



# Nanodiamond as an effective reinforcing component for nano-copper

V. Livramento<sup>a</sup>, J.B. Correia<sup>a,\*</sup>, N. Shohoji<sup>a</sup>, E. Ōsawa<sup>b</sup>

<sup>a</sup> INETI, Instituto Nacional de Engenharia, Tecnologia e Inovação, Estrada do Paço do Lumiar, 22, 1649-038 Lisboa, Portugal

<sup>b</sup> NanoCarbon Research Institute, 301 Toudai Kashiwa Venture Plaza, 5-4-19 Kashiwa-no-Ha, Kashiwa, Chiba 277-0882, Japan

Received 10 January 2006; received in revised form 27 April 2006; accepted 9 May 2006

## Abstract

This work reports for the first time the use of nanodiamond (nD) particles as a reinforcing component for alloying with nano-copper (nCu). Significant rise in Vickers microhardness (HV) was realised for nCu after ball milling together with nD. Thus, mechanical alloying (MA) proved to be an effective strategy for strengthening copper with nD, and perhaps for other metallic alloys as well. The absence of detectable wear and contamination for the MA-processed nCu specimens with nD is also considered as one of the promising aspects of this work. Short milling time of only 2 h was enough to achieve the reported rise in HV.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** A. Composites; B. Nanoparticles; C. Nanocrystalline; D. Mechanical properties

## 1. Introduction

In the last few decades there have been growing interests in nanostructured materials. In the case of metals, e.g. copper, there is a sharp increase of hardness with smaller grain sizes. However, this strategy to increase the hardness has several limitations. The smallest possible particle size that one can reach is limited to about 10 nm and, in the lower range of grain size the hardening effect stagnates [1]. Hence, the concept of composite material is also used in the field of nanostructured materials in order to tailor their properties to suit particular mechanical or functional purposes [2–4]. Nanocomposites are conveniently produced by mechanical alloying (MA: high-energy milling). The reinforcement can be mixed and dispersed during milling [2] or can be formed in-situ via chemical reaction [3,4]. The in-situ composites usually have better mechanical performance due to the existence of coherent interfaces between matrix and reinforcement [5].

Conventional reinforced copper materials are produced industrially via internal oxidation of Cu–Al alloys to give Al<sub>2</sub>O<sub>3</sub> particles that are 10 nm in diameter and dispersed in copper matrix particles in the micron range [6]. These are extremely stable at high-temperatures, but the Vickers' hardness is modest, 152 HV,

partly because the maximum volume fraction is only 2.7% Al<sub>2</sub>O<sub>3</sub>, and partly because the matrix contribution to strengthening is very small.

Nanostructured copper composites reinforced with Al<sub>2</sub>O<sub>3</sub> and several transition metal carbides have been synthesised using MA. In particular the Cu–Al<sub>2</sub>O<sub>3</sub>, Cu–NbC and Cu–Fe<sub>3</sub>C systems that have been prepared via mechanical alloying show significant hardening depending on volume fraction of carbide, ranging from 250 to 480 HV (10–30 vol.%) [2–4]. In contrast, reinforcement with graphite has never been very effective. The hardness obtained, about 200 HV for 10 at.% C (corresponding to 8 vol.%), was identical to that of the nanostructured copper itself [7,8].

In the present research diamond particles with single-digit nano-sizes [9,10], originally produced by detonation of explosives, were used as the reinforcement component for nano-copper (nCu). We were much surprised to find virtual absence of significant wear of steel balls during high-energy milling.

## 2. Experimental procedures

The nD particles used in this work were obtained by disintegrating commercially available but agglutinated product into a 10 wt.% aqueous colloidal solution in a stirred-media mill using zirconia beads that have an average diameter of 30 μm [9,10]. Dynamic light scattering measurements of particle size-

\* Corresponding author. Fax: +351 21 716 65 68.

E-mail address: [brito.correia@ineti.pt](mailto:brito.correia@ineti.pt) (J.B. Correia).

