



In-situ synthesis of AgCu/Cu₂O nanocomposite by mechanical alloying: The effect of the processing on the thermal behavior



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ABSTRACT

The influence of the mechanical alloying processing parameters on the elaboration of AgCu-based bimetallic matrix composites reinforced by in-situ synthesized Cu₂O has been studied. The milling time (20, 45 and 80 h) of the initial 72% mass Ag + 28% mass Cu micrometric powders mixture influences the particle size distribution of the obtained composite particles. After 80 h of mechanical alloying, AgCu/Cu₂O nanoparticles of 60–80 nm are obtained and their chemical composition at bulk/surface level has been determined by X-ray diffraction and photoelectron spectroscopy. The effect of milling time on the thermal behavior of the powders samples has been studied by thermogravimetry and differential scanning calorimetry measurements in argon atmosphere. The argon chemisorptive reaction from the particles surface has been identified and the binding energy (0.9–1.99 eV) has been calculated. The isothermal drop calorimetry and the linear thermal expansion measurements were used to evaluate the correlation between thermal stability and thermal expansion properties of the in-situ synthesized AgCu/Cu₂O nanocomposite.

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1. Introduction

In engineering applications, the materials could be exposed to severe functioning conditions that combine high mechanical loads, elevated temperature environment, and high corrosion and wear settings. In the most of such applications, the assembled parts are made of ceramics+ceramics (i.e., Si₃N₄, Al₂O₃) [1], ceramics (Si₃N₄) + metallic alloys (CrMo steels) [2] or intermetallics (TiAl-based) + metallic alloys (CrMo steels, Ti alloys) [3], special joining technologies being developed: brazing, diffusion bonding, partial transient liquid phase bonding [4] and vacuum brazing [5].

One of the most recommended filler materials that improve the well-known poor wettability of the ceramics are the AgCuTi alloys [3,6]. However, these joints present some differences in physical properties comparatively with the ceramics/intermetallics or even metallic counterparts, especially as concerns the coefficient of thermal expansion (CTE) which determines low performing functional behavior in the above mentioned extreme conditions. In order to improve this aspect, a new generation of filler materials

has been developed, namely the AgCuTi-based composites reinforced by borides (TiB whiskers) or carbides (SiC, WC, SiC) [1,2,7]. The CTE is accordingly decreased from 18–19 × 10⁻⁶ K⁻¹ [1,2,7] which corresponds to AgCuTi alloy [1,7], up to 16 × 10⁻⁶ K⁻¹ for composite reinforced by 20% vol. WC particles [7] and 9–11 × 10⁻⁶ K⁻¹ for 10% vol. SiC particles reinforcement [1].

On the other hand, for a certain reinforcing level, the carbides presence in the alloyed filler may have negative consequences on the bonding strength [1] that determines a novel class of brazing composite fillers to be designed using the principle of in-situ synthesis of the ceramic reinforcing elements.

Suitable reinforcing elements for a Cu matrix is Cu₂O that can be in-situ synthesized at nanometric scale (100–300 nm) [8] and controlled by the oxidation agent's quantity. Another method for Cu oxidation is the use of the ethylene glycol (EG) [9]. The EG may act as a structural directing agent [10] on the basis of the Ostwald ripening effect [11].

As far as the matrix concerns, the Ag–Cu system is recommended for this research by good mechanical properties (micro-hardness values up to 350–400 units and tensile strength to 1420 MPa) [12] respectively improved physical characteristics (optical, electrical) due to their ultrafine crystalline grain size of 200–400 nm [13]. Solid state processing technologies [12,14,15] are

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the most recommended because of the positive mixing enthalpy of Ag–Cu system ($\Delta H = 6\text{--}10\text{ kJ/mol}$). However, special technologies (i.e., severe plastic deformation = SPD; mechanical alloying = MA) [16,17], are highly recommended to produce AgCu-based composite filler [7]. Moreover, specific reaction mechanism may occur during the MA process, able to provide the conditions for direct mechanochemical synthesis of advanced materials [18] including AgCu-based materials.

In a previous paper [19], is shown the processing technology of the Ag–28Cu powder mixture by mechanical alloying (MA). The experimental results on the particle size distribution have been determined by the Brookhaven 90Plus BI-MAS equipment (15 mW solid laser; $\pm(1\text{--}2)\%$ accuracy for the mono-dispersed samples; measurement range: 2 nm ... 3 μm) because it allows the measurements for micronic and submicronic powders. The powder samples were processed for 20 h, 45 h (up to 45 h of MA, micronic and submicronic powders are obtained) and 80 h (only submicronic powders are obtained).

In the present paper, the same powder mixture Ag–28Cu is analyzed by NANOSIGHT LM 10, but only the samples processed for 80 h by MA route are discussed (MA80 samples). The new results are: (a) MA80 samples are analyzed by NANOSIGHT LM 10 because they are submicronic and nanometric size range; (b) Due to the agglomeration of MA80 powder particles, they need to be diluted for accurate measurements. There are three diluted samples: MA80-1st, MA80-2nd and MA80-3rd.

