

# Microstructure and electrical properties of near-eutectic alumina-zirconia composites

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The paper deals with the influence of the phase composition and growth rate on the microstructure and electrical properties of alumina-zirconia eutectic composites. The presence of monoclinic zirconia can be detected by impedance analysis. Although the conduction activation energies of composites are similar to those reported for zirconia ceramics and single crystals, the conductivity of composites is lower.

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## 1. Introduction

In many applications, there is a need for materials with sufficiently high strength and fracture toughness at high temperatures [1]. Oxide eutectic composites based on  $\text{Al}_2\text{O}_3$ , prepared by directional solidification, have good mechanical properties up to nearly their melting temperature. In last years, the investigation of the growth, microstructure and mechanical properties of eutectic composites in systems  $\text{Al}_2\text{O}_3 - \text{GdAlO}_3$ ,  $\text{Al}_2\text{O}_3 - \text{Y}_3\text{Al}_5\text{O}_{12}$ ,  $\text{Al}_2\text{O}_3 - (\text{Y}_2\text{O}_3)\text{ZrO}_2$  was performed [2-5].

Eutectic point in system  $\text{Al}_2\text{O}_3 - \text{ZrO}_2$  is located at 38 mol%  $\text{ZrO}_2$  and  $\sim 1870^\circ\text{C}$ . Yttrium dissolves in  $\text{ZrO}_2$  up to 12 mol% of  $\text{Y}_2\text{O}_3$ , forming solid solution. Dependent upon the amount of  $\text{Y}_2\text{O}_3$ , zirconia is stabilized either in a monoclinic, tetragonal, or cubic form. When 1 mol%  $\text{Y}_2\text{O}_3$  is added to zirconia, a small amount of zirconia is stabilized in tetragonal form, but a major amount of zirconia is in a low-temperature monoclinic form. When  $\sim 3$  mol%  $\text{Y}_2\text{O}_3$  is added, a major amount of zirconia is stabilized in a tetragonal form. At 5 mol%  $\text{Y}_2\text{O}_3$ , also a cubic zirconia appears. The amount of 9 mol%  $\text{Y}_2\text{O}_3$  is considered to be sufficient for stabilizing zirconia in a cubic form.

It is well known, that alumina is the leading phase of eutectic transition in system  $\text{Al}_2\text{O}_3 - \text{ZrO}_2$ . The microstructure of  $\text{Al}_2\text{O}_3 - (\text{Y}_2\text{O}_3)\text{ZrO}_2$  is cellular, due to constitutional supercooling caused by yttria, and due to faceting the solid-liquid interface of alumina phase. It is assumed, that solidification occurs in two steps. At the first step, the eutectic colonies are formed in the growth direction. During this stage, a part of yttria is rejected into intercolony spaces. At the next step, the intercolony spaces solidify. This suggestion is supported by experimentally found higher amount of yttria in intercolony spaces [6]. Microstructure containing eutectic colonies was found in composites prepared by Bridgman method [7], LFZ method [8], Stepanov /EFG technique [9] and micropulling down method [10]. The type of resulting

microstructure and thermal and elastic properties of eutectic phases, generally, strongly affect the residual thermal stresses during cooling the samples of eutectic composites [11].

The measurement of electrical properties of  $\text{Al}_2\text{O}_3 - (\text{Y}_2\text{O}_3)\text{ZrO}_2$  eutectic composites was done by Zhuykov [12]. His results indicate, that these materials can be applied as electrolyte in high-temperature oxygen sensors. To improve their performance, it would be necessary to enhance the oxygen conductivity of electrolytes. This paper deals with a description of microstructure and measurement of ionic conductivity of eutectic composites  $\text{Al}_2\text{O}_3 - (\text{Y}_2\text{O}_3)\text{ZrO}_2$ . The valuable tool for characterizing the electrical properties of non-metallic materials is impedance spectroscopy. Using this technique together with electron microscopy and measurement of optical properties often enables to describe the processes occurring in materials, as well as structural changes [13].

