulus and excellent resistance to thermal and chemical environments. $Al_2O_3$ has Young's modulus of 390 GPa and a density of 3.98 g/cm$^3$ providing a high stiffness and poor toughness typical for alumina, while Cu–Al metallic matrix improves the mechanical properties [4–8].

For economic viability of these materials they should be produced by a relatively simple process. The literature data shows some examples of Cu–Al/$Al_2O_3$ composite synthesis based mainly on *in situ* reduction by hydrogen of a homogenous mixture of finely divided CuO and $Al_2O_3$. Another way of synthesis is the internal oxidation of powder Cu–Al alloy. However, this method is a complicated and expensive one. Therefore mechanosynthesis seems to be an ideal way of metal matrix composite preparation. Thus, components of MMCs may be formed in single milling operation. Such an *in situ* route of composite synthesis results in the fact that synthesized $Al_2O_3$ reinforcement possesses much cleaner interface and thereby stronger binding strength with the Cu–Al matrix. Such a procedure has a strong influence on the mechanical properties of synthesized materials [9–11].

The aim of the present study is to compare the formation of Cu–Al/$Al_2O_3$ composite from mechanically alloyed mixture of copper oxide with aluminium using two energetically different planetary ball mills.

## EXPERIMENTAL

### *Materials*

The materials used in experiments were powdered copper oxide and aluminium (99.9 % purity). The two-component system, CuO−Al, was prepared as a physical mixture with the amount of aluminium 27.4 mass % and CuO 72.6 mass %, towards $Cu_9Al_4$ phase composite formation.

### *Instrumentation and milling procedure*

Mechanochemical treatment was provided in two laboratory planetary mills − Fritsch Pulverisette 6 and Pulverisette 5 with vials and balls made of hardened steel. They worked at maximum rotational speeds, equal to 550 and 250 rpm, respectively.

The milling processes were performed under protective atmosphere of argon. The total mass of powders was 5 g and the ball-to-powder mass ratio was 10 : 1. A small amount of powder was taken out from the vial after selected milling times for the solid phase analyses.

### *Equipment and methods of phase identification*

X-ray powder diffraction patterns were obtained using a Philips X'Pert diffractometer ($CuK_\alpha$) in the $2\theta$ range of 10−90°.

A Hitachi S-4700 instrument (SEM) equipped with an energy dispersive X-ray spectrometer was used for the microstructural examination and elemental microanalysis. The BSE imaging and EDX elemental analyses were carried out at an electron beam voltage of 20 kV.

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.

## RESULTS AND DISCUSSION

When CuO and Al react directly, the reduction process may be combustive and/or rapid. It can involve the melting of product and/or separation of composite phases. Therefore, in order to produce homogenous $Cu-Al/Al_2O_3$ composite, the combustive reaction must be suppressed. This can be achieved by reducing the activity of aluminium, through its dilution by adding copper and then using Cu−Al intermetallic compound for aluminothermic reaction. Another way of slowing the rate of SHS reaction in CuO−Al system is using a process control agent (PCA), *e.g.* toluene. Thus, PCA suppresses the combustion reaction promoting the progressive reaction. It helps in reducing temperature generated during the reactive milling making the synthesis of materials in nanocrystalline form possible [12−14].

In the presented work we try to slow down the rate of SHS reaction occuring during milling of the CuO−Al system by changing the amount of energy supplied to the materials in

