

SILVER COATED TUNGSTEN CARBIDE POWDERS FOR COMPOSITES IN ELECTRICAL CONTACT APPLICATIONS

R. Ch. Hula, Ch. Edtmaier

Abstract

Composite materials based on tungsten carbide and silver (WCAg) are well known and widely used electrical contact materials. Most commonly infiltration methods are used for production as they are superior to mixing-pressing-sintering. Nevertheless, infiltrated WCAg shows certain inhomogeneities and more or less porosity. Moreover, the silver content and particle size of tungsten carbide is limited. Therefore new methods were investigated applying electroless deposition techniques. Aqueous solutions containing different complexing agents for silver, such as ammonium hydroxide, benzoic acid and ammonium acetate have been tested. It was found that the use of aqueous suspensions of tungsten carbide in solutions of ammonium hydroxide and ammonium bicarbonate shows the best coverage. The silver coated tungsten carbide powders were consolidated by uniaxial cold pressing and liquid phase sintering. The sintered WCAg had a distinctly higher homogeneity than infiltrated products.

Keywords: *tungsten carbide, silver, electrical contact material, electroless plating*

INTRODUCTION

Composites made of tungsten carbide and silver (WCAg) are widely used as electrical contact materials e.g. for heavy-duty circuit breakers and vacuum contactors [1]. The combination of thermal and electrical high conductive silver with refractory and hard tungsten carbide leads to high arc resistance and exceptionally low chopping currents [2]. The typical properties of such materials are standardized in ASTM B 663-89. The silver fraction is between 38 and 67 wt.%, most commonly around 40 wt.%. Even though silver is more expensive, the replacement by cheaper copper results in higher chopping currents and must therefore be checked carefully [3]. Commercial products are most commonly produced by infiltration of tungsten carbide preforms with liquid silver. Residual pores, tungsten carbide agglomerations and silver accumulation limit the properties of the contact material. Furthermore, the silver fraction and the grain size of tungsten carbide are restricted to certain values.

A new approach is the plating of tungsten carbide with silver by chemical methods (electroless plating) to produce a WCAg powder for subsequent pressing and liquid phase sintering [4]. The expectable advantages of this route might be a higher homogeneity of the products, a widely adjustable silver content and the opportunity to process submicron WC powders. Moreover, silver coated tungsten carbide minimizes the segregation of silver compared to standard powder metallurgical techniques (mixing-pressing-sintering) of elemental powder fractions.

Koura [5] gives an overview of electroless silver plating techniques for different applications. As a result of the required solubility, silver nitrate is nearly the only silver salt suitable for a wide range of applicable concentrations (solubility in water at 20°C: 2160 g/L [6]). Different reducing agents, including glucose [7,8], ascorbic acid [9], Rochelle salt [5], sodium hypophosphite, sodium borohydride, lithium aluminium hydride [8] or borane dimethylamine complex [5,8] have been described for use in silver plating. Due to the high purity required for the use as contact material, reducing agents such as hydrazine or formaldehyde are preferable as they dissipate completely without leaving impurities like boron or phosphorus [10,11]. One must consider that both hydrazine and formaldehyde are stronger reducing agents in alkaline solution. Therefore solutions containing ammonium hydroxide or alkali hydroxides are preferable, in order to maximize yield.

A central issue in electroless plating is to prevent undesired deposition e.g. on the wall of the reaction vessel. Due to the abrasive character of tungsten carbide, silver would be easily removed from the wall forming particles of pure silver in the WCAG powder, and furthermore causing inhomogeneity in the sintered products. Moreover, unwanted deposition makes it difficult to exactly hit the intended silver content of the WCAG composite. Because of that, intense stirring, sufficient dilution and the use of complexing agents is recommended. In the case of silver, the use of ammonium hydroxide is one of the easiest and most suitable methods. The solutions are stable at least for some days due to the formation of diamine silver complex. Nevertheless, such solutions should not be kept in stock, as they tend to form explosive silver azide and silver imide [12]. The addition of ammonium bicarbonate as described in [13] stabilizes the alkaline pH value for complexation and high reduction power of hydrazine.

