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THE INFLUENCE OF SnO_2 NANOPARTICLES AND METHOD OF THEIR INTRODUCTION ON MICROSTRUCTURE AND PROPERTIES OF Ag-SnO_2 ELECTRICAL CONTACTS

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ABSTRACT

The influence of SnO_2 nanoparticles and method of their introduction in silver matrix on microstructure and physical properties such as density, porosity, hardness and electrical conductivity of Ag-SnO_2 electrical contact materials were studied. The SnO_2 nanoparticles were introduced by conventional powder mixing and by template method using different templates. All investigated samples were produced by powder metallurgy method followed by mechanical treatment. When compared, samples with nano particle metal oxide exhibit higher dispersion than their microparticle counterpart. However, comparing the microstructures, the two materials produced by template method display further increase of dispersion. Consequently, after sintering and forging these samples have higher hardness, density and lower porosity. The observed enhancement of hardness of almost 30 % can be attributed to greater dispersion hardening of otherwise soft silver matrix. The measured values of electrical conductivity of all investigated samples are comparable with conductivities of commercial Ag-SnO_2 electrical contact materials.

Keywords: Ag-SnO_2, metal oxide nanoparticles, template method

1. INTROUCTION

Ever since the introduction of Ag-SnO_2 contact materials as an environmentally-friendly alternative to Ag-CdO they have been continually improved regarding their performance and applicability. In general, when the goal is to alter materials properties by altering the interaction of a silver matrix and base oxides, finer microstructures are more favorable. Although, the influence of the oxide particle

size on the switching behavior is still not well defined it is generally accepted that smaller metal oxide particles promote formation of anti-welding characteristics and under certain conditions decrease erosion rate of the electrical contact [1]. Nevertheless, in order to improve the anti-welding behavior, hardness and wear resistance of these materials it is necessary to obtain uniform dispersion of SnO_2 particles in a soft silver matrix [2]. For that reason, different methods of introduction of SnO_2 nanoparticles were investigated and compared. SnO_2 nanoparticles were introduced by conventional powder mixing using ultrasound irradiation of the powder mixture suspension and by template method using two different templates. Ag-SnO_2 contacts were then produced by conventional powder metallurgy route.

2. EXPERIMENTAL

Studied silver based electrical contact materials were produced by powder metallurgy method from pure silver powder obtained by chemical synthesis route and very fine commercial Ag-NO_3 and (SnO_2 - 99.9%) powders as well as commercial SnO_2 nano powder produced by Sigma-Aldrich. Particle size distribution and morphology of the used powders are given in previous study [3]. The technological procedure included dry and wet homogenization of the powder mixtures, pressing, sintering and forging and characterization. In order to illustrate the influence of nanoparticles and method of their introduction in silver matrix all samples were produced with the same Ag:SnO_2 weight ratio (92:8).

Samples 1 and 2 were produced by mixing Ag powder with SnO_2 micro and nano powders, respectively. Since the starting powders were in the form of agglomerates consisting of very fine particles, ultrasound irradiation was used and both wet and dry homogenization was done.

In order to produce composites with higher dispersion of SnO_2 nanoparticles in silver matrix samples 3 and sample 4 were produced by the template method. The method generally consists of three steps: template preparation process, insertion of the precursors into the template and template removal process. Sample 3 was produced by a modified method developed by [4] which uses commercial ashless quantitative filter paper (Whatman Inc., burning ash < 0.005%) as the template. SnO_2 nanoparticles were firstly suspended and then mixed with $AgNO_3$ solution, in quantities necessary to achieve desired Ag:SnO_2 ratio of (92:8) in final composite. Filter paper sheets were immersed in the obtained mixture solution, then dried in chamber dyer, then burned and put into a muffle furnace pre-heated at 500^{o}C, where they were calcinated for 2h. Because impregnated filter papers are dried after immersion, silver nitrate crystallizes in pores of the filter paper and takes their inner shape entrapping the dispersed SnO_2 nanoparticles within. During the combustion and later calcination two processes occur, silver nitrate is transformed to elemental Ag encapsulating SnO_2 nanoparticles, and template is being removed. The silver leaf mesh like structure was obtained which corresponds to pores structure of filter paper.

