SYNTHESIS OF LOW-AGGLOMERATED
NANOPRECURSORS IN THE ZrO$_2$-HfO$_2$-Y$_2$O$_3$ SYSTEM

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Received: June 17, 2005

Abstract. It is well known that so-called stabilized zirconia is a perspective material for application as a solid electrolyte in high-temperature oxygen sensors. Fabrication of solid electrolytes from nano-sized precursors significantly improves their characteristics. In this investigation low-agglomerated nanopowders with a cristallite size of 3-5 nm have been synthesized in the ZrO$_2$-HfO$_2$-Y$_2$O$_3$ system using the back-coprecipitation method. The effect of the experimental conditions on the size of cristallites and agglomerates in the powders obtained has been studied. It has been shown that synthesis in ultrasonic bath enables to obtain precursors with the lowest degree of agglomeration.

1. INTRODUCTION

Yttria-stabilized ZrO$_2$-based solid solutions with a fluorite-type cubic structure are widely used as a solid electrolyte in high-temperature oxygen sensors [1,2]. Such sensors are essential for analysis of gaseous and liquid media in glassmaking and blast furnaces, in cement production, in energetic plants to controle a completeness of a fuel burning-away and so on. The efficient and long-time use of the sensors is hampered by a number of physicochemical processes; the main of them are: (1) the possible formation of the Zr$_{7}$Y$_{3}$O$_{12}$ rhombohedral compound [3,4], which leads to a drastic change in the unit cell volume and, as a consequence, the destruction of a solid electrolyte material; and (2) the interaction of these composite compounds with oxide melts [5,6]. A transition layer containing the products of ceramic decomposition is formed at the interface between the solid electrolyte and the melt. As a result, a variable contribution from the junction potential to the galvanic cell emf appears; in turn, it substantially affects the measurement accuracy. So, an important problem is to develop new sensor materials which are free of the aforementioned disadvantages. HfO$_2$-based isomorphous solid solutions are suggested as a perspective materials here since they exhibit unique properties associated with oxygen conduction [7], does not form Hf$_{4}$Y$_{3}$O$_{12}$ compound [8], and posseses a sufficiently high chemical stability [9].

The synthesis of nanopowders through coprecipitation is complicated by the process of agglomeration due to excess surface energy of nanoparticles. It is known that the use of ultrasound in a
sol-gel synthesis permits suppressing agglomera-
tion processes. Moreover it improves the mixing of
the components in reactional mixture [10,11].

The aim of the present work was to synthesize
82 mol.% ZrO$_2$ - 10 mol.% HfO$_2$ - 8 mol.% Y$_2$O$_3$
low-agglomerated precursor nanopowders; to determine
the temperature of amorphous-crystalline transition
in these powders, and the phase composition of
the powders after crystallization; to evaluate the
mean size of crystallites; to investigate the process
of agglomeration and to determine conditions for
preparing precursor powders with the lowest degree
of agglomeration.

2. THEORY

The method of amorphous hydroxide coprecipitation
from salt solutions of ZrO(NO$_3$)$_2$·2H$_2$O, HfOCl$_2$·6H$_2$O,
and Y(NO$_3$)$_3$·6H$_2$O by ammonium aqueous solution
was chosen to obtain precursor powders in the ZrO$_2$-
HfO$_2$-Y$_2$O$_3$ system. Fig. 1 presents pH-metric curves
for precipitation of hydroxides Zr(OH)$_2$, Hf(OH)$_2$, and
Y(OH)$_3$. It is seen from the figure that pH values for
the precipitation of Zr(OH)$_2$ and Hf(OH)$_2$ are close
and equal to 2.3 and 2.5, respectively, whereas the
pH value for the precipitation of Y(OH)$_3$=7. This made
it possible to use the back-precipitation method with
the aim of attaining sufficiently high homogeneity of
the powders prepared. The salt solution was added
into the precipitant solution. A constant pH equal to
9.5 was maintained ($\text{не понят}$) at the expense of
excess NH$_4$OH.