It also, in the present paper, a new way for elaboration of AgCu-based bimetallic matrix composites reinforced by in-situ synthesized Cu_2O nanoparticles has been studied. The bimetallic matrix and the oxide reinforcements are simultaneously obtained by the MA process, applied to the 72% mass Ag+28% mass Cu powder mixture in an aqueous EG solution which acts as a controlling oxidation agent. The chemical composition at bulk/surface level of the composite nanoparticles has been determined by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) methods. The thermal stability of the AgCu-based nanoparticles processed at different milling times was investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC). The measurement of the enthalpy increment values $H_T - H_{298}$ by isothermal drop calorimetry in the temperature range of 200–1000 °C was used for the first time to further evaluate the thermal behavior of the nanocomposite particles. The correlation between thermal stability and thermal expansion properties was then evidenced by thermal expansion measurements in the temperature range of 25–700 °C.

2. Materials and methods

The materials used for this research are Ag and Cu powders whose main morphological and physical properties are presented in Table 1.

The chosen chemical composition of the powder mixture corresponds to the eutectic concentration of this binary system, namely (Ag + 28% mass Cu). The eutectic composition mixture is processed by MA route. The milling process is developed in a planetary ball mill Pulverisette 6 (Fritsch, Germany). The milling

conditions are: jar speed = 200 rpm; 80 ml agate jar; amount of sample = 36.40 g; ratio balls mass/sample mass = 5:1. As far as the size balls concerns, in order to get higher collision energy, three different size agate balls, namely $5 \times \Phi 20$, $9 \times \Phi 10$ and $9 \times \Phi 5$, are used [20]. The MA process developed in water and ethylene glycol mixture (1:1 mass ratio), hereinafter named EG solution, in order to improve the cooling effect especially when ductile nanopowders are involved [21]. The EG solution is added 1 cm^3 at 1 g metallic powder mixture. Milling for three different times (20, 45 and 80 h) was carried out. The sample codes are presented in Table 2.

The determination of the particle size distribution was developed using two different equipments based on light diffraction: the Brookhaven 9Plus/BI-MAS, respectively the Nanosight LM 10 equipment. For 20 h of milling time, particle sizes are mainly of 350–470 nm, and after 45 h they are 200–270 nm. Only after 80 h of MA process, AgCu nanoparticles in the 60–80 nm range have been depicted by using Brookhaven Plus BiMas technique [19]. The detailed particle size distribution for MA80 sample has been determined by Nanosight analysis which allows the visualization of the nanoparticles in on-line mode, in real time. The samples were prepared as diluted solutions, MA 80-1st, MA 80-2nd and MA 80-3rd (Table 3), and they consist in successively dilution of the genuine MA 80 powder sample in 2 ml of distilled water. Finally, the ultrasonic separation for accurate particle size distribution results is applied to get the median volume parameter: D10, D50, D70, and D90.

For MA80-1st dilution sample, D10 points out that less than 10% vol. of the sample represent powder particles or conglomerates larger than 1115 nm. This result is confirmed by Fig. 1a where visible white spots are related to these particles/conglomerates while other particles are not visible because the sample is too concentrated and higher dilution is requested.

As the dilution increases, D10 parameter decreases and this phenomenon points out that few powder particles of MA80-2nd dilution sample are smaller than 212 nm. D50 and D70 parameters are decreasing, too, along the dilution process. Thus, for MA80-1st dilution, more than 50% vol. of the powders is between 1115 and 231 nm (D50) and more than 70% vol. of powders are between 231 and 141 nm (D70). The MA80-2nd dilution sample (Fig. 1b) shows a more homogeneous distribution of the particle size: D70 points out powder particles between 96 and 83 nm. D90 is constant along the dilutions, showing that nanometric powders of 66–85 nm represent more than 90% vol. of MA80-1st dilution, MA80-2nd dilution respectively MA80-3rd dilution samples, Fig. 1c, confirmed by Gingu et al. [19] with Brookhaven Plus BiMas equipment for the same MA80 sample.

The influence of the milling time on the chemical and structural composition of the processed powder particles was studied by XRD and XPS analysis.

XRD data were collected using a Rigaku Ultima IV diffractometer, with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$), operating at 40 kV and 30 mA. Counts were collected from 10 to 80 degrees, with a step size of 0.02 and a rate of 5 degrees/min. Phase identification was performed using Rigaku's PDXL software connected to ICDD PDF-2 database. Reference intensity ratio (RIR) method was used for quantitative analysis.

Table 1
Morphological and physical properties of the starting materials.

Powder type	Sigma–Aldrich code	Morphological and physical properties				
		Purity, %	Shape	Size, μm	Density, g/cm^3	Melting point, °C
Ag	CAS 7440-22-4	≥ 99.9	flakes	10	10.49	960
Cu	CAS 7440-50-8	99	dendrites	<75	8.94	1083.4

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