Synthesis of novel $CuSn_{10}$-graphite nanocomposite powders by mechanical alloying

A. Canakci[1], T. Varol[1], H. Cuvalci[1], F. Erdemir[1], S. Ozkaya[1], E.D. Yalcın[2]

[1]*Department of Metallurgical and Materials Engineering, Engineering Faculty, Karadeniz Technical University, Trabzon, Turkey*
[2]*Abdullah Kanca Vocational School of Higher Education, Karadeniz Technical University, Trabzon, Turkey*
E-mail: aykut@ktu.edu.tr

Published in Micro & Nano Letters; Received on 10th December 2013; Accepted on 17th January 2014

$CuSn_{10}$-Gr nanocomposite powders were successfully synthesised by mechanical alloying of the powder mixtures of $CuSn_{10}$ and Gr (1, 3 and 5 wt%, respectively, of Gr). The effects of increasing the graphite particles weight percentage and milling time on the morphology, the particle size and the microstructure of the $CuSn_{10}$-Gr nanocomposite powders were investigated. The $CuSn_{10}$-Gr nanocomposite powders were characterised using a scanning electron microscope, a laser particle-size analyser, X-ray diffraction analysis and energy dispersive X-ray analysis. The results show that the addition of the graphite particles as the reinforcement and the milling time has an important effect on the particle size, the morphology and the yield of the powder. The electron microscopy studies showed the formation of the equiaxed grains with a wide size distribution ranging from 50 to 250 nm. It was found that the particle size decreased until the creation of a balance between the rate of welding and fracturing. Moreover, the powder yield dropped drastically with the increasing milling time and the decreasing graphite content.

1. Introduction: Nowadays, there are potential applications for the nanocomposite materials because of their superior mechanical properties (strength and ductility with attendant workability) in comparison with monolithic materials. However, the method of production and the amounts of the components are vital challenges for the researchers in this field. In recent years, nanocomposite materials have received serious attention from researchers in view of their superior properties compared to either monolithic material or composites containing a coarse-grained reinforcement phase [1].

Copper-based materials are widely used in many industrial applications because of their good wear resistance and friction ductility, remarkable corrosion resistance, as well as self-lubrication properties, such as sliding bearings, sleeves, brushes and other components. CuSn bronzes have been used for a long time in many tribological fields on account of their self-lubricating, high strength and corrosion resistance properties. At the same time, these materials have a high wear resistance and hardness. In these alloys, Sn was used at 4–10 wt%. These types of bronzes have been used in the chemical industry, navigation, pivots, springs in electrical engineering, machine production, gears against corrosion resistance and crank pivot bearings [2]. Cu-based P/M composites are extensively used in the friction devices of various machines and mechanisms because of a good heat conductivity, wear resistance and stable chemical properties. Solid lubricants can be added into the Cu matrix for improving the wear resistance. Solid lubricant-rich films which are beneficial for improving the wear resistance could be produced between the contact surfaces in the friction process because of the lamellar structure and the softness of these solid lubricants. Graphite as a solid lubricant is widely used because of its low cost and excellent lubrication performance [3].

Nanosized materials have attracted considerable attention because of their improved physical, mechanical, optical and magnetic properties in comparison to coarse-grained polycrystalline materials. These properties arise from the crystallite size refinement down to the nanoscale and the consequent high density of the interfaces as well as the significant fraction of the atoms residing at the grain boundaries. These materials are fabricated through various methods. Among these, mechanical alloying (MA) is one of the useful methods for the production of nanostructured powders by a solid-state reaction at room temperature. The nanosized materials can be readily produced by MA with relatively inexpensive equipment, and there is the potential for scale up production for commercial quantities [4]. MA is a solid-state powder processing technique involving repeated deformation, welding and fracturing of the powder particle. MA has been widely used to synthesise a variety of materials, such as amorphous alloys, nanocrystalline materials, intermetallic compounds and composites. In almost all the cases, the final product has a nanosized structure which exhibits better properties and performance compared with conventional coarse-grain materials [5].

Previous studies have discussed the production of composite powders, metal matrix composite and nanocomposite using the MA method. Different materials and methods have been used in these studies. For example, Khadem *et al.* [1], Woo and Zhang [6], Wang *et al.* [7] and Mostaed *et al.* [8] produced nanocomposite powders with different matrix and reinforcement materials by using the MA process. However, there are no studies on the synthesis and the characterisation of the $CuSn_{10}$-Gr nanocomposite powders by the MA method.

