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Production of Cu/Diamond composites for first-wall heat sinks

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Introduction

Reinforcement of a copper matrix with nanodiamond (nDiamond) [1] enables to tailor composite properties, such as, hardness, microstructural thermal stability and thermal conductivity. Dispersions of nDiamond in copper can be easily produced by mechanical alloying (MA), however processing these nanostructured materials present several challenges: (i) Diamond presents intrinsically difficult bonding with copper. Yet chromium incorporated in the copper matrix can improve its adhesion to diamond and provide enhanced thermal coupling. Chromium tends to segregate to the reinforcement/metal interfaces, forming a stable carbide interlayer that leads to enhanced heat and load transfer between the composite components [2]. (ii) MA is a well-known processing technique used to produce nanostructured composites [3]. However, one of its drawbacks is contamination arising from the milling media. This contamination can be minimized with appropriate milling parameters, but must be carefully monitored with high sensitivity techniques such as particle-induced X-ray emission (PIXE) spectroscopy. (iii) Consolidation of mechanically alloyed materials was developed by spark plasma sintering (SPS) [4] in which local heating resulting from intergranular plasma pulses enhances the mass transport at the powder particle surface, while keeping the particle bulk at lower temperature. The current research line aims to systematize the suitable processing conditions for Cu-nDiamond composites to be employed as heat-sinks integrated in first-wall panels.

Materials and methods

- Powder mixtures of Cu/nDiamond (10 at% nDiamond) with 0.1 at% Cr.
- Mechanical alloying 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.
- Dispersion homogeneity was monitored for1h/2h/4h/6h and 8h milling times.
- The 4h milling time powders were heat treated at 400 and 600ºC for 1 hour.
- Consolidation was carried out via spark plasma sintering with a sintering temperature of 800ºC under a pressure of 400 MPa for 3 min.
- The hardness and structural characterization of the as-milled powders, as well as the densification of the consolidated sample were investigated. SPS consolidation results were compared with hot extrusion data from previous studies.
- Contamination was evaluated with PIXE.

Results and discussion

Figure 1 shows the variation of Cu crystallites size with milling time, heat treatment and consolidation. The crystallite size decreased with milling time from 18 nm to 27 nm. These results suggest that the nDiamond particles contributed to break up the copper crystallites, acting as milling agents. The heat treatments and SPS consolidation resulted in modest grain growth, in general the exposure to high temperatures, even for short periods, leads to microstructural coarsening and deterioration of the mechanical properties [5].

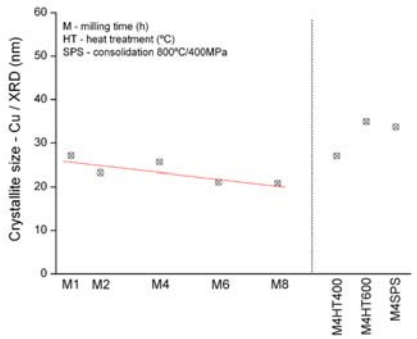

Figure 1 – Crystallite size of Cu/Cr/nDiamond nanocomposites. As-milled powders for milling times of 1h/2h/4h/6h and 8h, heat-treated powders at 400 and 600ºC, and SPS consolidated sample.

Figure 2 (a) presents the microstructure of the 8h as-milled powder and (b) shows an EDS spectrum of a typical inclusion. Microstructural homogeneity and extensive nDiamond dispersion were inferred from SEM observations for milling times higher than 4h. However, the number of Fe,Cr-inclusions originating from the milling media also increased with milling time. As a result, the 4h milling batch was selected as an optimized dispersion vs contamination condition and the resulting powder was further used for heat treatments and consolidation. Table 1 shows the average chemical composition determined by PIXE for the 4h milling condition. The ratio Cr/Fe (0.218) exceeds the nominal ratio of the stainless steel milling media (0.159) with the difference originating from the Cr doping. Figure 3 presents the microstructure of the 4h as-milled powder and annealed at 600ºC. The heat-treatments were used to promote a fine carbide precipitation at the interfaces. Although, due to its minute proportion, Cr carbides could not be detected at the interfaces. The nDiamond particles appeared equiaxed and homogenously dispersed (see arrows), with sizes in the 10-30 nm range. The nanocomposite exhibited apparent bonding at the interfaces.

