

## Processing of Copper-Graphite-Alumina Powders by High-Energy Milling

I. Rodrigues<sup>1</sup>, M. Guedes<sup>2,4</sup>, A. C. Ferro<sup>3,4</sup>

<sup>1</sup>Instituto Superior Técnico, ULisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.

<sup>2</sup>Department of Mechanical Engineering, School of Technology, Instituto Politécnico de Setúbal, 2910-761 Setúbal, Portugal.

<sup>3</sup>Department of Mechanical Engineering, Instituto Superior Técnico, ULisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.

<sup>4</sup>ICEMS, Instituto Superior Técnico, ULisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.

### ABSTRACT

Copper-matrix composites are versatile materials used in several electromechanical applications, but relatively low strength and thermal stability impair advanced uses. Development of robust solutions combining low wear and low electrical loss are thus paramount.

This work proposes high-energy milling of copper-graphite-alumina powders: graphite is conductive and self-lubricating; alumina toils as dispersion-strengthener and grain refiner. Tailored batches with 2wt%-graphite and 2wt%-alumina were milled up to 16h in planetary ball mill and characterized by XRD, FEG-SEM/EDS, microhardness and Raman.

Produced powders are nanostructured, containing graphite and alumina nanoparticles homogeneously distributed in copper. Increasing milling time results in some degree of nanographite amorphization and size decrease. Copper crystallite size and achieved hardness are affected mainly above 4 h milling.

Attained results suggest that efficient dispersion of graphite and alumina nanoparticles is achieved, envisaging high conductivity, high strength and thermal stability. The copper-graphite-alumina system thus seemingly opens an opportunity window for PM processing of advanced copper composites.

### INTRODUCTION

Copper-graphite composites offer a unique balance of physical and mechanical properties, including high friction and wear resistance in addition to high electrical conductivity [1,2]. As a result, several graphite-fiber and graphite-particulate copper reinforced composites are commercially used as tribological materials in sliding contacts, industrial bearings and electric motor and generator brushes [3-5].

There are still however two major problems hindering further development and application of advanced copper/graphite composites [2]. A major drawback consists in fabrication progress, resulting from the low affinity and poor wettability ( $\theta = 140^\circ$ ) of pure copper on graphite [2]. Powder metallurgy routes have been traditionally employed to consolidate the composites [1], but since graphite cannot be wetted by liquid copper, conventional liquid infiltration processes cannot be used [2]; pressure impregnation technologies are available, however with increased cost [1]. Secondly, the low affinity between copper and graphite results in weak interfaces, with deleterious effects upon mechanical, thermal and electric properties that limit performance and service life [2].

Mechanical alloying of copper powders with graphite particles has been studied as a route to solve the affinity and interfacial bonding issues in the system. Other authors [6-11] have shown that homogeneous distribution of the graphite particles, microstructural grain refinement to the nanoscale and increased hardness can be achieved. Powder metallurgy processing involving high-energy milling followed by consolidation operations thus appears to be a suitable route to process these composites with improved

mechanical properties. However, mechanical alloying of copper/graphite composites presents specific challenges: continued milling of graphite induces amorphization [12], altering the inherent properties of the allotrope; the intrinsically unstable carbon-copper bonding may originate deficient load transfer at moderate service temperatures; materials produced by high-energy milling tend to become contaminated by milling media debris [13], which can compromise the conductivity properties of the composite.

To overcome those issues a strategy was developed where copper, graphite and alumina powders are simultaneously milled using alumina as milling media, aiming at producing a nanostructured composite material where mechanical strength, low wear, thermal stability and low electric loss are combined. Alumina particles are a popular choice of reinforcement for copper matrix, owing to its high melting point, high hardness, thermal stability and chemical inertness [13,14]. The introduction of alumina aims to promote microstructural grain refinement and uniform introduction of small incoherent strengthening phases. Also, it is expected to accelerate the production of homogeneous nanostructured powders and to contribute to the incorporation and uniform distribution of the graphite phase in the nanostructure. Furthermore, copper-alumina composites have almost the same electrical and thermal conductivities as pure copper [14]. Another innovative feature of the developed work is the fact that it takes advantage of milling media wear, by intentionally incorporating the resulting debris into the developed microstructure. Milling media wear debris is unavoidably incorporated in the milled material, unintentionally modifying its chemistry and introducing inclusions [13]. Under this perspective, milling media with composition similar to one of the milled materials (alumina) was chosen in the current work, aiming to deliberately incorporate wear debris in the produced nanostructures.

