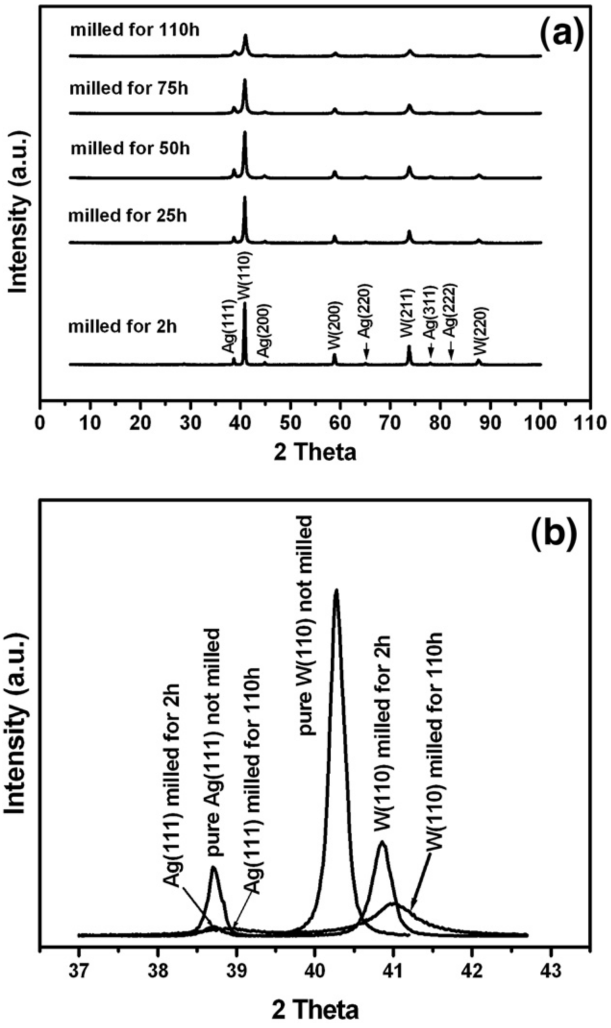

Fig. 6. XRD patterns of the powders milled for 2, 25, 50, 75 and 110 hours (a) and detail of the (111) and (110) peaks of Ag and W, showing the shift for higher angles with longer milling times (b).

HEM can amorphize crystalline phases [7]. XRD shows that neither phases are amorphized. However the diffraction peaks become wider and significantly less intense. This shows that milling has affected crystallite size and introduced lattice deformation. Costa [12] reported that neither W nor Cu were amorphized after 51 h of HEM, but the same author also reported [13] that Ta and Cu are amorphized after 100 h of HEM under more severe milling conditions than those used here. Considering the soft–hard character of the Ta–Cu and W–Ag couples, one can suppose that W and Ag could be amorphized, if heavier milling conditions were utilized.

Peak shift can be caused by both stacking fault and residual stress in the crystal lattice. Face centered cubic crystals like Ag are commonly affected by stacking faults, but not body centered cubic crystal like W. In this case, residual stress is likely the explanation.

4. Conclusions

Composite particles of W and Ag were formed by HEM in dry after 25 h of milling. Dispersion is improved with increasing milling times, but homogeneous dispersion could not be reached even after 110 h of milling. The mechanism of formation of composite particles consists of deformation of Ag particles, piercing of W particles in Ag, work hardening of Ag, fragmentation of the large composite particles, cold welding of different composite particles. Some of these steps are repeated, resulting in smaller particles with better phase dispersion. The collisions produce deformation and stacking faults of the crystal lattices, but is not able to amorphize any phase. Amorphization is a possibility, if heavier milling conditions are used.

