Structure and Electric Conductivity of a W-25w%Cu Pseudo-Alloy Prepared with a Composite Powder by Liquid Phase Sintering

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Abstract: The liquid phase sintering of W-Cu composite powders prepared by high energy milling produces very homogeneous structures of near theoretical density. This work discusses the effect of the preparation technique of a W-25%wt.Cu powder on the structure of the sintered material and the influence of this structure on the electric conductivity of the alloy. Mixtures of W and Cu powders containing 25%wt Cu were prepared by hand mixing and by dry high energy milling for 100 hours in a planetary mill. DRX had detected a significant reduction of the W and Cu crystallite sizes in the milled powder. The milling procedure did not contaminate the powders according to EDS. The sintered structures were observed under optical and electronic microscopes. Samples of the milled powders sintered at 1200°C for 1 hour exhibited 41 IACS of electric conductivity, high homogeneous structure and relative density above 95%. On the other hand, samples prepared from the hand mixed powders sintered at the same conditions reached only 30 IACS and 68% relative density.

Introduction

W-Cu pseudo-alloys are used in electric contacts, welding electrodes, heat sinks and microwave absorbers [1,2]. The base for these applications is the high resistance to welding, to arch erosion, thermal and electric conductivities and a thermal expansion coefficient that can be adjusted the match those of the materials used as substrates of the semiconductor pieces in the electronic devices [3].

Powder metallurgy is the technique used to produce such alloys. Liquid phase sintering is utilized to densify the structure. However, the W-Cu system is hard to sinter due to the poor wettability of liquid copper in tungsten and the mutual insolubility of these phases [4]. This results in a porous and heterogeneous structure with concentration of tungsten grains and large Cu lakes [5.6].

High energy milling (HEM) has been used to prepare composite W-Cu powders with nanocrystalline W grains which are much easier to liquid phase sinter, producing homogeneous and fine granulated structures [7-9]. Additionally, the composite powders can be sintered at lower temperatures than the conventional powders [10,11].

This work reports the preparation of a W-25w%Cu using high energy milling in a planetary mill and compares its characteristics to those of a powder with the same composition prepared with mechanical mixture. These powders are sintered and the resulting structures and electric conductivities are discussed.

Experimental

A tungsten powder with mean size of 0.78µm supplied by WOLFRAM GmbH and a copper powder with mean size of 28µm supplied by METALPÓ Ind. Com. Ltda were used. Fig. 1 is SEM micrographs of both powders.

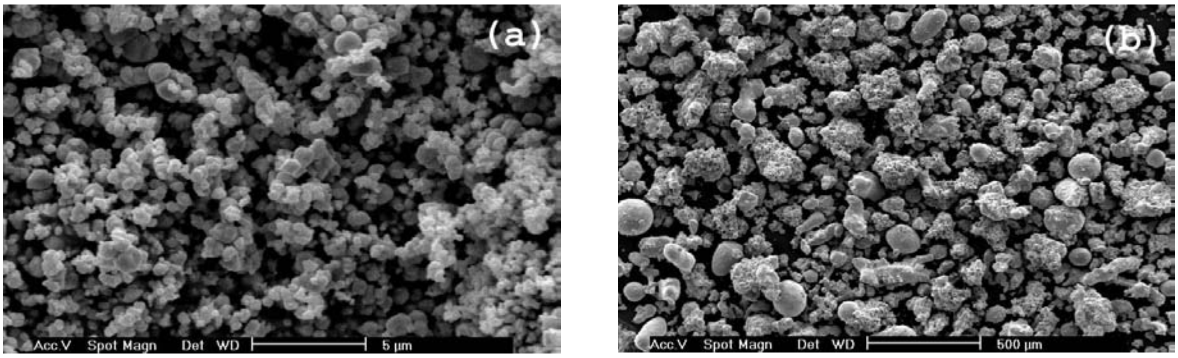

Figure 1: SEM micrographs of the tungsten (a) and copper (b) as supplied powders.

A high energy planetary mill model Fritsch Pulverisette 7 was used to prepare the composite powder. The powders were milled under room atmosphere for 100 hours using 4 hard metal balls with 15 mm of diameter and total mass of 100g. 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 the presence of contamination of the powder introduced during milling.

Cylindrical green bodies were dye pressed under 210MPa. The relative green densities of the composite and the mechanically mixed powders are 55% and 60% respectively. The samples were sintered in a resistive furnace at 1200ºC for 1 hour in a flow of hydrogen. The heating rate is 10ºC/min.

After sintering, the samples were prepared to be observed under SEM and the electric conductivity was measured.

