

Copper- μ Diamond Nanostructured Composites

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Introduction

Reinforcement of a copper matrix with nanodiamond (nDiamond) [1] or microdiamond (μ Diamond) enables to tailor composite properties, such as hardness, microstructural thermal stability and thermal conductivity. Multiscale dispersions of diamond in copper can be used to obtain optimal thermal conductivity vs strength and thermal stability, in fact dispersions of diamond in copper can be easily produced by mechanical alloying (MA), resulting in superior matrix refinement [2,3].

In the present work, pure Cu was milled with nDiamond in order to determine the lowest reinforcement fraction required to simultaneously refine the matrix and homogeneously disperse the diamond nanoparticles, while preventing powder agglomeration. In addition, pure Cu powder was milled with natural μ Diamond to directly assess the integration and distribution of the micro sized particles in the metallic matrix, as well as the milling media wear and concomitant contamination of the composite produced. Furthermore, pure Cu powder simply mixed with natural μ Diamond has been extruded at 600°C to access the consolidation process feasibility and analyse the resulting material. The production of a Cu-nDiamond- μ Diamond nanostructured composite is expected to be viable, and eventually the material can be employed as heat-sinks integrated in first-wall panels.

Materials and methods

- Mechanical alloying was performed using a Retsch PM400 planetary ball mill.
- Rotation speed of 400 rpm.
- The mill container was charged with:
 - 20 g mixture of the elemental powders.
 - 400 g of hardened stainless-steel balls.
- For Cu- μ Diamond, the μ Diamond fraction tested was 10 at.% of μ Diamond, and the milling times were 1 and 2 h.
- For Cu-nDiamond, the nDiamond fractions tested were 1.5, 2.5, 3 and 4 at.% of nDiamond, and the milling times were 1, 2 and 4 h (the best trade-off between particle dispersion and milling media contamination was obtained for 4 h of milling time).
- Consolidation was carried out by hot extrusion at 600°C, with the elemental powders simply mixed using a conventional powder mixer for ½ h.
- The materials produced were characterized by X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM and TEM, respectively). Microhardness measurements were performed.

Results and discussion

Figure 1 shows the microstructure of as-milled Cu- μ Diamond powder milled for 1 h. Pores resulting from a continuous integration and subsequent extraction of μ Diamond particles during the synthesis process are observed. The milling media wear has been indirectly assessed through EDS analyses, and showed a significant presence of Fe (> 2 at.%) and Cr (0.5 at.%). After 2h of milling time, the powder was fully aggregated and pasted onto the container walls. These results demonstrated that Cu- μ Diamond production is not viable by mechanical synthesis.

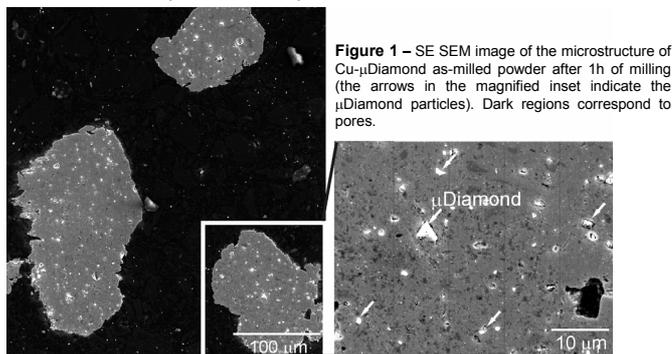


Figure 1 – SE SEM image of the microstructure of Cu- μ Diamond as-milled powder after 1h of milling (the arrows in the magnified inset indicate the μ Diamond particles). Dark regions correspond to pores.

Fine non-agglomerated powders could only be obtained for composites with nDiamond fractions above 4 at.%. Neither Fe nor Cr have been detected by EDS analyses for 4 at.% Cu-nDiamond composite. Figure 2 shows the homogeneous microstructure of the Cu-nDiamond (4 at.%) as-milled material (4h) observed by, respectively, (a) SEM and (b) TEM. The nDiamond particles are equiaxed and homogeneously dispersed in the matrix (see arrows in Figure 2 (b)), with sizes in the 10-20 nm range. This implies that the nDiamond agglomerates, resulting from the hydrogel drying, have not been fully disintegrated by the high-energy milling operation. The matrix presents grain sizes in the 20-50 nm range and good bonding with the diamond nanoparticles.

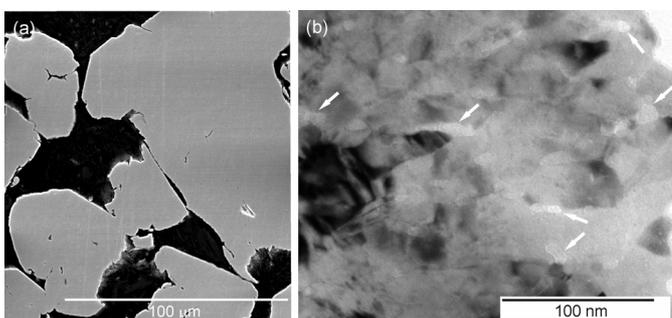


Figure 2 – (a) SE SEM image and (b) bright-field TEM image of the 4 at.% Cu-nDiamond as-milled powder after 4h of milling (the arrows indicate nDiamond particles).