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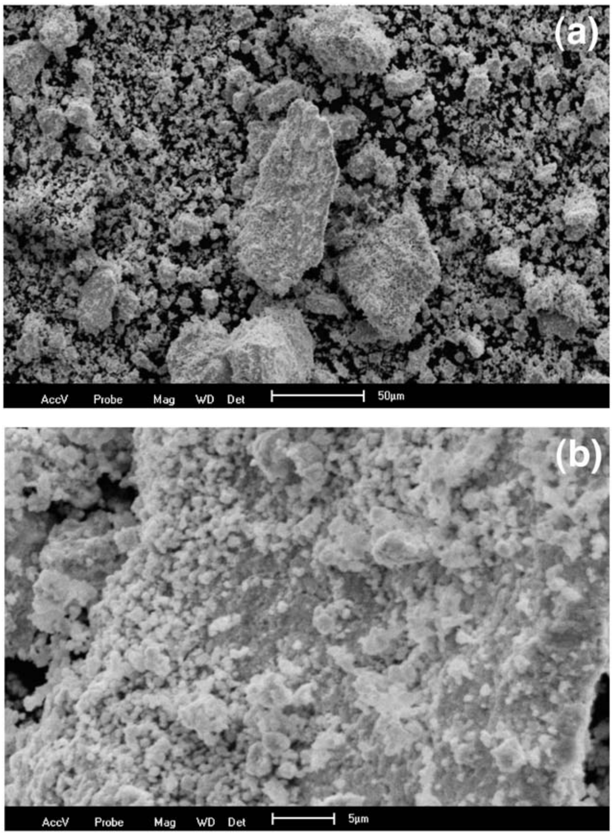

Fig. 4. General view of the powder milled for 25 h (a) and view of a large composite particle showing a W enriched surface (b).

of collisions intensifies the process of deformation of Ag and piercing of W in Ag. This results in Ag particles covered by a layer of pierced W particles, as shows Fig. 4(b). The outer surface of the Ag particles, where this layer is formed, is severely damaged. Thus, this region strain hardens earlier than the inner part. The large deformed particles preferentially fragment in the extremities. This is the reason for so many more fine particles at this milling time. The particles that contain W pierced in Ag are called composite particles. In this stage, the W and Ag are not homogeneously dispersed.

With continuation of milling, the particles evolve. The fracture of the composite particles exposes fresh Ag. Collisions of different composite particles can cold weld them. This process causes coarsening of the particles. At the same time, the collisions harden the particles. This favors fragmentation. Thus, two antagonistic processes simultaneously act. One produces particle refinement. The other produces particle coarsening. The predominance of one of these mechanisms determines the evolution of the particle size distribution. Nevertheless, both processes improve dispersion. For longer milling times, the fragmentation mechanism prevails, since strain hardening is cumulative.

Fig. 5(a,b,c) are SEM micrographs of the powders milled for 50, 75 and 110 h respectively. Large particles are still seen. But they are not necessarily large composite particles. They may be agglomerates that formed as the small composite particles stick at the vial wall and are compressed together by the collision of the milling balls. This process can be hindered by using wet milling.

The mean particle size of the powder milled for 110 h is 4.7 µm. The particle size ranges from 0.7 µm to 10.6 µm. It must be taken into account that agglomerates of small composite particles are considered as individual particles. Therefore, the actual composite particle mean size is smaller. X ray fluorescence detected 0.05 wt.% of Co in the powder milled for 110 h. This contamination is caused by the wear of the milling media and the vial's lining that are made of hardmetal.

EDX mapping for Ag of large composite particles formed during milling for 50 and 110 h (not included) shows that phase homogenization is not attained. Homogenization is reached by the sequence piercing, fracture, welding, fracture and agglomeration. Although complete homogenization is not reached even after 110 h, the phase dispersion produced by HEM is much higher than that obtained by milling, because in HEM the phases are dispersed in each particle of the powder.

Fig. 6(a,b) exhibits XRD patterns of the powder milled for 2, 20, 50, 75 and 110 h (a) and the detail of peak shift for both Ag and W (b). According to the Scherrer's equation, the coherent crystallite size of both W and Ag are 13.1 nm and 8.4 nm respectively. This measurement was done in the plane (110) for tungsten and (111) for Ag in the powder milled for 110 h. The crystallite sizes of both phases in the as supplied elemental powders are 52.4 nm for W and 54.4 nm for Ag, measured in the same planes. This significant decrease of the crystallite size is consequence of the severe deformation caused by milling.