The developed PM procedure is expected to produce a uniform nanostructure resulting in improved copper composite strength and thermo-electrical performance, while keeping the graphite anti-sticking characteristics. The resulting copper-alumina-graphite nanostructured materials are envisioned for high strength, high conductivity, and low wear structural applications.

## EXPERIMENTAL

The starting materials used in the experiments were commercially pure electrolytic copper (impurities < 0.03 wt%), alumina (impurities < 0.12 wt%) and synthetic graphite (impurities < 0.2 wt%), all in the powder form. As-supplied materials were characterized by particle size analysis and scanning electron microscopy.

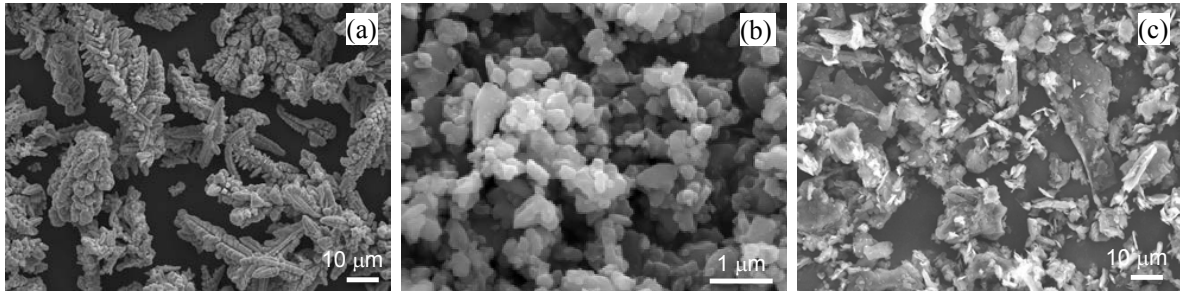
Tailored batches containing copper, 2 wt%-graphite and 2 wt%-Al<sub>2</sub>O<sub>3</sub> were milled in a planetary ball mill during 2, 4, 8 or 16 hours. Milling took place in an alumina-coated jar, using alumina balls with ø 15 mm, in air. A ball-to-powder weight ratio of 10:1 and milling speed of 400 rpm were used.

The produced powders were characterized by particle size analysis. Microstructural observations on both loose and resin-mounted polished powders were carried out using field emission gun scanning electron microscopy coupled with energy dispersive spectroscopy microanalysis (FEG-SEM/EDS). The carbon present in the microstructures was analyzed by micro-Raman spectrometry (532 nm laser, 100x objective lens, 600-grooves/mm grating, 5 accumulations and acquisition time of 10 seconds); Raman spectra were obtained after linear background subtraction and normalized to maximum intensity. The produced powders were also characterized by X-Ray diffraction (XRD) using CuK<sub>α</sub> radiation; samples were scanned with step size of 0.006° and step time of 2 seconds. Copper crystallite size was estimated from the Williamson-Hall equation using the (111), (200), (311), (222) and (331) Bragg reflections, after correction for instrumental broadening. Vickers microhardness measurements were carried out on powders mounted in resin, using a load of 0.245 mN (HV 0.025) during 10 s.

## RESULTS AND DISCUSSION

### Characterization of the starting powders

Fig. 1 is a micrograph of the starting powder materials. As-supplied copper is dendritic with measured median particle size of approximately 32.4  $\mu\text{m}$ , while alumina particles ( $d_{50} \sim 0.8 \mu\text{m}$ ) are regular and equiaxed and graphite ( $d_{50} \sim 12.1 \mu\text{m}$ ) is somewhat flaky.