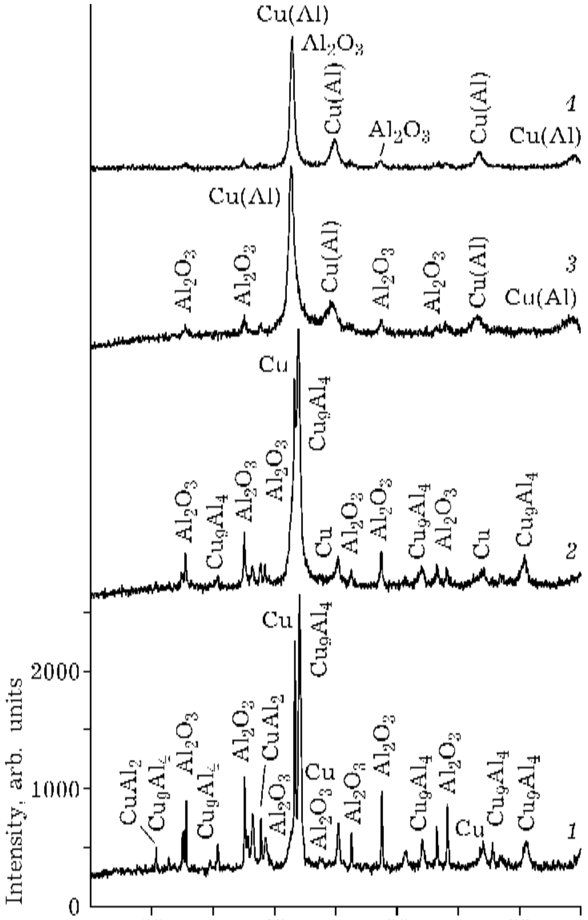

Fig. 1. X-ray diffraction patterns for CuO and Al mixture after different times of mechanochemical treatment realized in Pulverisette 6 mill (higher energetic). Milling time, h: 1 (*1*), 2 (*2*), 10 (*3*), 20 (*4*).

planetary mills Pulverisette 5 and Pulverisette 6, energetically different.

In fact, the results presented below point to two different mechanisms of Cu–Al/$Al_2O_3$ composite formation conditioned by the energy transfer to the ground materials during mechanical alloying process.

Mechanosynthesis in a copper oxide–aluminium system realized in Pulverisette 6 mill operated at 550 rpm caused the formation of two intermetallic phases, *i.e.* $CuAl_2$ and $Cu_9Al_4$ within the first hour of milling (Fig. 1). Elongation of milling time caused the disapperance of both intermetallics, however, with different kinetics. The first of them, $CuAl_2$, decays after one hour of milling, while $Cu_9Al_4$ exists in the system up to 2 h of milling. Everything points out that further milling process causes the consumption of aluminium from these phases to form Cu(Al) solid solution. This is confirmed by the shift of the Cu(111) peak from $2\theta = 42.57–43.33°$ observed for the system treated for 20 h.

An increase in temperature in the milling vial registered by the GTM system indicates that during the first hour of milling the combustion process occurs (Fig. 2). In this case the reaction between CuO and Al is complete, which is confirmed by the absence of peaks corresponding to initial components.

Considering the phase evolution of the CuO–Al mixed powders in higher energetic mill, one can suggest that the intermetallic phase is formed under the applied conditions only as intermediate products. During further milling they transform to the Cu(Al) solid solution.

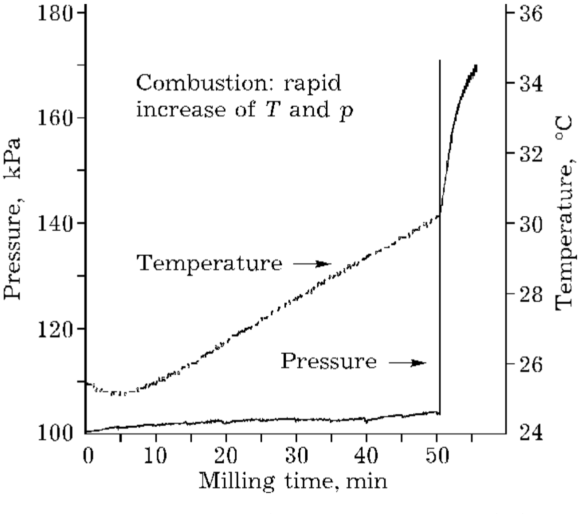

Fig. 2. Temperature and pressure registered during combustion process occurring in CuO–Al system milled in Pulverisette 6 mill.