## 2. Experimental procedure

Rod-shaped eutectic composites were directionally solidified from the melt by the Stepanov/EFG method at growth rates 10 – 80 mm/h. Powders of pure (99.9%) alumina, zirconia and yttria were used as reactants. RF heating (8 kHz) through a graphite susceptor in Ar, at a pressure of 0.12 MPa, a molybdenum crucible and a molybdenum rod-shaped die were used. A [0001] crystallographically oriented sapphire single crystal was used as a seed. The compositions of the melt were (in mol%):

- 1) 59  $\text{Al}_2\text{O}_3 - 40 \text{ZrO}_2 - 1 \text{Y}_2\text{O}_3$
- 2) 57  $\text{Al}_2\text{O}_3 - 41.3 \text{ZrO}_2 - 1.7 \text{Y}_2\text{O}_3$
- 3) 58.6  $\text{Al}_2\text{O}_3 - 39.2 \text{ZrO}_2 - 2.2 \text{Y}_2\text{O}_3$
- 4) 63  $\text{Al}_2\text{O}_3 - 35 \text{ZrO}_2 - 2 \text{Y}_2\text{O}_3$

The samples were cut parallel or perpendicular to the growth direction. The description of samples is given in Tables 1 – 4.

Table 1. Description of samples with composition 1.

| sample             | 1a | 1b |
|--------------------|----|----|
| growth rate (mm/h) | 20 | 60 |

Table 2. Description of samples with composition 2.

| sample             | 2b | 2d | 2e | 2e II |
|--------------------|----|----|----|-------|
| growth rate (mm/h) | 20 | 60 | 80 | 80    |

Table 3. Description of samples with composition 3, symbols II denote samples cut parallel to the growth Direction.

| sample                      | 3g  | 3h  | 3hII | 3i   | 3iII  | 3j   | 3k |
|-----------------------------|-----|-----|------|------|-------|------|----|
| growth rate (mm/h)          | 40  | 40  | 40   | 40   | 40    | 40   | 40 |
| distance from the seed (cm) | 1.2 | 5.2 | 6÷7  | 10.1 | 11÷12 | 21.5 | 28 |

Table 4. Description of samples with composition 4.

| sample             | 4a | 4b | 4c |
|--------------------|----|----|----|
| growth rate (mm/h) | 40 | 40 | 40 |

Some of small pieces of the composites were crushed and ground into powder. The X-ray phase analysis was performed using the  $\text{CuK}\alpha$  radiation. Different forms of zirconia were identified by microhardness measurements. The microstructure of the composites was observed using the scanning electron microscopy (in back scattered electrons), after coating the observed surfaces by carbon, to prevent the electrical charging of samples. Electrical measurements were performed, in a two-terminal arrangement in air, at 1 Hz – 10 MHz, for 4÷5 temperatures in the temperature range of 180 – 600 °C, using impedance/gain analyzer Solartron 1260. The data analysis was done using Boukamp's equivalent circuit software. Supporting measurements were performed at frequency of 1 kHz, in the same temperature range. Before measurements, the opposite planes of samples were coated by silver paste and then fired under infrared lamp, during 5 minutes, to form the electrodes.

### 3. Results

The X-ray diffraction studies show, that the hexagonal  $\text{Al}_2\text{O}_3$  is the major phase in all samples. As the diffraction peaks of monoclinic, tetragonal, and cubic zirconia are close each other, microhardness measurements were also made. According to [14,15], for microhardness of zirconia holds: microhardness of cubic form > microhardness of tetragonal form > microhardness of monoclinic form. The microhardness of investigated samples of eutectic composites  $\text{Al}_2\text{O}_3 - (\text{Y}_2\text{O}_3)\text{ZrO}_2$  was measured using Vickers indenter, at a load of 0.65 N. The values of microhardness, determined from statistics of 10 indentations, are given below:  
composition 1:  $(14.78 \pm 0.62)$  GPa

composition 2:  $(18.88 \pm 0.91)$  GPa

composition 3:  $(24.98 \pm 0.37)$  GPa

composition 4:  $(22.83 \pm 0.61)$  GPa

Using the results of X-ray diffraction and microhardness measurements, the phase composition of zirconia in composites was estimated:

- at a low content of yttria (composition 1), monoclinic and tetragonal  $\text{ZrO}_2$  are present.
- at a medium content of yttria (composition 2), mainly tetragonal  $\text{ZrO}_2$  and small amounts of monoclinic and cubic  $\text{ZrO}_2$  are present.
- at a high content of yttria (compositions 3, 4), mainly cubic  $\text{ZrO}_2$  is present.

