Synthesis of a Composite Nanocrystalline W-25w%Ag Powder Using High Energy Milling

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Abstract: W-Ag pseudo-alloys used in electric contacts are produced by sintering of W-Ag powder mixtures followed by hot pressing or rolling to increase density. High energy milling (HEM) is used to produce a W-Ag composite powder. These powders exhibit good dispersion of the phases and fine granulation of W. These characteristics enhance sintering. This work investigates the effect of HEM a W-25wt%Ag on phase dispersion, on the shape and size of the particles and on the crystal structure of the milled powders. The W-Ag mixtures were dry milled in a planetary mill for 110 hours. XRD has detected a significant reduction of the crystallite size of both W (13.05nm) and Ag (8.34nm) phases and a shift of the W diffraction peaks to higher angles. EDS and X ray fluorescence detected contamination by Co during milling. The changes of particle shape and size were observed under optical and electronic microscopes. The dispersion of the W and Ag phases was characterized by EDS mapping. Composite W-Ag powder consisting of nanometric W particles dispersed in a Ag matrix was obtained by HEM

Introduction

A refractory carbide or refractory metal such as W, Mo and WC and a transition metal like Cu or Ag are used to produce a composite material utilized as electric contact and welding electrodes [1-3]. This composite combines the high resistance to welding and electric arch erosion of the refractory phases with the 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 can be adjusted to match those of the ceramic substrates used with semiconductor devices. Thus this composite can be also used as heat sinks and microwave absorbers.

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 [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 and higher densities of the sintered bodies.

The elevated oxidation resistance of the composite W-Ag 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 powders 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-25w%Ag powder is prepared by HEM under dry conditions (room atmosphere) for up to110 hours in a planetary mill. The influence of the milling time on the size, shape, composition, dispersion and crystal structure of the particles is investigated.

Experimental

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

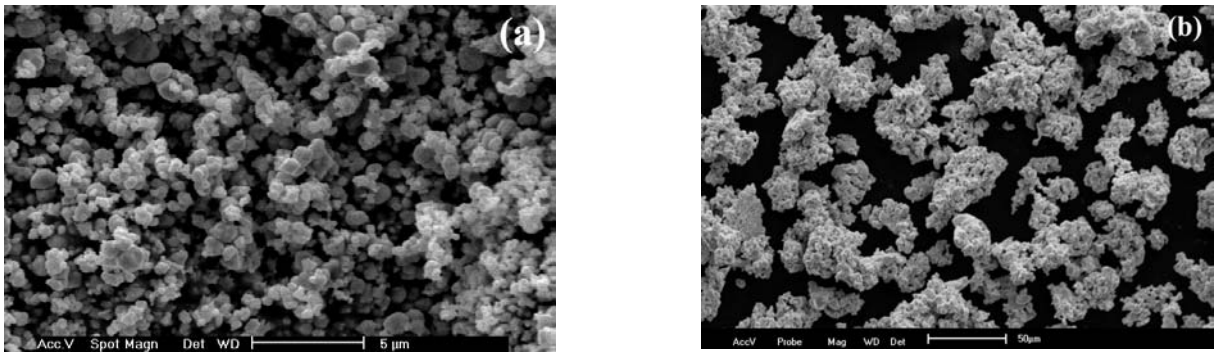

Figure 1: Morphology of the initial powders: (a) tungsten (b) silver.

The W and Ag powders in the 25w% Ag proportion were placed in the bowl of the Fritsch Pulverisette 7 planetary mill and milled for 110 hours under room atmosphere. WC-Co balls with ¼" diameter and total weight of 150g 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.

During milling after 2, 25, 50 and 75 hours the process was interrupted and samples were collected. Thus the evolution of the particles could be determined. Morphology, shape and size distribution of the particles were investigated by means of SEM. The mean particle size was determined by LASER scattering. X ray fluorescence and EDX were used to detect contaminants introduced during milling. XRD was used to investigate the evolution of the crystal lattice and the crystallite size of tungsten. The crystallite size is given by Eq. 1.

$$D = \frac{0.9\lambda}{B\cos\theta}(nm) \qquad (1)$$

λ is the X ray wave length (1.54Å for Cu Kα), θ is the diffraction angle and B is width of the peak at half height.

Results and Discussion

Figure 2(a-d) exhibits micrographs of samples collected at different times during milling.

