

Solid state sintering of a W–25 wt% Ag powder prepared by high energy milling

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Abstract

A composite W–25 wt% Ag powder was prepared by high energy milling (HEM). The mean particle size is 4.7 μm , although agglomerates of composite particles around 50 μm can be found. Neither phases were amorphized under the used milling conditions. Samples prepared with the composite powder and with a mixed powder were sintered in solid phase under the same conditions. The composite powder exhibited much higher sinterability, reaching 80% of relative density against 60% of the mixed powder. The composite powder also produces sintered structures with higher homogeneity. The high sinterability in solid phase of the composite powder is based on the sintering of a Ag layer that is formed on the surface of the composite particles by diffusion of Ag from the bulk. The layers build necks that sinter the structure.

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1. Introduction

The W–Ag pseudo-alloys are metal–metal composites used as electric contacts in circuit breakers [1–4]. Its properties are a combination of the high welding and erosion resistance to arcing of W and high thermal and electric conductivity, and good workability of Ag [5]. Furthermore, the composite's thermal expansion coefficient can be adjusted by changing its composition to match those of ceramic materials used as substrates in semiconductor devices. In these cases, the W–Ag composite may be used in heat sinks and microwave absorbers in microelectronic devices.

Powder metallurgy is the technique utilized to manufacture this material, but due to the mutual insolubility of W

and Ag [4] and to the poor wettability of liquid Ag on W (contact angle in the 20–30° range [6]), sintering cannot easily produce dense and homogeneous structures. Sintering of mixed or milled powders with the same characteristics as those of W and Ag (as W and Cu) produces porous and heterogeneous structures with local concentrations of both metals [7,8]. Nevertheless, sintering of powders milled under high energy produces structures which are denser and more homogeneous than powders mixed or milled. This is explained by the improved dispersion of the phases and the presence of composite particles that are formed by this kind of milling [9–12].

High energy milling (HEM), also referred to as mechanical alloying, differs from the conventional milling due to the high kinetic energy of the milling media. High kinetic energy can be produced by shaking, vibration and rotation. Some milling equipments are able to meet this condition. As the powder particles are trapped between colliding milling media, the high collision energy is transferred to the

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material, causing severe deformation besides other important effects, as the formation of composite particles. These particles are formed by fragments of the original particles of the harder phase, embedded by a matrix of severely deformed softer phase.

Reports on high energy milling (HEM) and solid state sintering of W–Ag composites are rarely found in the literature. Aslanoglu et al. [13] prepared W–35 wt% Ag electric contacts using high energy milled powders. Pressed bars were solid state sintered and then hot pressed. The authors reported a much higher erosion resistance of this material in comparison to another alloy prepared with mixed powders due to the improved homogeneity of the material prepared with HEM.

This work focuses on the preparation of a composite W–25 wt% Ag powder using HEM and its sintering below the Ag melting temperature. The results are compared to those of a mixed powder sintered under the same condition.

2. Experimental procedure

Elemental W (Wolfram mbH) and Ag (COIMPA Ind. Ltd.) powders with mean particles sizes of 0.78 μm and 10 μm, respectively, as informed by the suppliers, were used. Figs. 1a and b exhibit SEM micrographs of the as supplied powders. The W particles are softly agglomerated but the large Ag particles look like hard agglomerates of fine primary particles.

The elemental powders were placed in a proportion of W–25 wt% Ag in hard metal lined vial, together with 150 g of hard metal balls with diameter of 6 mm. The pow-

der to ball weight ratio is 1:3. The powders were dry milled under room atmosphere for 110 h in a planetary Fritsch Pulverisette 7 model, at a velocity set at 5 in a range from 0 to 10. This milling time was selected based in a previous study [14]. This milling time produces composite particles with good dispersion of the Ag and W. No process control agent was added. In dry milling the powders tend to stick to vial's wall, forming agglomerates. At each two hours, milling was interrupted, the powder stuck to the wall was removed, the powder was de-agglomerated and the milling operation restarted. After milling, the mean particle size was determined by laser scattering. SEM was used to observe the milled powder. XRF was used to detect any contamination during milling. XRD was used to determine the crystallite size of the phases by means of the Scherrer's equation [15].