The coprecipitation products are X-ray amorphous
gels containing nanoparticles of Zr(OH)$_2$, Hf(OH)$_2$,
and Y(OH)$_3$ hydroxides. Upon further thermal de-
composition, they are transformed into nanocrystallites of ZrO$_2$, HfO$_2$, Y$_2$O$_3$ system. The
structure and size of agglomerates of crystalline
oxide particles completely inherit the structure and
size of the agglomerates of amorphous hydroxide
particles [12]. Therefore, it is very important to obtain
particles with a low degree of agglomeration at the
coprecipitation stage. The size, density, and
strength of agglomerates can be controlled by vary-

The precipitation rate should be minimal;
• upon pouring, the solutions should be mixed thor-
roughly;
• the reaction should be carried out at room or lower
temperature, because a decrease in the precipi-
tation temperature makes it possible to control
the amount of nuclei of gel-forming particles and
their size;
• surface-active substances, like NH$_4$Cl or TSA,
should be introduced into the reaction mixture
in order to blockade agglomeration;
• coprecipitation should be carried out under ultra-
sound so that an ultrasonic wave may directly
act on the entire volume of reaction mixture. An
ultrasonic wave gives rise to intensive tensions in
gel precipitates and favors a decrease in the
size of the agglomerates;
• the time of keeping the precipitate in a mother
solution upon completion of the reaction should
be sufficiently short to exclude the agglomerate
growth in the course of ageing.

3. EXPERIMENTAL

The precipitation of amorphous hydroxides was
performed from 0.1M diluted salt solution. A 1M
ammonium aqueous solution was used as a precipi-
tant. The salt solution was added dropwise at a rate
of 10 ml/min into the precipitant solution upon vigor-
ous stirring with a many-paddled glass agitator. The
precipitation was carried out at three temperatures
- at room temperature 20 °C, 0 °C, and -5 °C. At

![Fig. 1. pH-metric curves for precipitation of amorphous hydroxides: Zr(OH)$_2$ (1), Hf(OH)$_2$ (2), and Y(OH)$_3$ (3).](image-url)
room temperature the precipitation was also performed with the use of an ultrasonic bath. The bath has an output of 50 watts and an operating frequency of 35 kHz. Immediately after the completion of the reaction, the precipitate was separated from the solution and washed using a Buchner filter. The amorphous hydrides obtained were dried and heat treated at 550 °C for 30 min and 1000 °C for 10 min.

After the calcination and heat treatment, the samples were examined using differential thermal analysis (DTA) by a MOM-3 derivatograph on air. The powder samples were heated up to 1000 °C in an electrical furnace at a rate of 10 °C /min. The temperature was measured with Pt/Pt-Rh thermocouple.

X-ray powder diffraction analysis was performed on a D-500/HS Siemens diffractometer (CuKα radiation, Ni filter, 2θ = 15-65°) at room temperature on air.

The crystallite size was calculated from the X-ray powder diffraction data. The X-ray powder diffraction curves obtained in the electron form were processed with the ‘Winfit version 1.2.1 @ St. Krumm’ program using the Fourier transformation. The Gaussian model was used as an approximation function of the Fourier transformation.

The agglomerate size was determined using an HORIBA LA-920 laser sedimentograph.

4. RESULTS AND DISCUSSION

The DTA curves for amorphous hydrides are shown in Fig. 2. As can be seen from the figure, the DTA curves for sample 1 (precipitation at 20 °C) and for sample 2 (precipitation at 0 °C) exhibit a pronounced endothermic effect in the temperature range 160-165 °C (Table 1) due to a considerable loss of structural water by crystal hydrates of amorphous hydrides. This process is accompanied by a considerable weight loss which is observed in the thermal gravimetric (TG) curves. For sample 4 (precipitation at 20 °C in an ultrasonic bath), the above-mentioned effect is shifted to the range of lower temperatures and equals 120 °C. In the DTA curves for sample 3 (precipitation at -5 °C) the endothermic effect due to dehydration (220 °C) is preceded by the exothermic effect at 120 °C. According to TG curve, this effect is not accompanied by the weight loss, and, most likely, is associated with the formation of crystal hydrates of amorphous hydrides (with a low water content) from hydrated adducts of variable composition which were obtained through the precipitation at -5 °C.

