THE INFLUENCE OF THE MILLING MEDIA ENVIRONMENT ON THE CHARACTERISTICS OF A W-Cu COMPOSITE POWDER

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ABSTRACT. W-Cu composite powders were prepared by high energy milling under two milling environments: cyclohexane and air. Composite particles are formed in both cases. The W particles are fragmented and embedded into the Cu particles. Both, W and Cu, are heavily strained, mainly in the first hours of milling. The composite powder has high homogeneity and is much finer than the original Cu powder. The mean particle size of the powders milled in both conditions is very close, but the wet milling was near 25% longer than dry milling and the size distribution is wider. This is consequence of the higher milling intensity of dry milling.

INTRODUCTION

The W-Cu composite material exhibits high electric and thermal conductivities. Furthermore its thermal expansion coefficient may be adjusted to values close to those of ceramic materials used as substrate of semiconductors. These properties make this material an alternative to be used in heat sinks and microwave absorbers that work coupled to microelectronic devices [1-3].

High relative density and homogeneous structures are not reached for this composite by means of conventional powder metallurgy due to the mutual insolubility of W and Cu and the poor wettability of liquid Cu on W [4,5]. Liquid phase sintering of W-Cu conventionally milled powders or infiltration of a porous tungsten skeleton by liquid copper result in a porous structure with large lakes of copper and agglomerates of tungsten particles [6,7]. Small additions of Ni, Pd or Fe increase the final density [8,9], but deplete the electric and thermal properties of the material [10,11].

High energy milling has been used to prepare W-Cu composite powders containing nanocrystalline W grains with improved sinterability in liquid phase. The sintered structures reach near theoretical density with high homogeneity, and still showing fine granulation [12-15]. Furthermore, the temperatures used to produce these superior results are lower than those used to sinter the conventional W-Cu milled powder [16,18].

The characteristics of high energy milled powders are influenced by a series of parameters such as milling velocity, density of the milling media, powder charge to milling media charge ratio among others. This work focuses on the influence of the milling environment. Crystallite size and the lattice strain were determined in the milled powders.

EXPERIMENTAL

Elemental W and Cu powders were used as starting materials. The tungsten powder has with a mean particle size of 0.78μm. It was supplied by WOLFRAM GmbH. The copper powder has a mean particle size of 28μm, and was supplied by METALPÓ Ind. Com. Ltda, Fig. 1 shows SEM micrographs of both powders.
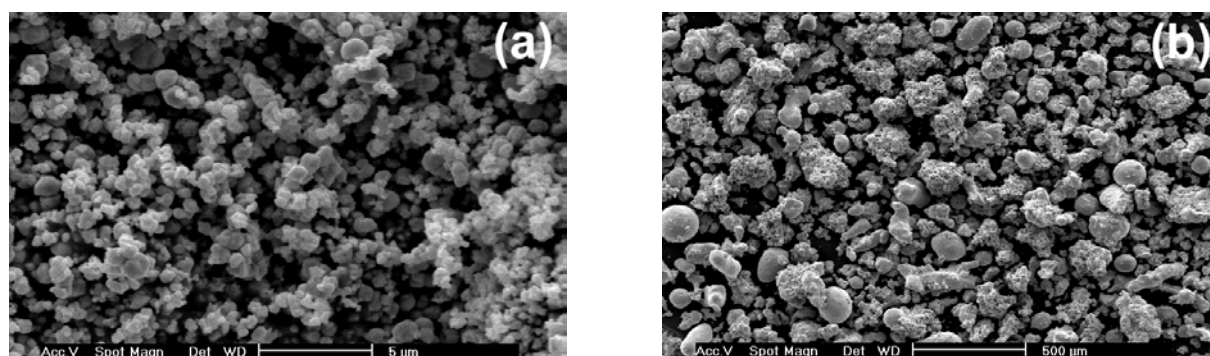

Fig. 1: SEM micrographs of the tungsten (a) and copper (b) as supplied powders.

A Fritsch Pulverisette 7 high energy planetary mill was used to prepare the composite powder. The milling environments were room atmosphere and cyclohexane. The powders

were milled for 100 (in room atmosphere) and 124 hours (in cyclohexane), using four hard metal balls with 15 mm of diameter and total mass of 100g. Samples were collected during milling and characterized. The powder to milling balls mass ratio is 2:5. The milling velocity is set at 5 in a scale from 0 to 10. No control process agent was used.