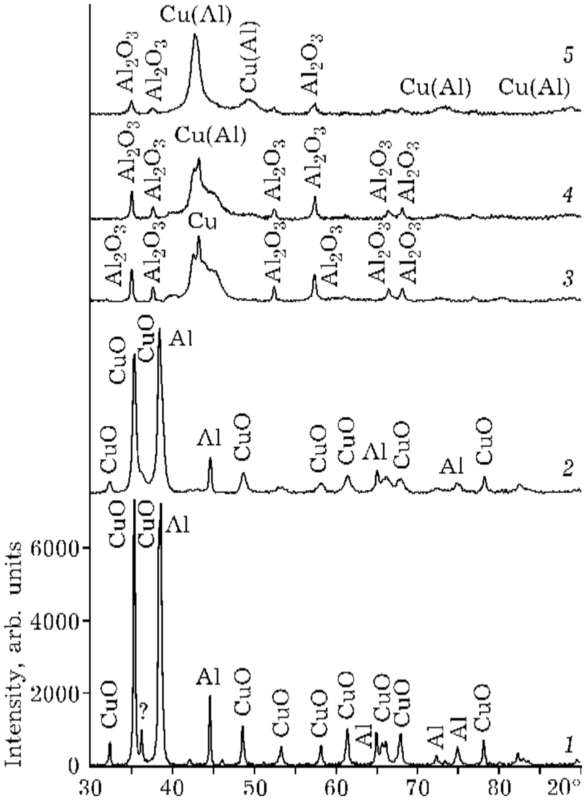

Fig. 3. X-ray diffraction patterns for CuO and Al mixture after different times of mechanochemical treatment realized in Pulverisette 5 mill (lower energetic). Milling time, h: 1 (*1*), 2 (*2*), 4 (*3*), 10 (*4*), 20 (*5*).

In the second mill (Pulverisette 5) reactions proceed in a slower manner than in Pulverisette 6 mill. Initial reagents exist in the ground mixture up to 4 h (Fig. 3). This time is considerably longer than in the case of the mixture milled at 550 rpm, where CuO and Al disappeared within the first hour of milling. In this case 4 h of mechanosynthesis is required for the reduction of CuO by Al to occur. After this time XRD patterns show only reflexes from $Al_2O_3$ and copper. Elongation of milling time up to 10 h caused the transformation of copper to Cu(Al) solid solution. In the case of this system, formation of intermetallic phases is not observed. It means that the formation of Cu(Al) solid solution proceeds directly without intermediate products.

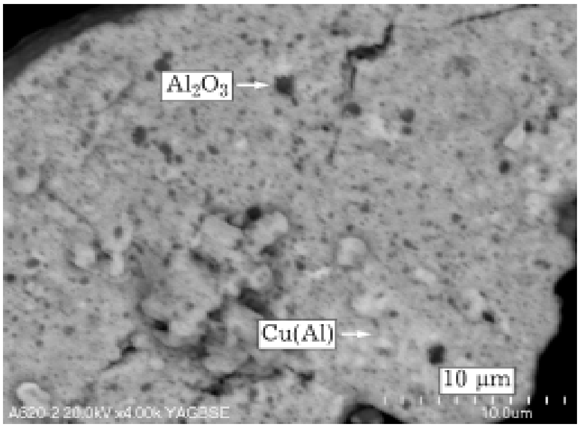

Fig. 4. Backscattered electron micrograph of mechanochemically synthesized Cu(Al)/$Al_2O_3$ composite ($Al_2O_3$ – dark grey spots, Cu(Al) – bright grey spots).

It was found that, independently of milling devices used, the expected $Cu_9Al_4$ phase is not formed in the final product. In both cases composites consist of Cu(Al) solid solution besides of alumina. This is due to deficiency of Al probably caused by its sticking onto milling tools. These phenomena are typical for ductile substances such as aluminium, which easily adheres to the milling media.

Characteristics of microstructure of milling products were provided using scanning electron microscopy. Figure 4 shows the typical morphology of composite powder after being milled for 20 h. It was proved by EDS analysis that the dark phase is alumina while bright phase is a Cu(Al) matrix. The micrographs definitely confirmed that $Al_2O_3$ particles are evenly embedded in the Cu–Al matrix, their particle size ranging from 100–500 nm. It indicates that milling of the CuO–Al system with stoichiometry to $Cu_9Al_4$ formation brings about the formation of metal matrix composites in which Cu(Al) is a matrix while alumina is its reinforcement.

## CONCLUSIONS

The Cu–Al/$Al_2O_3$ nanocomposite with components having a crystallite size close to 100 nm can be successfully synthesized by reactive ball milling of the mixture CuO–Al.

It was found that using energetically different mills one may change the mechanism and kinetics of mechanochemically induced reactions. However, the final product is the same.

$CuAl_2$ and $Cu_9Al_4$ are formed as intermediates when mechanosynthesis occurs in a combustive way, whereas progressive nature of synthesis gives directly the formation of Cu(Al) solid solution.

## Acknowledgement

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