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Ag/ZnO and Ag/SnO_2 Electrocontact Materials Obtained from Fine-Grained Coprecipitated Powder Mixture

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The manufacturing processes of Ag/ZnO and Ag/SnO_2 electrocontact materials concerns to chemical precipitation of precursors are represented in this paper. At all stages, obtained powders and compacts were characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD), thermal analysis (TG, DSC, DMA) and scanning electron microscopy (SEM). The size of particles in the sintered molded article is in the range of 0,1-0,3 nm for ZnO and 1-5 μm for SnO_2. The particle's size mostly depends on chemical precipitating conditions and metallurgical stage parameters. Relative density of final compacts is about 0,97-0,99. Resistivity is 2,5 μΩ cm for the concentration of ZnO equal 8 % and 2.4 μΩ cm for the concentration of SnO_2 equal 10 %. Electrical wear (AC, test device, 380 V, 30 A, cos φ=0,8) depends on oxide content and exceeds Ag/CdO series contacts wear.

Keywords: chemical precipitation, powder mixture, electrocontact materials.

Introduction

Silver-metal oxide composites are used as an arcing contact material in contactors, switches, and other devices [1-3]. Today Ag-CdO is the most widely used because the particles of CdO strengthen the contact structure without reducing the matrix conductivity and extinguish an arc. Ag-CdO suffers from a serious drawback of toxicity of cadmium fumes and hence is likely to be completely banned. Many research centers are carrying out work aimed to obtain a material for electrical contacts which would not contain the harmful cadmium oxide.

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Ag-SnO_2 and Ag-ZnO could be used to replace toxic Ag-CdO contact materials. Sn, Zn and Cd have similar physical and chemical features. Therefore, the materials with SnO_2 and ZnO are characterized by high functional properties [3-5] and they are widely studied [6-9].

In this work the improved technique of the electrocontact production by co-precipitation using a surface-active agent are presented.

Experimental

Materials

The initial materials are: $AgNO_3$, $Na_2SnO_3•3H_2O$, $Zn(NO_3)_2•6H_2O$, NaOH, Na_2CO_3, polyvinylpyrrolidone (PVP). All the reagents used were analytical grade. The relative molecule weight of PVP is 35000±5000.

Characterization

Thermogravimetric analysis (TGA) was carried out in argon on the Netzsch STA 449C Jupiter thermoanalyzer at the heating rate of 10 ˚C/min. The phase composition was analyzed by X-ray diffraction (XRD) using Cu Kα (λ = 1.54056 Å) radiation on the X'Pert-Pro X-ray diffractometer. Microstructure was characterized by scanning electron microscope (Jeol JSM-7001F, EJUC SFU). The electrical conductivity of contact materials was measured by dual-probe technique.

Synthesis

The processes used for making of Ag/SnO_2 and Ag/ZnO materials shown in Fig. 1. In the process (Fig. 1a) aqueous solutions containing an unstable-oxide-forming metal and silver are mixed with aqueous solutions containing a soluble hydroxide or carbonate causing co-precipitation of the metals as metal hydroxide or metal carbonate. The following chemical reaction took place (Fig. 1a, 1-4):

$$2AgNO_3+Na_2CO_3=Ag_2CO_3\downarrow+2NaNO_3, \quad (1)$$

$$5Zn(NO_3)_2 + 2Na_2CO_3 + 6NaHCO_3=Zn_5(CO_3)_2(OH)_6\downarrow+ 10NaNO_3 + 6CO_2\uparrow, \quad (2)$$

$$Na_2[Sn(OH)_6] + 2AgNO_3=Ag_2[Sn(OH)_6] + 2NaNO_3= \\ =Ag_2O\downarrow+SnO_2•nH_2O\downarrow+ 2NaNO_3, \quad (3)$$

$$2AgNO_3 + 2NaOH = Ag_2O\downarrow+ 2NaNO_3 + H_2O. \quad (4)$$

Then the precipitates were filtered, washed with deionized water and dried at 373 K to steady weight (Fig. 1b). After washing and filtering, the solid products were heated at 723 K for 1,5h in an oven for the decomposition of co-precipitates, yielding Ag and ZnO (or SnO_2) (Fig. 1c). The process (Fig. 1d) consists of pressing the powder in a die into the shape of the desired contact (P=300MPa), sintering the pressed compact (T=1123 K), repressing (P=1000MPa), and annealing the compact (T=773 K).