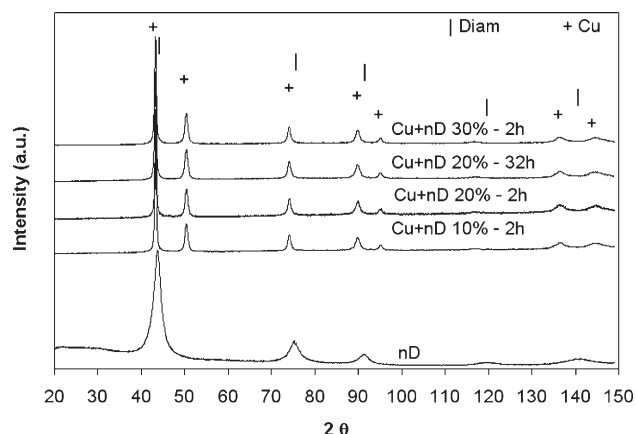


Fig. 1. XRD patterns for Cu MA-powders with 10, 20 and 30 at.% nD and nD powder.

distribution on diluted and transparent colloidal samples revealed that more than 90 wt.% of nD particles in the colloid have a mean diameter of 4–5 nm, which coincides with the size of diamond crystallites originally grown during detonation [9]. For this reason, it was considered that the stirred-media milling isolated primary particles of nD. After evaporating water from the colloid in an oven heated at 65 °C for 24 h to remove 99% of the water, visible agglomerates of nD particles that have diameters of 2–3  $\mu\text{m}$  were obtained and the agglomerate powder was used for mechanical alloying. Pure elemental Cu (99.9% purity; particle size 44–149  $\mu\text{m}$ ) was used as the matrix.

Mechanical alloying was performed in a Retsch PM400 planetary ball mill, charging 250 ml stainless-steel containers with 20 g of a mixture of the matrix and reinforcing component powders, and 400 g of stainless-steel balls that are 10 mm in diameter in each container. At first, we added synthetic graphite (99.9995% purity; average size 74  $\mu\text{m}$ ) to the milling mixture in order to avoid abrasion of the stainless-steel balls and the container by the nD particles. However, as no significant abrasive wear could be detected after introduction of nD, this cautionary step was abandoned.

The nominal atomic compositions used were 8:1:1 for Cu+graphite+nD, and 9:1, 8:2, 7:3 for Cu+nD. The mill was operated at a rotational speed of 400 rpm for several hours. In order to prevent oxidation of the mixed powder, the container was first evacuated and then filled with argon. In the case of Cu+graphite+nD mixture, the milling was carried out in two steps: a) milling of Cu and graphite for 4 h, in order to disperse graphite in the Cu powder, followed by b) milling after the addition of nD.

All the resulting alloys were characterized by XRD, optical microscopy, SEM, chemical analysis using energy-dispersive X-ray analysis (EDX) and microhardness measurements (HV). XRD was carried out using Cu  $K_{\alpha}$  radiation. The average crystallite size of copper was determined from X-ray diffraction results. The evaluation was performed from the highest intensity low angle Bragg reflections for Cu(111), using Scherrer's equation. Microhardness was measured with a Shimadzu HMV 2000 instrument in accordance with the ISO 6507-1 standard. A load of 25 g (0.245 N) and a 15 second dwell time were used.

### 3. Results and discussion

The X-ray diffraction patterns for Cu powders mechanically alloyed with 10, 20 and 30 at.% nD for several hours are shown in Fig. 1 together with that of nD powder alone. The absence of extra reflections from nD in the milled copper is due to the partial overlap of reflections of both nCu and nD.

High-magnification secondary electron SEM examination of the ball milled products revealed surprisingly good milling effect (Fig. 2A). Well-distributed bright spots are assigned to disintegrated nD particles based on EDX analysis: areas rich in the bright spots have high carbon contents (Fig. 2B). The sizes of bright spots are in the range of 30–50 nm. This means that the