Results and Discussion

During HEM the copper particles are deformed by the collisions. The hard tungsten particles fracture and fragments are incorporated to the soft Cu particles under action of the collisions. The composite particles then are produced. Initially, the soft copper particles are deformed in form of plates. With successive collisions, copper hardens and the plates are fragmented. Continuous cold welding, tungsten incorporation into the copper phase and fragmentation decreases the mean particles size up to an equilibrium is reached between the opposite mechanisms of fragmentation and agglomeration by welding. Nevertheless, the dispersion of the phases is always improved.

Fig. 2 shows a sequence of images of the powder during milling. It is possible to observe the evolution of the powder. Fig. 2a shows the mechanically mixed powder. This powder was simply hand mixed for 5 minutes. The coarse Cu particles are easily discernible. They keep the original shape and size. These particles are surrounded by the finer tungsten particles. The differences of size, density and flowability favor segregation of the phases. Fig. 2b shows the powder after 2 hours milling. Very coarse and plate like particles are seen. Around them there are few small particles, indicating that most of the tungsten particles were incorporated to the copper particles. One can expect that all tungsten is incorporated in copper short after 2 hours of milling.

Fig. 2c exhibits the image of the powder after milling for 50 hours. The particles are large and equiaxed. This shape is result of successive collisions in several directions and cold welding. After 100 hours of milling the particles are much finer, as shown in Fig 2d. This is consequence of the fragmentation of the large composite particles due to the hardening of the copper matrix.

In the composite particles tungsten and copper are intimately dispersed and in direct contact. In the mixed powder, on the other hand, bas dispersion and segregation are expected.

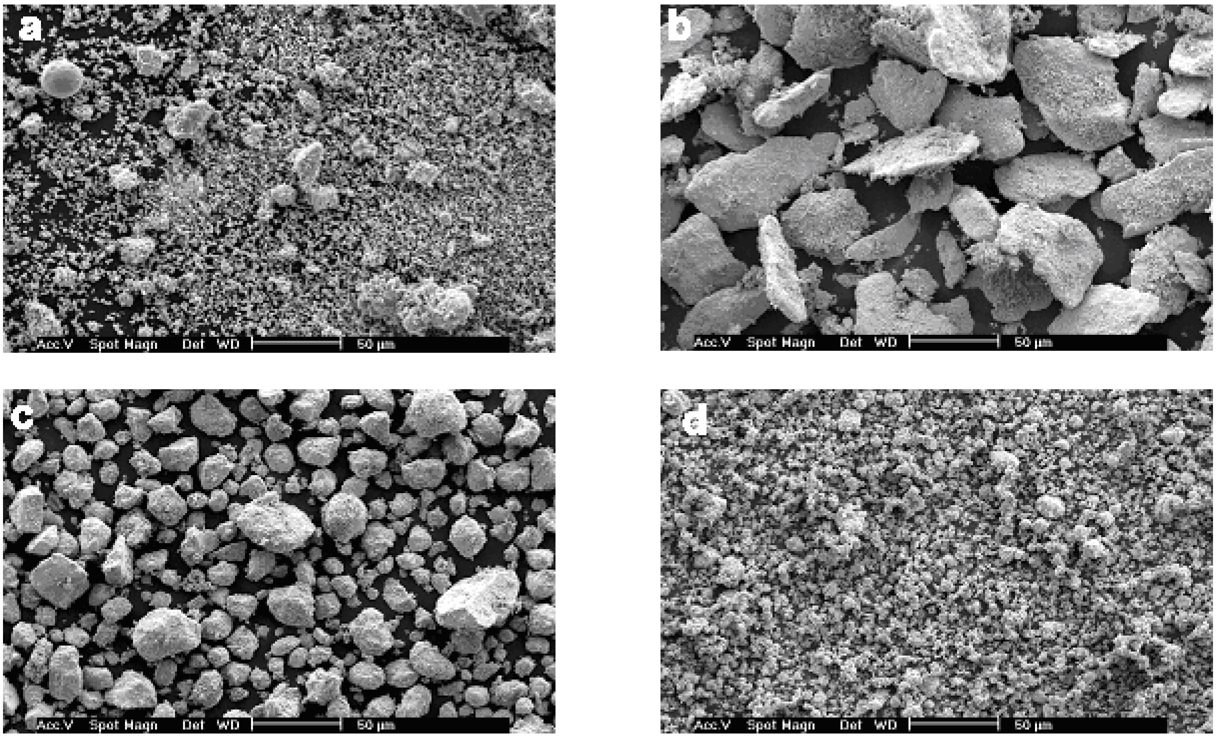

Figure 2: SEM micrographs of W-25w%Cu prepared by mechanical mixture (a) and high energy milling for 2 (b), 50 (c) and 100 (d) hours.