Results and discussion

Fig. 2 represents TG-DTA curves of mixtures of silver carbonate with basic zinc carbonate (Fig. 2a) and silver oxide with stannic acid (Fig. 2b). This analysis was made for the experimental justification of the decomposition temperatures of precipitates.

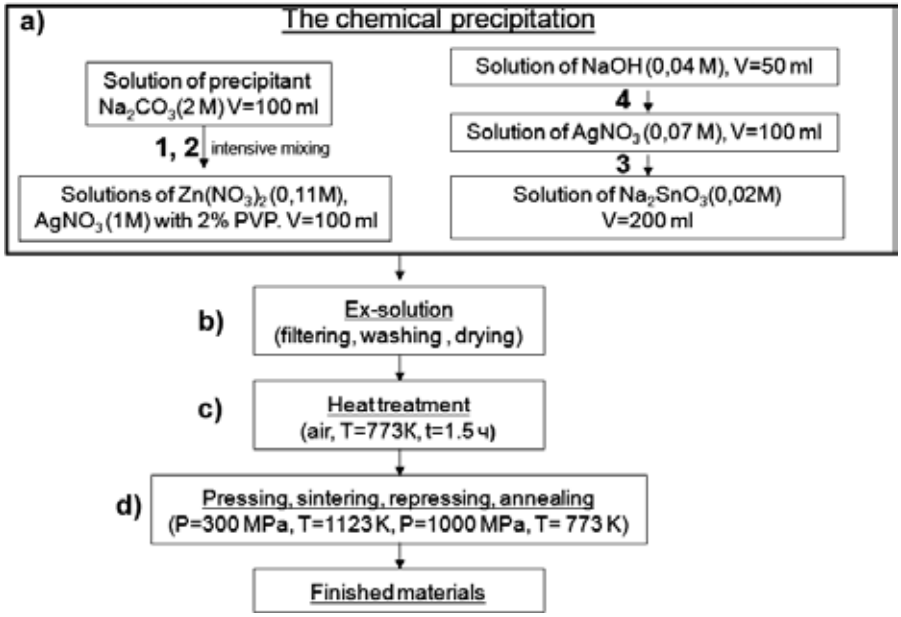

Fig. 1. The production model of making of Ag/SnO_2 and Ag/ZnO materials

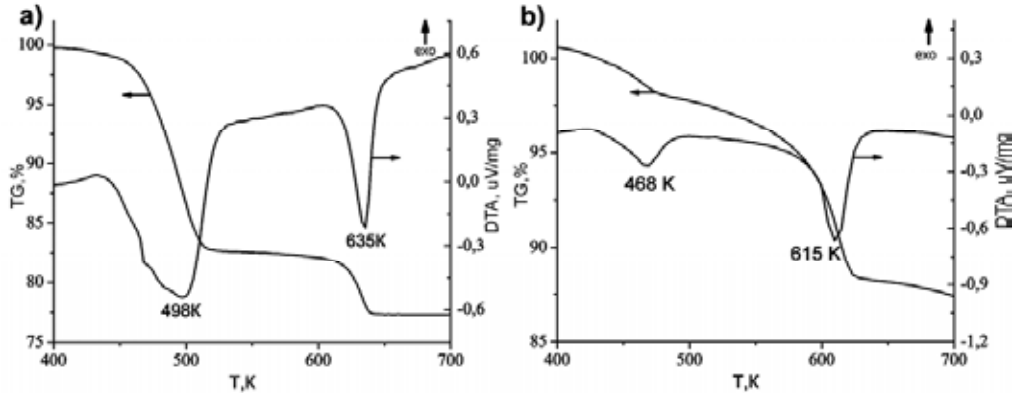

Fig. 2. The TG-DTA curves: a) precipitate of silver carbonate with basic zinc carbonate, b) precipitate of silver oxide with acid stannic