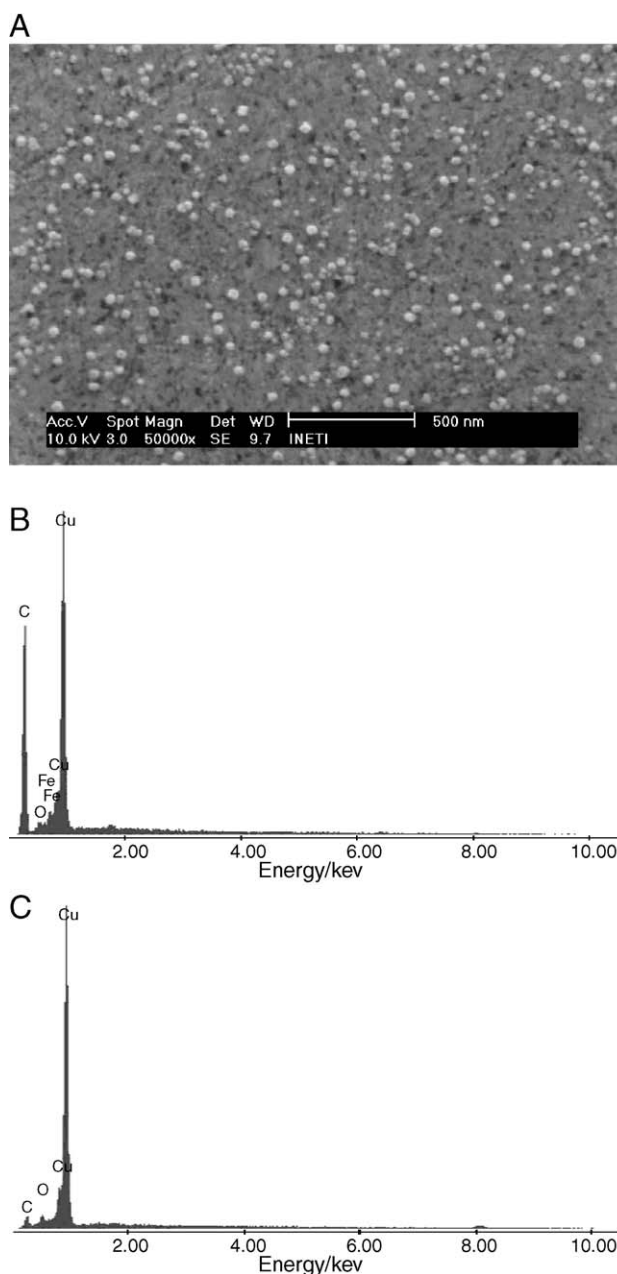


Fig. 2. High-magnification secondary electron SEM image of 8:2 Cu+nD milled for 2 h (A), and corresponding EDX analysis charts of the brighter particles (B) and the darker area (C).

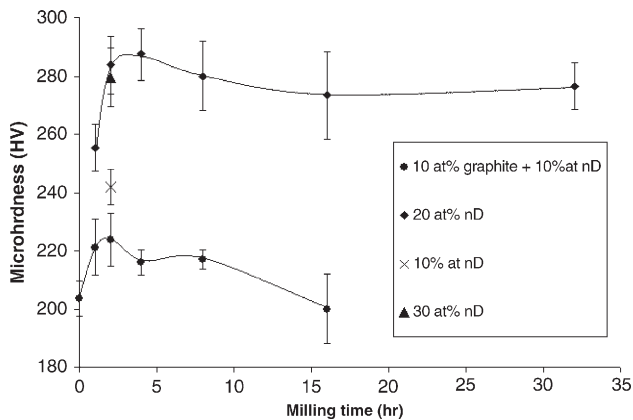


Fig. 3. Microhardness vs. milling periods in the mechanical alloying of Cu–nD for varying nD contents.

starting agglomerates of nD did not completely disintegrate into primary particles that are 4–5 nm in diameter but only to the double-digit nano-range under the ball milling conditions employed. Dark areas consist almost exclusively of copper (Fig. 2C). Although we could not distinguish individual copper particles due to poor contrast in Fig. 2A, XRD intensity analysis (using Scherrer's equation) revealed that Cu also disintegrated to a similar size-range of 20 nm.

A major achievement in this research was a good dispersion of the reinforcing nD (Fig. 2A). The fact that both nD and copper were disintegrated to a narrow range of 20–50 nm indicates that the nD agglomerates and copper powder were disintegrated by ball milling almost at the same speed and that the disintegration stopped when the size of particles reached the roughness level of the ball-surface. Note that the milling simply separated the boundaries between primary particles of diamond in the aggregates. For this reason, ablation of the stainless-steel ball by diamond did not occur to any significant extent, as can be inferred from the very small Fe peak in the XRD spectrum (Fig. 2B).

Addition of graphite to Cu+nD proved not only ineffective in hardening the alloy, but also annihilated the effect of nD: Vickers hardness of 8:1:1 Cu+graphite+nD alloys (HV 200–220, filled circles in Fig. 3) remained at almost the same level as nano-copper itself and that of Cu+graphite composite previously reported (HV 200 [7,8]). In this case, it is likely that the aggregates of graphite nanoparticles absorbed much of the nD particles as the latter were milled to smaller and smaller sizes, and killed the alloying effect of nD. However, in the absence of graphite, 9:1 Cu+nD showed 20% increase in the microhardness (HV 242, cross in Fig. 3) after milling for 2 h.