Another powder of the same composition was prepared for comparison. This powder was just mechanically mixed for 2 h.

Both powders were pressed in single action dye at 210 MPa to produce cylindrical pieces of diameter 9.7 mm and height in 2.0 ± 0.2 mm range. The relative density of the green pieces produced with the mixed and the milled powders are 54 ± 1% and 60 ± 1%, respectively. Four pieces of each powder were measured.

The green pieces were sintered at two temperatures for different times as shows Table 1 in a resistive, tubular furnace under a flowing hydrogen atmosphere. In all experiments a heating rate of 10 °C/min was used.

After sintering, density was measured. Then, the samples were sectioned, mounted and prepared by the standard metallographic technique to be observed under SEM. The sintered density was measured with use of a caliper. The geometrical regularity of the sample minimizes the error. The existence of open porosity in the structure does not allow the use of the Archimedes' method.

During sintering, the structure becomes denser. The volume of the porosity decreases, the pores are isolated from the outer surface and the structure shrinks. The level of sintering can be quantitatively represented by the densification, defined by Eq. (1), independent of the green density,

$$d = \left| \frac{d_s - d_g}{d_t - d_g} \right| 100 \tag{1}$$

In which d_s is the sintered density, d_g is the green density and d_t is the theoretical density.

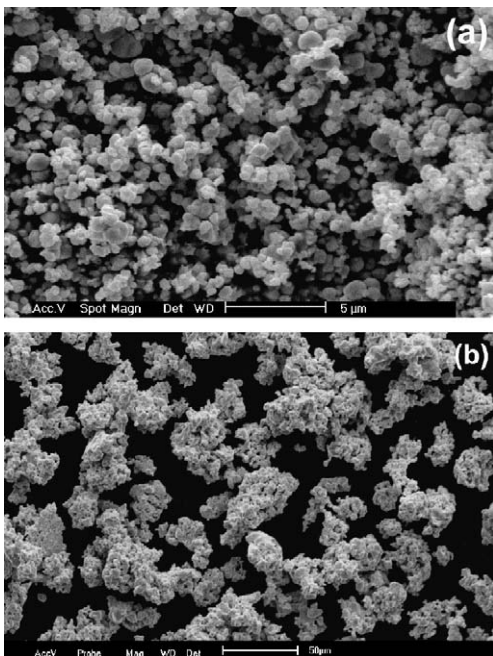


Fig. 1. SEM pictures of the original W (a) and Ag (b) powders.

Table 1

Conditions of sintering for the samples prepared with the mixed and composite powders

Powders used to prepare the samples	Sintering temperature (°C)	Dwelling sintering time (isotherm)
Mixed and milled	900	5
Mixed and milled	950	5
		120
		300

3. Results and discussion

Figs. 2a and b exhibit SEM micrographs of the mixed and the milled powders. As it can be seen (Fig. 2a), the mixed powder consists of particles of Ag and W that still have the original characteristics. Now, small W particles are attracted to the surface of the large Ag particles. The W particles can be seen forming a layer that covers the Ag particles and as loose particles (see in the up right corner of Fig. 2a).

In the HME powder, all particles are composite. The mean particle size of the milled powder is $4.7\ \mu\text{m}$. The micrograph shows that a considerable fraction of the particles is as small as the original W particles and much smaller than the original Ag particles. However, there are also particles as large as $50\ \mu\text{m}$. The large particles are not of Ag. They are agglomerates of smaller composite particles. These agglomerates are formed as the particles stick to the wall of the milling vial. Wet milling could minimize the presence of such agglomerates. The as milled powder was used without separation of the coarser particles.

During milling, the large Ag particles were fragmented. The literature [8,11] describes well HEM of mixtures of hard (as W) and soft (as Ag) phases. The soft phase is deformed by the collisions. The harder phase can be both deformed and fragmented, depending on its ductility. The harder particles are pierced in the softer ones. The latter are transformed into lamellae that cold weld, forming layered plates. The soft phase gradually strain hardens and fractures. This is the mechanism that fragments the large Ag particles.

