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Chemical synthesis and sintering behaviour of highly dispersed W/Cu composite powders

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The paper reports the preparation of W/Cu composite powders by a wet process based on the reduction of selected copper precursors in ethylene glycol and in the presence of tungsten powders. Reactions were performed in different conditions of temperature, time and concentration of the copper precursor. Two different Cu compounds, $Cu(AcO)_2{\cdot}H_2O$ and CuO (coarse or fine) and two W powders (coarse or fine) were used. The reaction yields ranged from 75% to 98%. Dense bodies (up to 97% fractional density) with highly homogeneous microstructure as well as high electrical conductivity (up to 41% IACS) were obtained by sintering W/Cu powders at 1350 °C.

1. Introduction

Tungsten-base electrical contacts exhibit excellent resistance to mechanical wear and electrical erosion. Therefore, tungsten-copper (W/Cu) composites, which benefit from the high thermal conductivity of copper, have been used for many decades for applications such as current-carrying contacts, vacuum interrupter, arcing tips and electrical discharge machining electrodes. Moreover, W/Cu composites benefit from the low coefficient of thermal expansion of tungsten. For this reason they have been recently used as heat sinks, manufactured by powder metallurgy (PM), for microprocessors, microwave modules, wireless telecommunication devices as well as other power and radio-frequency packages for the microelectronics industry.

Conventionally, full-density W/Cu composites are produced by copper infiltration of tungsten preforms. Infiltration is a two-step process that wicks molten copper into the open pores of a previously sintered tungsten porous structure. Since copper and tungsten are mutually insoluble, alloying does not occur in the conditions (i.e. pressures and temperatures) usually employed in the infiltration process. Following infiltration, the parts are mechanically machined to the final dimensions. Moreover, the infiltration process does not result in an homogeneous microstructure and it is not a net shape process, thus causing high production costs [1]. Further, the range of W/Cu compositions is limited because the amount of copper which may be incorporated in the tungsten skeleton is determined by the porosity of the presintered body [2].

In order to reduce costs and to produce net shape components with homogeneous structure, high density W/Cu parts can be produced by liquid-phase sintering of composite powders characterised by very fine dispersions of both metals [1, 3, 4]. Such composite powders can be obtained by the reduction of copper and tungsten oxides [5, 6]. The first step in this process consists in producing cupric tungstate ($CuWO_4$), *via* solid state reaction of tungsten trioxide (WO_3) or ammonium tungstates (meta, $(NH_4)_6W_{12}O_{39}{\cdot}xH_2O$ with $0.75 \le x \le 1.25$ or para, $(NH_4)_{10}W_{12}O_{41}{\cdot}5H_2O$) and copper oxides (CuO or Cu_2O) or copper hydroxide ($Cu(OH)_2$) [6]. After the formation of the cupric tungstate, powders are reduced in flowing hydrogen at 800 °C to yield a fine W/Cu composite powder. If the stoichiometric ratio of the starting components is employed, only $CuWO_4$ will be formed, leading to a W/Cu composite powder containing 25.7 wt.% Cu. If excess of WO_3 is present in the starting oxide mixture, then metallic powders with lower copper contents can be obtained after the high-temperature reduction step.

More recently, it has been found that W/Cu composites having fractional densities as high as 97% or more can be produced by sintering Cu_2O/W compact in reducing atmosphere at 1050–1250 °C [7].

Main disadvantages of these methodologies are time-consuming milling of the starting powders and/or firing of the solid mixture in H_2 atmosphere at temperature as high as 800 °C. More than a decade ago, Fievet *et al*. developed a simple single step chemical method which allowed to produce finely divided metallic powders [8, 9]. The general synthesis procedure, also known as the *polyol process*, requires either suspending or dissolving a metallic precursor in polyol (or a mixture of polyols); the mixture is then heated at temperatures higher than 85 °C, preferably to reflux.

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The reaction mechanism as described by Fievet *et al.* [9] involves the reduction of the precursors by the liquid organic phase and the subsequent nucleation and growth of metallic particles from the solution.

Synthesis of each metal powder, however, requires different process conditions and in some cases particle coalescence might lead to inhomogeneous powders [10]. The polyol process has been extended to synthesize nanocrystalline metallic powders and films, as well as composite Fe-Cu, Co-Cu and Ni-Cu powders [11, 12].

Recently, some of the Authors successfully developed magnetoresistive sensors in thick film form made up of Ni-Co metallic powders obtained *via* the polyol process [13–16].

In this paper we first report the synthesis of tungsten-copper powders by a wet process where selected Cu(II) precursors, dissolved or suspended in ethylen glycol, are reduced in the presence of W powders. It has been found that, when tungsten actively takes part to the the redox process, composite W/Cu powders can be prepared at temperatures as low as 60 °C and sintered to give parts with fractional densities as high as 97%.

2. Experimental procedure

Cupric acetate monohydrate ($Cu(AcO)_2{\cdot}H_2O$, Carlo Erba RPE) and two cupric oxide (CuO) powders of distinct morphologies were used as copper precursors. The coarse CuO powder (Aldrich, 99.99%) will be indicated in the following as CuO_c and the fine CuO powder (99.9% Kojundo Chemical Lab. Co, Ltd.) as CuO_f.

