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Cu-Al/Al_2O_3 CERMET SYNTHESIZED BY REACTIVE BALL MILLING OF CuO-Al SYSTEM

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Abstract. A mechanochemical method of a single-stage synthesis of a metal matrix composite consisted of copper aluminides, Cu_9Al_4, reinforced by fine particles of aluminium oxide was investigated. It was demonstrated that CuO and Al can react forming directly γ-Cu_9Al_4 intermetallic compound when the initial content of aluminium is higher than stoichiometric one. It is shown that Al_2O_3 particles in the synthesized cermet have a size ranging from 500 to 100 nm.

1. INTRODUCTION

The ordered intermetallics based on aluminides of transition metals have been evaluated for their potential applications after consolidation as high temperature structural materials. In order to improve the strength of intermetallics, especially at elevated temperatures, ceramic particles can be added as reinforcement. Composite material formed in this way is called as a cermet.

Cermet materials, which contain light metal alloys, have very good mechanical properties and therefore they are applied as construction materials in defence, aircraft and cars technology [1-4].

The mechanical properties of composite materials reinforced with ceramic particles depend on the matrix properties, mutual wettability of interphase and the amount of reinforcing particles. Currently copper-based composite materials are produced by using several routes such as mixing of Cu and alumina powders, internal oxidation of Cu-Al alloy in powdered form or by mechanical blending of copper with dispersed Al_2O_3 powder and subsequently cold pressed. The mechanochemical approach to the MMCs synthesis is likely to be the most promising because it allows obtaining materials characterized with nanocrystalline structure. This technique allows incorporating the metallic and ceramic phases into particles. It causes that material is more homogenous in microstructure and therefore has high strength and better interfacial contacts between reinforcements and the matrices [5-8].

Copper–based composites have relatively good mechanical properties and electrical conductivity. However, it is worth to mention, that even small amount of alumina additions into Cu matrix, increases its mechanical properties, simultaneously lowering considerably electrical conductivity [9-13].

In this work, the *in situ* technique to carry the SHS reaction between pure Al and CuO powders was used. Al-Cu intermetallic compounds directly formed during this reaction. Our objectives are to produce a Cu_9Al_4 intermetallics reinforced by alumina. Two different proportions of initial components, stoichiometric into Cu_9Al_4 intermetallics and excess of aluminium, were tested to mechanochemical synthesis of composite.

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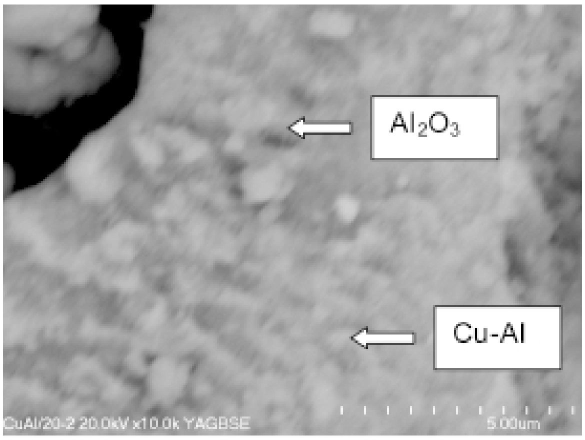

Fig. 1. SEM micrograph of mechanochemically synthesized Cu-Al/Al_2O_3 composite powders.

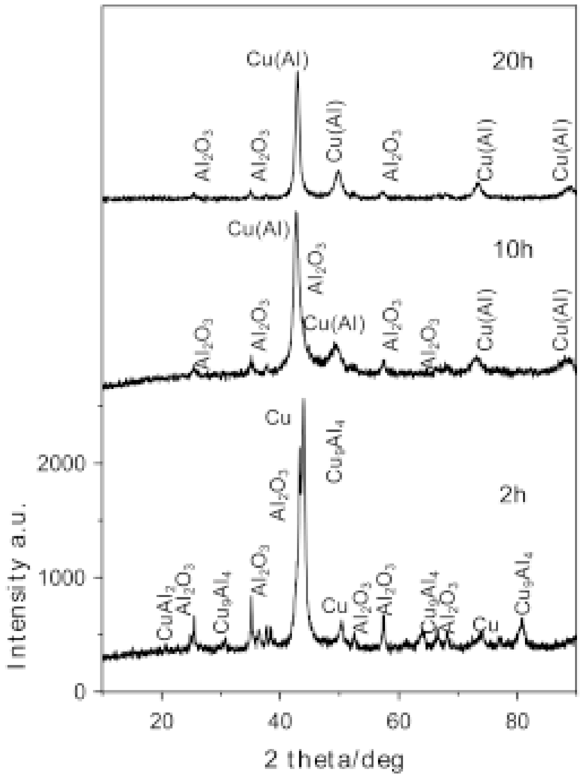

Fig. 2. X-ray diffraction patterns for mixture with 27.4 wt.% content of aluminium at different stages of composite formation.