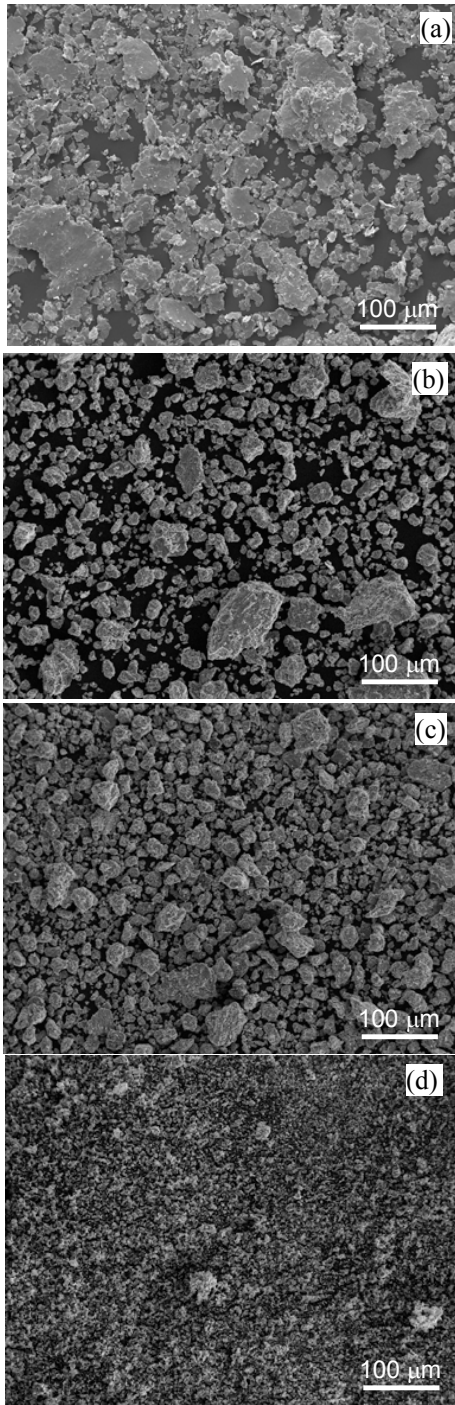


**Figure 1.** SEM secondary electron (SE) image of as-supplied powder materials: (a) copper; (b) alumina; and (c) synthetic graphite.

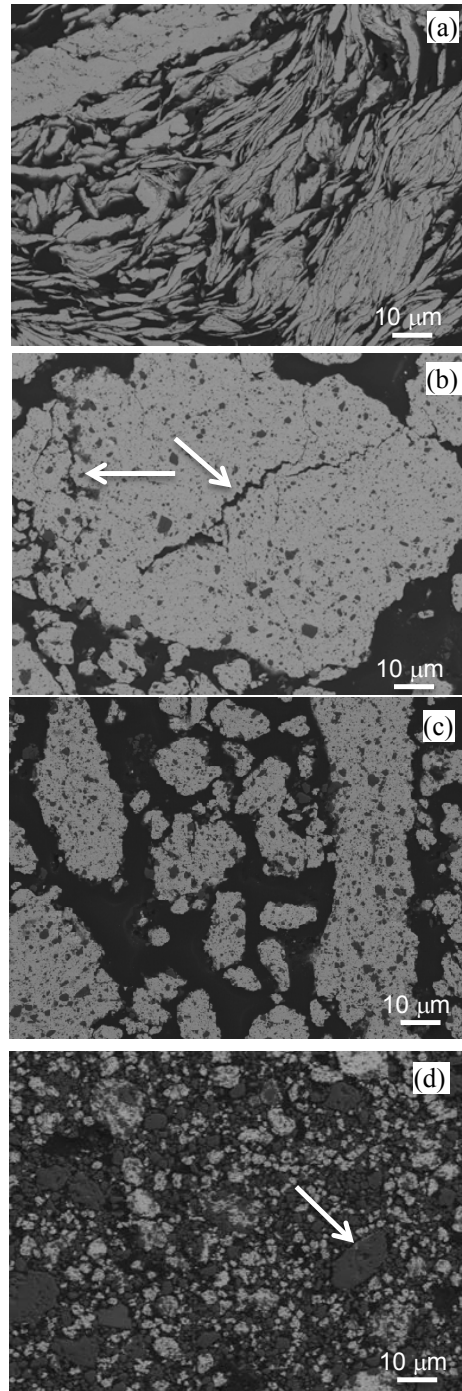
### Size, Morphology and Microstructure of the Produced Powders

Mechanical Alloying (MA) of the studied copper-graphite-alumina (Cu-G-A) mixture results in the production of copper-matrix nanostructured composites. The evolution of the morphological and microstructural features of the Cu-G-A powders with milling time (Figures 2 and 3) is typical of ductile-brittle systems [13].