Corse and fine tungsten powder were selected, the average particle size being respectively 4 μm (Eurotungstene) and 1 μm (H.C. Starck GmbH). In the following, the former will be indicated as W_c and the latter as W_f. SEM micrographs reported in Figs 1 and 2 illustrate the morphology of W and CuO powders, respectively.

The polyol used was 1,2-ethanediol (ethylene glycol, EG, b.p. 196–198 °C, Carlo Erba RPE). In preliminary tests both W_c and W_f were used. In particular, 3 g of W powder and 8.2 mmol of the copper precursor were added to 60 ml of EG. Mixtures were stirred and heated at different temperatures. The concentration of the copper precursor in the starting mixture was 0.13 M. In the case of CuO, the concentration has to be considered as moles of solid CuO suspended in one liter of EG. In this conditions, a final composite powder containing a nominal copper content of 15 wt.% Cu is expected. Reactions were also performed utilising only one component, i.e. W powder or copper precursor.

In order to test the sintering behaviour of fine grained W/Cu powders, larger amounts of composite powders were prepared according to the following procedure. The copper(II) compound was dissolved or suspended in 600 ml EG in presence of 90.0 g of W_f. The mixture was mechanically stirred (250 rpm) and heated at 70 °C for 6 h or at T_b for 2 h. Experimental conditions are reported in Table I. The concentration of the copper precursor in the starting mixture was 0.42 M or 0.59 M, to obtain a final composite powder containing a nominal copper content of 15 or 20 wt.% Cu, respectively. The

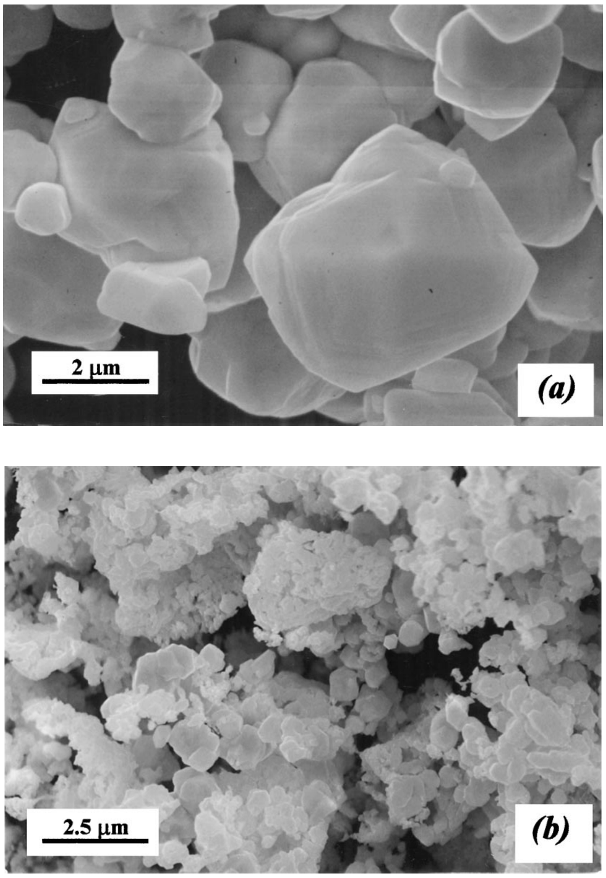

Figure 1 SEM micrographs of tungsten powders (a) coarse (W_c) (b) fine (W_f).

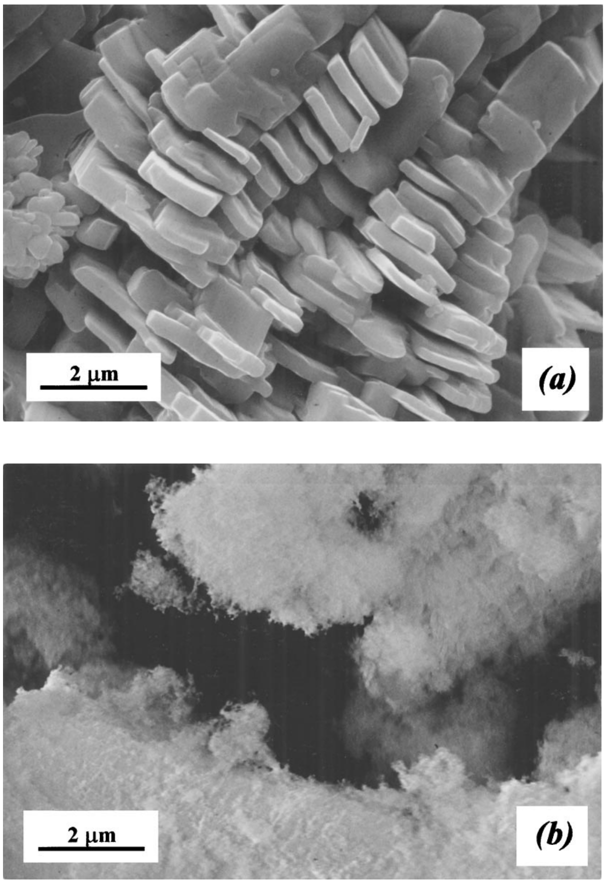

Figure 2 SEM micrographs of copper oxide powders (a) coarse (CuO_c) (b) fine (CuO_f).