The wear produced by HEM in the parts of the mill is an important factor to consider because impurities are introduced into the powders. The wear parts of the mill are made of hard metal (WC and CO). WC does not affect both sintering and the structure of the material, if introduced in small amounts as contaminant. Co influences both the structure and sintering. It can activate sintering in proportions as low as 1w% and promotes intensive grain coarsening of the W grains. Fig. 3 exhibits an EDX spectrum of the powder milled for 100 hours. Co is not detected. Thus a possible contamination by Co during milling is not significant.

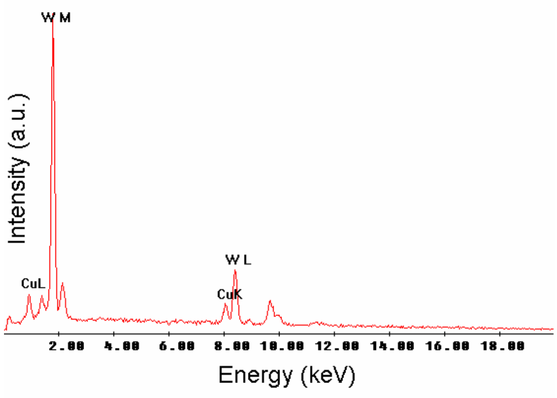

Figure 3: EDX spectrum of the composite W-25w%Cu after 100 hours of milling.

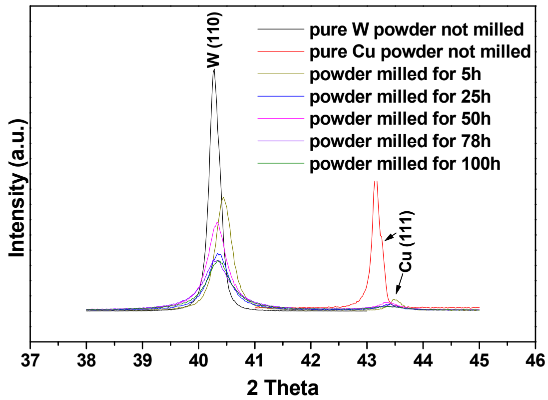

Figure 4: Diffraction peaks of tungsten (110) and copper (111) of powders milled for different times and the hand mixed powder.

HEM can also affect the crystal lattice of the milled material. Fig. 4 exhibits the (110) and (111) diffraction peaks of the hand mixed and milled powders for several times. Three effects are observed: intensity decrease, peak broadening and peak displacement. The broadening of the peaks is related to both grain fragmentation and lattice distortion. Both of these factors contribute to reduce the crystallite size of the milled powders. The decrease of intensity and peak displacement are related to distortion of the crystal lattice caused by milling. Although distorted, the structure of neither phases become amorphous.

Fig. 5 exhibits SEM micrographs of the powder mechanically mixed sintered at 1200°C for 1 hour. The structure is very heterogeneous. Large and numerous pores and lakes of copper are seen in a matrix of fine tungsten grains embedded in copper. This is a typical structure obtained with sintering of conventional powders. The bad dispersed together with the coarse used Cu powder results in local concentration of tungsten and copper. The large pores are formed by the infiltration of liquid copper into the small interstices between tungsten particles. Some pores have still the shape of the large copper particles. The infiltrated copper does not return to refill the left pores and the capillary pressure is not strong enough to shrink these pores. The copper lakes are formed by the non-infiltrated liquid copper. This structure has only 65% of relative density.

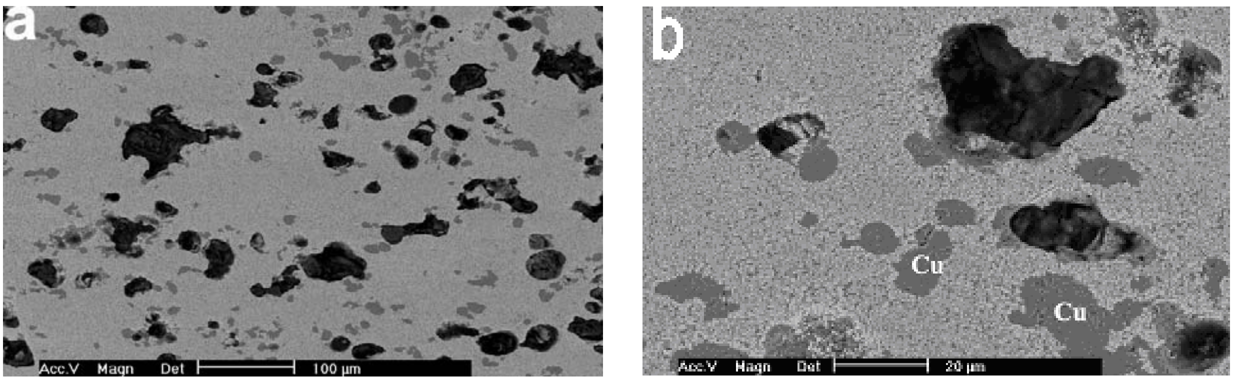

Figure 5: SEM of the alloy W-25w%Cu prepared with mixed powder and sintered at 1200ºC for 1 hour. A view of the structure (a) and details of the pores and Cu lakes (b).

