ELECTROPHYSICAL AND PHYSICAL-MECHANICAL PROPERTIES OF THE COMPOSITE SnO₂-Ag (SEMICONDUCTOR-METAL) CERAMIC MATERIAL

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ABSTRACT

We investigated the physical and electrical properties of ceramics based on SnO₂-Sb₂O₃-AgO. Electrical properties were investigated in the temperature range 20-1000 K. It is shown that in the temperature range 200-450 K dependence of the electrical resistivity ceramics with temperature shifts from an exponential curve to another, characterized by a high electrical resistivity. This is explained by the closure of the mesh silver percolation channels formed in the synthesis of ceramics.

Keywords: ceramics based on tin, high electrical conductivity, percolation channels silver.

INTRODUCTION

The SnO₂-based ceramics is being widely used in many industries (Nistro, 2003). Tin dioxide is a semiconductor with the forbidden band energy 3.54 eV (Knunyats, et al., 1988) having unique properties - in the first place high electrical conductivity and chemical resistance.

Chemically resistant ceramics of a high electrical conductivity is of great interest as electrode material (Jinhuai, et al., 2003) operating at high temperatures, for instance in aluminium electrolysis and glass production (Kirko, et al., 2010).

Without additives SnO₂ has a low sinterability and electrical conductivity (Bueno and Varela, 2006). The poor sinterability is caused by the domination of evaporation-condensation processes over diffusion. The intensive evaporation starts at 1100 °C (Haarber, et al., 2010). To improve sinterability there are used additives such as ZnO (Bureno, et al., 2008), CuO (Kirko, et al., 2012), MnO₂ (Yatao, et al., 2010; Zuca, et al., 1991), CoO (Cerri, et al., 1996), Fe₂O₃ (Zuca, et al., 1991). And electrical properties are improved with V₂O₅ (Mahipal and Mastikhi, 1992) and Sb₂O₃ (Ciorcero, et al., 2011).

In spite of the substantial improvement of the material’s electrophysical properties at high temperatures (above 600 °C), its electrical conductivity remains low at the room temperature, that makes it difficult for the material to be used and requires additional conditions (Dobrosmislov, et al., 2010). The reduction of the material’s electrical resistance at low temperatures will allow widening the field of its application (Figure-1).

In semiconductors the total electric current is a sum of partial currents, provided by p- and n-type conductivities (Zeeger, 1981). In case of a contact of a p-type semiconductor with a metal there appears a space charge region of ionized donors and the blocking contact, or Schottky barrier, forms (Parker, 1994).

This means that the addition of Ag superdispersed particles into the ceramics structure will allow an additional number of charge carriers to appear in the semiconductor-metal contact zone that will increase the electrical conductivity (Lakishev, 1996).

Figure-1. Phase diagram Ag-O.

It can be seen from the phase diagram Ag-O in Figure-1 that in the range 850 - 900 °C there takes place
the reduction of silver from its oxide. Accordingly, the addition of the silver oxide into the initial furnace charge allows making a ceramic material with silver particle additives.

THE EXPERIMENTAL TECHNIQUE

The synthesis technique: The material was synthesized according to the following technique: the furnace charge preparation→ pressing the powder with 5% polyvinylalcohol (PVA) → sintering at 1300 and 1400°C. For physical-mechanical tests the ceramic specimens were made in the form of cylinders 15 mm in diameter and of 10 mm height. For electrophysical measurements the specimens had the rectangular shape 5×4×50 mm.

The research of physical-mechanical properties of the specimens was carried out according to the State Standards 24468-80, 530-95, 20419-83. The resistivity within the temperature range 20-1000 °C was measured with the four-point probe method (Dharmasema and Wadley, 2002). To measure mechanical characteristics there was used the instrument Instron 3369. The material structure was identified by the X-ray phase analyzer XRD 6000 and electron microscope JEOL JSM-6490 LV.

To increase the electrical conductivity at high temperatures antimony oxide additives were used. When sintering at high temperatures the dissolution of antimony atoms in the SnO2 crystal lattice occurs (Galahov, et al., 1987) that provides the p-type conductivity of the material and substantial reduction of the band-gap energy (Ciorcero, et al., 2011). To improve the conductivity at low temperatures there are used superdispersed metallic silver particles that increase the charge carrier’s concentration in the semiconductor-metal contact zone.

The physical-mechanical properties of the SnO2-Ag (semiconductor-metal) material are presented in Table-1.

