Electrophysical and mechanical properties of SnO_2–Sb_2O_3–C ceramic-based composite material**

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Materials based on tin oxide and antimony oxide are of great interest as they are conductive at high temperatures and possess high corrosion resistance in corrosive environments such as the electrolytes used in aluminium electrolysis. Hence these tin dioxide-based materials can find wide application as current-carrying anodes in aluminium production. In this work the electrophysical and mechanical properties of SnO_2–Sb_2O_3–C ceramics have been studied. Materials have been synthesized by: preparing the mixture, pressing with polyvinyl alcohol, drying and firing at 1573 K. Specific electrical resistivity in the range 20–1000 °C was measured by a four-contact method. Thermophysical characteristics were obtained by a laser flash method. Material phase composition was determined by X-ray analysis, and microstructure by electron microscopy. It was demonstrated that the specific electrical resistance of 96%SnO_2–2%Sb_2O_3–2%MnO_2–2%C at 600–700 °C is practically temperature-independent. Above 700 °C the specific electrical resistivity of the material begins to increase catastrophically due to carbon oxidation. At temperatures 700–1200 °C the specific electrical resistivity becomes the same as that of a classical semiconductor and practically the same as that of carbon-free ceramics with composition 96%SnO_2–2%Sb_2O_3–2%MnO_2. The replacement of MnO_2 by Al_2O_3 allows enlarging the temperature range of the electrical resistivity stability up to 1200 °C.

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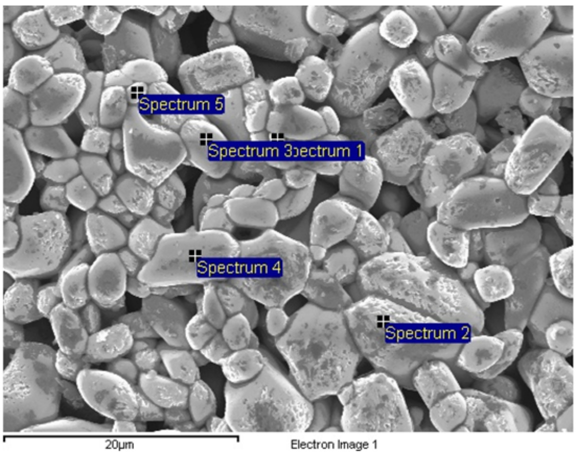
1. Introduction

Materials made from tin and antimony oxides are of interest because they are electrically conductive at high temperatures and have high corrosion resistance in aggressive substances such as the electrolyte used in the electrolysis of aluminium [3–9]. The main problem in using these materials is low electrical conductivity at low temperatures. To prevent destruction of electrodes when lowering them into the electrolyte, preheating is therefore necessary, at least up to the aluminium electrolysis temperature.

With that proviso, tin dioxide materials can become widely applied as current-carrying anodes in aluminium production. In the work reported here, electrophysical, physicomechanical and thermophysical features of SnO_2–Sb_2O_3–C ceramics have been investigated.

2. Experimental

Material synthesis: mixing of precursors in an agate mortar → mould powder containing 5% polyvinyl alcohol → isostatic pressing at 100 MPa → drying → thermal treatment. Pressed samples were dried in an air cabinet at 383 K to 2–4% moisture content. Thermal treatment was carried out in an open muffle furnace at 1673 K. Fig. 1 shows that the resulting structure of ceramics is granular—the particles are clinkered only in certain areas.



Spectrum	O	Si	Mn	Sn	Sb
Spectrum 1	79.87	0.68	0.59	18.71	0.82
Spectrum 2	73.17	0.57	0.56	25.55	0.71
Spectrum 3	62.20	0.60		37.8	
Spectrum 4	62.41		2.40	31.88	3.31
Spectrum 5	65.28	0.57		34.72	
max.	79.87	0.68	2.40	37.88	3.31
min.	62.20	0.57	0.56	18.71	0.71

Figure 1. (Left) scanning electron micrograph of 96%SnO_2–2%Sb_2O_3–2%MnO_2–2%C ceramics obtained at a firing temperature of 1673 K; (right) atom% from energy-dispersive X-ray spectroscopy (EDX) at the places marked on the micrograph.

To obtain the SnO_2–C composite, porous ceramics were soaked for 30 min in an aqueous solution of glucose prepared by boiling 150 g of glucose ($C_6H_{12}O_6$) in 100 g distilled water. Following soaking, the material was dried in an air cabinet for 4 h at 383 K. Samples 1 and 3 were then burnt at 773 K in air, and samples 2 and 4 at 873 K in carbon powder.

According to X-ray phase analysis using an XRD 6000 instrument, in 96%SnO_2–2%Sb_2O_3–2%MnO_2–2%C and 96%SnO_2–2%Sb_2O_3–2%Al_2O_3–2%C, only SnO_2 with the rutile structure has been detected. Oxides of antimony, manganese and aluminium, as well as of carbon, have not been found due to their low concentrations.