The sintered structure of the sample prepared with composite powder is quite different. It is shown in Fig. 6. Neither large pores nor Cu lakes are seen. The composite powder resulted in a granulated structure (Fig. 6a). The granules of different sizes are discernible due to the higher concentration of tungsten grains (the brighter phase). The contour of such granules is filled by copper. However, this is a much more homogeneous structure than that produced by sintering the mixed powder. The composite powder is able to sinter in both solid and liquid phases. While in the mixed powder the copper particles are surrounded by tungsten particles and the contact between the copper particles depend on the quality of the dispersion and the composition of the mixture, in the composite powder copper is present in each single particle of the powder as the matrix. Thus the copper matrix of a particle “touches” the copper matrix of the neighbour composite particles. This is of prime importance to sintering under the Cu melting point because at these temperatures only Cu-Cu contacts can form necks and sinter. Thus, solid state sintering is favored by the composite powder. In fact, around 35% of the whole shrinkage suffered by the sample produced with the composite powder during sintering occurred before the Cu melting. A final relative density of 95% was reached by the sintered structure.

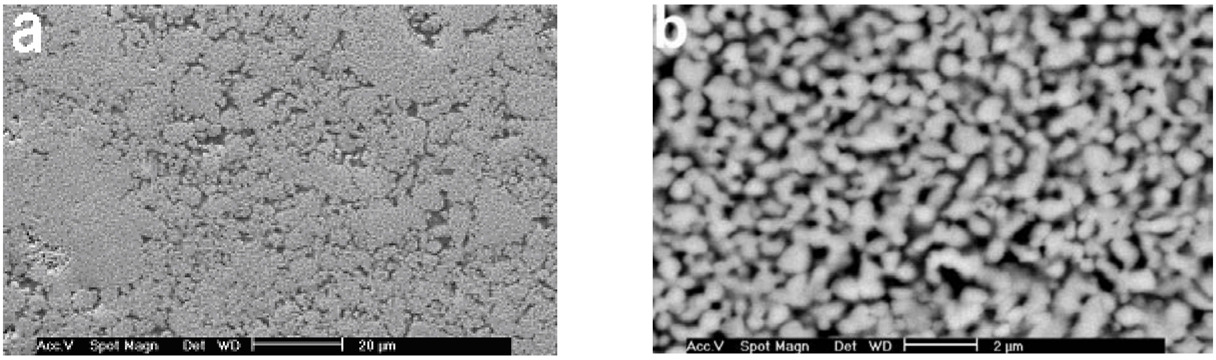

Figure 6: SEM micrographs of the alloy W-25w%Cu sintered at 1200ºC for 1 hours. Granulated dense structure (a) and detail of a granule of the structure showing the fine grains of tungsten in a copper matrix (b).

When copper melts, liquid is formed in all composite particles. The copper necks, which connected the composite particles before melting, become liquid that can flow to fill the remaining pores. The tungsten grains in each composite particle sinter together forming a skeleton. See Fig. 6b. The formation of such a skeleton is facilitated by the insolubility of tungsten in liquid copper and the high dihedral angle between tungsten and the liquid. This skeleton inhibits the rearrangement of the tungsten grains throughout the structure that would produce a homogeneous structure. Each original composite particle is a domain a skeleton. Thus the granules in the sintered structure, shown in Fig. 6a, are constituted of tungsten grains of composite particles that sinter. The interstices between the tungsten grains are filled with copper as well as the interstices between the granules.

The higher density and homogeneity of the structure contribute to elevate the electric conductivity of the material prepared with the composite powder (41 IACS) in comparison to the alloy prepared with the conventional powder (30 IACS).

Conclusions

HEM produces powders with different characteristics of those produced by mechanical mixture. The powder produced by this technique has composite particles. In these particles, small tungsten particles are embedded in a copper matrix. The fineness of the tungsten particles and the better dispersion improve sintering and homogenization. The sintering structures are consequently denser and more homogeneous. Higher electric conductivities are attained by this structure.

Acknowledgement

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