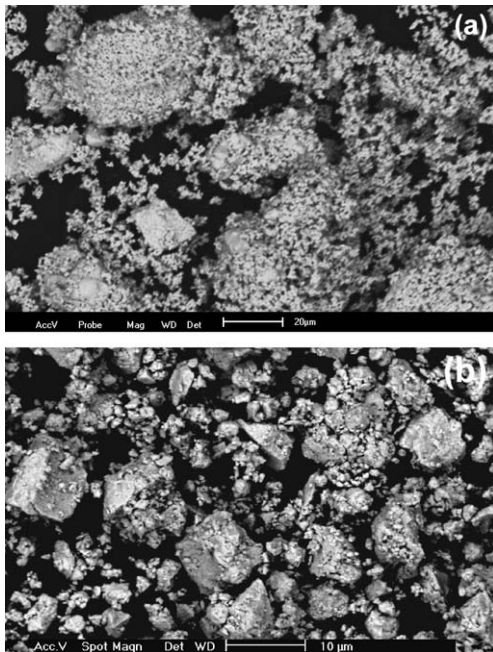


Fig. 2. SEM pictures of the mixed powder (a) and the composite powder after HEM for 110 h (b).

Fig. 3a shows the XRD pattern of the powder milled for 110 h. The peaks of W and Ag can be clearly seen in the pattern of the milled powder. Although HEM can cause amorphization, neither phases were amorphized here [11]. The literature reports amorphization of Ta and Cu after 50 h of HEM [16,17]. On the other hand, Costa [8] did not report amorphization neither of W nor Cu in HEM of W–Cu powders for 51 h. In this work W and Ag remain crystalline after 110 h of milling. Nevertheless, the intensity of the peaks significantly decreases while they become wider. Additionally, a peak shift for higher angles is observed for W and Ag, as shown in Fig. 3b. Costa [8] reported a peak shift for Cu but not for W.

Stacking faults can cause peak shifts. Cu and Ag are fcc metals. Stacking faults are common for this group of metals. W is a bcc metal. Stacking faults are not comparatively common for this group, but peak shift can also be caused by residual stresses in the crystal lattice [18], as that introduced by the severe milling process.

The apparently diverging results reported in the literature about amorphization can be explained by the milling conditions. The same mill and milling velocity was used in the present work and in the works [8,16]. However, in [8] the powder to ball weight ratio was 1:2.5 and the milling was in liquid. In [16], in which amorphization was verified, milling was in dry and the powder to ball weight ratio was

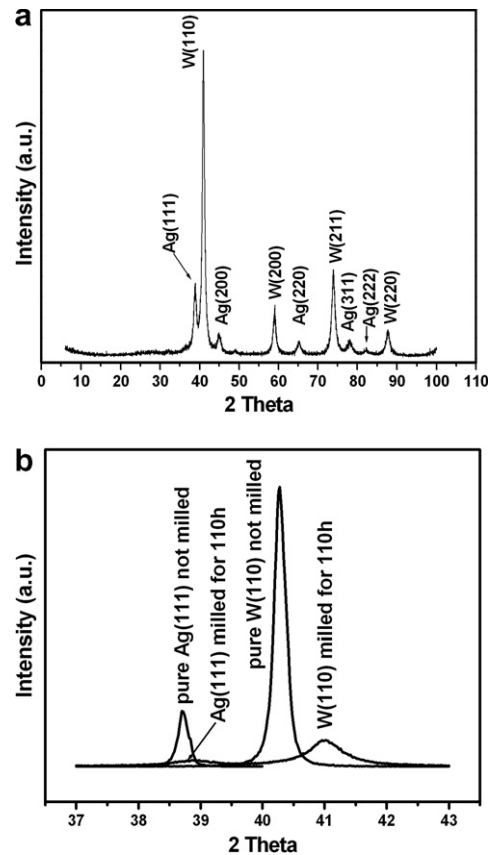


Fig. 3. XRD of the milled powder (a). Peak shift of the Ag and W peaks due to milling (b).

1:5. Therefore, the milling conditions used in this work and in [8] were milder than in [16]. This suggests that amorphization of W and Ag could be achieved by using heavier milling condition.