In addition to ammonium hydroxide, complexing agents like benzoic acid, acetic acid or ethylenediaminetetraacetic acid (EDTA) are possible variations. For the deposition of silver-tungsten films on oxidized silicon wafers for electronic purposes, the use of ammonium acetate/EDTA solutions and benzoate solutions has been described [14-16]. In both cases, the addition of sodium tungstate seems to be necessary as it acts as a catalyst for silver deposition. Without the presence of tungstate it was not possible to get SiO_2/Si plated. It is suggested that tungsten is most likely deposited as WO_3 .

EXPERIMENTAL

The substrate was tungsten carbide powder of 3 μm average particle diameter (Fig.1) and an oxygen concentration of 550 $\mu\text{g/g}$ (used as delivered by H.C.Starck without further treatment). Purity of the silver nitrate was 99.97 % (Umicore). In all cases, hydrazine hydrate (>99 %, Merck) was used as the reducing agent.

We investigated the usability of the following aqueous systems for plating and the effects on the morphology of the plated carbide:

- solutions of silver nitrate without additives (Solutions A/B)
- solutions of ammonium acetate, benzoic acid and ammonium hydroxide with the addition of different amounts of sodium tungstate (Solutions C/D)
- solutions of ammonium bicarbonate/ammonium hydroxide (Solutions E/F)

The detailed compositions of the solutions are shown in Table 1. Plating was performed in a glass flat flange reaction vessel with a PTFE stirrer and dropping funnel. All reactions were carried out at room temperature without further temperature control. In some cases, the substrate was placed in the silver containing solution while the reducing agent (hydrazine hydrate) was added over a period of 180 minutes (sequence a). In other cases, the tungsten carbide was suspended in the solution of the reducing agent while the aqueous silver solution was added (sequence b). The solution was stirred for another 30 minutes to

complete the reduction of silver. The plated powders sediment easily was separated by filtration. After washing with water and ethanol they were dried in a desiccator under vacuum at 50°C.

The plated powders were characterized by SEM (Philips XL30, 20kV). The silver concentration was checked by volumetric method (Volhard) or XRF (Philips X'Unique II). Oxygen content was measured by N/O/H-analyzer (LECO TCH 600).

Apart from the morphology of plated tungsten carbide powder, our interest focused on the microstructure of the products made out of it. Therefore, consolidation of the plated powders was done by uniaxial cold pressing (300 MPa) and subsequently liquid phase sintering under flowing hydrogen (1-2 l/min.) at 1100°C (dwell time: 30 minutes). The solid samples were characterized by optical light microscopy and density measurement.

Tab.1. Composition of plating solutions investigated.

Without additives	Solution A [mol/l]	Solution B [mol/l]
AgNO ₃	0.063	-
N ₂ H ₄ .H ₂ O	-	0.103
WC	-	0.052
Benzoate/Acetate/Tungstate	Solution C [mol/l]	Solution D [mol/l]
AgNO ₃	0.030 - 0.060	-
N ₂ H ₄ .H ₂ O	-	0.027 - 0.082
NH ₄ OH	0.636 - 6.675	-
C ₇ H ₆ O ₂	0 - 0.600	-
Na ₂ WO ₄	0 - 0.014	-
CH ₃ COONH ₄	0 - 0.472	-
WC	-	0.012 - 0.064
Bicarbonate/Ammonia	Solution E [mol/l]	Solution F [mol/l]
AgNO ₃	0.127	-
N ₂ H ₄ .H ₂ O	-	0.082
NH ₄ HCO ₃	1.897	-
NH ₄ OH	3.340	-
WC	-	0.105

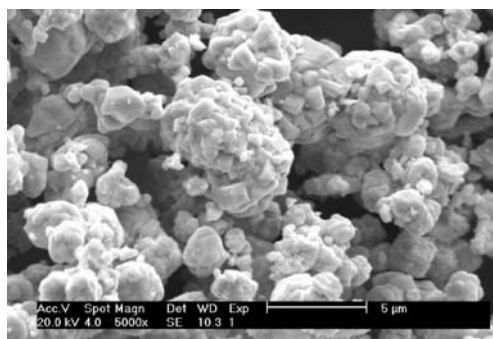


Fig.1. SEM image of tungsten carbide before plating.