In the case of the sample 4 soluble starch [5,6] was used as a template providing good dispersion of SnO_2 nanoparticles and breaking up of $AgNO_3$ solution in fine droplets. Previously prepared SnO_2 nanoparticle suspension is slowly added during vigorous mixing to the water solution of soluble starch and $AgNO_3$ water solution is slowly added. Both $AgNO_3$ and SnO_2 are added in quantities necessary to achieve desired Ag:SnO_2 ratio of (92:8) in final material. The prepared mixture is then dried in chamber dryer until water is evaporated and solid composite is obtained. The solid composite is subsequently burned and put into a muffle furnace pre-heated at 650^{o}C, where it is calcinated for 4h. During the combustion and later calcination, silver nitrate is transformed to elemental Ag, with embedded SnO_2 nanoparticles and the starch template is removed.

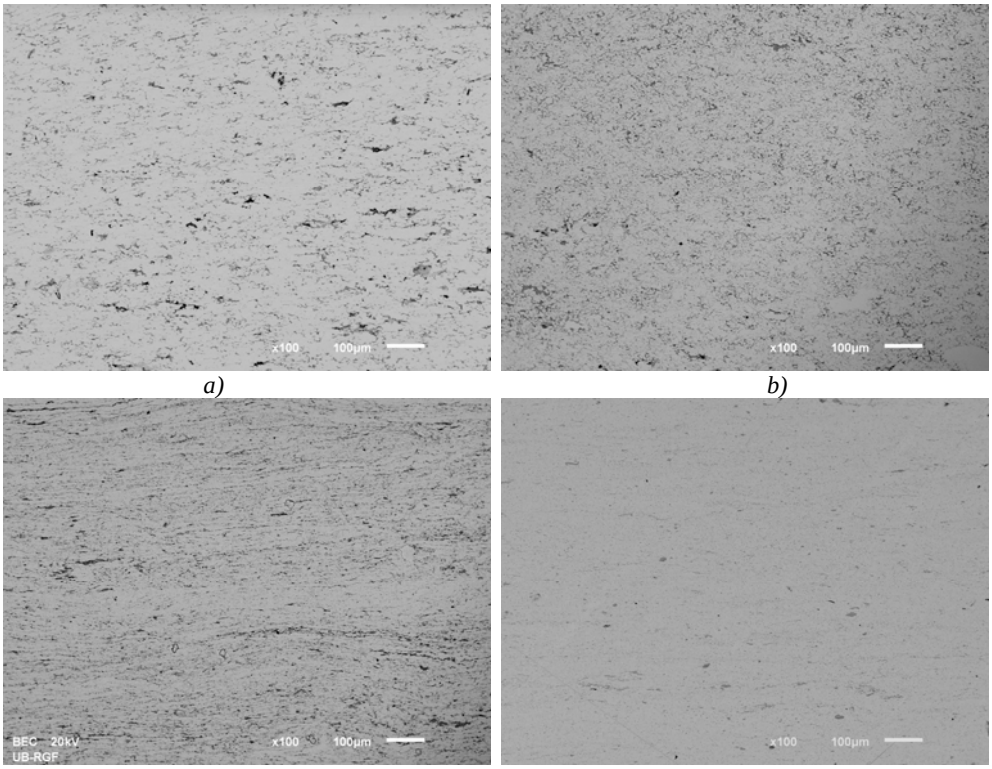
The investigated Ag-SnO_2 samples were produced by cold pressing of powder mixtures with micro (sample 1) and nano SnO_2 particles (sample 2) and particles of two composites (sample 3 and 4) obtained by template method into blocks with dimensions 25.4×11×3 mm, under pressure of 360 MPa. The obtained Ag-SnO_2 green compacts were then sintered for 3h at 820^{o}C in electro-resistive oven in the air atmosphere. The samples were subsequently forged (at 800^{o}C) with the low degree of reduction and then annealed at 750^{o}C for 30 min followed by quenching in water.