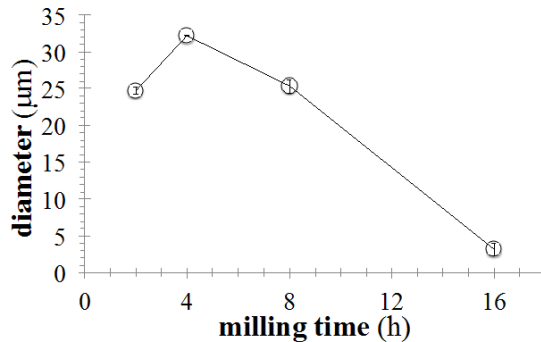
The ductile copper dendrites are flattened by the ball-powder-ball collisions and the powders change from the dendritic morphology of as-supplied copper (Fig. 1.a) to lamellar shape during the first 2h of milling (Fig. 2.a and 3.a). The newly created lamellar surfaces enable the particles to cold weld together [13], resulting in a slight  $d_{50}$  value increase to approximately 32  $\mu\text{m}$  (corresponding to a 30 % increase) after 4 h milling (Figure 4). Deformed and welded particles are thus predominant at this stage and the interfacial boundaries due to welding are visible and randomly oriented. The produced welding effect is somewhat small, which is expected to result from the presence of graphite. Graphite toils locally as a “process control agent” (PCA) [15], acting as a solid lubricant that prevents welding between particles and between particles and the milling media. With further milling the plastic deformation of the ductile powder particles eventually leads to the predominance of work hardening and fracture, with considerable size reduction. After as soon as 4 h milling there are substantial changes in powder morphology, which become more equiaxed, smaller and contain more abundant second phase particles. Welding boundaries are no longer visible and fracture appears to be the dominant stage (Fig. 3.b, arrow). From 4 h milling onward the mean powder diameter decreases reaching a final particle size of approximately 3.2  $\mu\text{m}$  after 16 h. The powder produced after 16 h are considerably smaller than as-supplied copper particles (approximately 10 % of starting particle size, Fig. 4) and equiaxed (Fig. 2.d and 3.d).



**Figure 2.** Low magnification SE image of powder after milling during (a) 2 h; (b) 4 h; (c) 8 h; and (d) 16 h.



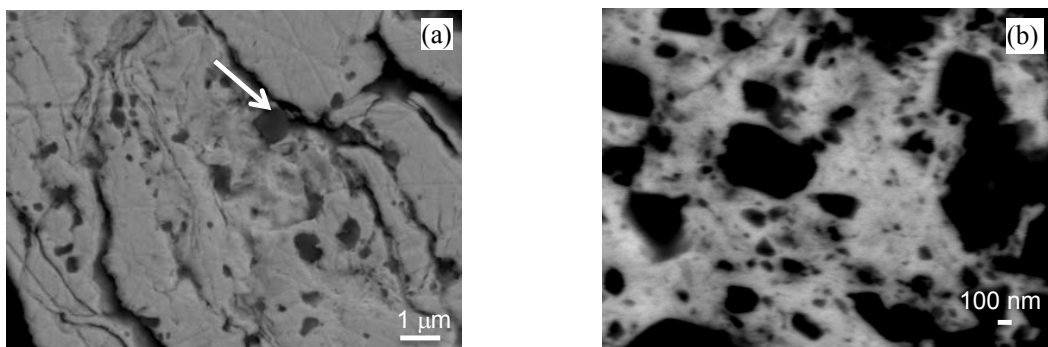
**Figure 3.** Powder backscattered electron (BE) image after milling during (a) 2 h; (b) 4 h (arrow: fracture); (c) 8 h; and (d) 16 h (arrow: alumina worn from the milling wear).



**Figure 4.** Variation of  $d_{50}$  with milling time for Cu-A-G powders.

During milling the copper powder suffers repetitive welding and fracture allowing for the formation of new interfaces across all the different powders. Meanwhile the reinforcement phases are fragmented and their particles tend to become occluded by copper and trapped in the ductile particles. This enables the incorporation and distribution of nanoscaled reinforcement particles inside the copper matrix powders [13]. As a result produced powders are nanostructured, containing second phase nanoparticles homogeneously distributed in copper (Figure 5).