2. EXPERIMENTAL

Materials

Copper oxide (Fluka, purity 99.9%) and aluminium (POCh, purity 99.9%), both in microcrystalline form, were used in experiments. The two-component system, i.e. CuO-Al, was prepared as two physical mixtures: with 27.4 wt.% and 31.2 wt.% of aluminium, respectively. The second mixture contained 20% of aluminium excess in relation to stoichiometry of Cu_9Al_4.

Instrumentation and milling procedure

Mechanochemical treatment was provided in a laboratory planetary mill - Fritsch GmbH *Pulverisette 6* with vials and balls made of hardened steel. The rotational speed rpm was equal of 550.

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. Small amounts of powder were 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_α) in the 2θ 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.

3. RESULTS AND DISCUSSION

Testing of Al-Cu system relates to industrial importance, because Al-Cu alloys are used as components in the production of commercially important structural materials defined as a duraluminium [14]. The binary Al-Cu phase diagram [15] shows several intermetallics, among them the main are $CuAl_2$, Cu_9Al_4, Cu(Al) and Al(Cu) solid solutions. It worth to mention that $CuAl_2$-Al(Cu) is the promissing metal matrix composite widely used in automobile industry, because its cost is relatively low and Al(Cu)

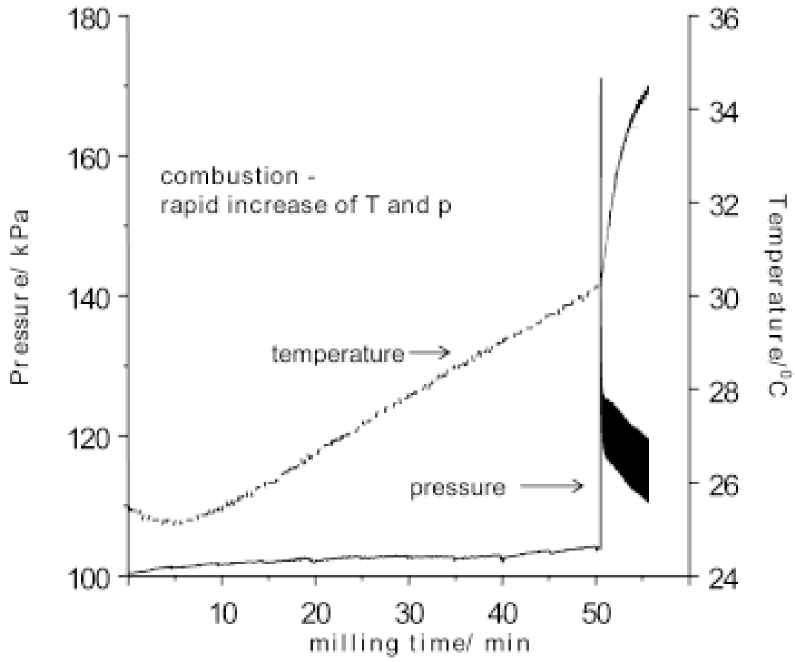

Fig. 3. Temperature and pressure changes during combustion process occurring in tested mixture of CuO-Al.

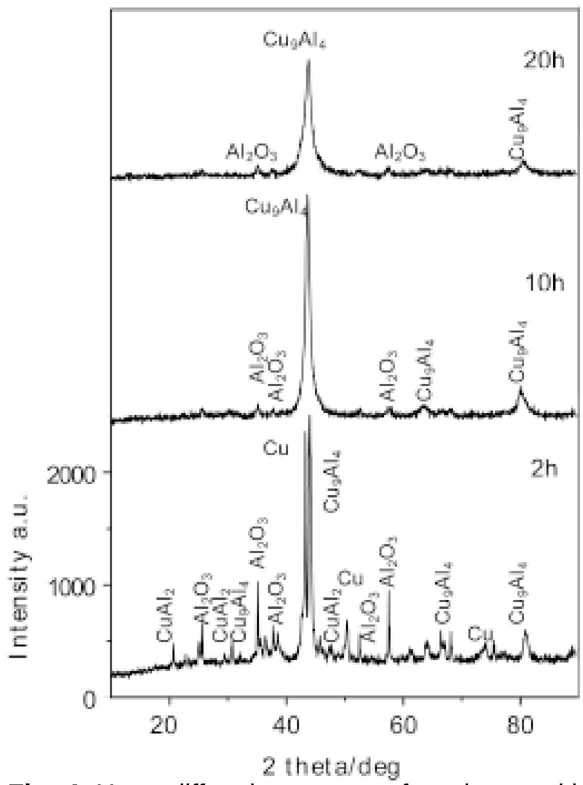

Fig. 4. X-ray diffraction patterns for mixture with 31.2 wt.% content of aluminium at different stages of composite formation.

solid solution matrix is mechanically tougher than a pure Al matrix. It has been pointed out that, from practical point of view, the Al-rich region in Cu-Al phase diagram is more important. However, in the present study we have tried to obtain Cu_9Al_4 phase by mechanochemical route from Cu-rich region, according to the below equation:

$$9\,CuO + 10\,Al = Cu_9Al_4 + 3\,AL_2O_3.$$

The γ-Cu_9Al_4 phase has a cubic primitive cell with relatively high lattice parameter (*a*=0.87023 nm) and space belongs to group P-43m. This phase is a typical Hume-Rothery phase, which conventionally is formed peritectoidally at 870 °C [16].