Microstructure of the samples after sintering and mechanical treatment and chemical composition of the observed phases were studied on polished cross-section surfaces using JEOL JSM-6610LV scanning electron microscope (SEM). Density of the obtained samples was determined by standard methods. Applying the procedure given in more detail in [7] theoretical density of the samples was calculated and by comparison between experimental and theoretical densities [7,8] the porosity of

samples was determined. Hardness measurements were carried out after sintering and forging on polished samples at room temperature using a Vickers hardness tester applying load of 5 kp. Electrical conductivity of the investigated materials was measured using Foerster SIGMATEST 2.069 eddy current instrument with the 8 mm probe.

3. RESULTS AND DISCUSSION

Metallographic images of polished cross-sections of the investigated electrical contact materials after sintering, mechanical treatment and subsequent annealing are presented in Figure 1.



a) *b)*

c) *d)*

Figure 1. SEM images of microstructures of the obtained Ag-SnO_2 electrical contact materials

Presented images illustrate notable differences in homogenity of the obtained Ag-SnO_2 contact materials. Comparing the microstructures of the samples with micro (Fig. 1a) and nanoparticle SnO_2 (Fig. 1b) it is evident that introduction of nanoparticles has improved SnO_2 dispersion in the silver matrix. Furthermore, when compared to the two materials produced by introduction of nanoparticles by template method (Fig. 1c and 1d) further increase of dispersion is observed, particularly in case of sample 4 (Fig. 1d).

Summarized experimental results of density, porosity, hardness and electrical conductivity measurements of the obtained Ag-SnO_2 electrical contact materials are presented in the Table 1.

Table 1. Physical properties of the investigated Ag-SnO_2 electrical contact materials

Sample	Density, g/cm^3	Porosity, %	Hardness, HV5	Electrical conductivity, MS/m
1	9.53	4.68	97	43.89
2	9.69	3.01	111	37.32
3	9.74	2.40	124	42.13
4	9.77	2.10	136	38.21

From Table 1, it is obvious that as a result of finer and more homogenous microstructure i.e. greater dispersion hardening, values of density and hardness are increasing for samples 1-4 and at the same time porosity decreases (Table 1). However, values of electrical conductivity do not follow this trend. As expected, sample 1 has the highest value of electrical conductivity given that it is the least homogenous and presence of denuded zones (pure Ag) can be observed (Fig. 1a). Electrical conductivity generally decreases with the increase of SnO_2 dispersion, as in case of the sample 2. Nevertheless, although sample 3 appears to have better SnO_2 dispersion considering the values of hardness, on Fig. 1c partial segregation of SnO_2 particles can be observed forming almost lamellar structure thus giving the raise to electrical conductivity. In terms of hardness, density and porosity sample 4 is due to greater SnO_2 dispersion better than other samples, making it superior in terms of wear resistance and exploitation life. Consequently its electrical conductivity is somewhat lower however it is still in the required range for commercial electrical contacts of this type.

4. CONCLUSION

Introduction of SnO_2 nanoparticles in silver matrix by conventional powder mixing and by template method was studied as a way of improving dispersion of metal oxide in Ag-SnO_2 contact materials. Structure and properties of the obtained silver-nanoparticle metal oxide composites are discussed and presented in comparison to their microparticle metal oxide counterpart. The obtained results of characterization of the investigated electrical contact materials showed that their physical, mechanical and electrical properties are comparable to Ag-CdO and are within the required range of values for commercial electrical contact materials of the same composition. Results of microstructural analysis confirm that by introduction of SnO_2 nanoparticles higher dispersion was obtained than for microparticle counterpart. When compared, the samples prepared by template method have exhibited greater dispersion than sample prepared by conventional mixing of Ag and nanoparticle SnO_2 powders. Consequently, after sintering and forging these samples have higher hardness, density and lower porosity. The observed enhancement of hardness of almost 30 % can be attributed to greater dispersion hardening of otherwise soft silver matrix. The obtained results illustrate importance of method of introduction of nanoparticles and demonstrate that the template method can be successfully used in production of Ag-SnO_2 contact materials.

5. ACKNOWLEDGEMENT

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