RESULTS AND DISCUSSION

The order of addition was varied as described. In most of the investigated systems shown in Table 1, it was more preferable to add silver solutions drop by drop to the tungsten carbide containing hydrazine solutions (sequence b) than the other way, in order to prevent unwanted silver precipitation on the reaction vessel.

Silver nitrate solutions without additives showed massive silver deposition on the reaction vessel leading to silver concentrations of WCAg powder much lower (30-32 wt.%) than targeted. The results were not dependent on the order of addition. Looking at the SEM images (Fig.2a), the tungsten carbide is only partially plated, uncovered surfaces of tungsten carbide are still present. The composite made out of this powder shows high porosity (Fig.2b) and therefore low density of 9.2 g/cm^3 (68 % of theoretic value). The only significant benefit of unbuffered aqueous silver nitrate solutions was an oxygen content of the silver plated tungsten carbide ($811 \text{ } \mu\text{g/g}$) significantly lower than with other methods. Because of the uncontrollable silver content and the poor microstructure, this method seems not suitable for the intended purpose.

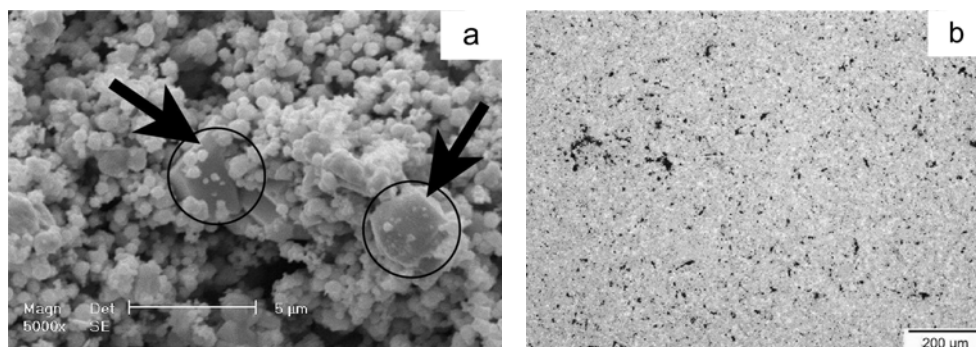


Fig.2. a) SEM images of tungsten carbide plated in a silver nitrate bath without additives (uncovered WC surfaces marked, 5000x). b) Micrograph of sintered WCAg from silver nitrate bath without additives. (Resolution: 100x).

Solutions of benzoic acid/ammonium hydroxide with additives yielded different results. To prevent unwanted deposition and incomplete silver precipitation, it was necessary to optimize the concentrations of all ingredients. Regarding this, experiments without benzoic acid and ammonium acetate (while all other components leaved unvaried) showed insufficient complexation and uncontrollable silver deposition on the reaction vessel. Since complexation and reduction of silver are competitive reactions, increasing concentrations of benzoic acid and ammonium acetate yielded in increasing amounts of hydrazine necessary for complete reduction of silver.

We also compared solutions of the same composition, except for sodium tungstate. Without the addition of tungstate, the WCAg powder obtained, had a silver concentration of 21.8 wt.%. By adding 0.002 mol/l sodium tungstate, the silver concentration in the powder increased to 33.6 wt.%. This observation is in accordance with results reported in [14-16] showing some kind of catalytic effect of tungstate in silver reduction. The mechanism of this effect remains unclear.

Optimum performance was achieved using the concentrations shown in Table 2. The oxygen concentration in the composite powder was in the range of $1400 \text{ } \mu\text{g/g}$.

Tab.2. Optimized composition of benzoic acid plating solutions

	Solution C [mol/l]	Solution D [mol/l]
AgNO ₃	0.060	-
N ₂ H ₄ ·H ₂ O	-	0.082
NH ₄ OH	1.214	-
C ₇ H ₆ O ₂	0.600	-
Na ₂ WO ₄	0.004	-
CH ₃ COONH ₄	0.472	-
WC	-	0.064

The WCAg powder produced with this optimized composition has promising morphology of the plated surface (Fig.3a). The tungsten carbide seemed to be completely covered by interleaved platelets of silver. Even so, after pressing and sintering, the obtained product was not as homogeneous as expected. The light microscopy image (Fig.3b) shows areas of concentrated tungsten carbide next to silver accumulations. This lack of homogeneity is a probable limitation for usage in electrical contact applications. The density was 9.9 g/cm³ (73 % of theoretic value).