Backscattered electron images show that a significant amount of second phase particles is already incorporated within copper at such early time as 2 h (Fig. 5.a). This amount increases with milling time. Two types of second phase particles are present in this system: irregular angular particles with dimension range between approximately 200 nm and 2  $\mu\text{m}$  (after 16 h milling), which were identified as alumina by EDS microanalysis; and nanoparticles (with diameter clearly below 100 nm), presenting more regular and equiaxed shape, which composition could not be surely assigned to either carbon or alumina, since the relatively close equivalent atomic numbers (6 and 10, respectively) results in similar contrast in the presence of the much brighter copper matrix (Fig. 5.b). The second phase particles are frequently localized at the copper boundaries, as a result of occlusion during the many deformation events that produce convolutions and subgrain recombinations.



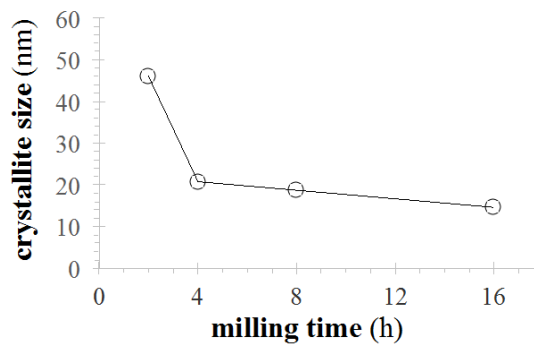
**Figure 5.** SEM BE images of the produced copper matrix powder after milling for (a) 2 h (arrow: alumina wear particle); and (b) 16 h.

The large irregular alumina particles are suggested to result mainly from milling media wear. A control 8 h milling experiment in the absence of alumina and graphite powder additions has shown that both the size and morphology of alumina particles originated exclusively from milling media wear are larger ( $d_{50} = 3.25 \mu\text{m}$ ; size span = 4.1) and more irregular (Fig. 6) than the equiaxed as-supplied alumina powder shown in Fig. 1.c ( $d_{50} = 0.8 \mu\text{m}$ ; size span = 2.5). It should be noted that particles attributed to wear are

visible after as soon as 2 h milling (Figure 5.a, arrow), but its amount clearly rises with increasing milling time, with a step increase above 8 h (Fig. 3.d). This delay is expected to result from the PCA action of graphite in the mixture, coating the ball and jar surfaces, which prevents excessive wear of the grinding medium and contamination of the powder [13]. It is suggested that for the longer milling times degradation of the graphite structure hampers its lubricant action [16], increasing the energy transferred to the milled powders.

In this way, alumina particles eroded from the media during milling become available for the reinforcement of the copper matrix, increasing the overall amount of dispersed reinforcement particles. Additionally the continuous milling action decreases the particle sizes of dispersed alumina, generating an increasingly more homogeneous spatial distribution of finer particles. It should be noted however that for milling duration above 8 h the amount of worn alumina introduced in the system is apparently too high: a significant amount of worn alumina particles in the micrometric range remain amongst the copper powders, not being incorporated in the composite (arrow in Fig. 3.d).

Simultaneously to the overall powder size reduction process, increasing milling times also lead to copper structural refinement. While a crystallite size of 198.1 nm was determined (Williamson-Hall method) for as-supplied copper, the crystallite size step decreases to 46.2 nm after 2 h milling, reaching 14.6 nm after 16 h (Fig. 6). For the longer milling times (4 hours onward), copper crystallite size is consistently lower than that observed by several authors for the Cu-Al<sub>2</sub>O<sub>3</sub> and Cu-graphite systems [6,10,17,18]. Such discrepancy is suggested to result from the use of different starting powders and milling conditions: in the absence of graphite (Cu-Al<sub>2</sub>O<sub>3</sub> system) milled particles tend to agglomerate and weld and part of the milling energy is consumed on fracture, delaying structural refinement to longer milling times; the absence of alumina (Cu-graphite system) prevents the additional milling efficiency introduced by the small hard particles, that can break up copper crystallites at a much smaller scale than that of the milling balls [19].

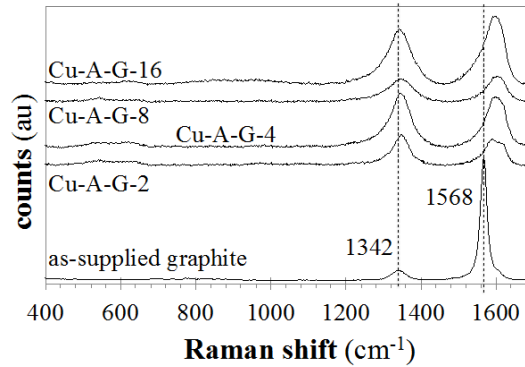


**Figure 6.** Copper crystallite size evolution with milling time in the produced Cu-A-G nanostructured composites (crystallite size in as-supplied copper is 198.1 nm).