The microstructure of composites consists from eutectic colonies and from coarse zirconia and alumina particles in intercolony spaces (Fig. 1). The colonies are elongated in the growth direction (Fig. 2), but only short zirconia fibers are formed (Fig. 3). The directional disordering of fibers results from the curved crystallization front due to:

- a heat transport to the lateral surface of the composite,
- an accumulation of yttria in front of the crystallization front.

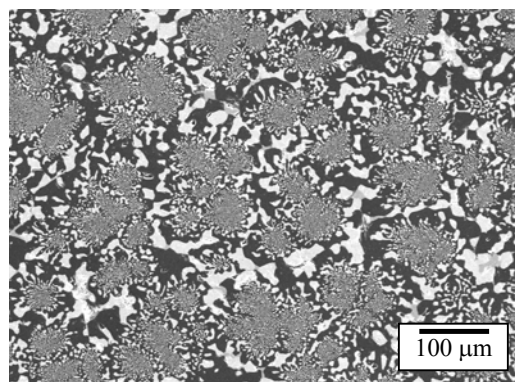


Fig. 1. Microstructure of  $\text{Al}_2\text{O}_3 - (\text{Y}_2\text{O}_3)\text{ZrO}_2$  eutectic composites, sample with higher yttria content (composition 3), growth rate 40 mm/h; perpendicular to the growth direction (dark phase is  $\text{Al}_2\text{O}_3$ , white phase is  $\text{ZrO}_2$ ).

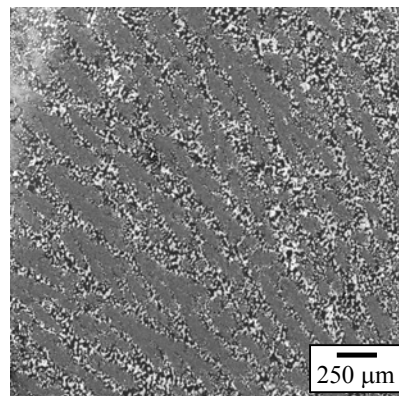


Fig. 2. Microstructure of  $\text{Al}_2\text{O}_3 - (\text{Y}_2\text{O}_3)\text{ZrO}_2$  eutectic composites parallel to the growth direction.

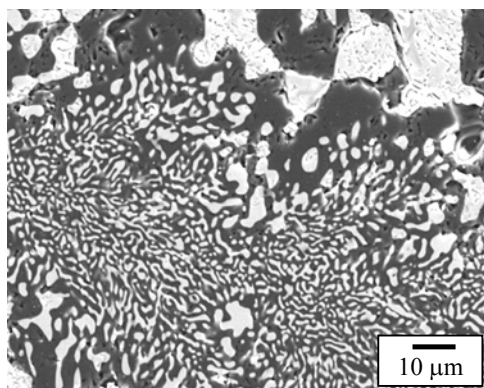


Fig. 3.  $ZrO_2$  fibers in eutectic colony; parallel to the growth direction

At higher growth rates and lower contents of yttria, the  $Al_2O_3$  phase tends to facet the crystallization front, and faceted colonies are formed (Fig. 4). In a close neighborhood of facets, zirconia fibers are relatively well ordered, but their length does not exceed 20  $\mu m$  (Fig. 5). In hypereutectic composites (composition 2), zirconia dendrites are present (Fig. 6). In hypoeutectic composites (composition 4), cellular dendrites of  $Al_2O_3$  and faceted eutectic colonies (also at low growth rates) appear (Fig. 7).

