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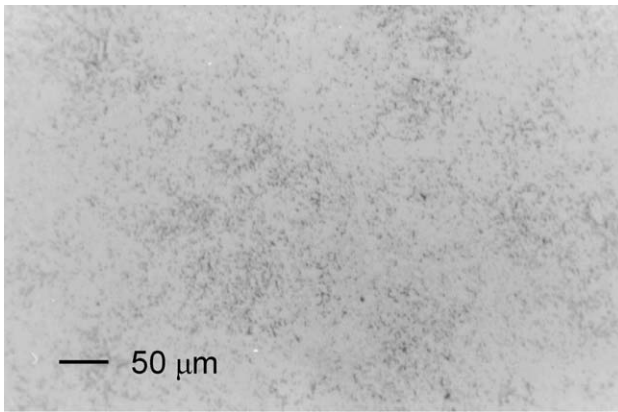


Fig. 21. Structures of alloys C19P sintered at 1170 °C (Fig. 20) and C19P56-f at 1200 °C, both for 1 h. The latter, milled for longer period, is much more dense than the former.

2 h. The other was milled for 56 h. They were milled in the planetary mill and sintered under the same conditions (1200 °C for 60 min). Alloy C19P was prepared with the 2.03 μm tungsten powder and alloy C19P56-f with the 0.54 μm tungsten powder. Fig. 18 shows the curves of the sintering rate for both alloys. The curve of alloy C19P56-f looks like the curve for alloy C47P92 in Fig. 15, which has 47v/o copper. Alloy C19P56-f began to shrink at 745 °C and reached a final relative density of 94%. There is a significant shrinkage in the solid state. Alloy C19P began to shrink just before the melting point and attained a relative density of 68%. Therefore, the low copper content, at least in this composition range, did not negatively influence the sintering of W–Cu composite particles due to the optimal copper dispersion and the fineness of the tungsten phase.

Fig. 19 shows the powder of alloy C19P56-f. Some large composite particles are seen together with much plate-like debris and very fine particles, possibly still free tungsten particles. The sintering of finer composite particles is easier than that of coarse ones. Figs. 20 and 21 show the structure of alloy C19P sintered at 1170 °C for 1 h and C19P56-f sintered at 1200 °C also for 1 h, respectively. Alloy C19P has a porous structure. The large pores are formed when copper particles melt. The liquid flows to the surrounding regions and a large pore appears where the particles were placed [5]. These pores are filled later only if there is liquid in excess. This is not the case for an alloy with only 19v/o copper. Alloy C19P56-f has a denser structure with small isolated pores. Most stains seen in the image are the effect of the chemical etching.

5. Conclusions

The milling of Cu and W powders in rod or planetary mill for long periods produces particles that contain very fine tungsten particles embedded in copper, the composite particles. The formation of such particles is dependent on

the kinetic energy of the milling media and the number of collisions per unit time of the milling media against the particles. The composite particles are formed by the deformation of the copper particles, the continuous insertion of broken tungsten particles into the copper plates and the fragmentation of the plates caused by the work hardening of copper due to the successive collisions. These composite particles can be formed even in Cu-poor powders such as W-19v/oCu.

The sintering of W–Cu composites depends mostly on the copper phase. In the solid state, a network of copper particles sintering together should be formed. In the liquid state, liquid copper must be available throughout the structure. Additionally, the tungsten phase must be as fine as possible. The composite particles fulfill all these conditions: copper is contained in each particle and the tungsten particle size is under 0.5 μm due to the fragmentation during milling.

The sintering process begins during the heating, before the melting, with the sintering of the composite particles. The necks linking these particles are built by copper that diffuses from the bulk, and a copper enrichment of the surface occurs. In consequence of the copper diffusion, the tungsten grains in the bulk come closer to each other and grow due to sintering and coalescence. When the liquid is formed, it flows, fills the remaining pores and rearranges the tungsten grains. The structure becomes denser and more homogeneous. The granulation of alloys prepared with composite particles is much finer than that prepared with conventional W–Cu powder mixtures. The large pores observed in alloys prepared with conventional W–Cu powders are not seen when copper melts because the copper phase is distributed throughout the structure in each composite particle and not localized as in the conventional powders.

Relative densities in the range 94–98% are obtained if powders consisting of composite particles are used, regardless the sintering time, the copper content, at least up to 19% in volume of copper and the sintering temperature, if the temperature is above the melting point.

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sintering of alloy C47P92 is shifted to lower temperatures, as compared to that of alloy C40B, so that the densification in solid state is more pronounced than that of alloy C40B. Additionally, when copper melts, the sintering rate decreases. This indicates that the density of the structure is already high and the total volume of remaining pores to be filled by the liquid is low.

Another factor that favors the densification of the powder consisting of composite particles is the size of the tungsten grains. During milling, the original tungsten particles are severely fragmented and become much smaller. Figs. 16 and 17 show the difference in the tungsten grain size of alloys milled in the planetary mill for 2 and 92 h, respectively. The latter is much finer.

The size of the original tungsten particles is about 2 μm . The size of the tungsten grains in alloy C47P2, shown in Fig. 16, seems to be larger. The back scattering electron mode used to photograph the structure does not resolve well the grain boundaries. Thus agglomerates of tungsten grains seem to be large grains. Nevertheless, the growth of the tungsten grains is possible by sintering and coalescence of the tungsten particles.

The milling process is able to fragment the original tungsten particles, so that the mean size of the grains in alloy C47P92 is around 0.5 μm . The grains were probably smaller because a great number of tungsten grains sintering together is seen. The very fine tungsten grains embedded in copper in the composite particles should have a great tendency to grow by sintering and coalescence due to the high Cu–W interface energy in comparison to the energy of the W–W interface. Contamination by cobalt during milling did not occur. An EDS analysis did not detect this element and the tungsten grains did not grow as they would grow in the presence of Co.