The DTA curves for all the samples exhibit an exothermic effect in the temperature range 460-500 °C (Table 1) due to crystallization which is confirmed by the X-ray powder diffraction data (Fig. 3). Analysis of the TG curves indicates weight losses at these temperatures (Fig. 2). Therefore we can conclude that the crystallization is accompanied by the decomposition of amorphous hydrides.

XRD analysis of 82 mol.% ZrO2 - 10 mol.% HfO2 - 8 mol.% Y2O3 powders revealed in all the samples lines associated only with a fluorite-type cubic structure. X-ray powder diffraction patterns for samples 1 and 4 calcined at 550 and 1000 °C are shown in Figs. 3 and 4, respectively. As can be seen, they differ only by the half-widths of the diffraction peaks. It is associated with the mean size of crystallites.
Table 1. Temperatures of endothermal and exothermal effects observed during heating the synthesized powders (DTA).

| effect | sample | T, °C | | |
|-------|--------|------|---|---|---|---|---|
|       |        | 1    | 2 | 3 | 4 |   |   |
| exo   | -      | -    | - | - | - |   |   |
| endo  | 165    | 165  | 165| 160|   |   |   |
| exo   | 480    | 480  | 500| 460|   |   |   |

Fig. 3. X-ray diffraction patterns for the powders after calcination at 550 °C: a) precipitation temperature 20 °C, b) precipitation temperature 20 °C, in an ultrasonic bath.

Fig. 4. X-ray diffraction patterns for the powders after calcination at 1000 °C: a) precipitation temperature 20 °C, b) precipitation temperature 20 °C, in an ultrasonic bath.

The calculated mean sizes of crystallites are given in Table 2. As the table indicates, the mean crystallite sizes for all the studied samples are in the nanometer range and don’t exceed 5 nm for the samples calcined at 550 °C and 28 nm for the samples calcined at 1000 °C.

Table 2. Mean crystallite sizes calculated from the X-ray powder diffraction data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Precipitation temperature, °C</th>
<th>The average size of crystallites at 550°, nm</th>
<th>σ%</th>
<th>The average size of crystallites at 1000°, nm</th>
<th>σ%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>3.7</td>
<td>92.1</td>
<td>27.6</td>
<td>98.9</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>5.0</td>
<td>93.9</td>
<td>23.3</td>
<td>98.0</td>
</tr>
<tr>
<td>3</td>
<td>-5</td>
<td>2.7</td>
<td>90.8</td>
<td>26.5</td>
<td>96.8</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>3.1</td>
<td>91.6</td>
<td>19.6</td>
<td>94.5</td>
</tr>
</tbody>
</table>

(Note: σ is the confidence of the theoretical description of the experimental X-ray powder diffraction peak).
The investigation of the agglomeration processes of nanoparticles obtained can be summarized as follows: the mean agglomerate sizes at precipitation temperature of 20, 0, and -5 °C are equal to 14.41, 5.91, and 5.03 μm, respectively. For the samples precipitated at 20 °C in an ultrasonic bath the mean agglomerate size is equal to 600 nm.

5. SUMMARY

1. Using the back-coprecipitation method, 82 mol.% ZrO₂ - 10 mol.% HfO₂ - 8 mol.% Y₂O₃ powders were prepared. After calcinations at 550 °C the mean crystallite size in the powders doesn’t exceed 5 nm. A decrease in the precipitation temperature and the use of ultrasound don’t affect the mean crystallite size in the powders.
2. A fluorite-type cubic structure only is observed for all the studied samples after heat treatment at 7–550 °C.
3. A decrease in the precipitation temperature causes a decrease in the mean agglomerate size in the powders under investigation from 14.4 μm at 20 °C to 5 μm at -5 °C. The use of ultrasound allows to obtain the precursor powder with the mean agglomerate size of 600 nm.

ACKNOWLEDGEMENTS

This work was supported by Ministry of Education and Science of Russian Federation Program Development of Scientific Potential of High School.

REFERENCES