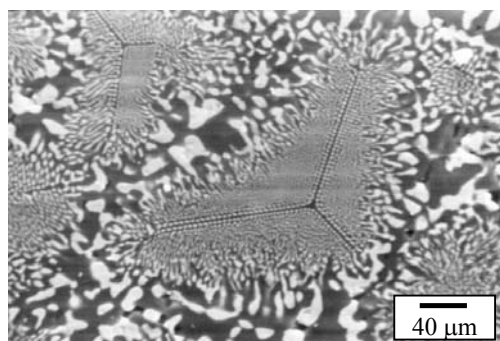


Fig. 4. Faceted eutectic colonies in sample with middle yttria content (composition 2), growth rate 60 mm/h; perpendicular to the growth direction.

The electrical measurements were performed on samples with composition 2 and composition 3. Impedance spectra of samples with composition 2 show two overlapping semicircles (Fig. 8a). As the conductivity of alumina is negligible, the first semicircle was ascribed to tetragonal  $ZrO_2$  and the second semicircle to monoclinic zirconia in these samples. Such a response can be described by equivalent circuit containing two parallel R-CPE elements (R – resistance, CPE – constant phase element), resistor  $r$ , and inductor L. The last two elements ( $r$ , L) represent the resistance and inductance of measuring cell (Fig. 8b). Resistor  $R_1$  determines the resistance of tetragonal  $ZrO_2$ , resistor  $R_2$  determines the resistance of monoclinic  $ZrO_2$ . The conductivity of sample was calculated according to:

$$\sigma = \frac{1}{R_1 + R_2} \frac{h}{S}, \quad (1)$$

where  $h$  stands for the thickness of the sample,  $S$  is the area of one surface of the sample, coated by silver electrode.

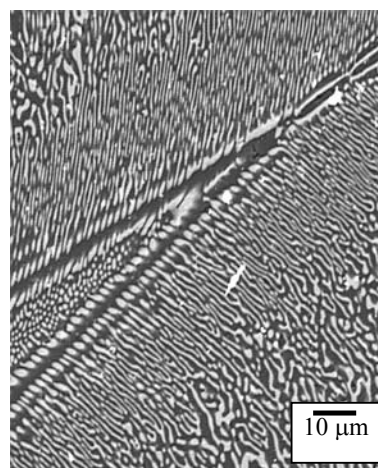


Fig. 5.  $ZrO_2$  fibers in faceted eutectic colony, parallel to the growth direction.

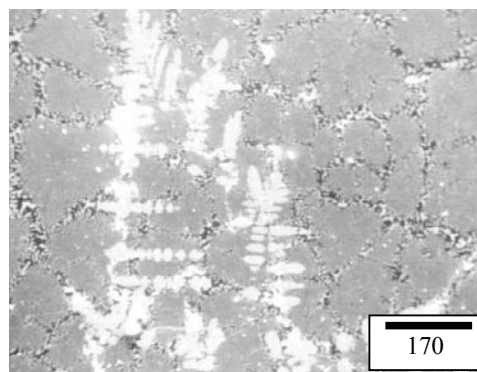


Fig. 6. Dendrites of  $ZrO_2$  in sample with hypereutectic composition (composition 4); perpendicular to the growth direction.

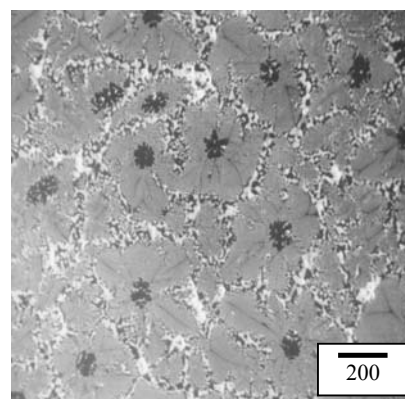


Fig. 7. Cellular dendrites of  $Al_2O_3$  in sample with hypoeutectic composition (composition 4); perpendicular to the growth direction.