Table 3 shows that alloy C40M, prepared by mechanical mixture, has the lowest sintered density and a low densification. Alloy C40P, prepared by 2 h of planetary milling densified a little more, but the relative sintered density of

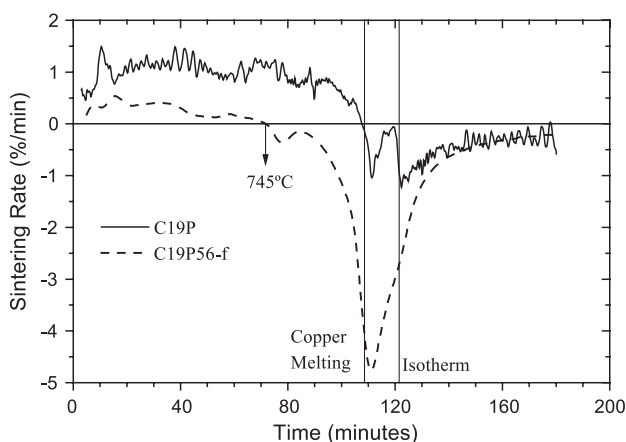


Fig. 18. Sintering rate curves of alloys C19P and C19P56-f sintered at 1200 °C for 1 h.

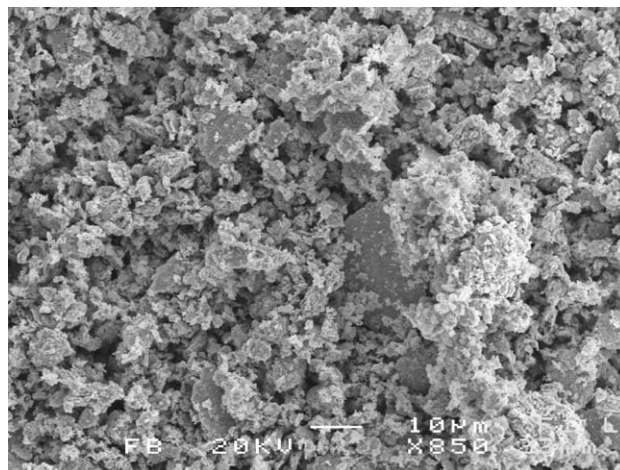


Fig. 19. Powder of alloy C19P56-f after dispersion. Large plate-like particles and fine particles are seen together.

both samples is under 80%. All alloys prepared with powders consisting of composite particles have relative density above 90% and densification above 30%. This is evidence of how high is the sinterability of powders consisting of composite particles.

The sintering temperature seems to have a limited influence on the final relative density, if the temperature is above the melting point. Alloy C47P92 sintered at 1200 °C and at 1300 °C for 1 h reached the same relative density, 98%. Alloys C47P25-f and C47P92-f sintered at 1170 °C for only 5 min also attained high relative densities, 94% and 98%, respectively. Although alloys C47P25-f and C47P92-f were prepared with the originally finer tungsten powder (0.54 μm), they can be directly compared to the alloy made with the coarser tungsten powder because the milling procedure fragments the coarser tungsten powder to a comparable size.

In order to prove how efficient are the composite particles in improving the sintering of W–Cu powders, two additional alloys were prepared, C19P and C19P56-f, with the same composition W-19v/oCu. One was milled for

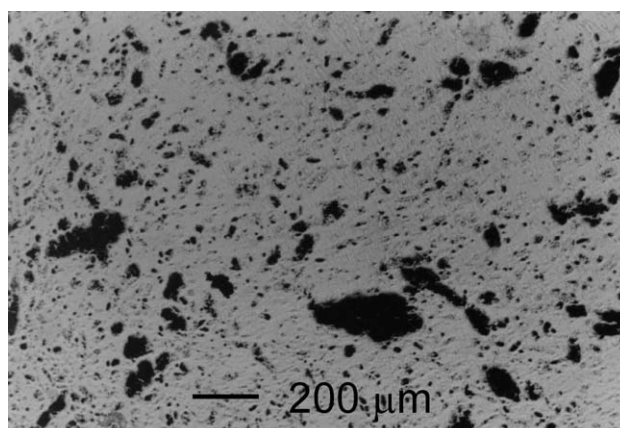


Fig. 20. Structures of alloys C19P sintered at 1170 °C and C19P56-f at 1200 °C (Fig. 21), both for 1 h. The latter, milled for longer period, is much more dense than the former.

plates and the tungsten particles are embedded in these plates. As milling continues, the number of copper plates and embedded tungsten particles increases. Fig. 7 shows a powder whose particles are either plates or small “free” tungsten particles. At this moment, all copper particles were deformed and few tungsten particles were still not inserted into the plates. Successive collisions against the same copper particles cause deformations in several directions and insertion of more tungsten particles. Copper is continuously cold worked and hardens. More collisions break the particles. This is observed when the powder is milled for longer than 25 h, as shown in Fig. 8. No free tungsten particles are seen.

Particles which contain copper and embedded tungsten particles are called W–Cu composite particles. The tungsten particles, which are smaller than the original size, are localized not only on the surface, but also in the bulk of the composite particles.

In the case of rod milling, the milling media have such a high kinetic energy that both copper and tungsten particles become platelet-shaped. However the number of collisions per unit time is not as high as in the planetary mill. Thus the platelets are not heavily cold worked and do not break into smaller pieces. The final result of this rod milling is a powder consisting of W–Cu composite particles in the form of plates. The tungsten particles, also in the form of plates, are embedded on the surface of the copper plates, building a waffle-like structure (Fig. 2).