Table-1. The physical-mechanical properties of the composite material.

<table>
<thead>
<tr>
<th>No.</th>
<th>Charge composition, %</th>
<th>Sintering temp., °C</th>
<th>Density, kg/m³</th>
<th>Open porosity, %</th>
<th>Strength, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SnO2</td>
<td>Sb2O3</td>
<td>AgO</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>4366</td>
</tr>
<tr>
<td>2</td>
<td>96</td>
<td>2</td>
<td>2</td>
<td>1300</td>
<td>4552</td>
</tr>
<tr>
<td>3</td>
<td>92</td>
<td>2</td>
<td>6</td>
<td>1300</td>
<td>4619</td>
</tr>
<tr>
<td>4</td>
<td>96</td>
<td>2</td>
<td>2</td>
<td>1400</td>
<td>3760</td>
</tr>
<tr>
<td>5</td>
<td>92</td>
<td>2</td>
<td>6</td>
<td>1400</td>
<td>3798</td>
</tr>
<tr>
<td>6</td>
<td>90</td>
<td>2</td>
<td>8</td>
<td>1400</td>
<td>4377</td>
</tr>
</tbody>
</table>

The conducted research of physical-mechanical properties of the SnO2-Ag composite material showed that the ceramics is badly sintered and has as a consequence a high porosity and low strength. This is caused by the following. It is well known that to intensify sintering it is necessary that the material should be well wetted by a liquid phase (Savitskiy, 1991). However, the limiting wetting angle for SnO2 at the porosity 0.01 % and within the temperature range 950-1020 °C is (72.4 ± 4.3) degrees (Denisova, 2009). Silver reduced from its oxide inhibits the SnO2 diffusion. The degradation of basic physical-mechanical properties of the material, when increasing the sintering temperature from 1300 to 1400 °C, supports the fact that silver inhibits sintering.

The X-ray phase analysis (Figure-2) of the material confirmed the presence of a metallic silver phase in the ceramics structure.
Figure-2. The X-ray diffraction pattern of a specimen with the initial furnace charge composition 
90%SnO₂-2%Sb₂O₃-8% AgO.

The raster electron microscopy showed (Figure-3) that silver segregates in the form of superdispersed 
particles. And there are pores of a significant size in the 
material that supports poor sintering and low physical-
mechanical properties.

Figure-3. The raster electron microscope photography of the specimen with the initial furnace charge 
composition 90%SnO₂-2%Sb₂O₃-8% AgO a) – x2000; (b) – x100.

The micro X-ray spectroscopic analysis results 
(Figure-4) showed that silver is dispersed quite uniformly, 
but its concentration is not high that may be associated 
with its partial dissolution in the tin dioxide structure.
ELECTROPHYSICAL PROPERTIES OF THE CERAMICS

In Figure-5 there are presented the resistivity measurement results of the SnO$_2$-Ag composite material sintered at 1300 °C.

As follows from the research carried out the superdispersed silver particles affect significantly the electrical conductivity of the material. Firstly, a significant drop of the temperature of the percolation beginning is observed. Secondly, the shape of the curve in Figure-5 suggests that there is a possibility of the electron passage from the metallic particles into the tin dioxide conduction band. It can also be noted that when the silver portion increases, there takes place saturation of the conduction band by charge carriers, and the resistivity doesn’t depend on the silver concentration any more.

In Figure-6 there are presented the resistivity measurement results of the SnO$_2$-Ag composite material sintered at 1400 °C.

The increased sintering temperature leads to increased resistivity in the low temperature range. In the range above 900 °C the resistivity is almost independent of the silver concentration. An influence of the additional space charge on the material conductivity at high temperatures is almost absent. This effect can be explained by the fact that the potential barrier value on the semiconductor-metal boundary doesn’t depend on temperature.
CONCLUSIONS

The usage of the silver oxide additives when making SnO2-based ceramics allows decreasing significantly the composite material resistivity, especially at low temperatures, which is associated with silver reduction from its oxide. This effect is associated with the formation of the space charge region in the semiconductor-metal contact zone.

Temperature dependencies of the resistivity for the materials with 4 and 8 weight % of silver and sintered at 1300 °C are practically the same.

For the ceramics sintered at 1400 °C there is observed an obvious dependence of the resistivity on the concentration. The percolation beginning temperature increases by 150 °C compared to that of the material sintered at 1300 °C. The sintering temperature increase may lead to silver particles being distributed more uniformly along the grains’ boundaries.

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