The powders were observed under SEM. The mean particle size was determined by LASER scattering. EDX was used to detect a possible contamination of the powder during milling.

The crystallite size of the phases and the strain of the crystal lattices were determined by XRD. The mean crystallite size of both W and Cu phases was determined by the Scherrer's equation (Eq. 1) [19]

$$D = \frac{0,9\lambda}{B\cos\theta} \quad (nm) \tag{1}$$

In which λ is the X Ray wave length (1,54 Å for CuKα), θ is the diffraction angle and B is the width at half height of the diffraction peak. The lattice strain ε is determined by the Williamson-Hall method, according to Eq. 2.

$$B\cos\theta = \frac{K\lambda}{\delta} + (2\varepsilon)sin\theta \tag{2}$$

RESULTS AND DISCUSSION

The process of formation of composite particles during high energy milling is described elsewhere [15,17,18]. Only the differences related to the use of different milling environments are focused here. Figs. 1(a-f) are SEM micrographs of the powders milled under different environments for different times. Figs. 2(a,c,e) show the powder dry milled for 5, 50 and 100 hours. Figs. 2(b,d,f) show the powder wet milled for 2, 50 and 124 hours, respectively.

The evolution of the shape of the particles is the same for both milling environments, but they are shifted in time. In the first hours of milling, composite plates are formed. Figs. 2(a,b) show small agglomerates of tungsten particles on the surface of the plates and separated from them. Most of the W particles, however, are inside the plates. The size of the plates is close to the size of the Cu particles. They are formed by deformation, as Co particles are trapped between milling media that collide.

In wet milling, the plates are thinner. It is important to remark that milling in a liquid allows the circulation of the particles throughout the milling vessel and the separation of the particles. In dry milling, the particles tend to the bottom of the vessel and form agglomerates.

After 50 hours of milling, there are clearer differences in shape. While some particles of the wet milled powder keep still the shape of plate (Fig. 2d), the particles of the dry milled powder are smaller and equiaxial (Fig. 2c).

After 124 hours, the wet milled powder also presents small and equiaxial particles (Fig. 2f) as the dry milled powder for 100 hours (Fig. 2e). The first collisions of the Cu particles cause a significant strain, so that the particles take the shape of plates. Additionally, W particles are embedded in Cu. Later, the plates are fragmented and become rounded.
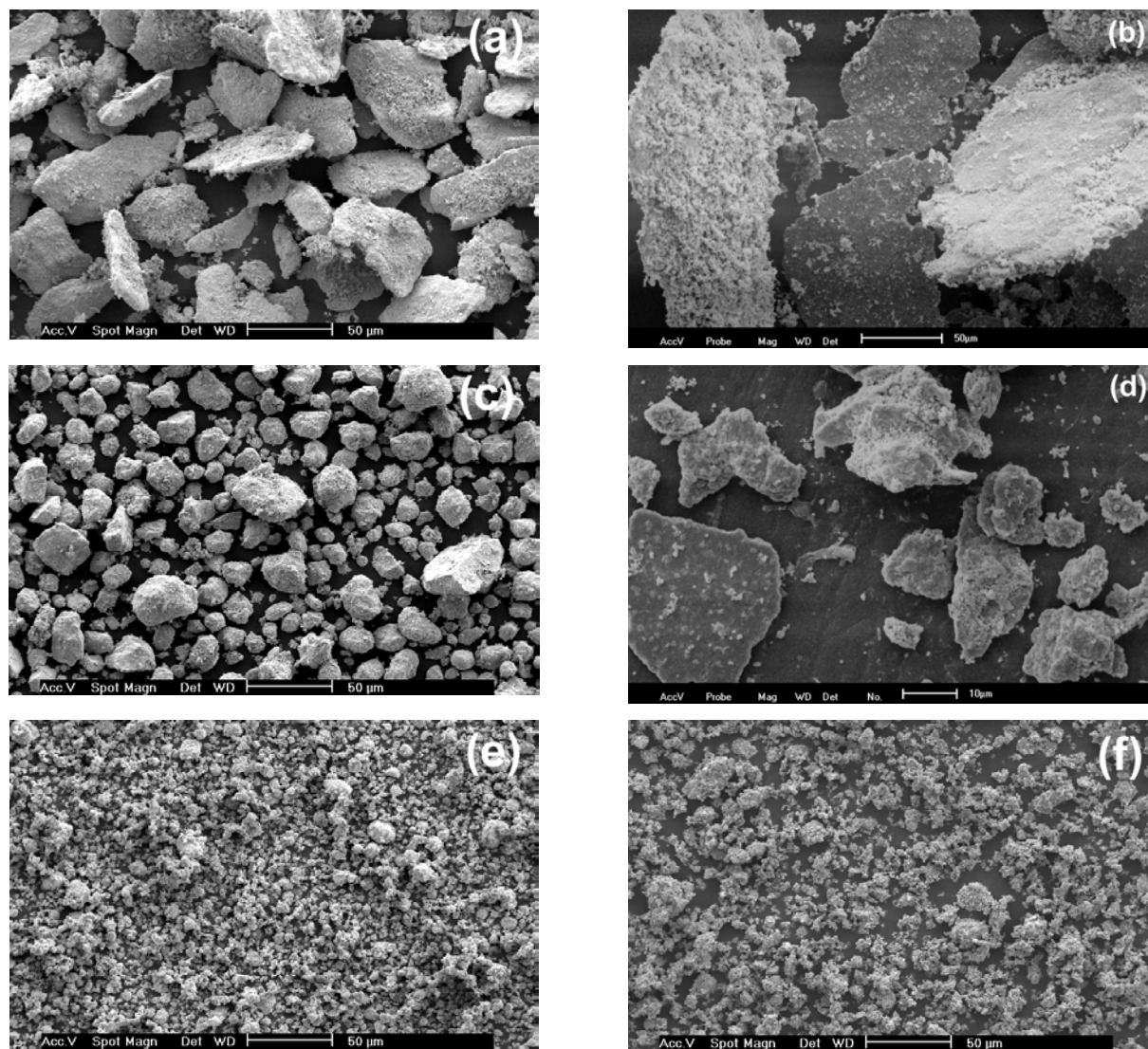

