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PARTICLE-REINFORCED SILVER-BASED CONTACT MATERIALS BY MEANS OF HIGH-ENERGY BALL MILLING

Wielage, B. / Lampke, Th. / Steger, H.

Chemnitz University of Technology
Institute of Materials Science and Engineering
09107 Chemnitz

ABSTRACT

Mechanical alloying is a well-known method to produce feedstock for diverse coating (e.g. thermal spraying) and sintering processes. Besides receiving loose powder materials, composites can be realized by means of pressing processes to obtain compact materials, e.g. wires. The high-energy ball-milling (HEM) process is an economic method to produce composite feedstock also with nanostructured composite powder particles. The contribution presents the morphology and microstructure of mechanically alloyed silver-based powders achieved by the HEM process as well as the microstructure and mechanical properties of the compact materials (e.g. wires). The objective of the present investigation has been the successful production of a feedstock for nano-structured compact metal-matrix composite materials (MMCs) as well as the reduction of the noble metal part by means of the incorporation of the oxide component. The results reveal that materials gained by HEM are suitable for producing contact materials related to phase distribution, grain size, impurities and, of course, mechanical and electrical properties.

Index Terms – Silver-based contact materials, particle-reinforcement; high-energy ball milling; mechanical alloying

1. INTRODUCTION

1.1. High-Energy Ball-Milling Process

In different investigations, the high-energy ball-milling process (HEM) was tested for different material systems and applications, e.g. as feedstock for thermal spraying processes or as composite powder for the production of compact materials [1-6]. The milling process is characterized by a fixed milling chamber and a spinning rotor (Figure 1). This rotor causes a very high acceleration of the milling balls. So, both the milling process and the cold-welding process can be used to produce composite powders. Using these permanent cold-welding, breaking and milling processes, a very homogeneous incorporation of particles can be obtained.

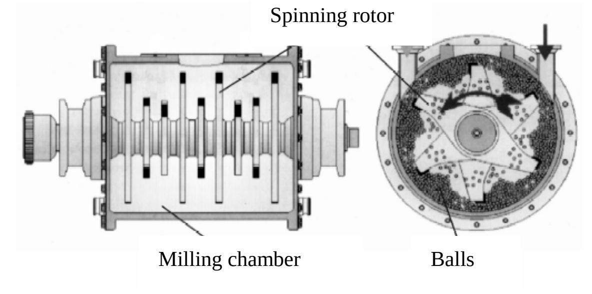


Figure 1: Scheme of a high-energy ball mill Simoloyer® [Fa. Zoz]

In particular, the mechanical alloying can be applied for ductile matrix materials and brittle reinforcements to achieve nanostructured particle-reinforced composite powders.

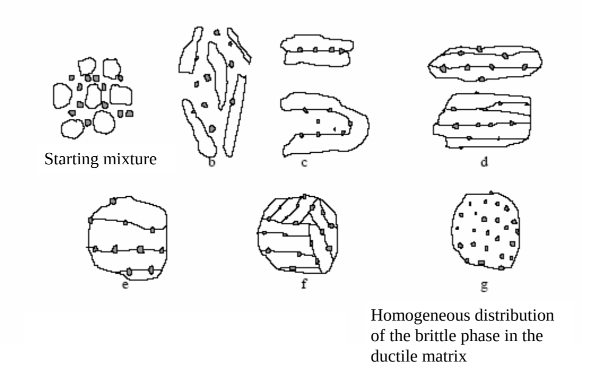


Figure 2: Development during the HEM process [8]

Within the process (Figure 2), first the ductile matrix is formed into lamellas or plates and the brittle particles are ground at the same time. After that, the small brittle particles are attached to the plate-forming matrix component and then the ductile phase encloses the brittle particles and the cold-welding process follows. So, a coarse lamellar structure is created. A deformation process follows another cold-welding process and again another breaking process. Thus, a refining process takes place. After repeated milling, the lamellar orientation has disappeared and there is a homogeneous distribution. Figure 2 shows this characteristic breaking, milling and cold-welding process for the combination of a ductile matrix material and a brittle reinforcement. [7, 8]

1.2. Contact Materials

Silver, the least expensive one of the noble metals, exhibits the highest electrical and thermal conductivity. Furthermore, noble metals do not form oxides in air. So they are appropriate for applications in open-air switchgear. On the other hand, silver sulphide will be formed in sulphur-containing atmosphere. For applications with small switch forces this silver sulphides will be a disruptive factor. In the field of the electrical energy technology with higher switching forces, these silver sulphides are not problematical. But because of its bad welding and wear resistance as well as its tendency to material migration in direct current applications, silver as a contact material satisfies the requirements only in a narrow range of electrical applications.