Therefore the objective of the reported work was the production of the $CuSn_{10}$-Gr nanocomposite powders and the investigation of the effect of the graphite content and the milling time on the morphology, particle size and microstructure of the $CuSn_{10}$ – 1 wt% Gr, the $CuSn_{10}$ – 3 wt% Gr and the $CuSn_{10}$ – 5 wt% Gr nanocomposite powders during the MA process.

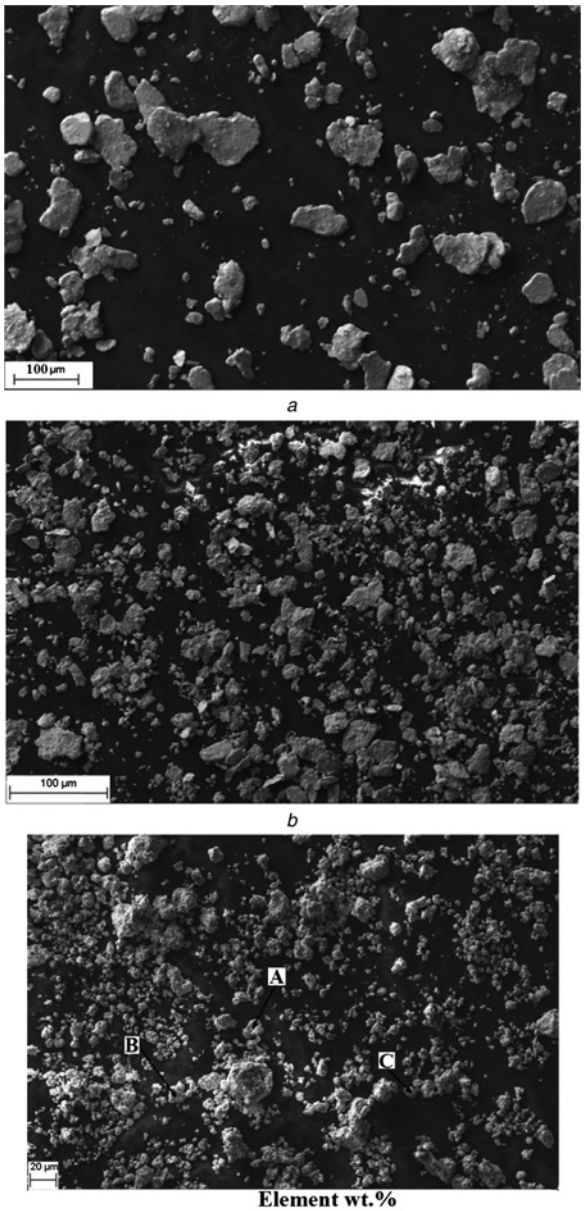
2. Experimental procedures: High purity $CuSn_{10}$ powder (Gündoğdu Exotherm Company, Turkey) with mean particles sizes of 28 μm and graphite powders (Alfa Easer, Germany) with particle sizes of 30 μm were used as the starting materials. MA was performed in a planetary ball mill (Fritsch 'Pulverisette 7, Premium line') by using a tungsten carbide container and balls. A total of 25 g powder with no process control agent was used in all the MA runs. The samples were milled at different graphite particles weight percentages (0, 1, 3 and 5 wt%), milling times (0.5, 1, 2, 5, 8, 12 and 24 h) and balls-to-powder weight ratio (10:1). The other parameters applied were: ball diameter (10 mm) and speed (400 rpm), respectively.

The size distributions (d50) of the as-received and milled powders were quantified by using a laser particle size analyser (Malvern, model 'Mastersizer Hydro 2000e'). The morphology

and microstructure investigations of the composite powders were performed using a scanning electron microscope (SEM) (Zeiss Evo LS10). Energy dispersive X-ray spectroscopy spot analysis was employed to quantify, determine and indicate the composition of the resulting powders. A Rigaku Corporation X-ray diffractometer was used to study the structural evolution of the milled powders.