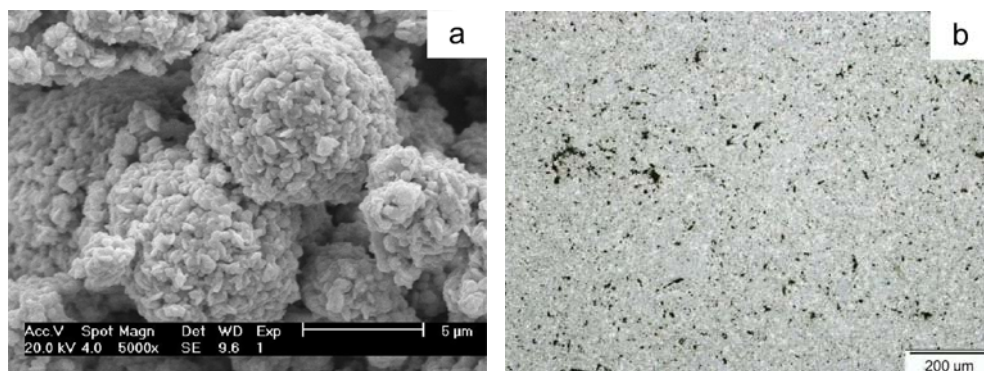


Fig.3. a) SEM image of tungsten carbide plated with 40 wt.% silver in optimized benzoic acid/ammonium hydroxide bath (5000x). b) Micrograph of sintered WCAg from optimized benzoic acid/ammonium hydroxide bath. (Resolution: 500x).

Solutions of ammonium bicarbonate/ammonium hydroxide showed high stability of the solutions and therefore less often unwanted silver deposition on the reaction vessel. The plating was performed with different concentrations of tungsten carbide, silver nitrate and hydrazine. The best results were obtained using solutions shown in Table 1. The oxygen amount of the WCAg powders was in the range of 1800 μg/g. This increase compared to the prior methods is most likely caused by the higher pH value. Andersson and Bergström [17] showed that the dissolution of tungsten carbide in aqueous solutions is a combined process of oxidation (formation of WO₃) and dissolving of the WO₃ forming different (poly)anions [18], dependent on the pH value. Exposure of tungsten carbide to aqueous media results in an increase of oxygen on the surface in an initial stage, followed by a decrease caused by dissolving of the generated WO₃. As the dissolution of WO₃ is associated with the release of protons, the pH value will decrease without further action. Even though the tungsten carbide dissolution is not limited by the oxidation rate but by the

dissolution rate of WO_3 , it seems that increasing pH values do promote initial oxidation of tungsten carbide. In electro-oxidation tests of tungsten carbide electrodes, Ma et.al [19] found that WC is oxidized in acidic solutions at 800-900 mV forming W_2O_5 (sulphuric acid) or W_8O_{23} (hydrochloric acid). In alkali solutions, WC was directly oxidized forming WO_3 . These results correspond to the measured correlation of oxygen content in WCAg powders and a higher pH value of used plating solutions.

The silver concentration of 40.2 wt.% was within the desired range. The use of even higher concentrated solutions is possible, but demands more care in sufficient stirring and unhasty addition of silver solution in order to prevent unwanted deposition on the vessel. Figure 4 shows the silver plated tungsten carbide (hereby called "WCAgTU"). The powder appears very homogeneous, having well plated, smooth surfaces without any detached silver precipitates.