Figure 3 presents the microstructure of the Cu- μ Diamond (10 at.%) material simply mixed (i.e., without high-energy milling) and consolidated by hot extrusion. Figure 3 (a) shows a homogeneous distribution of the μ Diamond particles (bright non-conductive particles) throughout the matrix. The apparent bonding between the matrix and the μ Diamond particles is evidenced in Figure 3 (b). Figure 3 (c) shows that the matrix presents grain sizes in the 0.5-1 μ m range and the observations have shown that abnormal grain growth has not occurred during the consolidation process at 600°C. No porosity could be detected by SEM and TEM observations, in agreement with results obtained for analogous materials, where hot extrusion has led to 99% of densification [2,4].

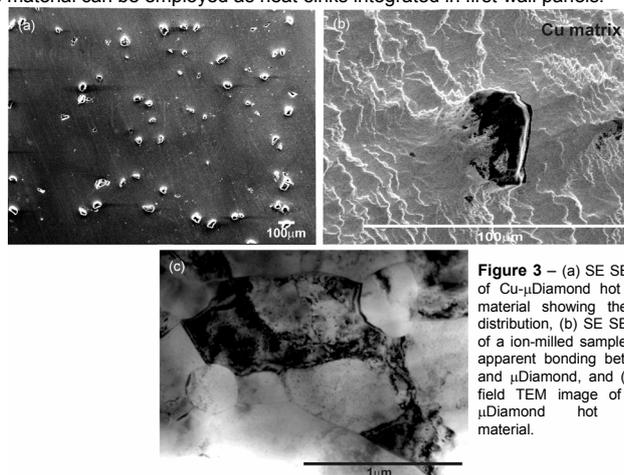


Figure 3 – (a) SE SEM image of Cu- μ Diamond hot extruded material showing the particle distribution, (b) SE SEM image of an ion-milled sample showing apparent bonding between Cu and μ Diamond, and (c) bright-field TEM image of the Cu- μ Diamond hot extruded material.

Table 1 shows the crystallite size evolution with milling time for the Cu-nDiamond (4 at.%) material (XRD data). The results show that the Cu crystallite size decreased essentially during the first hour of milling. The sizes attained with a nDiamond fraction as low as 4 at.% are similar to the values obtained in a previous study for 20 at.% nDiamond (~20 nm) [5].

Table 2 shows the microhardness evolution of the Cu-nDiamond 4 at.% composite with milling time. The values of the hot extruded Cu- μ Diamond together with reference values from the literature are also presented. As expected from the Cu crystallite size results, the microhardness values for the Cu-nDiamond 4 at.% nanocomposite showed no significant variation with milling time. Moreover, the reinforcement with nDiamond particles achieved significant microhardness enhancement relative to that of pure nanostructured Cu. Measurements performed around the μ Diamond particles in the Cu- μ Diamond extruded material revealed that the Cu matrix presented a microhardness comparable to that of pure micro sized Cu [6].

Production of Cu-nDiamond- μ Diamond nanostructured composites is currently underway and it can therefore be inferred that the multiscale dispersions are a viable approach for the production of composites with tailored properties.

Table 1 – Crystallite size evolution with milling time for the 4 at.% Cu-nDiamond composite obtained from XRD data.

Condition	Cu crystallite size (nm) - XRD
as-milled Cu-nDiamond (1h)	26
as-milled Cu-nDiamond (2h)	29
as-milled Cu-nDiamond (4h)	28

Table 2 – Microhardness evolution with milling time for 4 at.% Cu-nDiamond, as well as the microhardness value of the Cu matrix in the hot extruded Cu- μ Diamond material and reference values from the literature.

Condition	Microhardness (GPa)
Nanostructured pure Cu [7]	2.5
Microstructured pure Cu (1 μ m) [6]	0.9
As-milled Cu-nDiamond (4h) – 10 at.% nDiamond [3]	3.49
As-milled Cu-nDiamond (1h) – 4 at.% nDiamond	3.16 \pm 0.12
As-milled Cu-nDiamond (2h) – 4 at.% nDiamond	3.15 \pm 0.06
As-milled Cu-nDiamond (4h) – 4 at.% nDiamond	3.01 \pm 0.07
Hot extruded Cu- μ Diamond – 10 at.% μ Diamond	1.09 \pm 0.07

Conclusions

- High-energy milling of pure copper with μ Diamond is not a viable powder metallurgy process due to agglomeration/pasting onto the container walls and contamination from the milling media.
- High-energy milling of pure Cu with nDiamond resulted in fine powders with well-dispersed nDiamond particles in the matrix, displaying apparent interfacial bonding.
- Cu-nDiamond composite achieved significant microhardness enhancement relative to that of nanostructured pure Cu.
- Hot extrusion of mixtures consisting of milled Cu-nDiamond powder and μ Diamond powder is expected to be a feasible process and therefore the multiscale dispersion approach is viable for the production of Cu-Diamond composites.

References

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