The TGA traces confirm that the decomposition process starts at about 430 K (Fig. 2a) and 420 K (Fig. 2b) and finishes at about 660 K (Fig. 2a) and 645 K (Fig. 2b). In the Fig. 2a two evident plateaus appear on the TG curve corresponding to two endo-effects on the DTA curve with the minima at 498 K and 635 K. The first plateau in the temperature range of 430–540 K is connected with the simultaneous decomposition of $Zn_5(CO_3)_2(OH)_6$ and Ag_2CO_3. The second plateau is joined with the decomposition of Ag_2O. Therefore, the thermal decomposition of the sample (Fig. 2a) is expressed by the following chemical equations:

$$Ag_2CO_3 = Ag_2O + CO_2\uparrow, \quad (5)$$

$$Ag_2O=2Ag+1/2O_2\uparrow, \quad (6)$$

$$Zn_5(CO_3)_2(OH)_6 = 5ZnO + 2CO_2\uparrow + 3H_2O. \quad (7)$$

The mass losses on the TG curve (Fig. 2b) correspond to the decomposition of the silver compounds (eq. 5, 6) the same as the mass losses in Fig. 2b. The thermal decomposition of stannic acid wasn't registered.

Fig. 3 shows the XRD patterns of the precipitates and powders calcined at 773 K. The precipitate (Fig. 3a) is two-phase system and consists of silver carbonate (Ag_2CO_3) and basic zinc carbonate ($Zn_5(CO_3)_2(OH)_6$). The precipitate (Fig. 3c) contains an amorphous phase, therefore, the definite identification of diffraction peaks is difficult. After thermal processing the observed phases were Ag and ZnO (Fig. 3b) or SnO_2 (Fig. 3d).

The microstructure of the thermal decomposition powders and surface morphology of the sintering materials of Ag/ZnO and Ag/SnO_2 are illustrated in Fig. 4. The microstructure of Ag/ZnO and Ag/SnO_2 compacts are significantly different. The Ag/ZnO powder (Fig. 4, a) consists of particles of silver (dark area, ~ 2μm) and zinc oxide (light area, in the range of 15-25 nm). After sintering, the particle size of zinc oxide increases to 300 nm (Fig. 4, b, dark area). These ultrafine particles homogeneously distributed through the volume of the matrix of silver.

From Fig. 4 (c), it can be seen that the Ag/SnO_2 powder is silver coated tin oxide and the particle sizes are varied over a wide range. The microstructure of Ag/ SnO_2 sintering compact (Fig. 4, d) consist of larger tin oxide grains (dark area, in the range of 1-5 μm) and matrix of silver (light area).

Physical and mechanical properties of samples with different oxide metals were listed in Table 1.

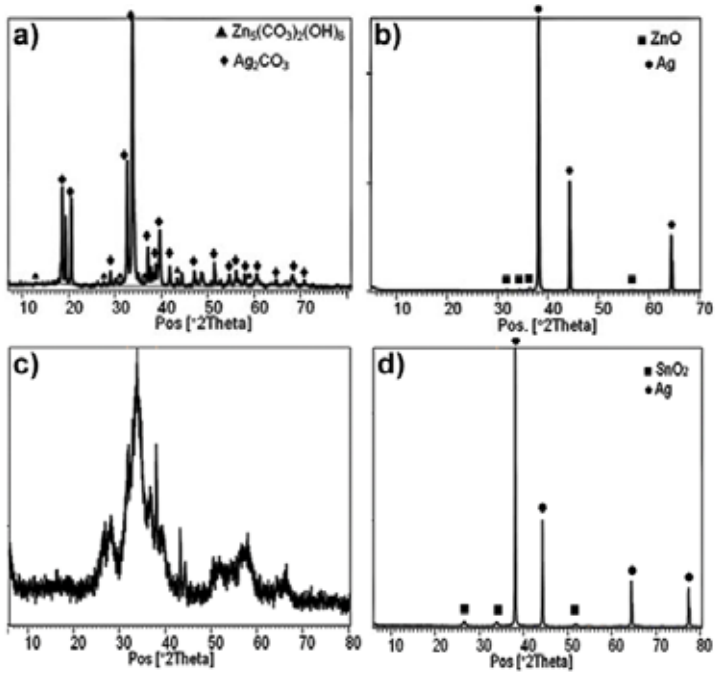

Fig. 3. The XRD patterns of the precipitates (a, c) and powders calcined at 773 K (b, d)