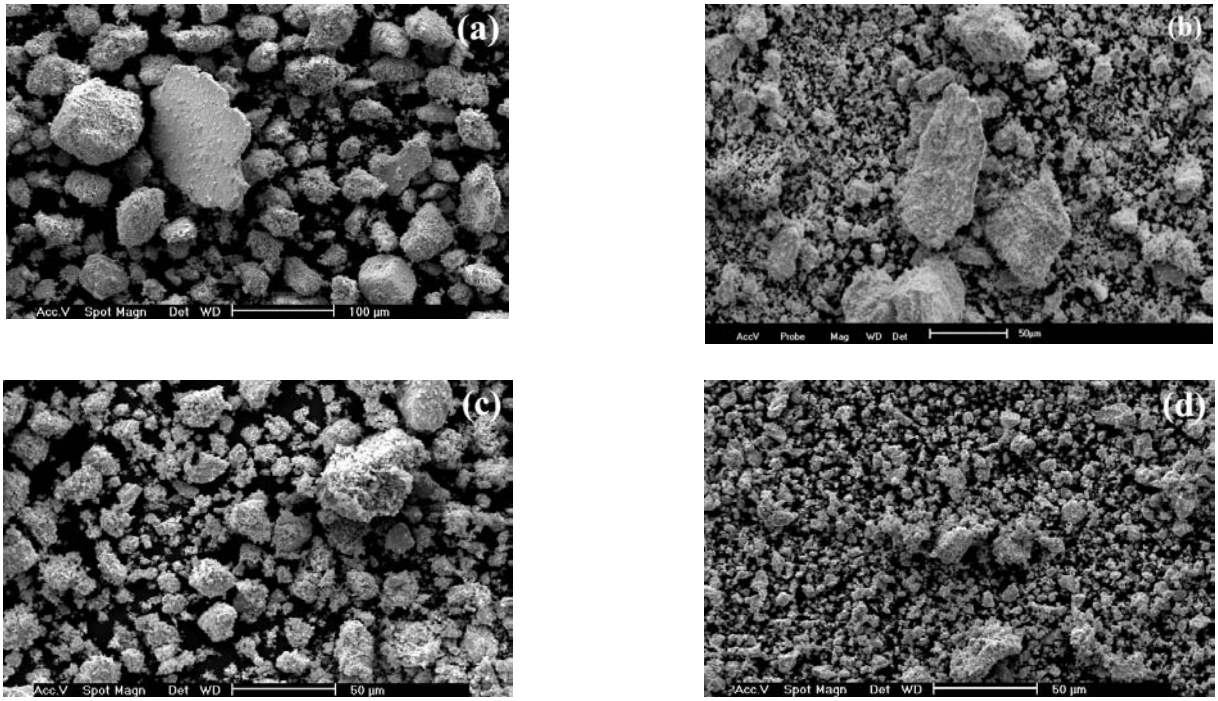

Figure 2: SEM micrographs of the samples collected after 2 (a), 25 (b), 50 (c), and 110 (d) hours milling.

After 2 hours free W particles are not seen anymore. The W particles were incorporated to the Ag particles by the successive collisions between the milling media and the W and Ag particles. The ductile Ag is deformed and the harder W is fractured. The W fragments can penetrate into the Ag particles. The composite particles are so formed. Figure 2a exhibits particles that are larger than the initial Ag particles. Some of them are platelike. This shape is produced by collisions of the milling balls against the ductile silver. The sequential collisions change continuously the shape of the Ag particles while they harden. The hardened particles then fracture.

After 25 hours of milling the particles show a different shape and size distribution. Most of the particles are much smaller than those present after 2 hours milling but still large and plate like particles are found. The fragmentation of the larger particles occurred due to hardening. Those still large particles suffered a retarded hardening process.

With longer milling times the particle size tend to decrease. The population of the largest particles decreases, but some of the smaller particles can agglomerate. This can be seen in Figs. 2c and 2d, for powders milled at 50 and 110 hours respectively. The successive deformation, fragmentation and incorporation of tungsten particles create composite particles of improved dispersion. After 110 hours of milling the mean particle size is 4.68µm. The particle size ranges between 0.70µm and 10.62µm. It is finer than the powder milled for 50 hours.

Fig. 3 exhibits a SEM micrograph of a section of a composite particles formed by 110 hours milling. These composite particles are in fact agglomerates of smaller composite particles. Individual Ag and W particles do not exist anymore. Fig. 4 exhibits the EDX

spectrum of the powder milled for 110 hours. Co is present in the amount of 0.05w% determined by X ray fluorescence. Co was introduced due to the wear of the WC-Co milling balls.