Products of both tested mixtures after 20 hours of milling consisted of a very fine powders in black colour. SEM micrograph in Fig. 1 indicates that synthesized composite powder is highly homogeneous. The EDAX analysis indicates that the dark uniformly distributed phase is Al_2O_3 and the lighter one consists mainly of copper with small amount of aluminium. It can state that this time of milling involved the formation of metal matrix composite consisted of Cu-Al matrix reinforced by embedded Al_2O_3 particles. The particle size of alumina ranges from 100 to 500 nm.

However, XRD data indicate that final products, namely, metallic matrix formed in two composite powders, are different and depend on the initial amount of aluminium in the mixture. Fig. 2 shows XRD patterns of the mechanochemically synthesized composite powders produced at different stages of milling mixture with 27.4% of Al. After 2h of milling, the XRD pattern does not show peaks related to initial components of the tested mixture. Although one can observe peaks corresponding pure copper and two intermetallics, i.e. $CuAl_2$ and Cu_9Al_4 beside of Al_2O_3. It means that during this time self-propagating high temperature synthesis (SHS) process occurred completely. The course of this SHS reaction was monitorred by measuring temperature and pressure in milling vial by the GTM system. The increase in the temperature indicates that during first hours of milling proceeds complete combustion of initial reagents (Fig. 3). The products of SHS reaction are heterogenous in nature. Prolongation of milling time caused that $CuAl_2$ phase disappeared. This is probably due to consumption of this phase during further reactions in mill. Presumably the aluminium from $CuAl_2$ is utilized for dillution of copper forming Cu(Al) solid solution and after 10 hours of milling, Cu_9Al_4 also disappears. Finally, Cu(Al) solid-solution and alumina are the only products of mechanical alloying in the tested system.

It is worth to notice that the expected Cu_9Al_4 phase is not present in the final MMC although, initial material contains enough amount of Al^0 for its formation. The real deficiency of Al is probably due to sticking of aluminium onto milling tools. It is typical for ductile substances like aluminium, which easy adheres to the milling media. Therefore, we tried to synthesize this phase by providing mechanochemical process in the system with 20 wt.% exccess of aluminium.

It was proved that milling of mixture containing 31.2 wt.% of Al caused synthesis of composite of Cu_9Al_4 and alumina phases. Fig. 4 shows XRD patterns of the mechanochemically produced composite powder at different stages of its milling. After two hours of milling XRD results reveal the presence of different products, i.e. Cu, $CuAl_2$, Cu_9Al_4, and alumina. The absence of inital components confirmed that aluminothermic reduction process proceeds within this time. It is pointed out that in both tested systems, independently on aluminum content, SHS reduction process occured in the nearly the same period of time. However, the evolution of the phases which compose of MMC is completely different. In the system with excces of Al^0, intermetallics Cu_9Al_4 after four milling hours is still present in the system. However, the $CuAl_2$ phase disappered in a similiar way as in the previous one. Increase of the X-ray diffraction peaks intensity of Cu_9Al_4 with prolongation of milling time suggests that $CuAl_2$ reacts with pure copper forming this phase. It is confirmed by gradual decreasing of intensity peaks related to copper up to its total disapperance after 10 hours of milling. Mechanosynthesis provided for 20 hours did not bring any changes. The final product, i.e. synthesized cermet consists of two phases, Cu_9Al_4 intermetallics and alumina.

4. CONCLUSIONS

The Cu_9Al_4/Al_2O_3 cermet with components having a crystallite size close to nanoscale can be successfully synthesized by reactive ball milling of the CuO-Al mixtures.

$CuAl_2$ and Cu_9Al_4 phases were formed as intermediate products independently on initial composition of the tested mixtures.

It was found that expected Cu_9Al_4 phase in final product appears only in the case of using amount of aluminium higher than stoichiometric one, probably due to its adhering to milling media.

The fact that in both tested mixtures formation of $CuAl_2$ phase precedes the formation of Cu_9Al_4 shows that nucleation of $CuAl_2$ requires lower energy than Cu_9Al_4 (structural reason). Therefore, it is likely that even with low Al^0 contain, $CuAl_2$ forms as the primary phase in the system.

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