3. Results and discussion

3.1. Morphology and particle size: Figs. 1 and 2 show the SEM images of the $CuSn_{10}$ – 3 wt% Gr and the $CuSn_{10}$ – 5 wt% Gr nanocomposite powders mechanically alloyed for different milling times. In the early stages of MA (from 0.5 to 2 h), the $CuSn_{10}$ powders are still soft, and cold welding predominates. Consequently, the particles size increases (Figs. 1 and 2). The particles shape has become flattened because of the cold working effects during the milling process (Figs. 1*a* and 2*a*). When the graphite content is low, the $CuSn_{10}$ particle deformation and the cold welding are the predominant mechanisms. By increasing the graphite content, the contribution of the fracture mechanism is increased and consequently the particle size is decreased (Fig. 3). Cold welding between the $CuSn_{10}$ powders decreased with increasing graphite content and so the efficiency of the ball-powder-ball collisions increased with increasing graphite content in the milling vial. Fracturing of some flattened powder particles is observed after 2 h. Continuation of the MA for 5 h resulted in

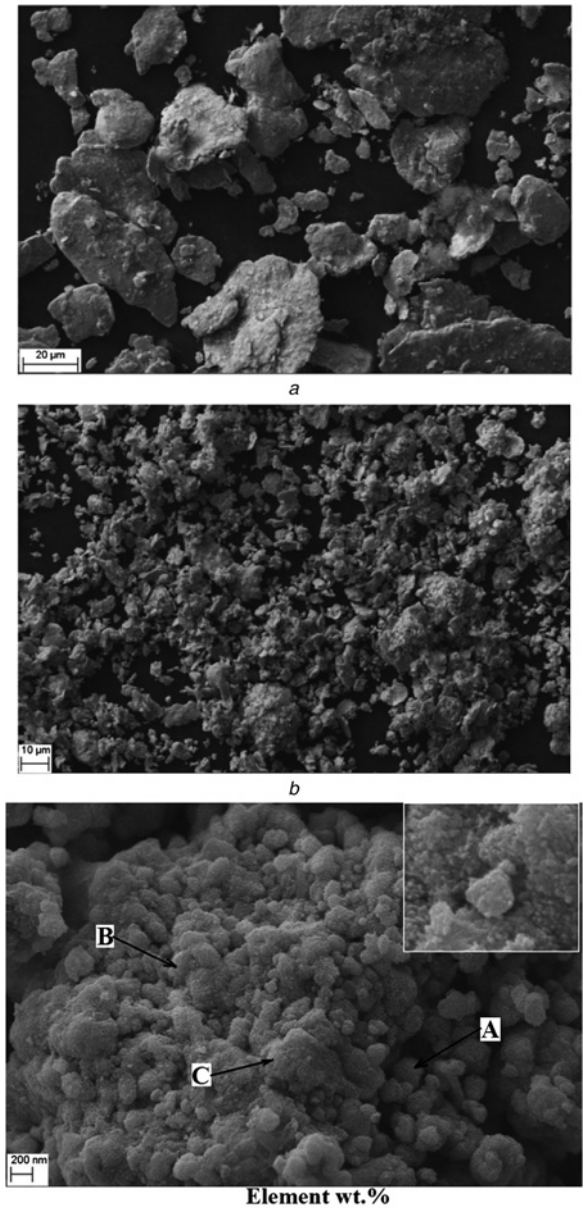


Element wt.%

	Copper	Tin	Carbon
A	76.11	7.23	16.66
B	89.08	4.44	6.48
C	86.45	10.54	3.01

c

Figure 1 *SEM images of the $CuSn_{10}$ – 3 wt% Gr nanocomposite powders*
a 1 h
b 5 h
c 24 h



Element wt.%

	Copper	Tin	Carbon
A	83. 35	10.15	6.50
B	75. 52	15.34	9.14
C	79.06	12.16	8.78

c

Figure 2 *SEM images of the $CuSn_{10}$ – 5 wt% Gr nanocomposite powders*
a 1 h
b 5 h
c 24 h

doi: 10.1049/mnl.2013.0715

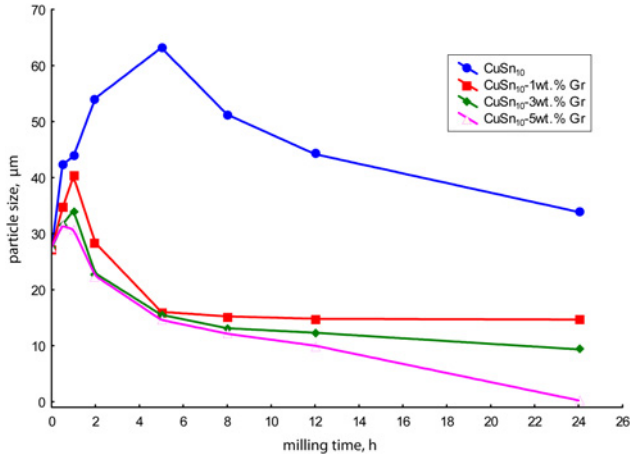


Figure 3 *Effect of the milling time and the graphite content on the particle size*

