PHYSICAL AND CHEMICAL PROPERTIES OF THE SOLID ELECTROLYTES
CONSISTING OF ZrO₂ STABILIZED PARTIALLY WITH
A MIXTURE OF Y₂O₃-Yb₂O₃-Sc₂O₃

T. V. Chusovitina, Yu. S. Toropov, M. G. Tretnikova, and S. A. Gladkovskaya

The application of stabilized zirconium dioxide in the production of solid electrolytes of the oxygen-sensing elements is well known. In view of the specific operational conditions of the sensing elements (abrupt temperature gradients and a high level of vibration), the solid electrolytes must possess adequate thermal stability and mechanical strength besides a significant oxygen ion conductivity.

This paper deals with a study of the physicochemical properties of zirconium dioxide containing a Y₂O₃ + Yb₂O₃ + Sc₂O₃ mixture (amounting to 4%) in order to use this material for the production of solid electrolytes having superior thermomechanical properties as compared to those of the electrolytes based on cubic zirconium dioxide.

The thermomechanical properties of the ceramics based on partially stabilized zirconium dioxide can be improved by retaining the high-temperature tetragonal phase right up to room temperature [1]. In order to obtain ceramics having mainly a tetragonal structure, it is necessary to use ultrafine powders [2, 3]; of equal importance is the regime of heat treatment of the obtained products [4].

In view of the fact that the production of the powders based on zirconium dioxide according to the method of coprecipitation of the components (that was developed at VostIO) makes it possible to obtain quite finely dispersed materials, we studied the aspects concerning the effect of heat treatment of the products obtained from the material consisting of ZrO₂ - 4% Y₂O₃ + Yb₂O₃ + Sc₂O₃ mixture on the phase formation, the strength characteristics, and the electrophysical properties; furthermore, we examined the stability of conductivity under cyclic thermal loads and during isothermal swells and the thermal stability of the electrolytes under different conditions of loading.

It is known that high-temperature firing of the ceramics based on partially stabilized zirconium dioxide leads to recrystallization of their grains; during subsequent cooling, the content of the tetragonal phase decreases abruptly and the content of the monoclinic structure increases [5]. In view of this, in order to produce strong ceramics from partially stabilized ZrO₂, it is necessary to obtain a sintered product at a lower temperature.

The hydroxide powder obtained according to the method of chemical coprecipitation was subjected to calcination at 1000°C and was milled using ball mills until the main size of the aggregates amounted to 1.5-2.5 μm; the specific surface of the milled powder was found to be 5.7 m²/g. Products were obtained according to the slip casting method and were fired under different thermal conditions.

The quantitative content of the phases present in the specimens was calculated according to the following equations [6]

\[ C_a = \frac{I_a(111) + I_a(111)}{I_d(111) + I_d(111) + I_{t, c}(111)}, \]  
\[ \frac{C_m}{C_t+ C_c} = 0.82 \frac{I_d(111) + I_d(111)}{I_{t, c}(111)}. \]  

*Here and elsewhere, mole fractions are given.*

TABLE I. Characteristics of the Specimens Containing ZrO₂ and 4% Mixture of Y₂O₃ + Yb₂O₃ + Sc₂O₃

<table>
<thead>
<tr>
<th>Firing temp., °C</th>
<th>App. density, g/cm³</th>
<th>Open porosity, %</th>
<th>Ult. bend strength, N/mm²</th>
<th>Content of phases, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1450</td>
<td>5.87</td>
<td>0.5</td>
<td>470</td>
<td>83</td>
</tr>
<tr>
<td>1400</td>
<td>5.79</td>
<td>0.6</td>
<td>500</td>
<td>90</td>
</tr>
<tr>
<td>1350</td>
<td>5.83</td>
<td>0.4</td>
<td>95</td>
<td>5</td>
</tr>
<tr>
<td>1350 (10)</td>
<td>5.86</td>
<td>0.5</td>
<td>500</td>
<td>90</td>
</tr>
</tbody>
</table>

*The duration of holding τ at the firing temperature, h, is indicated within brackets. In all the remaining cases, it amounted to 3 h.

\[
\frac{C_c}{C_t} = 0.88 \frac{I_c(400)}{I_t(400) + I_t(004)}
\]

\[
C_m + C_t + C_c = 100\%
\]

where \(C_m\), \(C_t\), and \(C_c\) are the contents of the contents of the monoclinic, the tetragonal, and the cubic phases, respectively; \(I_m(111)\) and \(I_m(111)\) represent the line intensity of the monoclinic phase due to x-ray diffraction from the (111) and (111) planes, respectively; \(I_c, t(111)\) is the total intensity of the lines of the cubic and the tetragonal phases due to diffraction from the (111) plane; \(I_c(400)\) is the intensity of the (400) line of the cubic phase; and \(I_t(400)\) and \(I_t(004)\) represent the intensity of the (400) and the (004) lines of the tetragonal phase.

The obtained data (Table I) show that the ceramic undergoes satisfactory sintering even at 1400°C; sintering of the ceramic can be improved by increasing the duration of holding at 1350°C up to 10 h. As the firing temperature and the duration of holding are increased, a change in the phase composition occurs: the content of the tetragonal phase decreases and the content of the monoclinic phase increases simultaneously; at 1450°C, the content of the cubic phase also increases along with them. The increased content of the monoclinic phase owes to the grain growth of the tetragonal structure that undergoes transformation during subsequent cooling. This is indicated by the data of the electron microscopic studies. The micrographs (Fig. 1) show that on increasing the firing temperature from 1350 up to 1450°C, the average grain size increases from 0.1-0.5 up to 0.5-2.0 μm. Increasing the duration of holding at 1350°C leads to the growth of the grains up to 0.3-0.7 μm.

According to us, the second reason underlying the phase redistribution in the system is as follows: with increasing temperature, the diffusion process of the lattice ions is activated and the cations of the stabilizer tend to occupy more stable positions owing to which formation of the cubic structure occurs. Most probably, the stabilizer-depleted tetragonal structure transforms into the monoclinic form during the process of cooling. The products are characterized by a fairly high ultimate bend strength (470-500 N/mm²); their strength tends to decrease as the content of the cubic and the monoclinic phases increase (Table I).

The electrical resistivity measurements carried out in the 500-1000°C range indicate (Fig. 2) that its magnitude decreases with increasing firing temperature and the decrease is most significant at temperatures exceeding 1400°C.

We note that the differences observed at low temperatures are more significant than those observed at high temperatures. The lower resistivity values of the specimens fired at 1450°C owe, probably, to the high content of the cubic phase whose lattice facilitates the diffusion of oxygen ions to a greater extent.

The stability of the electrical characteristics of the given materials was studied at 700 and 900°C; the duration of isothermal holding amounted to 300 h. It was established that the firing temperature does not have any effect on the aging process of the specimens. During the process of isothermal holding at 700°C, the electrical resistivity of the specimens was found to increase during the first 150 h; thereafter, it did not virtually increase and the overall degree of aging amounted to 18-20% (Fig. 3). When holding at 900°C, the resistivity