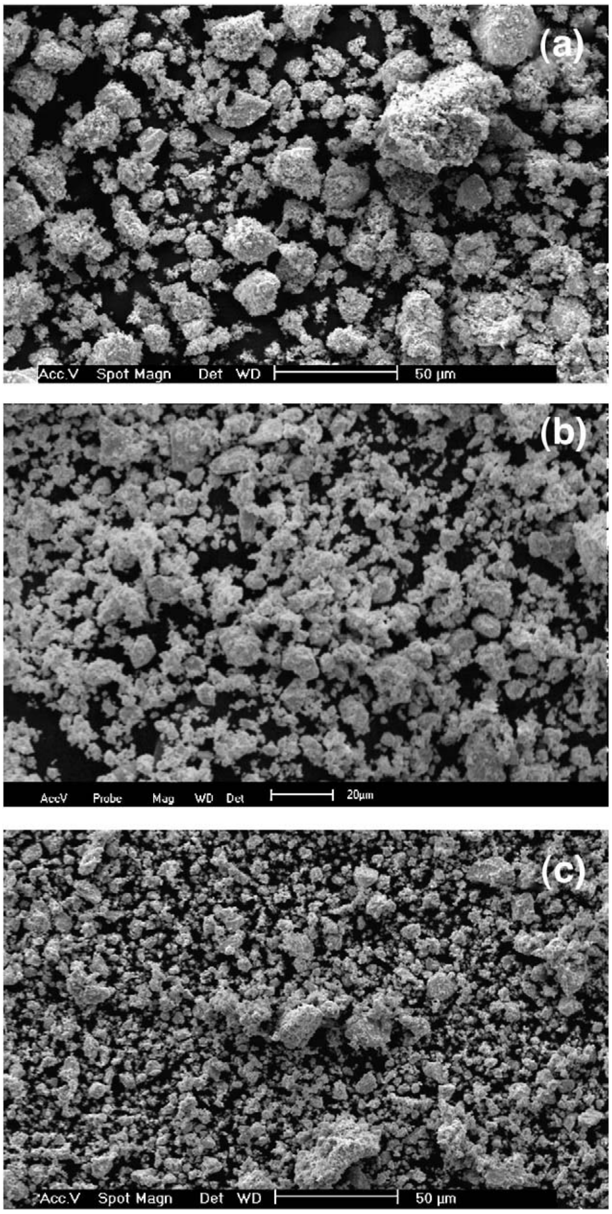

Fig. 5. SEM micrographs of the powders milled for 50 (a), 75 (b) and 110 hours (c).

2. Experimental

Powders of tungsten (mean size 0.78 µm, supplier WOLFRAM GmbH, Fig. 1a) and silver (mean size 10 µm, supplier COIMPA Industrial Ltda, Fig. 1b) were used.

The W and Ag powders in the proportion of 25 wt.%Ag were placed in a hardmetal lined bowl (diameter: 40 mm; height: 38 mm) of a Fritsch Pulverisette 7 planetary mill and milled for 110 h under room atmosphere in dry. Hardmetal balls with ¼" diameter and total weight of 150 g were used as the milling media. The ball to powder weight ratio is 1:3. The milling velocity is set at five in a mill scale from 0 to 10. No process control agent was used. This milling conditions were set based on a previous work [6] about HEM of the W–Cu system.

Milling was interrupted after 2, 25, 50 and 75 h for collecting samples. Thus the evolution of the particles could be determined. Another sample was prepared by simple hand shaking the powders of same composition for 3 min. This powder is used as reference. Morphology, shape and size distribution of the particles were determined by means of SEM. The mean particle size was determined by LASER scattering. X ray fluorescence was used to detect contamination introduced during milling. EDX mapping was used to investigate the quality of phase dispersion in the composite particles. XRD was used to investigate the evolution of the crystal lattice and to measure the crystallite size of tungsten and silver. The crystallite size is determined by the Scherrer's equation [11].

3. Results and discussion

Fig. 2 is a SEM micrograph of the mixed powder. A large fraction of W particles is attracted to the surface of the large Ag particles. Both Ag and W particles keep their original shape and size.

Fig. 3(a,b) are SEM micrographs of the powder milled for 2 h. It is noticed that the number of free W particles is reduced (Fig. 3(a)). Most particles are attached to the surface of the Ag ones. Agitation tends to agglomerate powders, mainly the finer ones. This could explain the increase of W particles attached to Ag. However, another factor should be taken into consideration. The collisions of the particles and the milling media produce deformation of the particles, in special of the softer Ag particles. This is shown in Fig. 3(a) that exhibits a plate-like particle. The collisions also produces the piercing of the harder, smaller W particles in the softer Ag phase. As a result, the W–Ag agglomerates now look different from those present in the mixed powder. The W particles that cover the Ag ones look to be more strongly attached to the Ag particles, Fig. 3(b). The particle size distribution of this powder is similar to that of the hand mixed powder, except that now more W particles are attached to Ag and few Ag particles were deformed into plates.