The high energy milling is able to dissolve, beyond the solubility limit, the materials being milled and to make these materials amorphous [13]. In the present case, both copper and tungsten remain crystalline even after 92 h of intensive planetary milling, considered a high energy milling technique, as seen in the XRD of the powder of alloy C47P92 (Fig. 9). Although copper has been intensively deformed, it retains its crystal form. The solution of some tungsten in copper due to the milling process and vice versa is not probable. Both elements are mutually insoluble (a very low solubility limit) even at temperatures above 1000 °C.

4.2. Effect of the dispersion technique on the sintering behavior

da Silva et al. [5] stated that the copper phase is the main agent responsible for the densification of the W–Cu composite. In order to obtain the highest densification in solid and liquid state sintering, the copper phase should be very fine and well dispersed. Under these conditions, the formation of a network of copper particles sintering together would be easier and favors the densification in solid state. The improved dispersion of copper throughout the structure makes the liquid phase available in the whole structure and favors the densification in liquid state. Additionally, for fine tungsten powders, the particles can be more easily rearranged and the capillary forces are stronger. All methods cited (6–12) that produce W–Cu powders with high sin-

terability are based on well-dispersed Cu and a fine tungsten phase. The only exception is the copper coated tungsten powder that contains coarse tungsten particles.

In the case of composite particles, each particle of the powder contains copper and tungsten. The tungsten particles inside the composite particles are very small and are already embedded by copper. During the sintering of composite particles, the copper phase in each particle sinters together, building up a network. Because copper sinters significantly in the solid phase, it is expected that the structure exhibits an advanced sintering stage before the copper melting point. This is indirectly supported by the sintering rate curve of alloy C47P92, shown in Fig. 15. The structure of this alloy begins to shrink at 635 °C. Alloys C40M and C40P begin to shrink at around 900 °C.

When the composite particles sinter together in solid state, copper necks grow. The copper to build the necks comes from the bulk of the particles. The bulk is dense or fairly dense. The diffusion of copper from the bulk of the particles to build the neck is energetically favorable because the copper–copper interface area increases due to the copper neck growth between the composite particles. When copper diffuses from the bulk to the surface of the composite particles, the distance between the small tungsten particles is decreased. The number of contacting tungsten particles increases and these particles can sinter together, increasing the tungsten–tungsten interface area and the grain size. Thus the total interface energy of the system decreases. The substitution of tungsten–copper interface for copper–copper and tungsten–tungsten interfaces lowers the total interface energy. Kim et al. [12] reported tungsten grain growth and copper enrichment of the surface of the composite particles before the copper melting. The intensity of the solid state densification should depend on the copper content and mainly on the mean size of the composite particles. Depending on the copper flow from the bulk to the different necks, the composite particles could deform, favoring the densification, but the tungsten particles offer resistance to this deformation.

At 1086 °C, copper melts and flows through the structure, filling the remaining pores. The presence of copper in each particle means liquid availability wherever a pore exists. The movement of liquid causes a rearrangement of the tungsten particles and the structure becomes more homogeneous. Kim et al. [12] referred to this movement as the second rearrangement in the sintering of W–Cu composite particles.

The difference between the sintering of a W–Cu powder containing composite particles and a conventionally prepared W–Cu powder is seen in the final density, in the curve of sintering rate and in the structures of the sintered pieces. As shown in Fig. 15, the sintering rate curve of alloy C47P92 is quite similar to that of alloy C40B (Fig. 11), whose powder also consists of composite particles, but in form of plates, and very different of the curves of alloys C40M and C40P, made of conventional powders. But the

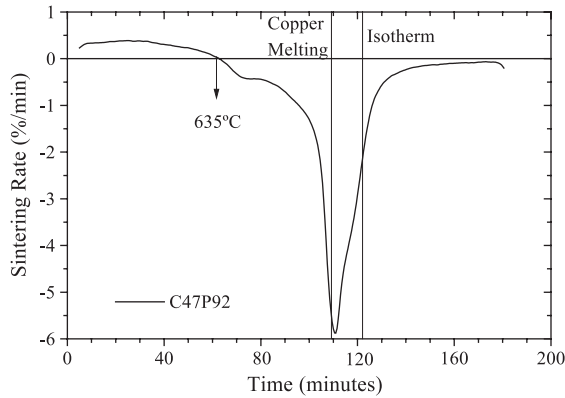


Fig. 15. Sintering rate of alloy C47P92 sintered at 1200 °C for 1 h.

Figs. 7 and 8 show the powders of alloys C47P25-f and C47P92-f after dispersion and Fig. 9 shows the XRD of the powder of alloy C47P92 after dispersion. The shape of the particles changes significantly between 25 and 92 h of milling. The 25 h milled powder consists of fine plate-like particles and a small number of “free” tungsten particles (Fig. 7). Neither the plates nor free tungsten particles are seen in the 92-h milled powder (Fig. 8).

Figs. 10 and 11 show the sintering parameter and the sintering rate for alloys C40M, C40B and C40P. Figs. 12–14 show the structures of these alloys after sintering at 1160 °C for 1 h. Even after 60 min at 1200 °C, alloy C40M did not shrink. Alloy C40P shrank a little. The curves of sintering rate for both alloys are quite similar. Nevertheless, alloy C40B suffered significant shrinkage and its sintering rate is the highest. The structure of this alloy is the most dense.

Table 3 shows the green and sintered densities of the alloys. The densification is also given as the difference between sintered and green densities.