Figure 7 shows micro-Raman results obtained for pristine synthetic graphite and milled powders. The graphite G-peak at 1568 cm<sup>-1</sup> corresponds to C-C bond stretching in the hexagonal lattice of graphite (E<sub>2g</sub> mode) [20], while the D-peak at 1342 cm<sup>-1</sup> (A<sub>1g</sub> mode) occurs exclusively in polycrystalline graphite [21]. The same peak profile is present after milling, but with increasing milling time the 1568 cm<sup>-1</sup> peak is displaced to higher wavenumber, accompanied by the increase of D- to G-peak relative intensity. These features are characteristic of nanostructured graphite [12]. Applying the empirical model proposed by Truinstra [20] results that graphite crystallite size decreases with milling time from approximately 66 nm in pristine graphite, stabilizing around 8 nm after 8 h milling, in good agreement with results by other

authors [6,10]. The peaks considerably broaden with milling time, which suggests some degree of graphite amorphization [12,20].

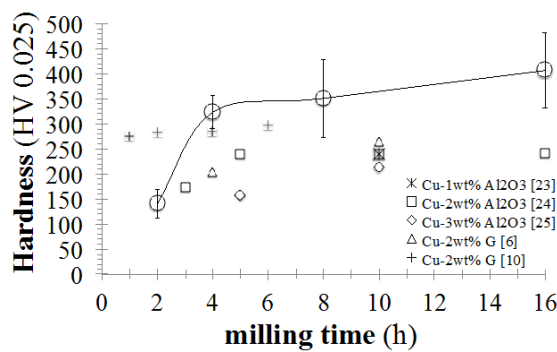
It should be noted that complete amorphization would correspond to a single broad asymmetric band corresponding to fully amorphous carbon [21], which was not observed.



**Figure 7.** Evolution of the Raman spectrum of the powder with milling time. The spectrum of pristine synthetic graphite is shown for comparison.

### Microhardness

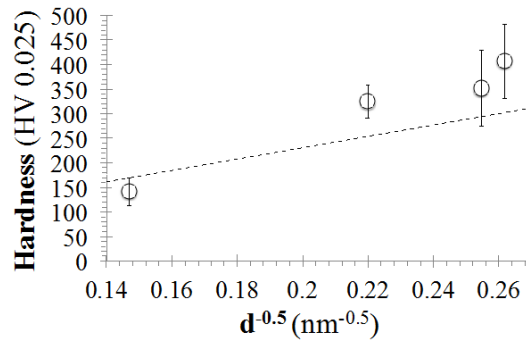
Figure 8 shows microhardness results for the produced powders. The microhardness value determined for as-supplied electrolytic copper is  $HV\ 104 \pm 4$  ( $1.02 \pm 0.04$  GPa); a significant hardness increase is achieved in the produced materials, consistently higher than that observed by several authors for the Cu- $Al_2O_3$  and Cu-graphite systems. After milling for 4 h that value step increases to approximately  $HV\ 324$  (3.18 GPa), and a maximum HV value around 407 (4.0 GPa) is attained after 16 h.



**Figure 8.** Increase in microhardness with milling time (O); results in other works shown for comparison.

Since carbon solubility in copper is extremely low [27], metal strengthening mechanisms leading to increased microhardness in the produced powders are expected to result from grain refinement of the copper matrix structure and from the presence of the nanosized reinforcement particles.

Grain size refinement gives way to Hall-Petch strengthening. Accordingly, in the produce powders microhardness increase with milling time matches copper crystallite size decrease (Fig. 9).



**Figure 9.** Relation between microhardness and copper crystallite size. The theoretical curve proposed for pure nanostructured copper [22] is shown for comparison.

However, Zhao [22] proposed that the contribution of the interplay between dislocation and grain-boundary processes during deformation vary as size changes, reaching a maximum in the 15-30 nm range. Pure copper with grain size in the 10-30 nm range attains a maximum hardness of approximately 2,5 GPa (256 HV) [26]. The Hall-Petch relation established for pure nanostructured copper (dashed line in Fig. 9) accounts for the effect of copper crystallite size upon hardness increase, indicating that the surplus must result from cumulative mechanisms.