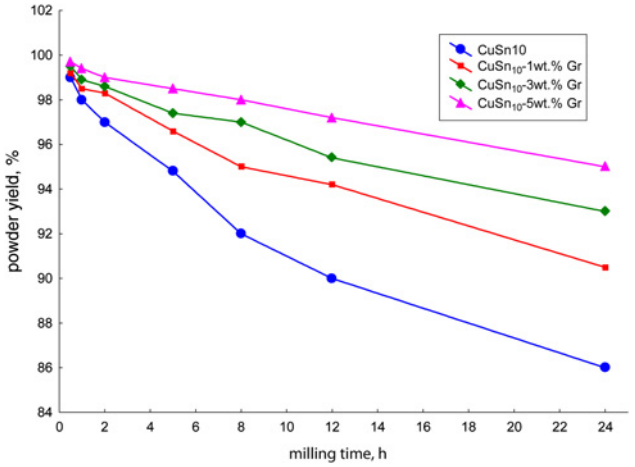


Figure 5 *Variation of the powder yield as a function of the milling time*

the fragmentation of the particles (Figs. 1*b* and 2*b*) and a reduction of the average particles size. However, the cold welding process continued until the end of a 5 h milling for the monolithic $CuSn_{10}$ powders (Fig. 3). Eventually, when the milling time increased to 24 h (Fig. 2*c*) a balance was established between the cold welding and the fracturing events and a steady-state situation was obtained. This means that the distribution of the graphite particles in the $CuSn_{10}$ matrix is very uniform at this stage. Also, the average particles size of the $CuSn_{10}$ – 5 wt% Gr powder at the end of 24 h milling was 50–200 nm (Fig. 2*c*). In all cases, a similar trend in the powder particle size was observed, that is, an initial increase followed by a decrease and then a steady state. This behaviour can be attributed to the cold welding of the initial ductile particles followed by a work hardening and thus the fracturing of the powder particles. When the rate of the cold welding and the fracturing process is equal, a steady state is achieved [1, 9]. Moreover, it should be noted that although a process control agent was not used in the MA process, graphite prevented excessive cold welding between the ductile particles and the ball-vial surfaces. Therefore it can be said that the graphite acted as a process control agent. In addition, it is observed that the powder agglomeration increased with the increasing milling time because of a decrease in the particle size (Figs. 1*c* and 2*c*). The agglomeration and the growth of the nanoparticles could be attributed to the surface free energy of the nanoparticles [10–12]. As can be seen in Fig. 4, there was no reaction between $CuSn_{10}$ and the graphite particles for different

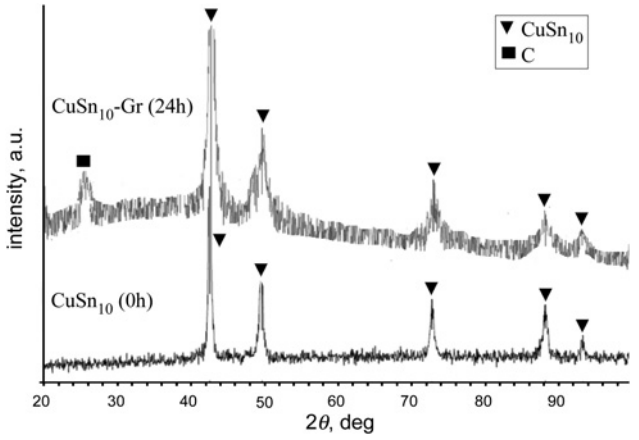


Figure 4 *XRD patterns of the $CuSn_{10}$ powders*

milling times as the $CuSn_{10}$ phase was still present in the powder mixtures.

3.2. Powder yield: Powder yield is one of the most important indicators to estimate the milled powders recovered after the MA process, which is commonly expressed by the ratio between the weight of the powders before and after ball milling. The powder yield can also quantificationally reflect the adhering degrees of the powders during MA. During the MA process, constant collisions among the milling balls, the powders and the milling vial result in the plastic deformation of the $CuSn_{10}$ powders. Owing to the increase of the surface activity, the refined powders will be inclined to get together and will be coated onto the milling balls and the vial spontaneously [13]. The yield of the MA process was calculated as the weight ratio between the total powder loaded into the milling vial and the powder collected at the end of the process. As a result, the increasing graphite content can greatly increase the powder yield, which is an important material in overcoming the adhering problem (excessive cold welding) during the ductile-brittle milling process. Fig. 5 shows the variation of the powder yield as a function of the milling time. It is shown in Fig. 5 that the increasing graphite content further led to an increasing powder yield. It should be noted that the effect of the graphite content on the powder yield is very important in milling without a process control agent.