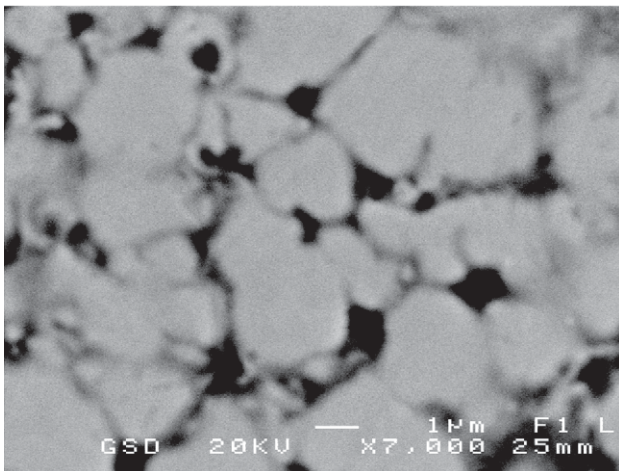


Fig. 16. Tungsten grains of alloy C47P2 sintered at 1200 °C for 1 h. The long milling period reduced significantly the size of the tungsten particles.

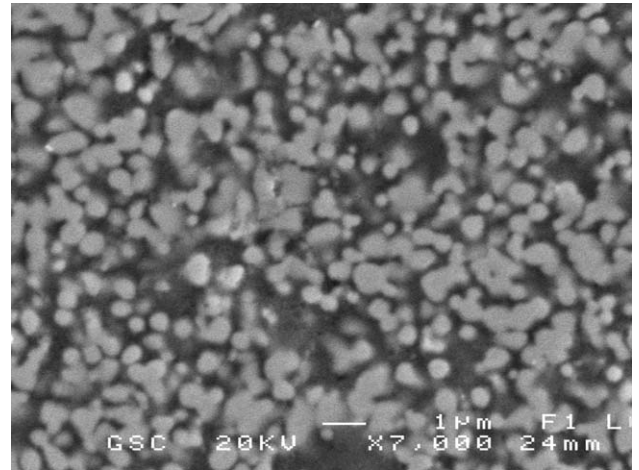


Fig. 17. Tungsten grains of alloy C47P92 sintered at 1200 °C for 1 h. The long milling period reduced significantly the size of the tungsten particles.

Fig. 15 shows the sintering rate curve of alloy C47P92 and Figs. 16 and 17 show the tungsten grains of alloys C47P2 and C47P92 after sintering at 1200 °C for 1 h.

4. Discussion

The dispersion technique used to prepare the powders affects the shape and size of the particles, the sintering behavior, the homogeneity of the structure, the sintered density and the size of the tungsten grains.

4.1. Effect of the dispersion technique on the shape of the particles

The mean size of the copper particles is around five times larger than that of the 2.03 μm tungsten particles. When these powders are dispersed by mechanical mixture the shape of the particles does not change regardless of the mixing time. Only the quality of the dispersion is affected by the mixing time.

The milling of the powders involves collisions between the particles and the milling media. When some copper and tungsten particles are trapped between two colliding milling bodies or between a milling body and the wall of the vessel, the copper particles can be deformed easily and the tungsten particles can either deform or break. Additionally, the harder tungsten particles are embedded in the copper particles during the collision. Depending on the kinetic energy of the milling media and on the number of collisions during the whole milling period, the shape of the particles differs for different milling techniques, milling times and milling velocities.

It is possible to accompany the evolution of the shape of the particles in the planetary mill. The movement of the vessel mixes copper and tungsten particles. When copper and tungsten particles hit each other in a collision between the milling media, the copper particles are deformed into

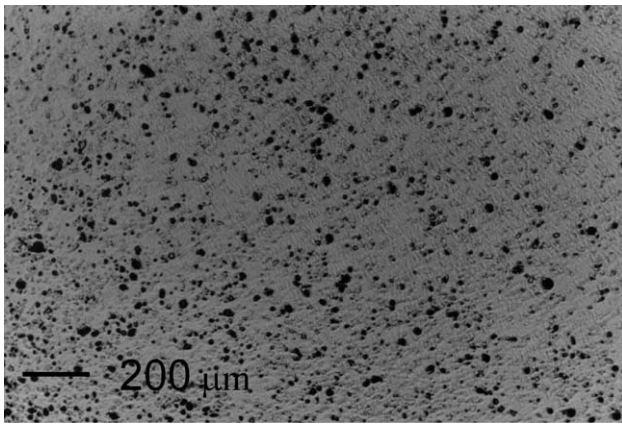


Fig. 12. Structures of alloy C40M sintered at 1160 °C for 1 h. Alloy C40M is the most porous and alloy C40B the least porous.

sintering parameter and the sintering rate, defined by Eqs. (1) and (2), respectively.

$$SP = \frac{L_s - L_0}{L_f - L_0} \times 100 \quad (1)$$

and

$$SR = \frac{d(SP)}{dt} \quad (2)$$

where L_0 and L_f are the initial and final lengths of the sample, respectively, and L_s is the length at a given instant during sintering. Positive values for both the sintering parameter and the sintering rate mean swelling of the structure.

3. Results

Figs. 1–3 show the powders of alloys C40M, C40B and C40P after dispersion. The mixed powders (Fig. 1) have

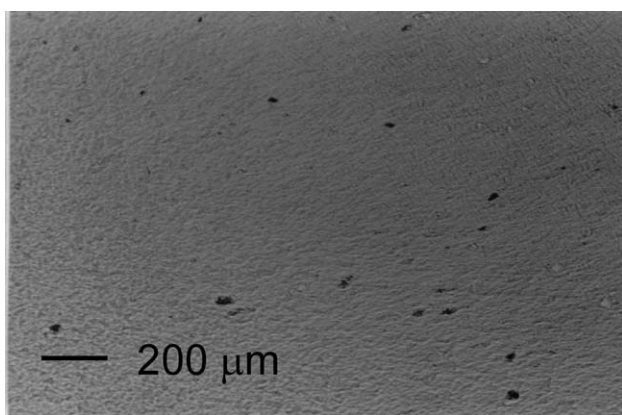


Fig. 13. Structures of alloy C40B sintered at 1160 °C for 1 h. Alloy C40M is the most porous and alloy C40B the least porous.