TABLE I Reaction conditions selected to prepare W-Cu powders with 15%wt or 20%wt nominal Cu content ([Cu] 0.42 M or 0.59 M, W 90 g, EG 600 ml) for sintering experiments. Reaction yields are reported in parentheses

Precursors	W_f	W/Cu Powder
$Cu(AcO)_2 \cdot H_2O$ (15%wt)	T_b, 2 h (85%)	A15
	70 °C, 6 h (80%)	A15lt
$Cu(AcO)_2 \cdot H_2O$ (15%wt) + $Co(AcO)_2 \cdot 4H_2O$	T_b, 2 h (85%)	A15Co
$Cu(AcO)_2 \cdot H_2O$ (20%wt)	T_b, 2 h (80%)	A20
CuO_c (15% wt)	T_b, 2 h (94%)	B15
CuO_c (15% wt) + $Co(AcO)_2 \cdot 4H_2O$	T_b, 2 h (94%)	B15Co
CuO_c (20% wt)	T_b, 2 h (95%)	B20
$Cu(AcO)_2 \cdot H_2O$* (20% wt)	90°C, 4 h	C20

*Pilot scale process.

concentration of CuO was considered as in the previous case.

In order to check the effectiveness of metallic Co as a sintering additive [2], in some cases a small amount of cobalt(II) acetate tetrahydrate ($Co(AcO)_2 \cdot 4H_2O$, Carlo Erba RPE) was added. The concentration of this precursor was 0.014 M (nominal 0.5 wt.%Co in the final product). Reaction yields ranged from 75 to 98%, depending on the experimental conditions. At the end of the process the composite powder was separated from the liquid phase by sedimentation, washed with acetone, dried in air at room temperature and weighted. The presence of both cupric and tungstate ions in the liquid medium was checked according to the qualitative essays described in ref. [17].

The composite powders were analyzed by X-ray diffraction (XRD, Philips mod. PW 1729), scanning electron microscopy (SEM, Leica Cambridge mod. Stereoscan 360 with LaB_6 source) and energy dispersive spectroscopy (EDS, Link mod. eXL II).

In order to determine the sintering behaviour of the composite powders, 10 g samples were uniaxially pressed in a cylindric dye of 20 mm diameter at loads in the 0.97–2.44 MPa and then heated in hydrogen atmosphere at temperatures ranging from 1200 °C to 1350 °C. The fractional density (ρ_s) of sintered bodies was determined by immersion technique using a Mettler AM 100 balance. The microstructure of sintered parts was observed by SEM, samples being previously etched by Murakami's reagent. The electrical conductivity of the sintered parts, expressed as % IACS [18], was measured by means of a Forster Sigmatest D2.068 instrument. Finally, a large scale experiment was performed using 5 kg of W powder (Eurotungstene, mean particle size 1 μm), 35 l EG (Fluka, RPE) and 2.82 kg of $Cu(AcO)_2 \cdot H_2O$. The mixture was mechanically stirred (120 r/min) and heated at 90 °C for 4 h. The obtained W/Cu (copper content 20 wt.%) powder was then formed (2.44 MPa) and sintered at 1350 °C.

3. Results

3.1. Blanks

Reactions were firstly performed in the presence of a single component, i.e. copper precursor or tungsten powder. When only W powder is present, either W_c or W_f, after 2 h at the boiling temperature (T_b), over 99 wt.% of tungsten was recovered. In the residual liquid organic phase no tungstate ions were detected and the morphology of the W powder was identical to the as-received one. The same result was obtained at low reaction temperature and longer reaction time.

At T_b , all the copper precursors were nearly quantitatively reduced by EG, yields ranging from 94 to 99.6%. On the contrary, no reaction was observed for both the copper(II) compounds at lower reaction temperatures, even for longer reaction times.

3.2. Reaction in the presence of W_c

3.2.1. Copper precursor: $Cu(AcO)_2 \cdot H_2O$

At the boiling point, the complete reduction of the 0.13 M copper(II) acetate occurred within 15 min. The reaction time increased on decreasing the reaction temperature. At 110 °C, the reaction was completed in 70 minutes. The completion of the reduction process was confirmed by the absence of cupric ions in the liquid phase. The weight of the resulting dried powder indicated that reaction yields ranged from 80% to 86%. The XRD spectra of the resulting powders showed only the presence of the metallic W and Cu.

Figures 3 and 4 show the morphology of the composite powders formed after 2 h at the boiling temperature

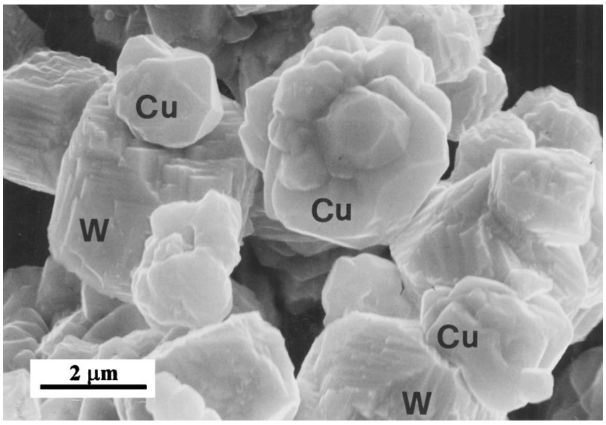

Figure 3 SEM micrograph of the W/Cu composite powder obtained from W_c and $Cu(AcO)_2 \cdot H_2O$ after 2 h at T_b.