Fig. 2. SEM micrographs of the W-25%Cu powder milled in dry for 5, 50 and 100 hours (a), (c) and (e) and in cyclohexane (b), (d) and (f) for 2, 50 and 124 hours, respectively.

Figs. 3(a,b) show high magnification images of the dry milled powder for 100 hours (a) and the wet milled one for 124 hours. It can be seen that the particles in both cases are composite, but the particles of the dry milled powder seem to be smaller. This observation is complemented by the curves of particle size distribution shown in Figs. 4(a,b) for both powders. The mean particle size of the powders is close, around 3μm, but the size distribution of the wet milled powder is bimodal. The population of the coarser particles of the wet milled powder is higher.
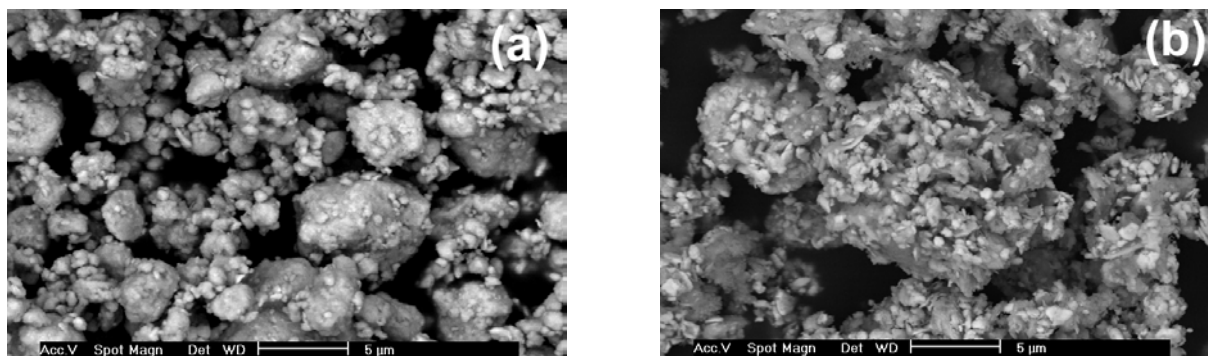