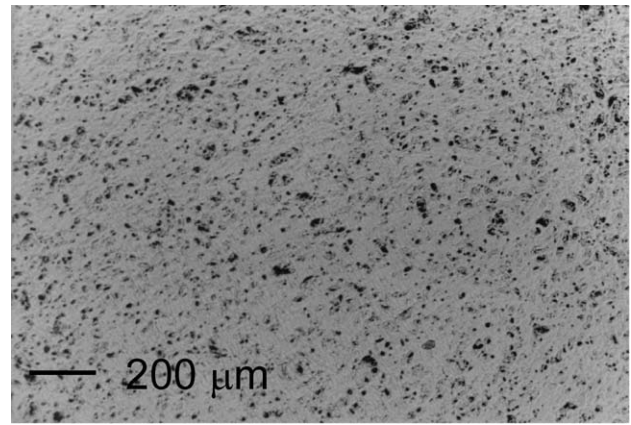


Fig. 14. Structures of alloy C40P sintered at 1160 °C for 1 h. Alloy C40M is the most porous and alloy C40B the least porous.

tungsten particles surrounding coarser copper particles. The original shape of the particles is retained. The copper particles in the powder of alloy C40P (Fig. 3) are deformed and surrounded by tungsten particles. Some tungsten particles are embedded on the surface of the copper particles. The powder of alloy C40B is completely different. The particles are plate-like (Fig. 2). Small tungsten plates are seen covering the large copper plates.

Figs. 4–6 show the powders of alloys C47P1, C47P3 and C47P6 after dispersion. It is possible to see a change of the powder with the milling time. With 1 h milling (Fig. 4), the copper particles are deformed and many tungsten particles are seen around the copper particles. With longer milling times (Figs. 5 and 6), the copper particles are more deformed and the number of tungsten particles around the copper plates decreases (free tungsten particles), because more and more tungsten particles are embedded in the copper plates with the successive collisions.

Table 3

Green density (GD), sintered density (SD), densification and sintering temperature of all alloys

Alloy	Sintering temperature, °C	Relative green density, %	Relative sintered density, %	Densification (SD-GD)
C40M	1200	68	72	4
C40B		64	94	30
C40P		72	78	6
C47P1	1075	81	82	1
C47P2		83	84	1
C47P3		83	85	2
C47P4		81	83	2
C47P5		83	84	1
C47P6		82	84	2
C47P92	1206	65	98	33
C47P92	1300	65	98	33
C47P92-f	1170	65	98	33
C47P25-f		68	95	27
C19P56-f	1200	64	96	32

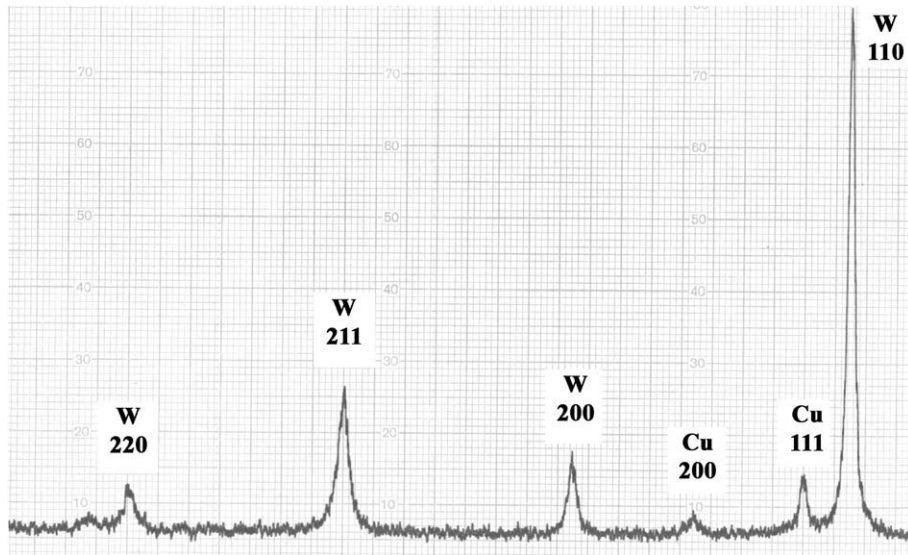


Fig. 9. X-ray diffraction of the powder of alloy C47P92. Tungsten keeps its crystalline structure but copper is highly deformed.

of the planetary mill, the vessel and the spheres used as the milling media were made of hardmetal. The milling velocity was set at 5 in a scale (dimensionless scale) ranging from 1 to 10. In all cases, the powders were wet dispersed using cyclohexane and the powder charge was about 20 g. Table 1 shows the characteristics of the powders used to prepare each composition and the respective dispersion conditions. The composition W-47v/oCu (W-30w/oCu) was used as standard for the planetary milling. Other compositions or sintering conditions not contained in the tables will be eventually mentioned.

After milling, the slurries were dried in a rotavapor and agglomerated. The milled powders were pressed at 220 MPa in a 6-mm diameter, cylindrical, single action die. Sintering was carried out in a dilatometer or in a resistive type furnace. Table 2 shows the sintering temper-

atures of each powder mixture. In all cases the sintering atmosphere was flowing hydrogen and the heating rate 10 °C/min.