The nanoscaled alumina and graphite particles finely distributed within the copper matrix and grain boundaries can produce such reinforcement effect through preventing further dislocations movement and propagation [23].

Additionally, the produced nanocomposites exhibit apparent bonding at the Cu/G and Cu/Al<sub>2</sub>O<sub>3</sub> interfaces, suggesting a potentially efficient mechanical load transfer. This effect must be enhanced by the presence of micrometric alumina particles introduced through wear of the milling media.

## CONCLUSION

Mechanically alloying of copper powder with 2wt%-graphite and 2wt%-alumina produces nanostructured powders containing graphite and alumina nanoparticles homogeneously distributed in the metallic matrix. Both powder particle size and copper crystallite size decrease become efficient above 4 h milling, the more so with increasing milling time. The higher refinement of the copper matrix in comparison with values reported in the literature is associated with an additional milling mechanism arising from the alumina milling media wear and the particles. However milling above 8 h step increases the amount of worn alumina in the system; this micrometric alumina is an impurity not incorporated in the metallic powders, which suggests a limit for the time parameter. Raman results confirm carbon inclusion within the metallic matrix, and show that for the studied conditions graphite amorphization is residual. Strengthening resulting from grain refinement and second phase particles renders the produced materials a remarkable microhardness. Additionally, the produced nanocomposites exhibit apparent bonding at the Cu/reinforcement interfaces, suggesting a potentially efficient mechanical load transfer.

Further experiments are on course regarding conductivity and wear performance, but these preliminary results envision the produced PM nanocomposite materials for high strength electromechanical applications.



## REFERENCES

- [1] Yeoh, C. Persad and Z. Elieze, "Dimensional Responses Of Copper-Graphite Powder Composites To Sintering", *Scripta Mater.*, 1997, vol. 37, n° 3, pp. 271-277.
- [2] Z. Tao, Q. Guoa, X. Gaoa and L. Liua, "The Wettability and Interface Thermal Resistance of Copper/Graphite System with an Addition of Chromium", *Mater. Chem. Phys.*, 2011, vol. 128, pp. 228–232.
- [3] K. Rajkumar, K. Kundu, S. Aravindan and M.S. Kulkarni, "Accelerated Wear Testing for Evaluating the Life Characteristics of Copper–Graphite Tribological Composite", *Mater. Design*, 2011, vol. 32, pp. 3029–3035.
- [4] M. Braunovic, N. Myshkin and V. Konchits, *Electrical contacts: fundamentals, applications and technology*, 2010, CRC Press.
- [5] Y. Zhan and G. Zhang, "Graphite and SiC Hybrid Particles Reinforced Copper Composite and its Tribological Characteristic", *J. Mater. Sci. Lett.*, 2003, vol. 22, pp. 1087–1089.
- [6] M. T. Marques, J. B. Correia and O. Conde, "Carbon Solubility in Nanostructured Copper," *Scripta Mater.*, 2004, vol. 50, n° 7, pp. 963–967.
- [7] X. Liu, Y. Liu, X. Ran, J. An and Z. Cao, "Fabrication of the Supersaturated Solid Solution of Carbon in Copper by Mechanical Alloying", *Mater. Charact.*, 2007, vol. 58, n° 6, pp. 504-508.
- [8] T. Yamane, H. Okubo, K. Hisayuki, N. Oki, M. Konishi, M. Komatsu, Y. Minamino, Y. Koizumi, M. Kiritani and S. J. Kim, "Solid Solubility of Carbon in Copper Mechanically Alloyed", *J. Mater. Sci. Lett.*, 2001, vol. 20, n° 3, pp. 259-260.
- [9] S. Saji, T. Kadokura, H. Anada and K. Notoya, "Solid Solubility of Carbon in Copper During Mechanical Alloying", *Mater. Trans. JIM*, 1998, vol. 39, pp. 778-781.
- [10] D. Nunes, V. Livramento, R. Mateus, J.B. Correia, L.C. Alves, M. Vilarigues and P.A. Carvalho, "Mechanical Synthesis of Copper–Carbon Nanocomposites: Structural Changes, Strengthening and Thermal Stabilization", *Mater. Sci. Eng. A*, 2011, vol. 528, Issues 29–30, pp. 8610-8620.
- [11] J.-H. Ahn, I.-H. Song and Y.-D. Hahn, "Cu-Based Cermets Prepared by Mechanical Alloying", *Mater. Trans. JIM*, 1996, vol. 37, n°4, pp. 733-737.
- [12] K. Niwase, T. Tanaka, Y. Kakimoto, K. N. Ishihara and P. H. Shingu, "Raman Spectra of Graphite and Diamond Mechanically Milled with Agate or Stainless Steel Ball-Mill", *Mater. Trans.*, 1995, vol. 36, n° 2, pp. 282-288.
- [13] C. Suryanarayana, "Mechanical Alloying and Milling", *Prog. Mater. Sci.*, 2001, vol. 46, pp. 1-184.
- [14] S. C. Tjong, "Novel Nanoparticle-Reinforced Metal Matrix Composites with Enhanced Mechanical Properties", *Adv. Eng. Mat.*, 2007, vol. 9, no. 8, pp. 639–652.
- [15] F.C. Robles Hernández and H.A. Calderon, "Nanostructured Al/Al<sub>4</sub>C<sub>3</sub> Composites Reinforced with Graphite or Fullerene and Manufactured by Mechanical Milling and Spark Plasma Sintering", *Mater. Chem. Phys.*, 2012, vol. 132, pp. 815-822.
- [16] J.-C. Rietsch, R. Gadiou, C. Vix-Guterl and J. Dentzer, "The influence of the Composition of Atmosphere on the Mechanisms of Degradation of Graphite in Planetary Ball Millers", *J. Alloys Compd.*, 2010, vol. 491, n° 1–2, pp. L15-L19.
- [17] V. Rajković, O. Erić and D. Božić, "Characterization of Dispersion Strengthened Copper with 3wt% Al<sub>2</sub>O<sub>3</sub> by Mechanical Alloying", *Sci. Sinter.*, 2004, vol. 36, pp. 205–211.
- [18] V. Rajković, D. Božić and M. Jovanović, "Characteristics of Copper and Copper-Al<sub>2</sub>O<sub>3</sub> Composites Prepared by High-Energy Milling," *Metalurgija*, 2007.
- [19] J.B. Fogagnolo, F. Velasco, M.H. Robert and J.M. Torralba, "Effect of Mechanical Alloying on the Morphology, Microstructure and Properties of Aluminium Matrix Composite Powders". *Mater. Sci. Eng. A*, 2003, vol. 342, pp. 131-143.
- [20] F. Tuinstra and J. L. Koenig, "Raman Spectrum of Graphite," *J. Chem. Phys.*, 1970, vol. 53, n° 3, pp. 1126.