The particle size distribution of the powder milled for 25 h is quite different, as shows Fig. 4(a). There are much more fine particles and the large ones are either deformed or became smaller, in comparison to the size of the large particles of the 2 h milled powder. The sequence

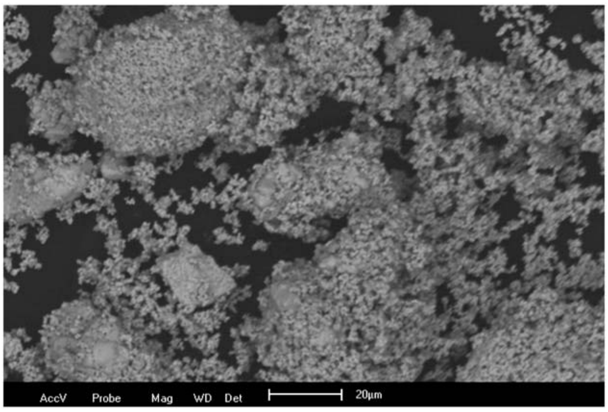

Fig. 2. SEM micrograph of the hand mixed powder.

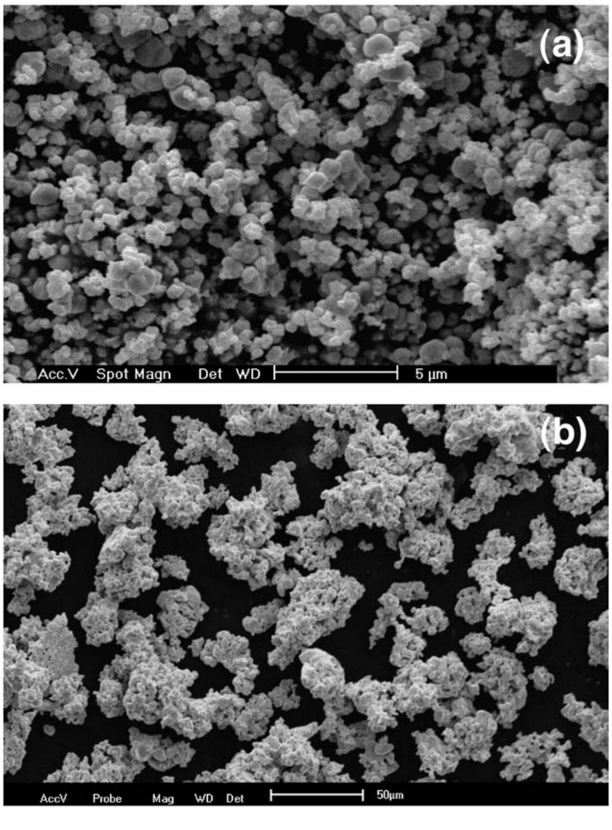

Fig. 1. Morphology of the initial powders: (a) tungsten (b) silver.

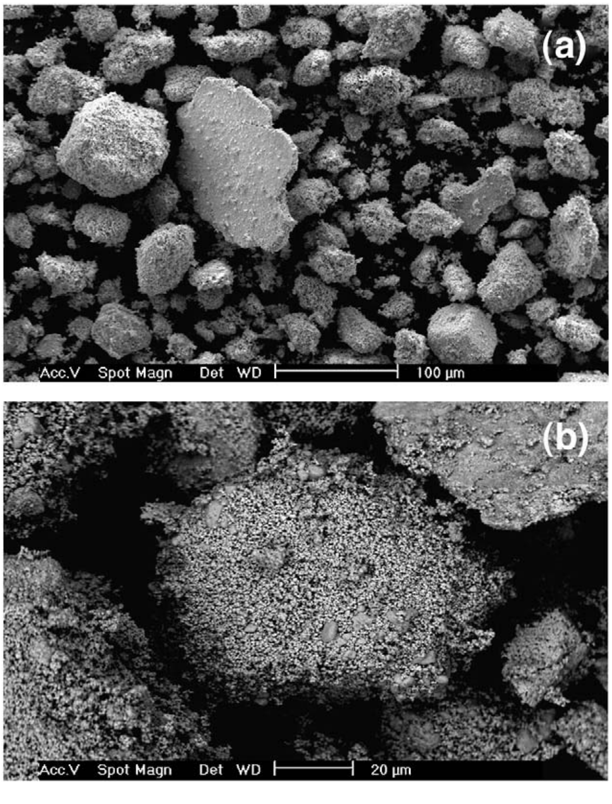

Fig. 3. SEM micrographs of the powder milled for 2 h.