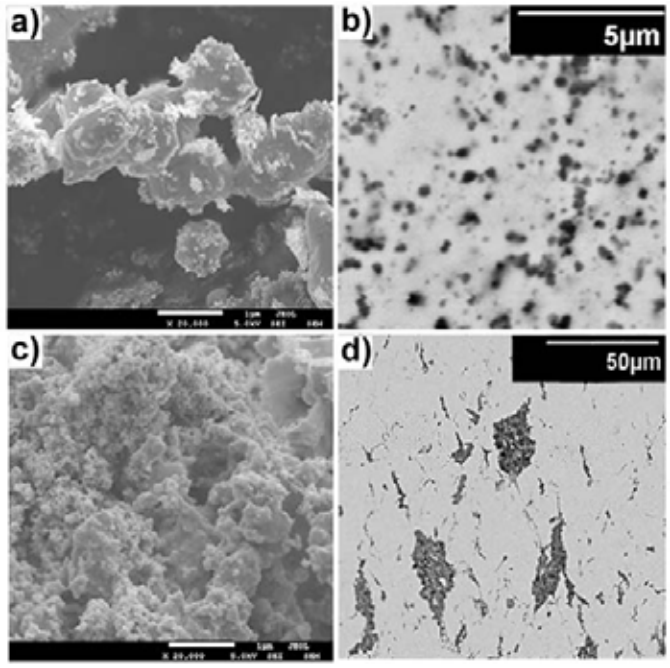

Fig. 4. SEM micrographs of the microstructure of Ag/ZnO (a), Ag/SnO_2 (c) powders and surface morphology of Ag/ZnO (b), Ag/SnO_2 (d) sintering materials

Table 1. Physical and mechanical properties of samples

Sample name	Density (g/cm^3)	Relative density (%)	Hardness, HV (MPa)	Resistivity (μΩ·cm)
Ag/8ZnO	9,62	98	91	2,5
Ag/10SnO_2	9,69	97	95	2,4

Conclusion

In this work the method of chemical precipitate for making uniformly mixed Ag/ZnO and Ag/SnO_2 composition is improved. The results can be concluded as follows:

1) The surface-active agent (PVP) has an effect on the dispersity of powders. It decreases size of particles.

2) The thermal decomposition of obtained precipitates takes place in the range of 430-660 K (for Ag- ZnO) and 420-645 K (for Ag-SnO_2).

3) The properties of obtained contact materials are: relative density is about 0.97-0.99; resistivity is 2.5 μΩ·cm for the concentration of ZnO equal 8 % and 2.4 μΩ·cm for the concentration of SnO_2 equal 10%.

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Получение электроконтактных материалов Ag/ZnO и Ag/SnO_2 из высокодисперсной соосажденной порошковой смеси

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*Рассмотрены процессы изготовления электроконтактных материалов Ag/ZnO и Ag/SnO_2 из химически соосажденных прекурсоров. На всех стадиях получения порошки и компакты охарактеризованы методами РСА, РФА, ТГА/ДСК и СЭМ. Размер частиц в спеченном компактированном образце находится в диапазоне 0,1-0,3 μм для ZnO и 1-5 μт для SnO_2. Размер частиц главным образом зависит от условия химического осаждения и параметров металлургического передела. Относительная плотность готовых компактов имеет значения 0,97-0,99. Сопротивление 2,5 μОт*см для образца, содержащего 8% ZnO, и 2,4 μОт*см для 10% SnO_2. Дуговая эррозия (условия испытания – постоянный ток, 380 В, 30 А, cos fi=0,8) зависит от содержания оксида и превышает износ контактов серии Ag/CdO.*

Ключевые слова: химическое соосаждение, смесь порошков, электроконтактные материалы.