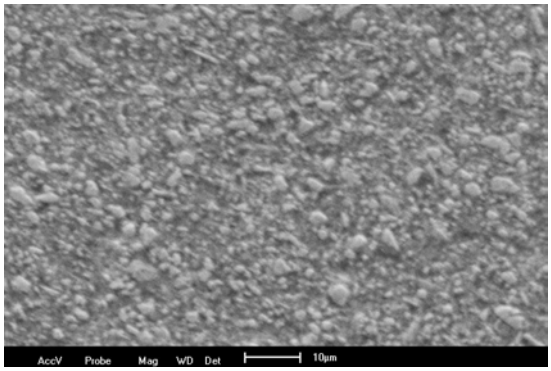

Figure 3: SEM micrograph of a section of a composite particle after 110 hours milling.

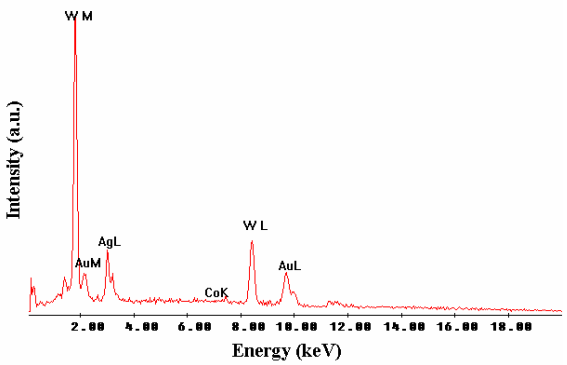

Figure 4: EDX spectrum of the powder milled for 110 hours. A small Co peak is detected.

Fig. 5 exhibits the XRD patterns of samples milled for different times. In all of the cases tungsten and silver are the only identified phases. Nevertheless broadening of the peaks of both phases can is observed, as shown in Fig. 6. Using Eq. 1, the crystallite size for both phases are 13.1µm and 8.4µm for tungsten and silver respectively after 110 hours. Furthermore there is a displacement of the diffraction peaks of W to higher angles, as can be seen in Fig. 6. This peak displacement is associated to the severe deformation of the crystal lattice during milling. The continuation of milling could cause amorphization of both phases.

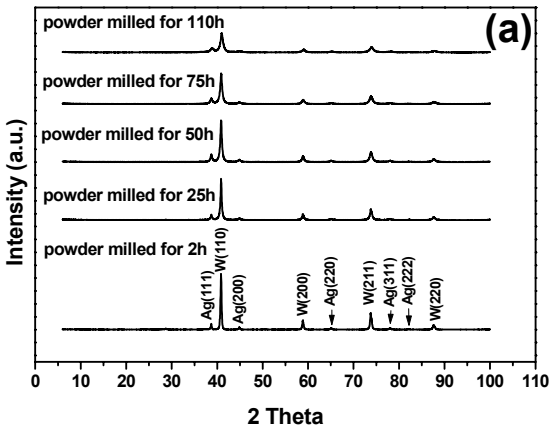

Figure 5: XRD patterns of the powders milled for different times.

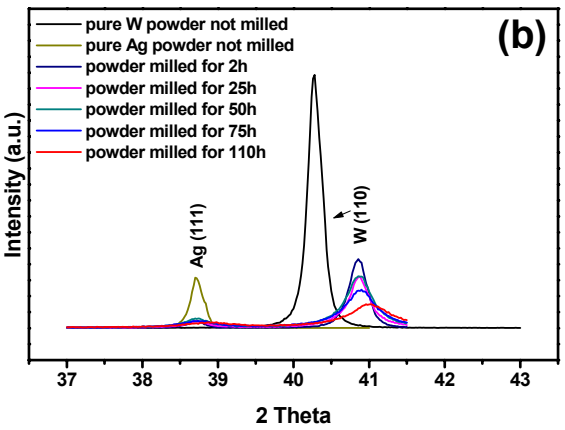

Figure 6: Peak broadening and displacement for (110) tungsten and (111) copper milled for different times

Conclusions

High energy milling of W and Ag powders can produce composite particles. These particles are formed during milling due to the deformation of the Ag particles and the incorporation of tungsten particles and fragments into the ductile Ag. The hardening caused by the cold work causes the breakage of the particles that tend to decrease the mean size. In spite of high milling energy and the long milling time, neither of the phases became

amorphous although the lattices were deformed as detected by the peak displacement and the crystallite size measurement.

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