After dispersion, the powders were observed under the electron microscope. The particle shape resulting from each dispersion technique and the shape evolution during dispersion were examined. The structures of the samples sintered at different temperatures were also observed under the microscope and the relative density measured. The Archimedes method and the mass/volume ratio (for samples with open porosity) were used to measure the density. Both methods yielded approximate results, unless the samples have deformations and/or pores open to the outer surface.

During sintering in the dilatometer, the size of the sample is measured as a function of the temperature and time. The length of the sample and its rate of change are shown as the

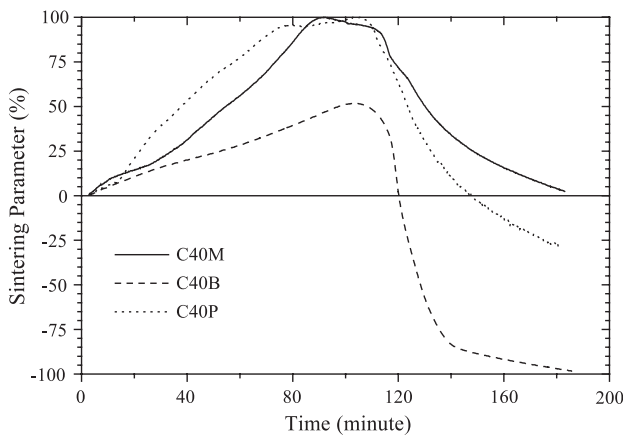


Fig. 10. Sintering parameter of alloys C40M, C40B and C40P.

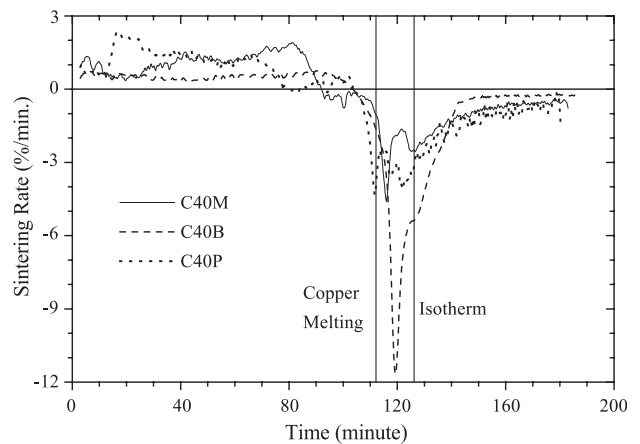


Fig. 11. Sintering rate of alloys C40M, C40B and C40P.

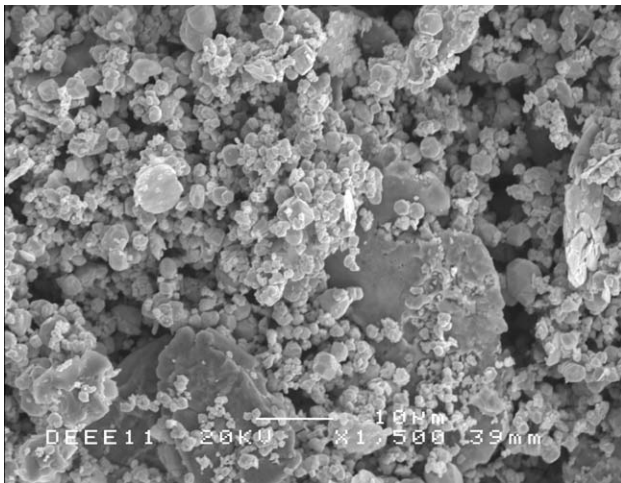


Fig. 3. Powders of alloy C40P after dispersion. Plate-like particles are seen in the powders of alloys C40B and C40P.

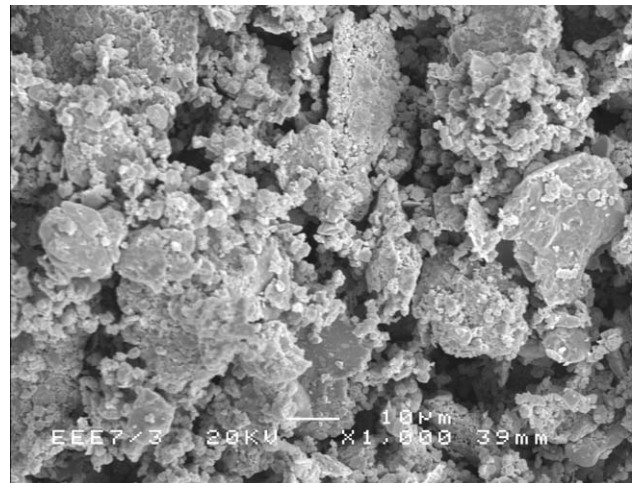


Fig. 6. Powders of alloy C47P6 after dispersion. The particles become plate-like with increasing milling time.

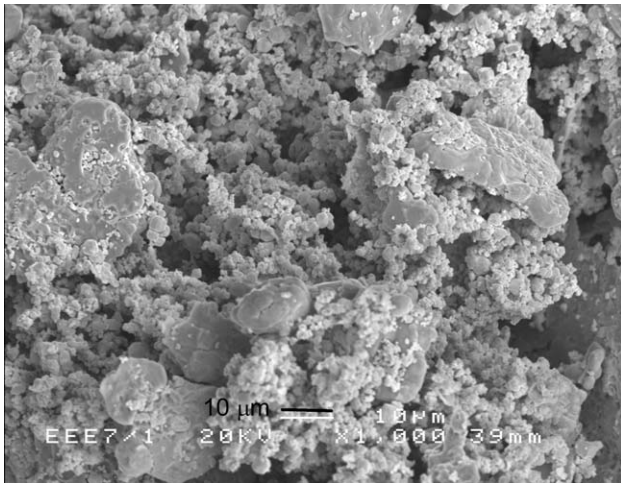


Fig. 4. Powders of alloy C47P1 after dispersion. The particles become plate-like with increasing milling time.