The coherent crystallite sizes determined by the equation of Scherrer for both were 13.1 nm and 8.4 nm, respectively, for W and Ag.

X-ray fluorescence has measured 0.05 wt% of Co in the milled powder. This indicates contamination by Co during milling due to the wear of the milling parts (vial and balls). Heavier milling condition would increase contamination. This level of contamination cannot influence sintering. However, if present in higher levels, Co can activate the sintering of the W particles [19].

Figs. 4a and b show diagrams of relative density versus sintering temperature and sintering time for powders mixed and milled. Densification at each sintering condition is also informed into parenthesis.

It is significant the difference in densification between the samples prepared with mixed and milled powders. In spite of the lower green density of the sample prepared with the mixed powder, this sample was much less sintered than that prepared with the milled powder. While the sample of the milled powder densified 31% at 900 °C, increasing to 42% at 950 °C, which represents almost half of the whole

densification, the sample of the mixed powder densified less than 5% at 950 °C.

Few below the Ag melting temperature (962 °C), therefore in the stage of solid state sintering, the sample made of the milled powder reached 77% of relative sintering density. This result shows how HEM can influence the sinterability of a system intrinsically difficult to sinter.

HEM is able to disperse phases much better than mechanical mixture and usual milling (low energy). HEM can also finely particulate the phases. Both factors positively influence sintering. Additionally, HEM forms composite particles. The existence of all phases in each particle favors sintering in both liquid and solid states. In the case of liquid phase sintering, liquid is formed throughout the structure and its diffusion path is shortened. Thus particle rearrangement is faster and more intense and higher homogeneity is attained.

In case of solid state sintering, powders constituted of W–Ag composite particles can sinter more than powders without composite particles (as mixed powders) due to a mechanism of Ag diffusion to the surface of the particles.

The composite particles are a dense arrange of W particles involved by Ag. The green structure is constituted of composite particles. In the 900–950 °C temperature range, Ag can sinter well in solid state, but not W. Furthermore, the W–Ag interface energy is higher than that of the Ag–Ag interface, as suggested by the high contact angle of liquid Ag on tungsten. Below the Ag melting temperature, necks of Ag are formed and grow between contacting composite particles. The higher Ag–W interface energy is the driving force to the diffusion of Ag from inside the composite particles to the surface. A layer of Ag is formed on the surface of the composite particles and contributes to solid phase sintering, since it supplies Ag to the necks and allows more Ag–Ag contacts between composite particles.

Fig. 4b shows the change of the relative sintering density with time for both powders. The green densities are 54% and 60% for the mixed and milled powders respectively. The densification reaches 42% during the heating up period, for the milled powder (composite particles), but it does not increase comparatively after 120 and 300 min. For the mixed powder, densification is comparable in all time intervals investigated (heating up, 0–120 min, 120–300 min). Therefore, there was a significant densification of the W–Ag powder prepared by milling in solid state sintering, in special during heating, in the last period of higher temperatures.

The structure of a sample prepared with the HEM powder sintered at 950 °C for 120 min is shown in Fig. 5. The composite particles are the brighter regions. They are separated by darker layers. They are the Ag layers formed by Ag diffused from the bulk of the composite particles to the surface of them. This sintering mechanism is able to promote high densification. Nevertheless, the composite particles keep their shape and size.

The structure of the samples sintered at 950 °C is still very porous, but it is denser than the structure of the