4. Conclusions: $CuSn_{10}$-Gr nanocomposite powders were synthesised by a MA process. The conclusions can be summarised as follows:

1. On increasing the milling time and the graphite content, the particle size of the $CuSn_{10}$-Gr nanocomposite powders is decreased. The average particle sizes of the $CuSn_{10}$ – 5wt% Gr powder after 24 h milling is about 50–200 nm.

2. It was found that the addition of graphite has a great influence on the powder morphology. Particle agglomeration is observed in the nanocomposite powders because of the surface free energy of the nanoparticles.

3. Graphite can be prevented from excessive cold welding in the mechanical alloying process without a process control agent.

4. The powder yield of the samples increased with increasing graphite content. In other words, higher graphite content leads to a higher powder yield.

5 References

[1] Khadem S.A., Nategh S., Yoozbashizadeh H.: 'Structural and morphological evaluation of Al–5 vol.%SiC nanocomposite powder produced by mechanical milling', *J. Alloys Compd.*, 2011, **509**, pp. 2221–2226

[2] Yılmaz O., Turhan H.: 'The relationships between wear behavior and thermal conductivity of $CuSn/M_7C_3$–$M_{23}C_6$ composites at ambient and elevated temperatures', *Compos. Sci. Technol.*, 2001, **61**, pp. 2349–2359

[3] Chen B., Bi Q., Yang J., Xia Y., Hao J.: 'Tribological properties of solid lubricants (graphite, h-BN) for Cu-based P/M friction composites', *Tribol. Int.*, 2008, **41**, pp. 1145–1152

[4] Yousefi M., Sharafi S., Mehrolhosseini A.: Correlation between structural parameters and magnetic properties of ball milled nanocrystalline Fe-Co-Si powders, http://www.dx.doi.org/10.1016/j.apt.2013.11.008

[5] Tavoosi M., Karimzadeh F., Enayati M.H.: 'Fabrication of Al–Zn/α-Al_2O_3 nanocomposite by mechanical alloying', *Mater. Lett.*, 2008, **62**, pp. 282–285

[6] Woo K.D., Zhang D.L.: 'Fabrication of Al – 7wt%Si – 0.4wt%Mg/SiC nanocomposite powders and bulk nanocomposites by high energyball milling and powder metallurgy', *Curr. Appl. Phys.*, 2004, **4**, pp. 175–178

[7] Wang H., Wu W., Sun S., Bian X., Tu G.: 'Characterization of the structure of TiB_2/TiC nanocomposite powders fabricated by high-energy ball milling', *Ceram. Int.*, 2011, **37**, pp. 2689–2693

[8] Mostaed E., Saghafian H., Mostaed A., Shokuhfar A., Rezai H.R.: 'Investigation on preparation of Al–4.5%Cu/SiCp nanocomposite powder via mechanical milling', *Powder Technol.*, 2012, **221**, pp. 278–283

[9] Alam S.N.: 'Synthesis and characterization of W-Cu nanocomposites developed by mechanical alloying', *Mater. Sci. Eng. A*, 2006, **433**, pp. 161–168

[10] Song A.J., Ma M.Z., Zhang W.G., *ET AL.*: 'Preparation and growth of Ni–Cu alloy nanoparticles prepared by arc plasma evaporation', *Mater. Lett.*, 2010, **64**, pp. 1229–1231

[11] Safari J., Akbari G.H., Shahbazkhan A., Delshad Chermahini M.: 'Microstructural and mechanical properties of Al–Mg/Al_2O_3 nanocomposite prepared by mechanical alloying', *J. Alloys Compd.*, 2011, **509**, pp. 9419–9424

[12] Suryanarayana C.: 'Mechanical alloying and milling', *Prog. Mater. Sci.*, 2001, **46**, pp. 1–184

[13] Zhu S.G., Wu C.X., Luo Y.L.: 'Effects of stearic acid on synthesis of nanocomposite WC–MgO powders by mechanical alloying', *J. Mater. Sci.*, 2010, **45**, pp. 1817–1822

doi: 10.1049/mnl.2013.0715