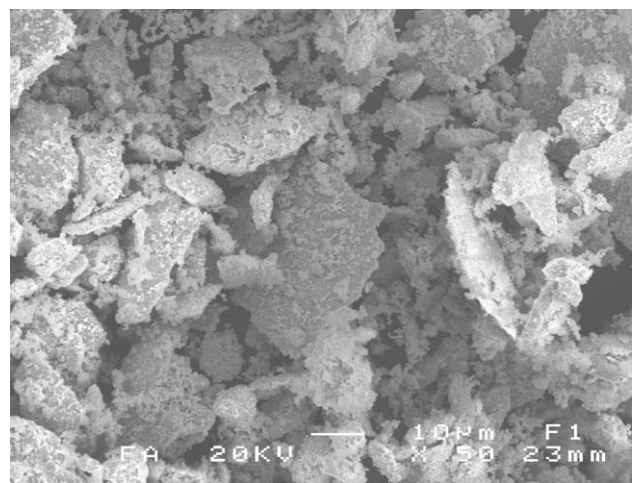


Fig. 7. Powders of alloy C47P25-f after dispersion. The plates formed during milling are broken into smaller particles with more prolonged milling.

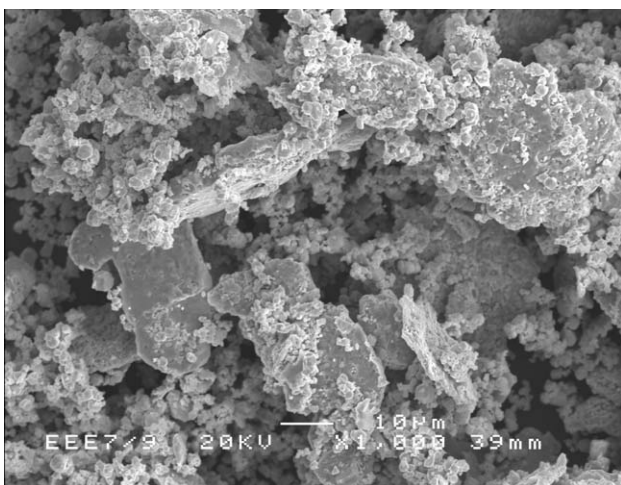


Fig. 5. Powders of alloy C47P3 after dispersion. The particles become plate-like with increasing milling time.

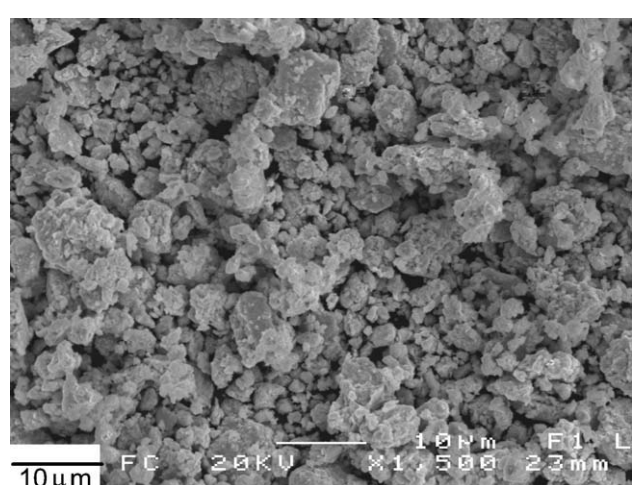


Fig. 8. Powders of alloy C47P92-f after dispersion. The plates formed during milling are broken into smaller particles with more prolonged milling.

Table 1
Alloys and dispersion conditions

Alloy	Copper content (vol.%)	Dispersion technique	Dispersion time (h)	Tungsten powder (μm)	
C40M	40	Mechanical mixture	24	2.03	
C40B		Ball milling	92		
C40P		Planetary milling	2		
C47P1		47			1
C47P2					2
C47P3					3
C47P4			4		
C47P5			5		
C47P6			6		
C47P92			92	0.54	
C47P92-f			92		
C47P25-f			25		

chemical methods which produce coated W particles or nanodispersed W and Cu phases [6]. There are combinations of chemical and mechanical methods which use milling of tungsten and copper oxides to produce a fine dispersion followed by reduction by hydrogen [7,8] or the production of copper tungstate followed by hydrogen reduction [7,9]. There are also purely mechanical methods [10–12]. All these methods produce very finely dispersed mixtures with which fully or near fully dense structures can be obtained after sintering.

This paper investigates the high sinterability of a W–Cu powder prepared by high energy milling and explains this sinterability in terms of dispersion and fineness of the W and Cu phases. The same arguments can be used to explain the high sinterability of powders prepared by other methods, like those mentioned before.

2. Experimental procedure

Two different tungsten powders and a copper powder were used. The copper powder was produced by atomiza-

Table 2
Sintering conditions

Alloy	Sintering temperature in $^{\circ}\text{C}$	
	Dilatometer	Resistive type furnace
C40M	1200	900, 1000, 1085, 1160
C40B	1200	
C40P	1200	
C47P1	–	1076
C47P2		
C47P3		
C47P4		
C47P5		
C47P6		
C47P92	1206, 1300	–
C47P92-f	1170	1170 (5 min)
C47P25-f	–	1170 (5 min)

The holding time is 60 min at the temperature for all alloys, except those whose sintering time in round brackets.