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Synthesis of a nanocrystalline composite W–25 wt.%Ag powder by high energy milling

Franciné Alves da Costa [a,*], Angelus Giuseppe Pereira da Silva [b], Francisco Ambrozio Filho [c], Uílame Umbelino Gomes [d], Francisco Antonio Vieira [e]

[a] *Laboratório de Materiais Cerâmicos e Metais Especiais, UFRN, Campus Universitário, 59072-970, Natal, RN, Brazil*
[b] *Laboratório de Materiais Avançados, UENF, 28015-620, Campos de Goytacazes, RJ, Brazil*
[c] *Laboratório de Metalurgia do Pó, IPEN, Cidade Universitária, 05508-900, São Paulo, SP, Brazil*
[d] *Departamento de Física Teórica e Experimental, UFRN, Campus Universitário, 59072-970, Natal, RN, Brazil*
[e] *Laboratório de Ensaios de Materiais, CTGás, 59063-400, Natal, RN, Brazil*

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ABSTRACT

W–Ag pseudo-alloys are used in electric contacts of circuit breakers. They are produced by sintering of W–Ag powder mixtures followed by hot pressing or rolling to increase density. High energy milling (HEM) can enhance sintering of systems that present low sinterability because it improves dispersion, promotes refinement of the phases and produces composite particles. This work investigates the effect of HEM upon a W–25 wt.%Ag powder mixture. Phase dispersion, evolution of the shape and size of the particles during milling and the influence of strain on the crystal structure are investigated. The milled powders consist of composite particles that were formed in the first 25 h of milling. Longer milling times improve the distribution of phases inside the composite particles. The formation of the composite particles involves sequential steps of deformation, fragmentation, cold welding, work hardening and piercing of particles of the hard phase in the soft phase. The crystal lattice of W and Cu is damaged, but is not amorphized.

1. Introduction

Refractory carbides or refractory metals such as WC, W and Mo and transition metals like Cu and Ag are used to produce composite materials utilized as electric contact and welding electrodes [1–3]. These composites combine high resistance to welding and to electric arch erosion of the refractory phases with the high electric and thermal conductivities and the ability to be machined of the transition metals [4]. The composite material has elevated corrosion resistance and its thermal expansion coefficient (TEC) can be adjusted by changes in its composition. This allows the match of TEC to those of the ceramic substrates used with semiconductor devices, for example. Thus this composite can be also used as heat sinks and microwave absorbers in microelectronic devices.

Powder metallurgy is the technique used to manufacture composites with immiscible components like W–Cu, W–Ag, Mo–Cu and Mo–Ag. The powders of the components can be mixed to produce the conventional powder mixture or can be high energy milled (HEM) to produce a composite nanostructured powder. The mechanical mixture is not able to produce a well dispersed mixture and local concentration of the individual phases is common. This results in heterogeneous structures and poor sintering [5,6]. On the other hand, HEM can produce severe deformation, fracture, cold welding of the particles as well as synthesis of non-equilibrium phases, super saturation of solutions and formation of composite particles and nanostructures [7–9]. This results in improved dispersion (more homogeneous structures) and higher densities of the sintered bodies.

The elevated oxidation resistance of the W–Ag composite in comparison to the concurrent materials (W–Cu and Mo–Cu) used to produce electric contacts, welding electrodes, heat sinks and microwave absorbers is its main advantage. Nevertheless, few studies have been made about the use of HEM to prepare composite W–Ag powders [10] and no detailed investigation about the effect of this technique on size, shape, composition and crystal structure of the particles has been reported. It is known that the properties of these materials are influenced by the composition and the manufacture route. Thus the electric, thermal and mechanical properties of the composites will be affected by the use of HEM because this technique highly influences sintering and the structure of the material.

In this work, a composite W–25 wt.%Ag powder is prepared by HEM under dry conditions in room atmosphere for up to 110 h in a planetary mill. The influence of the milling time on the size, shape, composition, dispersion and crystal structure of the particles is investigated.

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* Corresponding author. Tel.: +55 84 3215 3800; fax: +55 84 3215 3791.
E-mail address: francineac@yahoo.com (F.A. da Costa).

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