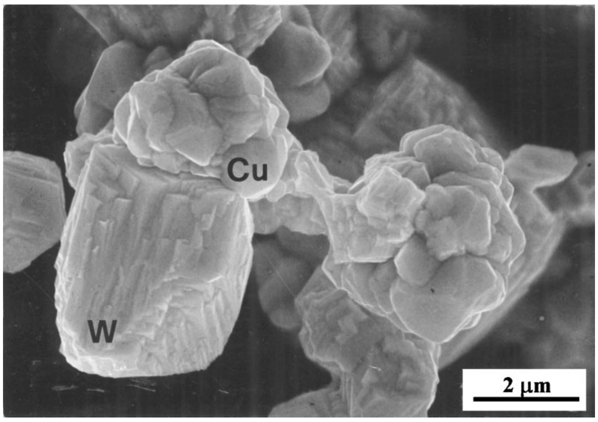

Figure 4 SEM micrograph of the W/Cu composite powder obtained from W_c and $Cu(AcO)_2 \cdot H_2O$ formed after 2 h at 110 °C.

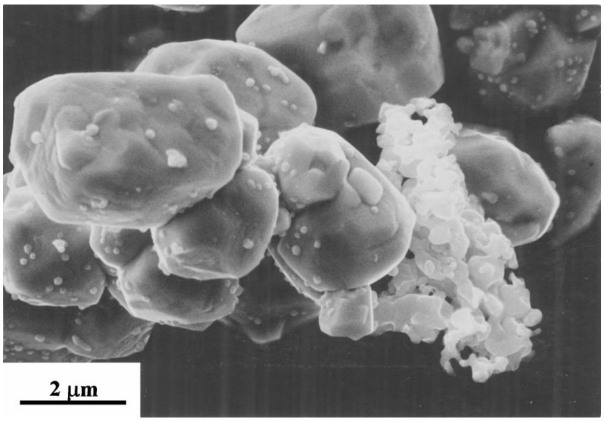

Figure 5 SEM micrograph of the W/Cu composite powder obtained from W_c and CuO_c obtained after 2 h at T_b.

and at 110 °C, respectively. SEM pictures clearly show that surface roughening of W particles occurred and copper aggregates, recognised by spot microanalysis, nucleated and grew at the surface of the W grains. Qualitative essays performed on the supernatant liquid phase put into evidence the presence of tungstate ions, while no Cu^{2+} ions were detected.

3.2.2. Copper precursor: CuO_c

In this case the recovered reaction yield was 98%. The XRD spectrum of the powder obtained in the presence of W_c suspended in EG showed only W and Cu metallic phases.

As shown in Fig. 5, the morphology of the resulting W/Cu composite powder was distinctly different with respect to the previous case. First of all, it is worth nothing that W particles retained their initial morphology and no surface roughening occurred. Moreover, micron size copper aggregates were detected among W particles; few small Cu nuclei were also present at the surface of W particles.

Besides SEM micrographs, the different dispersion of the two metallic phases formed using the two copper precursors can be also argued by considering EDS data. Fig. 6 shows the EDS spectra acquired at low magnification (500×) of the powders shown in Fig. 3 (Fig. 6a) and in Fig. 5 (Fig. 6b). In the spectra, Cu K_α and W $L_{\alpha 1}$ peaks are labelled as Cu and W, respectively.

It is evident that the intensity ratio Cu K_α/W $L_{\alpha 1}$ observed in the case of the powder prepared starting from cupric acetate (Fig. 6a) is more than two times larger than that of the powder synthesized from CuO_c (Fig. 6b).

3.2.3. Copper precursor: CuO_f

The chance of obtaining W/Cu powders without loss of W was very attractive. Thus, in order to prepare a more homogeneous material, the reaction was performed using a CuO powder with much finer particle size (CuO_f, Fig. 2b). The yield of the reaction at T_b was 90%, in between that obtained in the presence of $Cu(AcO)_2 \cdot H_2O$ (86%) and CuO_c (98%); the powder morphology was very similar to that recovered using $Cu(AcO)_2 \cdot H_2O$ as copper precursor.