Physicomechanical tests have been carried out with an Instron 3369 testing machine. Samples were made in the form of cylinders (diameter 15 mm and height 10 mm).

The specific electrical resistivity within the temperature range 20–1270 K was measured by a four-contact method. Samples were rectangular prisms ($5 \times 5 \times 50$ mm) and were heated in air.

Thermophysical characteristics have been obtained by a laser flash method using a Netzsch LFA 457 apparatus. Samples had a cylindrical shape (diameter 8 mm and height 5 mm). The measurements were carried out in an argon environment.

3. Results and discussion

Physicomechanical features are given in Table 1. The synthesized samples have a high open porosity, which is reflected in indifferent strength characteristics. The theoretical density of this ceramic is 6.9 g cm^{-3}, while the density of the synthesized ceramics does not exceed 5.65 g cm^{-3}. The porosity in the synthesized ceramic material is mainly open, which expedites qualitative infiltration of the entire material with the glucose solution.

Table 1. Physicomechanical features of the synthesized ceramics.

Sample №	Content of starting materials (wt%)					Density/ g cm^{-3}	Open porosity (%)	Strength/ MPa
	SnO_2	Sb_2O_3	Al_2O_3	MnO_2	C			
1	96	2	2	-		3.91	42.9	58.0
2	96	2	-	2	-	5.64	17.9	155.3
3	94	2	2	-	2	3.92	42.2	57.5
4	94	2	-	2	2	5.65	18.7	154.6

Fig. 2 shows the specific electrical resistivity of the ceramics with manganese dioxide. Curves 1 and 2 have three characteristic regions of behaviour. In the first (temperature range 300–720 K for curve 1 and 300–780 K for curve 2) the resistivity does not depend on the temperature. In the second, starting from 720 K (curve 1) and from 780 K (curve 2), the temperature engenders a sharp rise of electrical resistance. It is ascribed to burning off the carbon. When the samples are reheated to 1200 K after the carbon burning, the temperature dependence of the resistivity decreases exponentially and resembles that of the samples without carbon (curve 3).

Taking into account the fact that during aluminium electrolysis the anodes operate under anaerobic conditions, it can be assumed that the sharp rise in the second region will disappear and the resistivity, thus, will immediately reach its high-temperature values.

Fig. 3 shows the analogous behaviour of the materials with aluminium oxide. In this case it is also possible to distinguish three characteristic temperature regions: 300–650 K, where the resistivity is practically independent of the temperature; 650–800 K, where the resistivity starts to incease with increasing temperature; and finally the region with $T > 800$ K, where the resistivity approaching the high-temperature values of carbon-free ceramics.

The absence of an increase of resistivity can be attributed to the reduction of Al_2O_3 in the glucose environment and the formation of conductive aluminium layer as a result, just as it is in [1,2] with silver oxide added to ceramics.

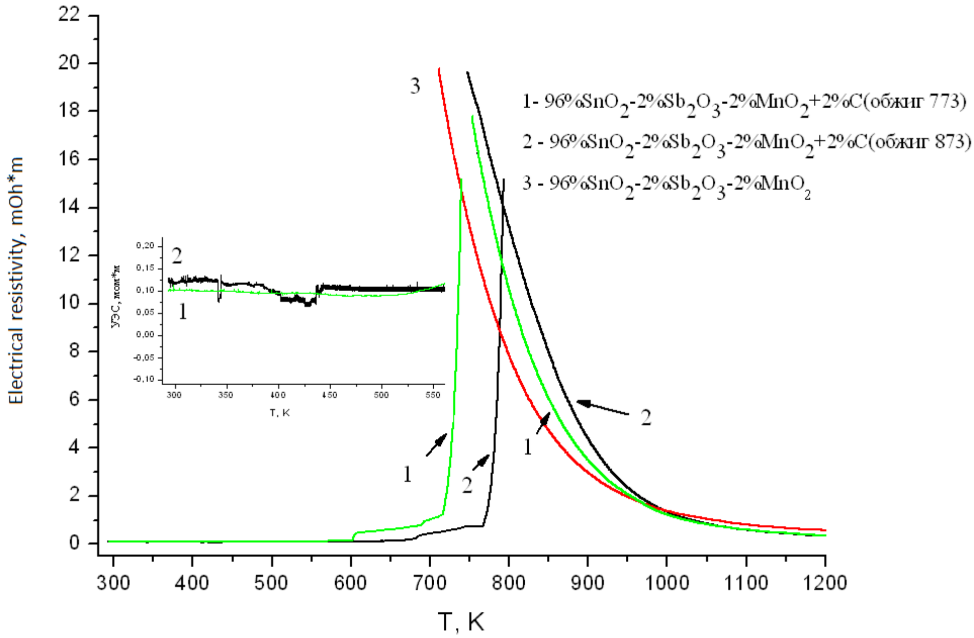


Figure 2. Temperature dependence of the specific electrical resistivity of ceramics with added manganese dioxide.