Impedance spectra of samples with composition 3 show only one slightly depressed semicircle in complex plane (Fig. 9a), which is ascribed to cubic  $\text{ZrO}_2$ . Then, the equivalent circuit contains one parallel R – CPE element, and resistance, and inductance of the measuring cell

(Fig. 9b). Resistor R determines the conductivity of cubic  $\text{ZrO}_2$  and conductivity of sample is calculated as:

$$\sigma = \frac{1}{R} \frac{h}{S} \quad (2)$$

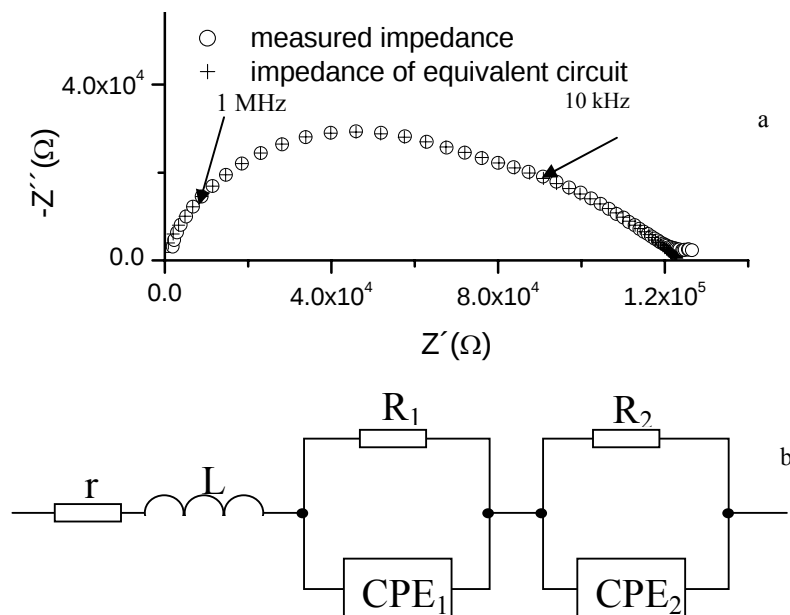


Fig. 8. Impedance spectra of  $\text{Al}_2\text{O}_3 - (\text{Y}_2\text{O}_3)\text{ZrO}_2$  eutectic composites with composition 2 at 406 °C (a) and equivalent circuit (b).

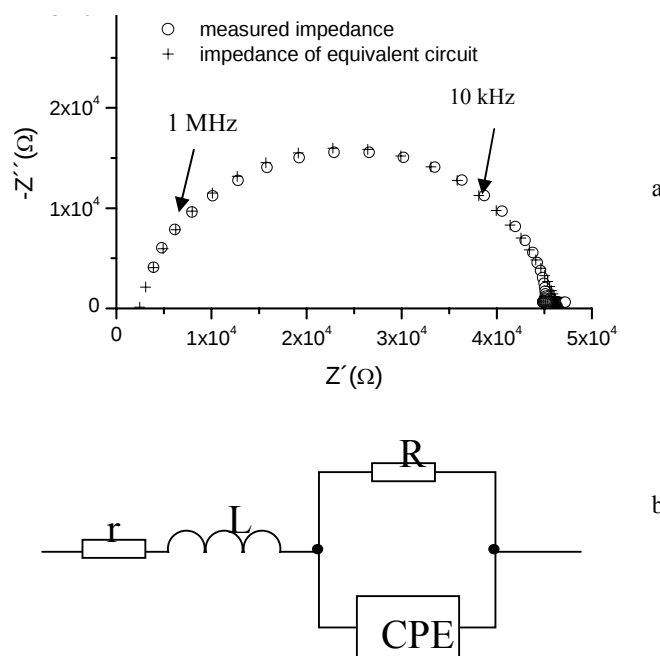


Fig. 9. Impedance spectra of  $\text{Al}_2\text{O}_3 - (\text{Y}_2\text{O}_3)\text{ZrO}_2$  eutectic composites with composition 3 at 440 °C (a) and equivalent circuit (b).