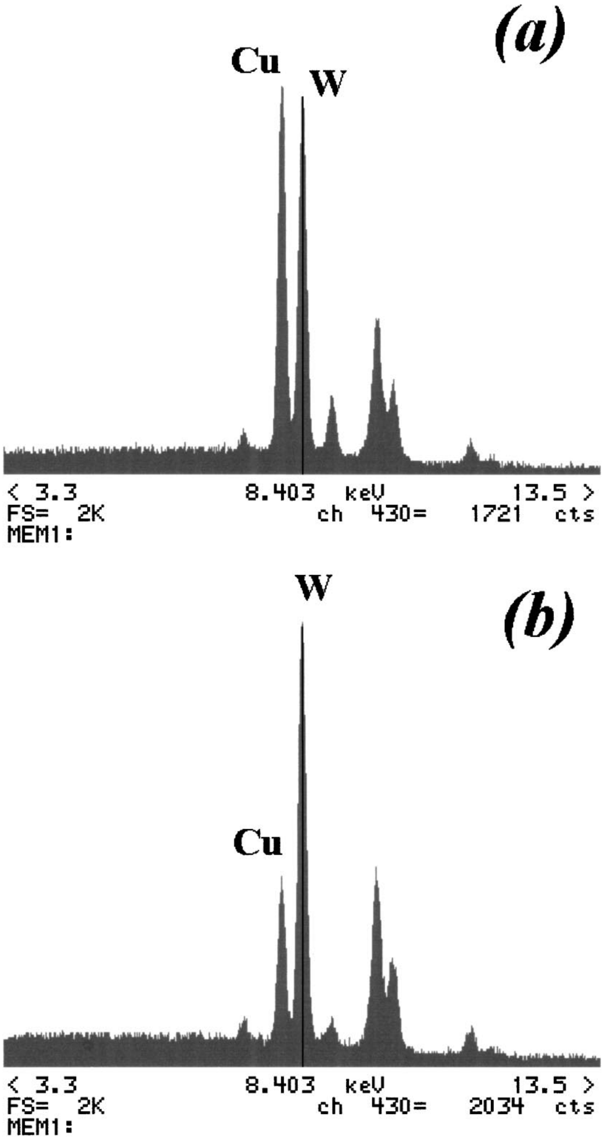

Figure 6 EDS spectra at low magnification (500×) of the powders shown in Fig. 3 (panel a) and in Fig. 5 (panel b).

3.3. Reaction in the presence of W_f

In this case, beside preliminary tests, W/Cu powders were also prepared for sintering experiments (Table I).

3.3.1. Copper precursor: $Cu(AcO)_2 \cdot H_2O$

Composite W/Cu powders have been obtained at 60 °C, 70 °C and boiling temperature after 12, 6 and 2 h, respectively. The yield of the reaction ranged from 75 to 85%. Fig. 7 shows the SEM micrograph of the composite powder prepared at 70 °C (powder A15lt in Table I). The powder was highly homogeneous, and small Cu aggregates, as detected by spot microanalysis, were finely dispersed between W particles. Fig. 8 shows the EDS spectrum of the powder acquired at low magnification (500×). The SEM and EDS characterization of the A15 powder containing the same Cu amount and prepared at boiling temperature did not show any significant difference.

For the sintering tests, W/Cu powders with 20 wt.% nominal Cu content were also prepared (powder A20 in Table I). After 2 h at the boiling temperature (T_b), the yield of the reaction was 80%. The morphology of

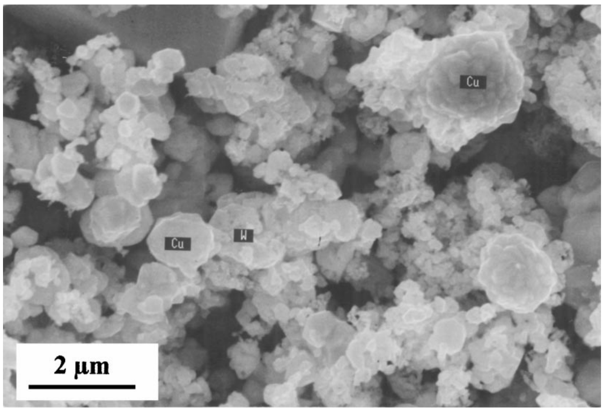

Figure 7 SEM micrograph of the W/Cu composite powder obtained from W_f and $Cu(AcO)_2{\cdot}H_2O$ after 6 h at 70 °C.

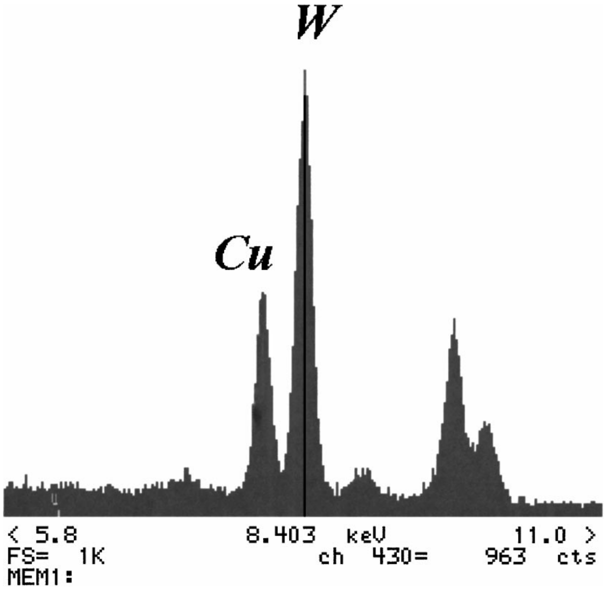

Figure 8 EDS spectrum acquired at low magnification (500×) of the of the W/Cu composite powder obtained from W_f and $Cu(AcO)_2{\cdot}H_2O$ after 6 h at 70 °C.