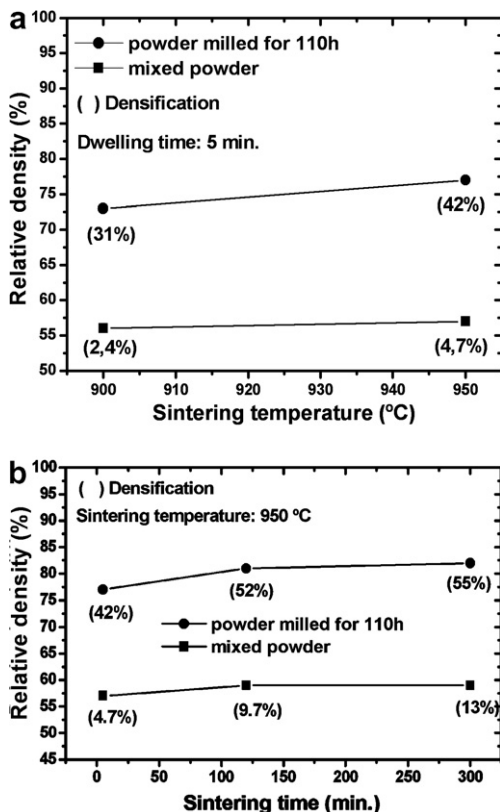


Fig. 4. Relative density and densification of the samples prepared with the mixed and with the composite powders against sintering temperature (a) and time (b).

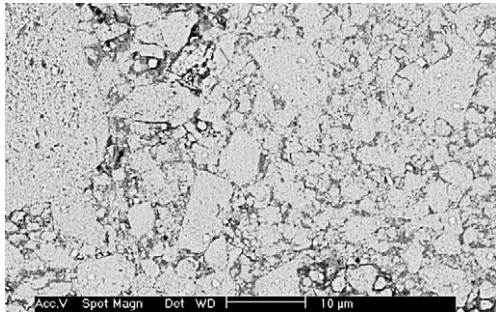


Fig. 5. SEM micrograph of the structure of a sample prepared with the composite powder sintered at 950 °C for 120 min. Ag layer can be seen separating the composite particles that still keep their shape and size.

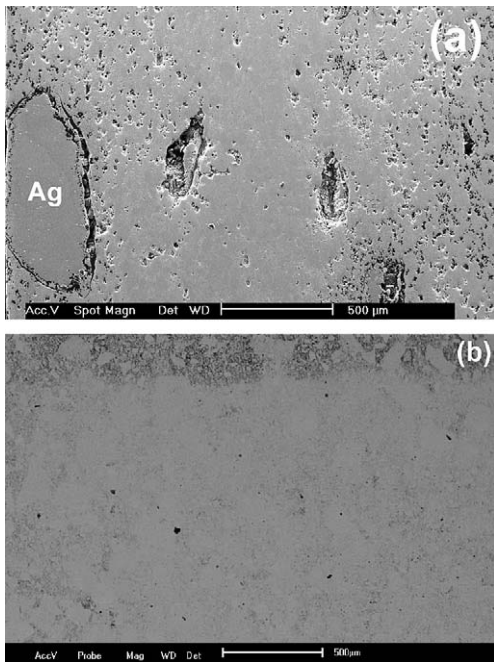


Fig. 6. SEM micrographs of the samples prepared with the mixed powder (a) and the composite powder (b) and sintered at 950 °C for 5 min. Large and small pores and a large Ag pool are seen in the sample prepared with the mixed powder. The structure of the sample prepared with the composite powder is much denser and more homogeneous, but a porous region is seen at the border of the sample.

sample prepared with the mixed powder as shown in Figs. 6a and b. Large and small pores are seen in the structure of the mixed powder together with large Ag pools. On the other hand, the structure prepared with the HEM powder is much denser and homogeneous, although density gradient caused during compaction defects is seen. This is result of the improved sinterability of the composite powder and the superior dispersion of the phases that HEM is able to promote.

4. Conclusions

HEM of W and Ag produced a composite powder whose characteristics are completely different from those

of the original particles. The large Ag particles were fragmented and deformed. The milling conditions were not heavy enough to amorphize Ag and W. The use of higher ball to powder ratio could lead to amorphization. The composite Ag–W powder sintered much more in solid state than a reference powder prepared by mechanical milling. Furthermore, it produced more homogeneous structure without the very large pores and W or Ag local concentrations obtained in the sample prepared with the mixed powder. Nevertheless, a density gradient was observed. The mechanism of solid state sintering of Ag–W particles is based on the sintering of a Ag layer formed on the surface of the composite particles. Necks of Ag link different composite particles and significant densification can be reached before Ag melting. Although the bulk of the composite particles lose Ag, they keep the shape and size.

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