Fig. 3. SEM micrographs of the W-25%Cu powders milled in dry for 100 hours (a), and in cyclohexane (b) for 124 hours, respectively.
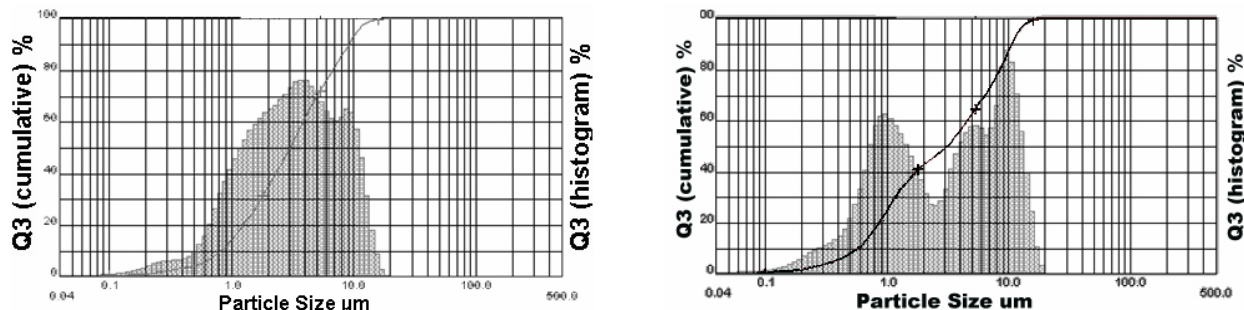

Fig. 4: Particle size distribution of the dry milled powder for 100 hours (a) and the wet milled powder for 124 hours (b).

Figure 5 shows the result of EDX for the dry milled powder milled for 50 hours. Only peaks of W and Cu were detected. The same result was obtained for all milling times. Therefore contamination with the milling media is discarded. This kind of contamination is likely in high energy milling due to the extreme wear of the mill. Nevertheless, another kind of contamination can occur. The powders can react with oxygen of the atmosphere during milling and during drying, the metal oxide is formed. The presence of oxides during sintering can be a problem.
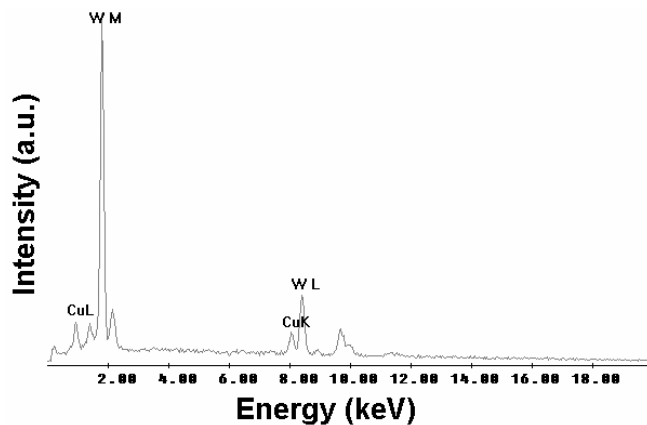
Fig. 5. EDX spectroscopy of the W-25%Cu powder dry milled for 50 hours.

The XRD pattern of the powders wet and dry milled in different times is shown in Fig. 6. Diffraction peaks of CuO_2 are detected in the patterns of the 100 hours dry milled and 124 hours wet milled powders. In the latter, the intensity of the peak was more intense. In the case of dry milling, oxidation can be explained through the reaction of oxygen in the milling atmosphere and the Cu particles. The local heating of the particles during collisions increases the reaction rate. The use of a liquid milling environment, as cyclohexane, should inhibit this kind of oxidation, since the oxygen-rich environment is eliminated and the heat caused by the collisions is dissipated by the liquid. Nevertheless, the drying of the powder/cyclohexane slurry was done under slight heating in a rotavapor. The Cu particles could have oxidized during this operation. The oxidation of W is also possible. In this case, the amount of tungsten oxide should be too small to be detected. The sintering of this powder must be done under a reducing atmosphere. Amorphization was not produced in neither cases.
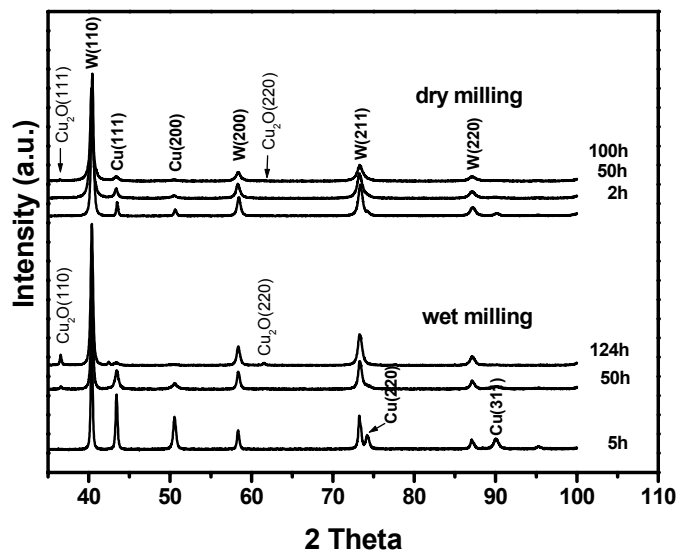