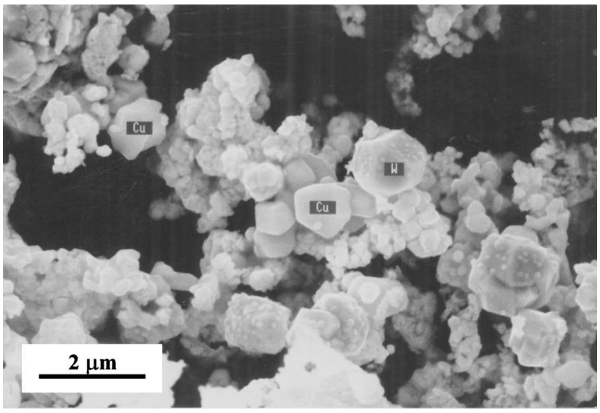

Figure 9 SEM micrograph of the W/Cu composite powder obtained from W_f and CuO_c obtained after 2 h at T_b.

the resulting powder was similar to those observed for the powders with the lower copper content. In all cases, at the end of the process tungstate ions were present in the liquid phase and no cupric ions were detected.

3.3.2. *Copper precursor: CuO_c*

Composite powders prepared using W_f and CuO_c as copper precursor were recovered after 2 h refluxing at the boiling temperature (Table I). The nominal content of the prepared powders was either 15 or 20 wt.%. At the end of the process, the yield of the reaction was 94–95%. Also in this case, the essay for the presence of tungstate ions in the residual liquid phase was positive.

Fig. 9 shows the SEM micrograph of the B15 composite powder (15 wt.% nominal Cu content). Besides W particles, micron size Cu particles were present. B20 (20 wt.% nominal Cu content) powder showed a similar morphology. In order to check the effectiveness of Co as sintering additive, some samples containing 0.5 wt.% Co were synthesized by dissolving the proper amount of cobalt(II) acetate tetrahydrate in EG. The yields of the reaction and the morphologies of the resulting powders were similar to those observed for the Co-free materials (Table I).

4. Discussion

When $Cu(AcO)_2{\cdot}H_2O$ was used as copper precursor, the results of the qualitative essays performed on the residual liquid phase suggest that the complete reduction of cupric ions occurred. Moreover, the presence of tungstate ions in the liquid phase at the end of the process was always detected. Thus, the observed reaction yield lower than 100% was ascribed to the loss of W caused by its oxidation to tungstate ions.

If cupric ions were reduced by metallic tungsten only, a 86% reaction yield should be expected on the basis of the following redox process:

$$3\mathrm{Cu}^{+2}_{\mathrm{solv}} + \mathrm{W_s} + 4\mathrm{H_2O} \rightarrow 3\mathrm{Cu_s} + \mathrm{WO}^{2-}_{4\mathrm{solv}} + 8\mathrm{H}^{+} \quad (1)$$

where Cu^{+2}_{solv} and WO^{2-}_{4solv} are cupric and tungstate ions which are solvated by EG, W_s and Cu_s are solid tungsten and copper, respectively.

It is worth noting that this yield value is quite close to the experimental ones we observed when tungstate ions could be detected at the end of the reaction (Table I). It thus can be hypothesized that copper ions reacted with W (see Equation 1) rather than with the polyol, and that the severe dissolution of W can be attributed to the high activity of cupric ions, due to the complete dissolution of the copper precursor in the organic medium.

The active role of metallic tungsten in the reduction of the cupric ions was also substantiated by the data of low temperature experiments, performed in the absence of W powder. As a matter of fact, cupric acetate was not reduced by the ethylene glycol, and no formation of metallic copper was observed.

In the case of W_c, the etched surface of the W particles visible in Fig. 3 should be ascribed to the reaction 1, which gave rise to suitable sites for the heterogeneous nucleation of the metallic copper.

Due to the partial dissolution of W, the true copper content in the powder was expected to be higher than the nominal one. Therefore, by taking into account the W loss, the copper content in the W/Cu composite powders was expected to be either 18 wt.% or 25 wt.% rather than the 15 or 20 wt% nominal values.

When CuO_c was used as copper precursor, the reaction yield at T_b was in the 95–98%, for both W_c and W_f. Therefore, coarse cupric oxide was quantitatively reduced to metallic copper and the compositions of the recovered W/Cu powders were expected to correspond to the nominal ones, i.e. 15 or 20 wt.% Cu.

Therefore, since CuO is only slightly soluble in the organic medium at T_b, it is reasonable to hypothesize that the inhibition of the W-oxidation process is substantially attributable to the lower electrochemical potential of the oxidating agent. This effect can be due to either the lower activity of cupric ions in the liquid phase or to the formation of different equilibria involving CuO dissolution products.

The reduction of CuO was thus performed by the ethylene glycol only, according to the mechanism described by Fievet *et al*. [8, 9]. Moreover, the SEM characterization of composite powders revealed that coarse tungsten (W_c) particles did not act as seeds for the nucleation of copper. In fact, most of metallic copper was present as isolated aggregates, suggesting that its nucleation occurred in the bulk of the liquid medium rather than at the surface of the tungsten particles.