So, silver alloys or silver composite materials are used according to the requirements. Typical examples for silver alloys are AgNi 0.15 (fine grain silver) and Ag/Cu alloys [9]. Contact materials of silver/metal oxide demonstrate very good anti-welding properties. In particular, the material system silver tin-oxide with an oxide quota between 8 and 12 and up to 14 wt.-% [9, 11, 13] shows

- best anti-welding properties, increasing with higher oxide content (silver metal oxides up to currents of 5000 A);
- lowest erosion rate of all silver/metal oxide materials for currents with more than 100 A;
- significantly less material migration (compared to Ag/CdO and Ag/ZnO);
- low contact resistance (compared to other silver/metal oxides) and
- excellent arc-extinguishing properties.

Furthermore, these Ag/SnO_2 contact materials are free of toxic and carcinogenic components and special additives keep the contact resistance stable throughout the service life. These special additives can offer different properties: CuO, for example, improves the ductility of the material. WO_3 and MoO_3 yield better contact resistance and therefore less contact warming but they also lead to lower ductility. Bi_2O_3, for example, produces better switching properties at special load performances and, together with WO_3, a decreasing ductility. [9-16]

2. EXPERIMENTS

2.1. HEM unit

The powders were milled in a laboratory-scaled high-energy ball-milling unit, type Simolyer® CM01 (1.6 l). The HEM process was performed in air atmosphere at various rotation speeds and milling times. To reduce impurities caused by a steel chamber and rotor as well as steel balls, a special ceramic configuration of a high-energy ball mill with a ceramic chamber, a ceramic rotor (Si_3N_4) and ceramic balls (ZrO_2) was used.

2.2. HEM of Ag/SnO_2 powder

In a first step, the ductile silver matrix material was reinforced with three different contents of the tin oxide component (8, 12 and 14 wt.-%) by means of the HEM process. Three different tin oxide fractions were applied (Table 1).

Table 1: Tin oxide fractions

SnO_2 fraction No.	1	2	3
D_{50} [µm]	7.7	4.2	0.7

The different particle sizes as well as the different contents of tin oxide were selected to identify possible agglomerations, especially by using the finest fraction of SnO_2 No. 3 and the highest oxide content of 14 wt.-%.

2.3. HEM of Ag/SnO_2 powder doped with different metal oxides

In a second step, the silver matrix was reinforced with a combination of tin oxide and other metal oxides. Copper oxide, tungsten oxide and bismuth oxide were selected in particular. The contents of SnO_2 were between 9.5 and 13.2 wt.-% and of Bi_2O_3 between 0.6 and 2.0 wt.-%. The CuO and WO_3 content was approx. 0.5 and 0.1 wt.-% respectively. Different particle sizes of the tin oxide component and different total oxide contents (12 and 14 wt.-% of the oxide) as well as different combinations and contents of the added components were selected to get an analogy to other manufacturing routes and benchmark materials. The aim was also to discover a possible influence of the combination and content of the added metal oxides with regard to possible agglomerations and dispersions in the silver matrix.

2.4. Further processing/consolidation

To obtain semi-finished products like wires, the HEM powder is pressed to a preform by means of cold isostatic pressing (CIP). After special heat treatment, the extrusion of the preform to wires follows.

3. MICROSTRUCTURE

3.1. Microstructure of the composite powder

In the case of the ductile silver matrix, a typical distinctive flake form of the composite particles is reached (Figure 3). The development of the distribution of the oxide component and so of the composite powder can be displayed by means of microstructural observation after different milling times. The process which is described in Figure 2 was validated and the evolution of the Ag/SnO_2 material is monitored in Figure 4. The distribution d, f and g in Figure 2 is discernable after 10, 20 and 60 min milling time (Figure 4 a, b and c). After reaching an optimum of such a homogeneous dispersion of the oxide component within the matrix material (Figure 4c), the composite powder can be consolidated to semi-finished products (e. g. wires). In the case of the very ductile silver matrix, no significant grinding process of the reinforcement can be detected.