Fig. 6. DRX patterns of the W-25%Cu powder milled wet and dry for different times.

The collisions between the particles and the milling media also cause strain of the lattice and decrease of the coherent crystallite size. Figures 7(a,b) show the curves of the lattice strain and mean crystallite size for the powders as a function of the milling time for both milling environments. It is seen that the strain increases and the crystallite size decreases for longer milling times. However, the effect of milling is far more pronounced in the first hours of milling. After 20 hours of milling in both environments the crystallite size and the lattice strain are stable.

It is seen that the W lattice is the most affected by milling, and the dry milling produces more strain and crystallite size decrease. These results can be explained by the differences in stress applied to the Cu and W particles during collision. The Cu particles are much larger than the W ones. Thus, for a load applied to a particle during a collision, the stress is higher for the smaller one. Furthermore, the milling media energy is lower in wet milling because the viscosity of cyclohexane decreases the kinetic energy of the milling balls.
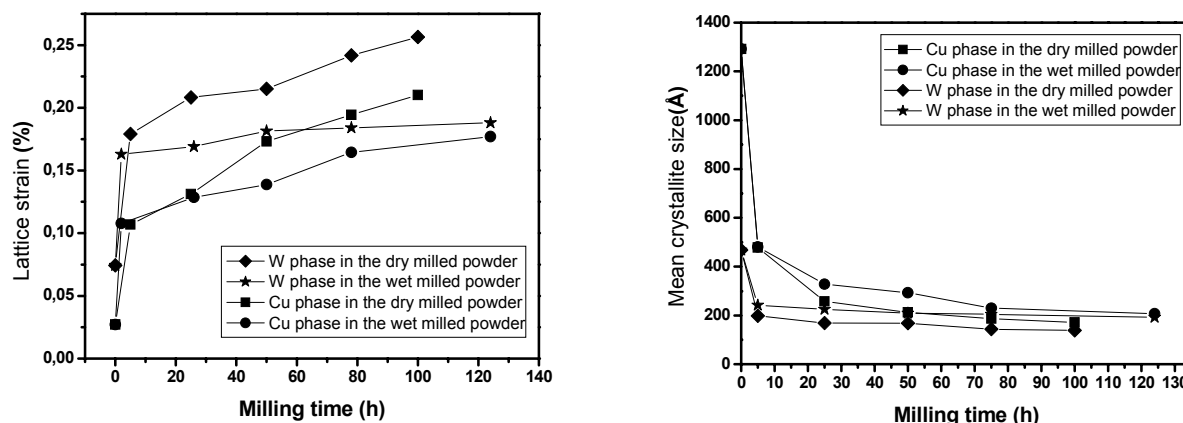

Fig. 7. Lattice strain (a) and mean coherent crystallite size (b) as function of the milling time for the W and Cu phases milled in dry and wet conditions.

CONCLUSIONS

Milling in air and in cyclohexane did not alter the composite particle evolution, but did promote a time shift in this process. Dry milling has a fast evolution. After 50 hours milling, it is possible still to find particles in form of plates in the wet milled powder. The final mean particle size is very close for both milling environments, but the distribution curve is wider for the wet milled powder. High energy milling did not produce contamination of the powder by wear of the milling media, but oxidation of Cu was produced in dry milling as a result of the reaction between the Cu particles and the oxygen of the milling atmosphere. Most of the

lattice strain and decrease of the crystallite size takes place in the first hours of milling. Tungsten is more affected than copper and dry milling is more energetic than wet milling.

ACKNOWLEDGEMENT

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