The much larger Cu K_α/W $L_{\alpha 1}$ ratio observed in the EDS spectrum of W/Cu powder prepared from cupric acetate (Fig. 6a) with respect to CuO (Fig. 6b) can not be ascribed to the slightly larger Cu content of the former powder (18 wt.% instead of 15 wt.%), the effect being attributable to the different dispersion of the two metallic phases within the composite powder. Particularly, when cupric acetate is employed, most of copper nucleates and grows as micrometric particles at the surface of roughened W particles, thus partly covering and surrounding them.

Finally, it results that the reaction yield is slightly lower when W_f is present (Table I). This can be explaneid, reminding that particles as small as few hundreds of nm are present in the as-received tungsten powder. Therefore, small amounts of more reactive, fine-grained tungsten particles might react with the scarcely concentrated cupric ions coming from the partial dissolution of CuO in EG at the boiling temperature.

The overall picture does not change when the Co precursor was added to the reaction mixture. It can be concluded that, in the presence of W powder suspended in EG, the reduction of the copper precursor can be accomplished by two chemical routes, i.e. a redox reaction within the copper-tungsten system and the reduction of the cupric ions by the polyol. The relative importance of the two mechanisms changes with reaction conditions (time and temperature) and with the copper precursor, while the size of the W particles does not appear to play a dominant role in the overall process.

5. Sintering behaviour

Since homogeneous phase distribution of fine-grained W/Cu insures isotropic behaviour of the composite, with respect to both the thermal conductivity and the thermal expansion, it was decided to check the sintering behaviour only of the composite powders prepared with 1 μm W powder. Firstly, air-dried powders were formed in 20 mm diameter disks by applying compaction pressures of 0.97, 1.62, 2.44 or 3.08 MPa. In Table II the results of the sintering tests are reported. The heating rate was 10 °C/min and the hold time at the maximum temperature was 50 min. The electrical conductivities of the sintered parts are also reported. The data in Table II show that W/Cu composite powders synthesized using cupric acetate as copper precursor led to sintered parts with fractional densities higher than 97% and with high electrical conductivities (39–41% IACS). The data also show that the powders are easily compacted, being the fractional density independent of the compaction pressure in the 0.97 ÷ 3.08 MPa range. The use of cobalt as a sintering additive did not allow to increase the density of the sintered part (sample A15Co). On the contrary, the presence of an amount of Co as small as 0.5 wt.% led to a significant reduction of the electrical conductivity.

TABLE II Fractional density (ρ_f), electrical conductivity (σ_e) of W/Cu bodies formed at various compaction pressure (P_c) and sintered at different temperatures (T_s)

Powder	Cu (%wt)	P_c (MPa)	T_s (°C)	ρ_f (%)	σ_e (% IACS)
A15	18	0.97	1350	97.1	41.0
A15	18	1.62	1350	97.0	41.3
A15	18	2.44	1200	89.3	-
A15	18	2.44	1300	96.0	39.1
A15	18	2.44	1350	96.9	40.5
A15	18	3.08	1350	97.0	40.0
A15Co	18	2.44	1350	96.7	25.8
A20	25	2.44	1300	97.4	46.3
A15lt	18	2.44	1350	97.0	38
B15	15	2.44	1350	88.4	34.8
B15Co	15	2.44	1300	96.4	26.5
B20	20	2.44	1350	86.5	36.0
C20	-	2.44	1350	-	40

The increase of copper content in the powders prepared from cupric acetate allowed both to reduce the sintering temperature and to increase the electrical conductivity (A20). Fig. 10 shows the homogeneous microstructure of the dense parts obtained from powder A15, pressed at 2.44 MPa and sintered at 1350 °C.

When CuO_c was used as a copper precursor, densification of the powders did not occur, being the fractional densities lower than 90%. Fig. 11 shows the inhomogeneous microstructure of the sintered part, where the formation of copper pools is evident.

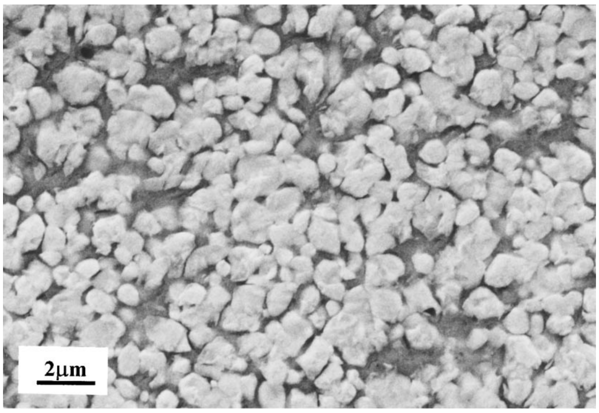

Figure 10 SEM micrograph of the dense W/Cu body obtained from the powder A15, formed at 2.44 MPa and sintered at 1350 °C.