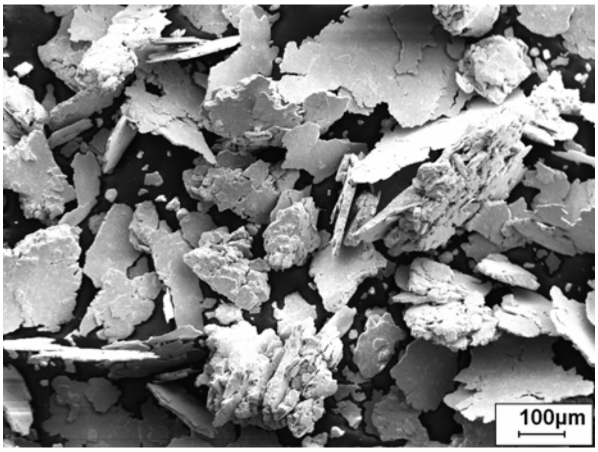
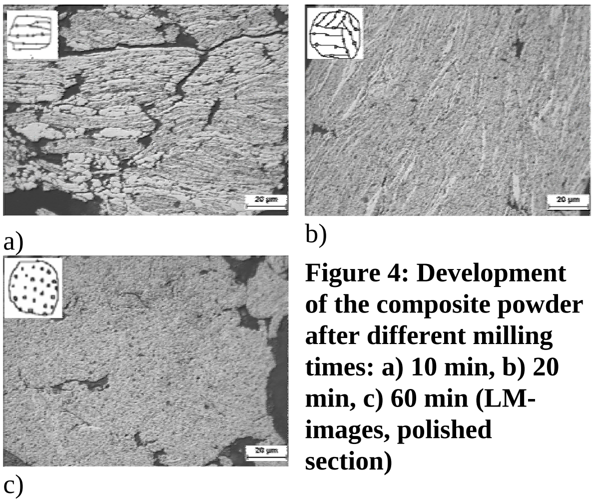


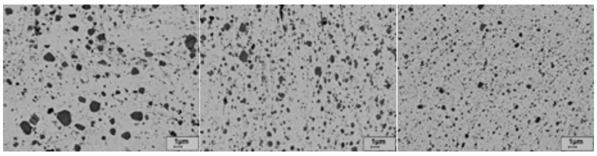
Figure 3: Morphology of the flake form of Ag/SnO_2 composite particles after HEM (SEM image)



a) b) c)

Figure 4: Development of the composite powder after different milling times: a) 10 min, b) 20 min, c) 60 min (LM-images, polished section)

Different tin oxide fractions and quotas are very homogeneously distributed within the flake-formed composite particles. The resulting powder of the silver/tin oxide/added oxide milling process also displays the same result of very fine particle dispersion. Figure 5 shows SEM images of the polished sections of three Ag/SnO_2 powders with three different tin oxide fractions. These images as well as image 4c show very dense silver tin oxide powders with a very finely distributed oxide component. Within the composite powder, the very fine fraction is distributed as well as the coarse fraction.



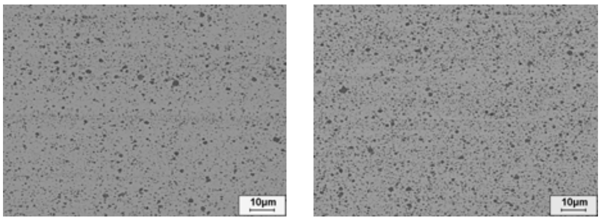
a) b) c)

Figure 5: Ag-SnO_2 HEM powder with three different SnO_2 fractions: a) No. 1; b) No. 2; c) No. 3 (SEM images)

3.2. Microstructure of the compact material

3.2.1. Microstructure of the Ag/SnO_2 material

After consolidation (pressing, heat treatment and extrusion) of the composite powder to wires, the microscopical investigations of the compact material show a very fine dispersion of the tin oxide component in the silver matrix. The oxide-free silver lines which can be observed especially in longitudinal sections of the wires are very fine and acceptable. The wires displayed in Figure 6 show a very homogeneously distributed tin oxide component also for a SnO_2 content of a) 8 and b) 14 wt.-% (longitudinal section).



a) b)

Figure 6: Compact Ag/SnO2 wires with a) 8 wt.-% and b) 14 wt.-% tin oxide (SEM image, longitudinal section)

The composite powders as well as the extruded wires are very dense and there are only a few micropores. Besides these pores, the oxide component is also well embedded in the silver matrix material (Figure 7). The FE-SEM image in Figure 7 also illustrates the integration of very fine oxide particles of a few nanometers which are very well-dispersed. These very small particles are located at the silver grain boundaries in particular.