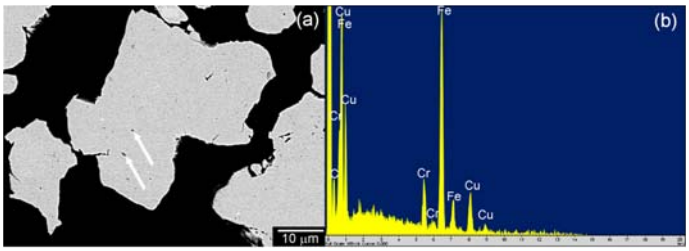

Figure 2 – (a) **SEM** BSE image of the microstructure of Cu/Cr/nDiamond powder after 8h of milling (arrows point to Fe,Cr-rich inclusions). (b) EDS analysis of a typical inclusion.

Acknowledgements

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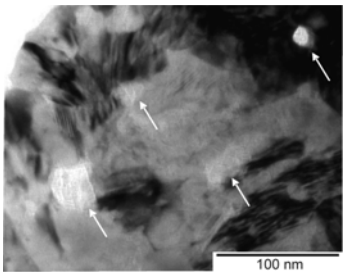

Table 1 – Average composition in wt% evaluated by PIXE analysis.

Sample	Cr	Fe	Cu
Cu/Cr/nDiamond	0.12	0.55	86.97

Figure 3 – TEM image of the Cu/Cr/nDiamond 600ºC annealed material. The arrows point to nDiamond particles at grain boundaries and inside copper grains.

Figure 4 presents the microstructure of the SPS consolidated sample. Prior particle boundaries (ppb) of the as-milled powder were bordered by pure copper (Figure 5 (a)). The nDiamond particles are homogeneously dispersed throughout copper matrix, while porosity could not be detected (Figure 5 (b)). The nDiamond particles showed sizes in the 20-50 nm range. SPS consolidated sample exhibited a density of 7.89 g/cm^3, representing 96% of densification, which is similar to the 99% densification obtained for analogous materials with hot extrusion [6].

Table 2 presents the microhardness evolution of the mechanically alloyed, heat-treated and consolidated materials, including reference values from the literature. Microhardness showed a slight increase with milling time, and the coarsening induced by the heat exposure during the SPS consolidation justifies the decrease in hardness relative to the as-milled powder (4h). The hardness value obtained with SPS is similar to results obtained with hot extrusion [7]. However, the microstructural heterogeneity (ppb) tends to embrittle the material. In consequence, as the microstructures resulting from hot extrusion are homogeneous, this consolidation method seems preferable.

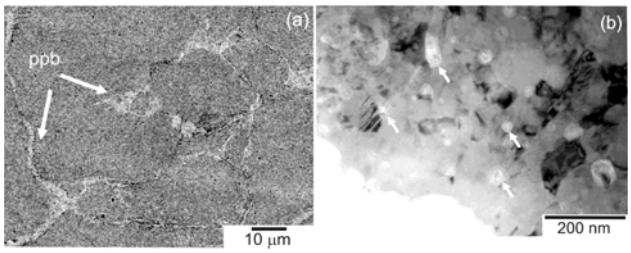

Figure 3 – (a) SEM BSE image, and (b) TEM image of the 4h milled SPS consolidated sample. The arrows in (a) point to prior particle boundaries and in (b) to nDiamond particles. Planar defects were observed in copper grains.

Table 2 – Microhardness values of Cu/Cr/nDiamond as-milled and heat-treated powders, and SPS consolidated sample.

Cu/Cr/nDiamond*	Vickers Microhardness (GPa)
Nanostructured Cu [8]	1.55
M1	3.34
M2	3.39
M4	3.52
M6	3.73
M4/without Cr doping	3.49
M4HT400	3.36
M4SPS**	2.45
M2HE [7]	2.50

* M – milling time (h), HT – heat treatment (ºC), and SPS – consolidation 800ºC/400MPa, and HE – Hot extrusion at 600 ºC.
** The microhardness was measured at the central part of the particles, i.e., avoiding the soft ppb.

Conclusions

- Microstructural observations showed well-dispersed nDiamond particles in the copper matrix, displaying an apparent interfacial bonding.
- Optimal nanoparticle dispersion vs contamination was obtained for 4h of milling.
- Contaminations by the milling media can be easily monitored by PIXE.
- Microhardness experiments demonstrated that in the case of nDiamond dispersions effective bonding can be achieved by mechanical alloying without Cr doping.
- Consolidation by hot extrusion leads to higher microstructural homogeneization than spark plasma sintering.

References

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