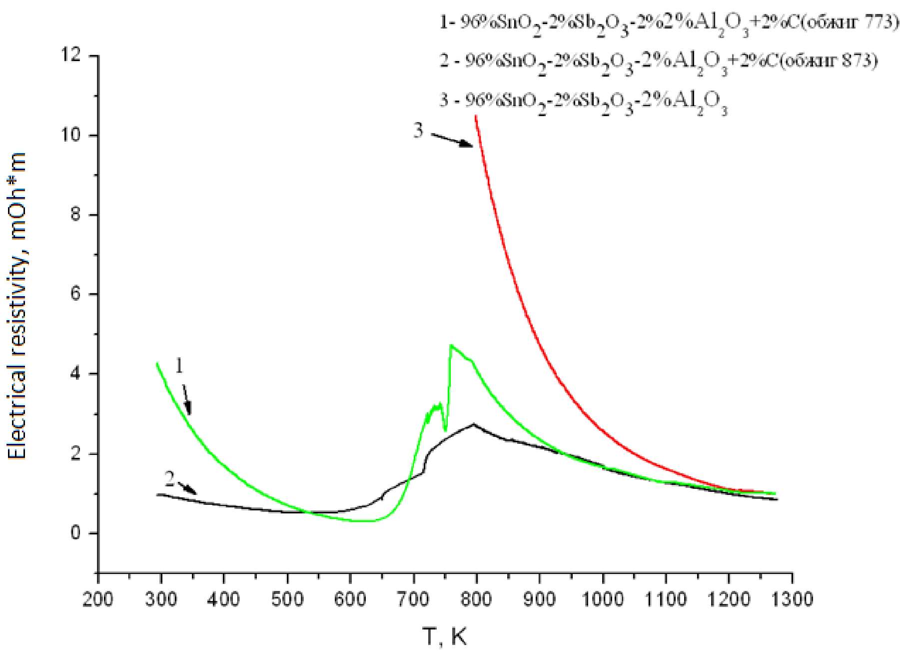


Figure 3. Temperature dependence of the specific electrical resistivity of ceramics with added aluminium oxide.

Thermal conductivities are presented in Fig. 4. It can be inferred that the main factor affecting thermal conductivity is porosity, which is about 42% for the Al_2O_3-containing ceramics and only about 17% for the MnO_2-containing ceramics; hence the increased thermal conductivity in the latter compared to the former. Note that the specific electrical resistivity does not affect the thermal conductivity.

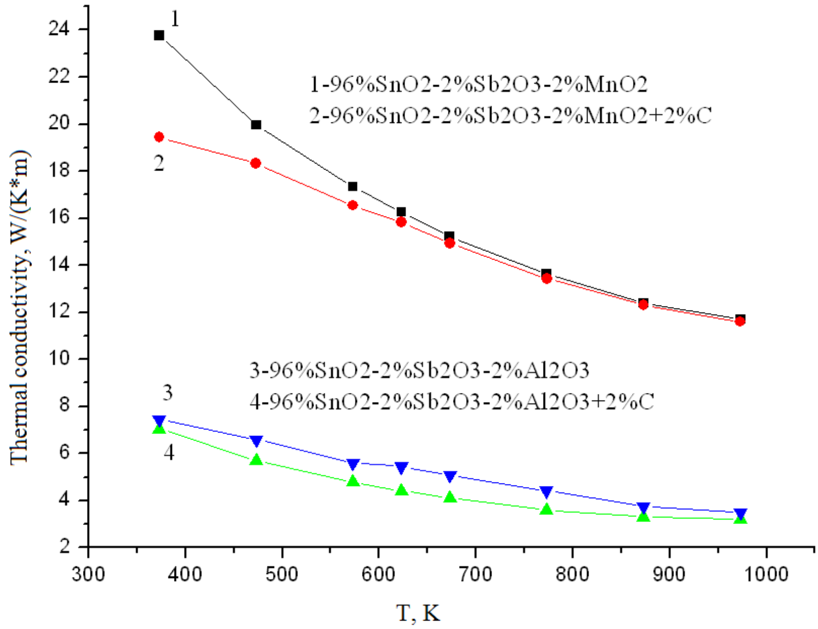


Figure 4. Temperature dependence of the thermal conductivity of tin dioxide-based ceramic composite materials.

4. Conclusions

1. Tin oxide-based ceramics containing antimony oxide admixed with manganese dioxide or aluminium oxide and synthesized with and without carbon have been investigated. The mechanical properties of the ceramics are poor with strength not exceeding 150 MPa, due to the low density.

2. The specific electrical resistivity of the MnO_2-containing ceramics with C barely depends on temperature up 700~800 K. Above 700 K, the resistivity starts rising sharply due to carbon oxidation. At 700–1200 K, the resistivity becomes that of a classical semiconductor and nearly coincides with that of the carbon-free samples.

3. Replacing MnO_2 by Al_2O_3 extends the temperature range of stable resistivity up to 1200 K and suppresses the sharp rise in electrical resistivity within the range 650–800 K.

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