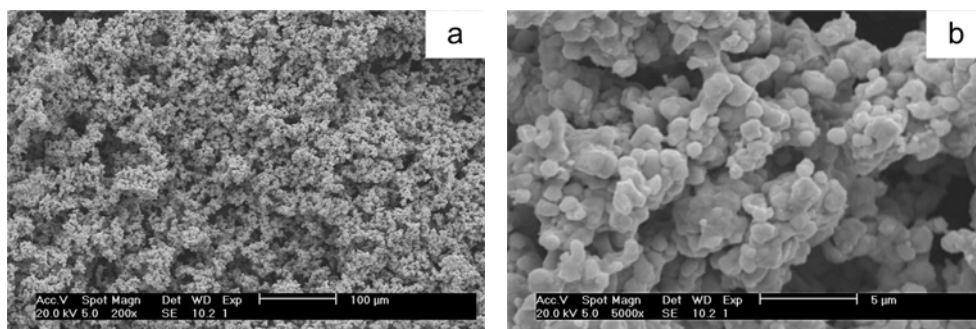


Fig.4. SEM image of tungsten carbide plated with silver (40 wt.%) by ammonium bicarbonate/ammonium hydroxide method. (Resolution 200x (left) and 1000x (right)).

As a result of surface porosity the overall density of the sintered product (calculated from weight and dimensions) was only 10.5 g/cm^3 (80% of theoretical value). Nevertheless, the samples had much higher density inside and remarkable homogeneity, even compared to industrial infiltrated WCAg manufactured, with the same sort of tungsten carbide (Fig.7). The aggregation of silver and tungsten carbide was significantly lower. A positive effect of this improved microstructure on the arc erosion resistance may be expected, but had not been measured yet.

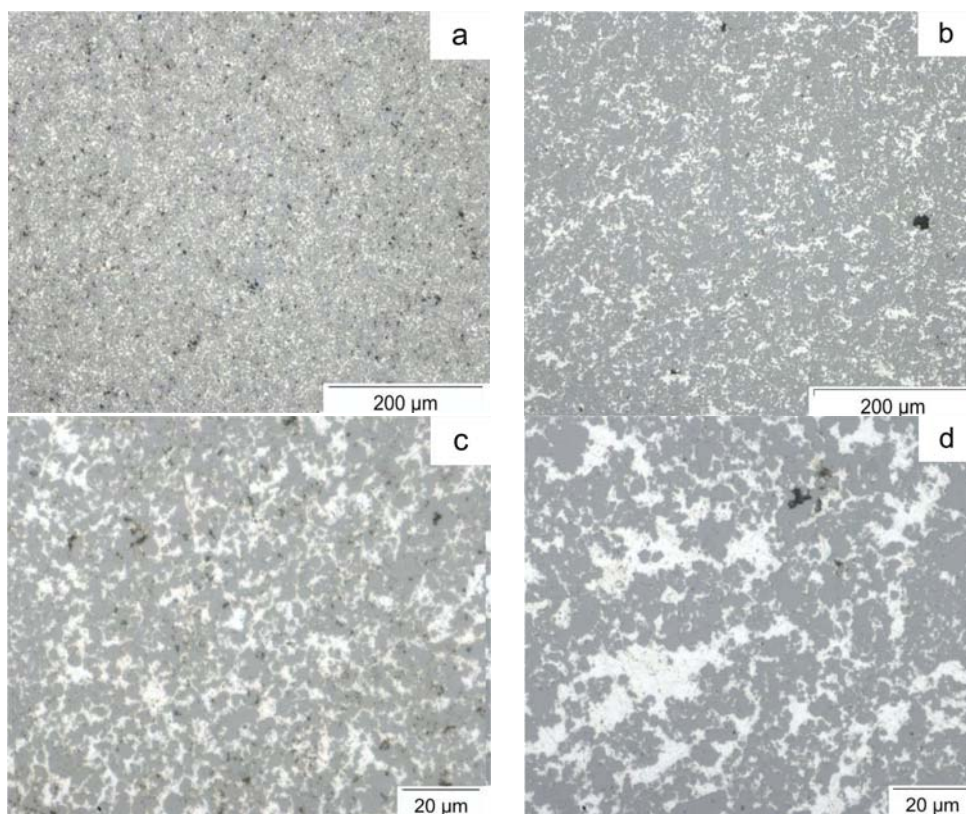


Fig.5. Micrograph of sintered "WCAgTU" (left) compared to industrial infiltrated WCAg with the same type of tungsten carbide (right). (Resolution 200x (top) and 1000x (bottom)).