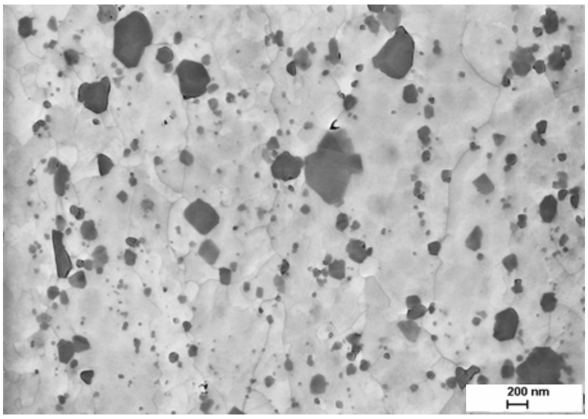


Figure 7: Compact Ag/SnO_2 wire with 12 wt.-% tin oxide (FE-SEM image, longitudinal section, ion-polished)

3.2.2. Microstructure of the $Ag/SnO_2/MeO$ material

In addition to the Ag/SnO_2 composites, the doped materials were also investigated. The focus of these investigations was on the quality of the distribution of the doped metal oxides (copper oxide, bismuth oxide and tungsten oxide). Because of its low atomic number, the copper oxide can be well-detected in the backscattered modus of the scanning electron microscope (SEM). The distribution of 0.5 wt.-% copper oxide (dark grey oblong particles) within a sample with a total oxide rate of 12 wt.-%.is illustrated in Figure 8. The picture shows that the copper oxide component is very finely distributed and embedded in the silver and also between the oxide particles.

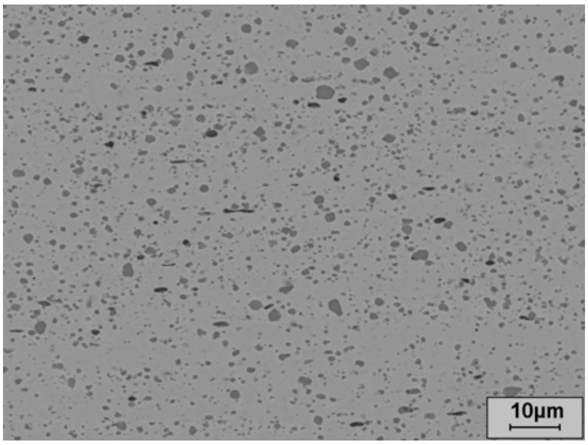


Figure 8: Compact Ag/SnO_2 wire (12 wt.-% total oxide content) with 0.5 wt.-% copper oxide (SEM image, longitudinal section, ion-polished)

Figure 9 displays a typical effect of the copper oxide in the longitudinal section. There, the copper oxide shows an oblong structure which is obviously attributable to the deformation process during the extrusion. Other investigations to detect the tungsten and bismuth oxide particles have shown that these oxides are also very well-dispersed and embedded. Analyses concerning possible impurities show that impurities of only $\leq$ 10 ppm were detected after milling in the special ceramic configuration of the high-energy ball mill.

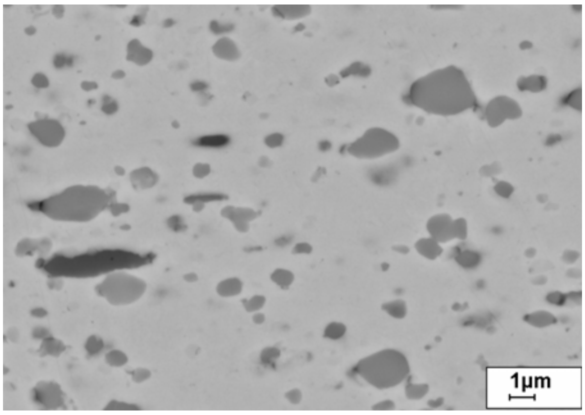


Figure 9: Compact Ag/SnO_2 wire (12 wt.-% total oxide content) with 0.5 wt.-% copper oxide (SEM image, longitudinal section)