- [21] T.D. Shen, W.Q. Ge, K.Y. Wang, M.X. Quan, J.T. Wang, W.D. Wei and C.C. Koch, "Structural Disorder and Phase Transformation in Graphite Produced by Ball Milling", *Nanostructured Materials*, 1996, vol. 7, pp. 393-399.
- [22] M. Zhao, J.C. Li and Q. Jiang, "Hall-Petch Relationship in Nanometer Size Range", *J. Alloys Compd.*, 2003, vol. 361, n°1-2, pp. 160-164.
- [23] V. Rajkovic, D. Bozic, A. Devecerski and M. T. Jovanovic, "Characteristic of Copper Matrix Simultaneously Reinforced with Nano- and Micro-Sized Al<sub>2</sub>O<sub>3</sub> Particles" *Mat. Char.*, 2012, vol. 67, pp. 129-137.
- [24] V. Rajkovic, D. Bozic and M. T. Jovanovic, "Effects of Copper and Al<sub>2</sub>O<sub>3</sub> Particles on Characteristics of Cu-Al<sub>2</sub>O<sub>3</sub> Composites"; *Mater. Design*, 2010, vol. 31, pp. 1962-1970.
- [25] Viselava Rajkovic, Dusan Bozic and Milan T. Jovanovic, "Properties of Copper Matrix Reinforced with Nano- and Micro-Sized Al<sub>2</sub>O<sub>3</sub> particles", *J. Alloys Compd.*, 2008, vol. 459, pp. 177-184.
- [26] KS Siow, A. O. Andrew Tay and P. Oruganti, "Mechanical Properties of Nanocrystalline Copper and Nickel", *Mater. Sci. Tech.*, 2004, vol. 20, pp. 285-294.
- [27] G.A. López and E.J. Mittemeijer, "The Solubility of C in Solid Cu", *Scripta Mater.*, 2004, vol. 51, pp. 1-5.