CONCLUSIONS

The use of chemical plating techniques for the production of homogenous WCAg composites is primarily limited by the stability of silver solutions used. Precipitation on the walls of the reaction vessel yields to inhomogeneous products. Moreover, the amount of silver deposited on the vessel is unknown, which yields to uncontrollable silver concentration of the WCAg powders. Therefore, adequate complexation of silver is required. Thus the sole use of aqueous silver nitrate solutions is not suitable. A feasible method is using complex solutions containing benzoic acid, ammonium acetate and sodium tungstate. One problem concerning these solutions is a relatively low limitation in silver concentration due to limited complexation compared to ammonium hydroxide/ammonium bicarbonate. Even so, an optimum composition of the plating bath was found, giving interesting morphologies of WCAg powders. However, the sintered product was disappointing due to inhomogeneity.

The best results were obtained by using a simple aqueous mixture of ammonium hydroxide and ammonium bicarbonate for complexing silver and preserving a high pH value for high reduction power of hydrazine. The WCAg powders produced showed good properties such as easy sedimentation, uniformity and good dispersion of the deposited silver. The oxygen content ($1808 \mu\text{g/g}$) was considerably higher than the as-delivered

tungsten carbide (550 µg/g). Compared to industrial infiltrated WC/Ag, the sintering of these silver plated powders gave products of a significantly higher homogeneity.

Acknowledgement

The authors wish to thank Plansee SE for the financial support of part of this work.

REFERENCES

- [1] Davis, JR: Metals Handbook – Electric-Contact Materials. Vol. 3. Ohio : ASM International, 1990
- [2] Temborius, S., Lindmayer, M.: 15. Fachtagung Kontaktverhalten und Schalten, Karlsruhe, 1999
- [3] Temborius, S., Lindmayer, M., Gentsch, D.: IEEE Transactions on Plasma Science, vol. 31, 2003, no. 5, p. 945
- [4] Hula, RC: Diploma Thesis. Vienna : TU, 2007
- [5] Koura, N. In: Electroless Plating: Fundamentals and Applications. Vol. 17. Ed. G.O. Mallory. Orlando : American Electroplaters and Surface Finisher Soc., 1990, p. 458
- [6] Lide, DR.: CRC Handbook of Chemistry and Physics. Boca Raton, Ann Arbor, London, Tokyo : CRC Press, 1999
- [7] Falbe, J., Regitz, M.: Römpps Chemielexikon. Vol. 5. Stuttgart, New York : Thieme, 1995
- [8] Jellinek, TW.: Praktische Galvanotechnik. Bad Saulgau : G. Lenze, 2005
- [9] Suber, L., Sondi, I., Matjevic, E., Goia, DV.: J. Colloids and Interf. Sci., vol. 288, 2005, p. 489
- [10] Djokovic, SS.: J. Electrochem. Soc., vol. 144, 1997, no. 7, p. 2358
- [11] Chou, KS., Ren, CY.: Mat. Chem. and Phys., vol. 64, 2000, p. 241
- [12] Beck, G., Beyer, HH., Gerhartz, W., Hausselt, J., Zimmer, U.: Edelmetalltaschenbuch. Heidelberg : Hüthig, 1995
- [13] Kozlov, AS.; Palanisamy, T., Narasimhan, D.: Patent WO02/04711A2, 2002
- [14] Inberg, A., Bogush, V., Croitoru, N., Dubin, V., Shacham-Diamand, Y.: J. Electrochem. Soc., vol. 150, 2003, no. 5, p. C285
- [15] Bogush, V., Inberg, A., Croitoru, N., Dubin, V., Shacham-Diamand, Y.: Microelectr. Eng., vol. 70, 2003, p. 489
- [16] Shacham-Diamand, Y., Inberg, A., Sverdlov, Y., Croitoru, N.: J. Electrochem. Soc., vol. 147, 2000, no. 9, p. 3345
- [17] Anderson, KM., Bergström, L.: Int. J. Refr. Metals Hard Mater., vol. 18, 2000, p. 121
- [18] Lassner, E., Schubert, WD.: Tungsten. New York, Boston, Dordrecht, London, Moscow : Kluwer Academic, 1999
- [19] Ma, C., Gan, Y., Chu, Y., Huang, H., Chen, D., Zhou, B.: Trans. Nonferrous Met. Soc. China, vol. 14, 2004, no. 1, p. 11