4. MECHANICAL PROPERTIES

4.1. Methods

There are two ways to obtain the mechanical properties of the consolidated silver-matrix composite materials: on the one hand, the use of customary tension tests and on the other hand, the application of compression tests with a much easier sample preparation. The disadvantage of this compression test is that information like breaking elongation is not possible. So, a combination of tension and compression tests was used. The mechanical properties at different deformation rates (0.1, 200 s^{-1}) and temperatures (room temperature, 200, 400 and 600 °C) were determined by means of compression tests of cylindrical samples (diameter = 5 mm, height = 5 mm). To validate the results of the compression test, simple tension tests on the wire material (diameter = 5 mm) were conducted at room temperature. These tension tests also deliver information about the breaking elongation.

4.2. Results

4.2.1. Compression tests

The true strain/true stress diagram in Figure 10 displays the mechanical properties of the HEM Ag/SnO_2 materials with 8, 12 and 14 wt.-% of tin oxide (SnO_2 No. 2) at different temperatures (room temperature, 600 °C) with a deformation rate of 200 s^{-1}. The influence of the different reinforcement quotas is recognizable for room temperature as well as for 600 °C. Also the influence of the temperature is displayed. At 600 °C, a nearly ideal plastic behaviour can be registered.

4.2.2. Tension tests

The results of the tension tests at room temperature have validated the compression test results and show the following expected correlations. In the case of the dispersion strengthening, the strength shown by means of the tensile strength and the yield strength rises with the increasing quota of the oxide component and the decreasing particle size of the reinforcement. The breaking elongation also decreases with the rising oxide component quota.

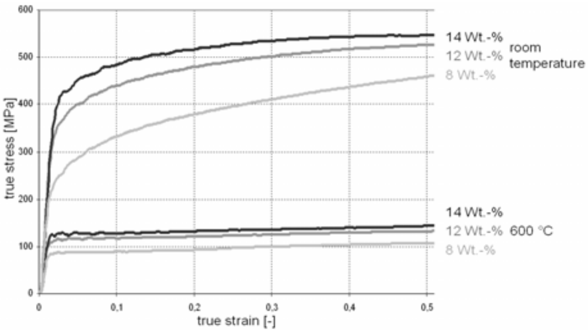


Figure 10: Compression tests of HEM Ag/SnO$_2$ with 8, 12 and 14 wt.-% tin oxide at room temperature and 600 °C and a strain rate of 200 s^{-1}

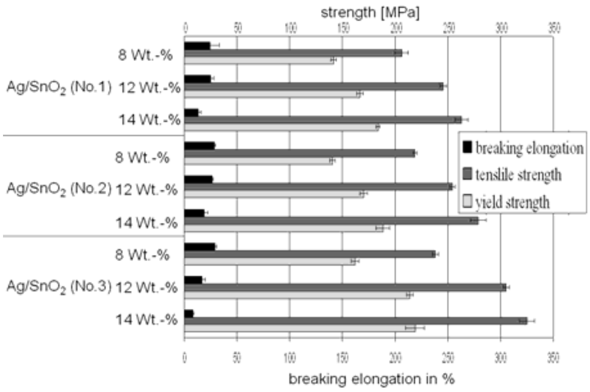


Figure 11: Tension tests of HEM Ag/SnO$_2$ with 8, 12 and 14 wt.-% tin oxide at room temperature

5. SUMMARY AND CONCLUSIONS

The investigations have shown that the high-energy ball-milling technology is a suitable means for mechanical alloying of particle-reinforced silver-based composite materials to produce feedstocks. It is possible to mill ductile matrix materials with different fractions and contents of brittle tin-oxide particles and to add other oxides such as copper oxide, tungsten oxide and bismuth oxide. The feedstocks as well as the finished compact materials show a very homogeneous particle distribution. Such fine structures are not feasible with other mixing and milling processes. By means of the oxide particles, the noble metal rate can be reduced rapidly. The current investigations on the switching properties of the HEM materials (e.g. contact resistance, material migration, anti-welding properties and erosion rate) will be compared with investigations on other manufacturing routes and benchmark materials.

6. ACKNOWLEDGEMENT

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