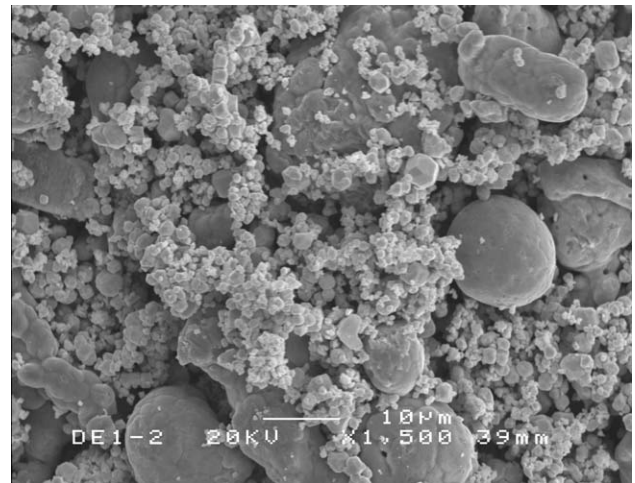


Fig. 1. Powders of alloy C40M after dispersion. Plate-like particles are seen in the powders of alloys C40B and C40P.

tion. Its particles are rounded or have a very irregular shape. According to an estimation with a SEM image, the size of the Cu particles ranges between 4 and 30 μm . The mean size is around 10 μm . The tungsten powders were supplied by the WBH Austria. The mean particle sizes of the Cu and W powders were respectively 0.54 and 2.03 μm , measured by the laser scattering technique.

The copper and tungsten powders were dispersed (milled or mixed) in certain compositions, pressed and sintered. Three dispersion techniques were used: mechanical mixture, rod milling and planetary milling. In the rod milling method, the powder is put in a vessel together with a rod type milling media. Both the milling media and the vessel are made of stainless steel. In the case of the mechanical mixture, the powder is put in the same vessel but without the milling media. In both cases the rotation velocity of the vessel was 210 rpm. In the case

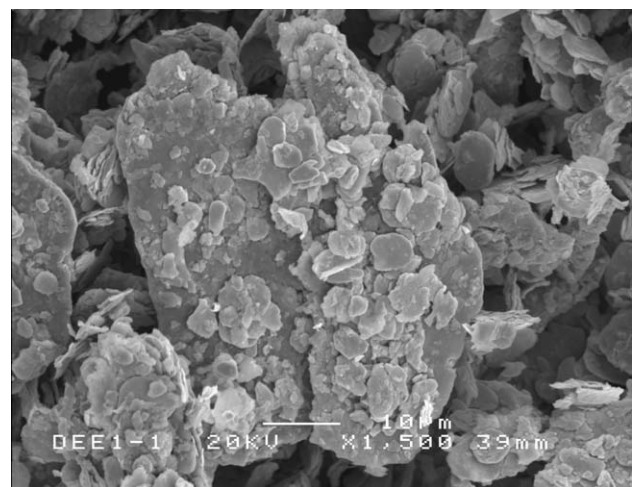


Fig. 2. Powders of alloy C40B after dispersion. Plate-like particles are seen in the powders of alloys C40B and C40P.

The influence of the dispersion technique on the characteristics of the W–Cu powders and on the sintering behavior

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Abstract

The influence of the dispersion technique on the sintering behavior of W–Cu composites is investigated. The dispersion of the copper phase and the fineness of the tungsten phase mostly influence the sinterability of W–Cu powders. By using high energy milling, particles containing very fine tungsten grains embedded in copper, called composite particles, can be produced. A powder consisting of composite particles has an optimal Cu dispersion and a very fine tungsten phase. This kind of powder improves significantly the sinterability of the W–Cu system in solid and in liquid states. Relative densities above 94% can be obtained easily for such powders at temperatures above the Cu melting point and for Cu contents as low as 19% in volume, even for short sintering times. A homogeneous fine structure is obtained. The sintering kinetics of such powders is described.

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1. Introduction

W–Cu composites are used in heavy duty circuit breakers and as heat sinks of microelectronic devices. The reason for this is the high resistance to welding and to arc corrosion, high electrical and thermal conductivity and a thermal expansion coefficient that matches those of the materials frequently used as substrates of semiconductor devices [1]. This composite material is commonly produced by infiltration of a porous sintered tungsten piece by liquid copper. This technique is limited because it produces defects in the structure (pores, copper lakes and tungsten agglomerates) and the properties are sensitive to these defects [1]. Additionally, the pieces must be post-worked to give the right shape to the infiltrated body and to eliminate surface irregularities. The mixing, pressing and sintering route could be a solution to this problem since the structures so produced are more homogeneous and it is possible to obtain net or near net shaped pieces. The use of powder injection molding would be specially interesting to produce complex shapes necessary for the heat sinks [2–4]. However, the structure of the

material must be dense, and the W–Cu system is difficult to sinter due to the mutual insolubility of W and Cu and the high contact angle of liquid copper on tungsten.

Denser structures of this system can be produced by sintering at higher temperatures, by using finer tungsten powder, by using milling instead of just mixing and by using sintering activators, but the gains are not enough to produce fully dense structures without activators and the presence of activators depletes the properties of the material.

da Silva et al. [5] described the sintering kinetics of W–Cu composites, the influence of the copper content and the tungsten particle size on the kinetics. According to the authors, copper plays the most important role in sintering. It is the main agent responsible for the densification both in solid and in liquid states. The existence of a copper network throughout the structure causes significant shrinkage before melting and a better distribution of liquid after melting. The availability of liquid throughout the structure promotes a more intensive particle rearrangement. Additionally, finer tungsten particles are easier to rearrange and the pores between these particles are smaller. This increases the capillary forces.

Several attempts have been successfully made to increase the sinterability of the W–Cu composite material. There are

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