Higher strengthening effect appeared when more nD was added to give 8:2 Cu+nD composite (filled rhombi, Fig. 3), producing 40% increase in the HV value. This increase turned out to be the highest attainable, see 7:3 Cu+nD (filled triangle). The saturation tendency is possibly caused by the brittleness produced by the increasing reinforcement component.

The hardness increment obtained by milling copper with nD is clearly larger than that obtained with copper–graphite [7]. This is not surprising as the size of the reinforcing particles is of the same order of magnitude as that reported for commercial Cu–Al<sub>2</sub>O<sub>3</sub> made by internal oxidation, about 10 nm [6], and

that of Cu–Al<sub>2</sub>O<sub>3</sub> composite made via mechanical alloying, 14 nm [2]. Unlike graphite, nD is an extremely hard material and can therefore pin the dislocation movement associated with plastic deformation of copper. However, the hardening mechanism is not straightforward. As with all nanostructured materials, the closely spaced nCu grain boundaries also give a major contribution to the hardening.

The size effect became evident by the fact that even copper itself acquires higher hardness when it is nanostructured, of about 200 HV [8].

Further, the addition of 10 vol.% of Al<sub>2</sub>O<sub>3</sub> by *ad hoc* mechanical alloying resulted in the improved microhardness value of 255 HV [2]. Assuming for nD a density similar to that of bulk diamond, 3.5, then the 20 at.% C material in the present research corresponds to 11 vol.% of C. The maximum hardness determined in this research, 280 HV, is comparable with those of nanostructured copper based materials with similar volume fraction, 10%, i.e. 255 HV with Al<sub>2</sub>O<sub>3</sub> [2] and 280 HV with NbC [4]. Unlike most reinforcing particles, diamond possesses higher thermal conductivity than copper [11]. Since it is natural to expect improved thermal conductivity for the Cu+nD composites, the simple alloying technique described above appears to offer a good option for injection moulds of plastics, heat sinks for nuclear fusion technology and electronic applications.

#### 4. Conclusions

The grinding of both the reinforcing component and the metal matrix down to nano-range by milling is a useful strategy for strengthening copper, and perhaps for the other non-carbide-forming metal alloys as well. Primary effect of the 'nano/nano alloying' is to create and keep good dispersion among each other, thus preventing the well-known tendency of ultrafine nanodiamond particles to aggregate quickly. The dispersion hardening obtained with nD is more favourable, compared to the mixing of nano-graphite platelets with nCu. Short milling time of only 2 h provides a favourable condition for the least contamination of ball material in the mechanical alloying. Due to the naturally improved thermal conductivity in Cu+nD composites, the simple alloying technique described above appears to offer a good option for thermal management applications.

#### References

- [1] H. Gleiter, Prog. Mater. Sci. 33 (1989) 223.
- [2] J. Naser, W. Riehemann, H. Ferkel, Mater. Sci. Eng. 234A (1997) 467.
- [3] P.A. Carvalho, I. Fonseca, M.T. Marques, J.B. Correia, A. Almeida, R. Vilar, Acta Mater. 53 (2005) 967.
- [4] M.T. Marques, V. Livramento, J.B. Correia, A. Almeida, R. Vilar, Mater. Sci. Eng., A Struct. Mater.: Prop. Microstruct. Process. 399 (2005) 382.
- [5] T. Weissgarber, B.F. Kieback, Mat. Sci. Forum 343–346 (2000) 275.
- [6] J. Groza, J. Mater. Eng. Perform. 1 (1992) 113.
- [7] M.T. Marques, J.B. Correia, O. Conde, Scr. Mater. 50 (2004) 963.
- [8] L. Lu, R. Schwaiger, Z.W. Shan, M. Dao, K. Lu, S. Suresh, Acta Mater. 53 (2005) 2169.
- [9] A. Krüger, M. Ozawa, F. Kataoka, A.E. Aleksenskii, A.Y. Vul', T. Fujino, Carbon 43 (2005) 1722.
- [10] E.D. Eidelman, V.I. Siklitsky, L.V. Sharonova, M.A. Yagovkina, A.Y. Vul', M. Takahashi, Diamond Relat. Mater. 14 (2005) 1765.
- [11] S.R. Phillpot, A.J.H. McGaughey, Materials Today 8 (2005) 18.