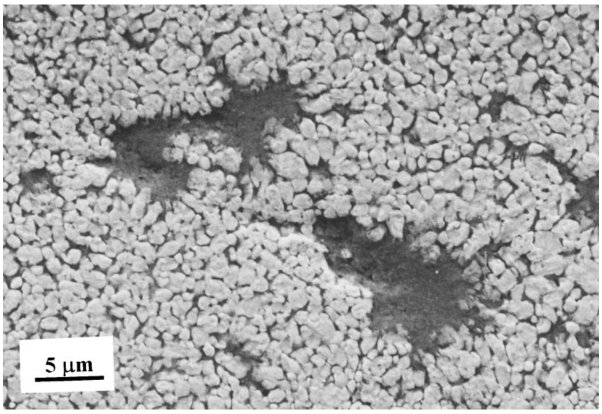

Figure 11 SEM micrograph of the dense W/Cu body obtained from the powder B15, formed at 2.44 MPa and sintered at 1350 °C.

In this case, the presence of Co was successful to achieve sintered parts with densities approaching 96–97% of the theoretical value. The lower electrical conductivity observed for samples A15Co and B15Co with respect to samples A15 and B15 (Table II) can be explained as the effect of alloying between Cu and Co. The different sintering behaviour of the composite powders obtained by reduction of CuO should be attributed to the less homogeneous dispersion of the metallic copper. The data obtained with the 4 μm W powder clearly put into evidence that, when copper(II) acetate oxidize tungsten, nucleation of metallic copper tends to occur preferentially *via* a heterogeneous process at the surface of W particles. This fact guarantees an intimate mixing of both the components which should be expected also when the finer W powder is employed. In contrast, when CuO is used as a precursor, the different nucleation process as well as the agglomeration of copper particles does not ensure a satisfactory dispersion of the two metals. Therefore powders prepared using CuO (B15 and B20) showed a lower densification than powders A15 and A20 synthesised using $Cu(AcO)_2{\cdot}H_2O$ as copper precursor (Table II).

6. Conclusions

Tungsten-copper composite powders have been prepared by reduction of copper(II) compounds in the presence of W powder suspended in ethylene glycol at temperatures as low as 60 °C. When copper(II) acetate is dissolved in the glycol, cupric ions are reduced by metallic tungsten, and the resulting copper particles are highly dispersed in the composite powder. This fact ensures that the W/Cu powder can be directly pressed and sintered at 97% fractional density, giving rise to parts characterized by a highly homogeneous microstructure. When CuO is employed, the W/Cu powders do not undergo a satisfactory densification when pressed and sintered under the same conditions.

These facts indicate how critical the choice of the copper precursor and the dispersion of the two metals are, whereas a powder suitable for powder metallurgy technology must be prepared.

Acknowledgements

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References

1. D. L. HOUCK, L. P. DORFMAN and M. PALIWAL, in Proceedings of the 7th International Tungsten Symposium of the International Tungsten Industry Association, Goslar, Germany, September 1996, p. 390.
2. R. M. GERMAN, “Sintering Theory and Practice” (John Wiley & Sons, New York, 1996).
3. A. K. BASU and F. R. SALE, *J. Mater. Sci.* **13** (1978) 2703.
4. J. S. LEE and T. H. KIM, *NanoStructured Materials* **6** (1995) 691.
5. L. P. DORFMAN, M. J. SCHEITHAUER, D. L. HOUCK and N.E. KOPATZ, U.S. Patent 5 468 457 (1995).
6. *Idem*., U.S. Patent 5 470 549 (1995).
7. D. E. JECH, J. L. SEPULVEDA and A. B. TRAVERSONE, U.S. Patent 5 686 676 (1997).
8. M. FIGLARZ, F. FIEVET and J. P. LAGIER, European Patent 0 113 281 (1987).
9. F. FIEVET, J. P. LAGIER, B. BLIN, B. BEAUDOIN and M. FIGLARZ, *Solid State Ionics* **32/33** (1989) 198.
10. C. DUCAMP-SANGUESA, R. HERRERA-URBINA and M. FIGLARZ, *J. Solid State Chem.* **100** (1992) 272.
11. L. K. KURIHARA, G. M. CHOW and P. E. SCHOEN, *NanoStructured Materials* **5** (1995) 607.
12. *Idem*., *J. Mater. Res.* **10** (1995) 1546.
13. A. BIANCO, G. GUSMANO, R. MONTANARI, G. MONTESPERELLI and E. TRAVERSA, *Materials Letters* **19** (1994) 263.
14. *Idem*., *Thermochimica Acta* **269/270** (1995) 117.
15. B. MORTEN, M. PRUDENZIATI, G. DE CICCO, A. BIANCO, G. MONTESPERELLI and G. GUSMANO, *Meas. Sci. Technol.* **8** (1997) 21.
16. A. BIANCO, G. GUSMANO, G. MONTESPERELLI, M. PRUDENZIATI, B. MORTEN, R. ZANONI and G. RIGHINI, *Thin Solid Films* **359** (2000) 21.
17. A. F. CLIFFORD, “Inorganic Chemistry of Qualitative Analysis” (Prentice-Hall, N.J., 1961).
18. P. LATTARI, J. GARDNER and H. WIEGARD, “Metals Handbook, Vol. 2” (ASM International, USA, 1990) p. 822.

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