The values of circuit parameters are determined using Boukamp's software "Equivalent circuit". Characteristic parameters of the conductivity (pre-exponential factor  $\sigma_0$ , conduction activation energy  $\Delta E$ ) are calculated using Arrhenius relation:

$$\sigma = \sigma_0 e^{-\frac{\Delta E}{kT}}, \quad (2)$$

where  $k$  is Boltzman constant and  $T$  denotes the temperature in K. The conduction activation energies and conductivities of samples are given in Table 5.

Table 5. Activation energies and conductivities of samples with composition 2 and composition 3 at 850 K.

| sample                                          | 2b   | 2d   | 2e   | 3g   | 3h   | 3i   | 3j   | 3k   | 3h   | 3i   |
|-------------------------------------------------|------|------|------|------|------|------|------|------|------|------|
| $\Delta E$ (eV)                                 | 1.01 | 0.98 | 1.00 | 0.86 | 0.91 | 0.92 | 0.95 | 0.99 | 1.03 | 1.02 |
| $\sigma_{850} \cdot 10^4$ (S.cm <sup>-1</sup> ) | 0.8  | 1.5  | 1.1  | 2.4  | 0.8  | 0.8  | 1.0  | 0.8  | 1.2  | 0.9  |

At 850 K, conductivities of all samples are in the range of  $(0.8 \div 2.4) \cdot 10^{-4}$  S.cm<sup>-1</sup>. The activation energies of samples containing tetragonal zirconia (composition 2) are in the range of  $(0.98 \div 1.01)$  eV. The activation energies of samples containing cubic zirconia (composition 3) slightly rise, from 0.86 eV to 0.99 eV, with distance from the seed.

The conduction activation energy in direction perpendicular to the growth direction is very similar to that measured in growth direction (sample 3h|| vs. sample 3h; sample 3i|| vs. sample 3i).

Table 6. Activation energies and conductivities at 850 K of zirconia single crystals [13] and zirconia ceramics [14,15].

|                                                                               | ZrO <sub>2</sub> form      | $\Delta E$ (eV) | $\sigma_{850} \cdot 10^4$ (S.cm <sup>-1</sup> ) | references |
|-------------------------------------------------------------------------------|----------------------------|-----------------|-------------------------------------------------|------------|
| single crystal ZrO <sub>2</sub><br>(1.13 mol% Y <sub>2</sub> O <sub>3</sub> ) | monoclinic +<br>tetragonal | 1.13            | 1.16                                            | [14]       |
| single crystal ZrO <sub>2</sub><br>(3.24 mol% Y <sub>2</sub> O <sub>3</sub> ) | tetragonal                 | 0.82            | 13.3                                            | [14]       |
| single crystal ZrO <sub>2</sub><br>(4.31 mol% Y <sub>2</sub> O <sub>3</sub> ) | tetragonal +<br>cubic      | 0.95            | 31.4                                            | [14]       |
| single crystal ZrO <sub>2</sub><br>(9.21 mol% Y <sub>2</sub> O <sub>3</sub> ) | cubic                      | 1.06            | 35                                              | [14]       |
| ceramics ZrO <sub>2</sub><br>(8 mol% Y <sub>2</sub> O <sub>3</sub> )          | cubic                      | 0.72            | 104                                             | [15]       |
| ceramics ZrO <sub>2</sub><br>(4 mol% Y <sub>2</sub> O <sub>3</sub> )          | tetragonal                 | 0.89            | 52.2                                            | [16]       |

The values of conductivity parameters of zirconia single crystals [16] and zirconia ceramics [17,18] are summarized in Table 6. Comparing these data with conductivity parameters of Al<sub>2</sub>O<sub>3</sub> – (Y<sub>2</sub>O<sub>3</sub>) ZrO<sub>2</sub> eutectic composites we can conclude:

- 1) the samples of composites with composition 2
  - the conduction activation energy  $(0.98 \div 1.01)$  eV is between the values of zirconia single crystals in monoclinic + tetragonal form (1.13 eV) and the values of zirconia single crystals in tetragonal form (0.82 eV)
  - the conductivity at 850 K  $(0.8 \times 10^{-4} \div 1.5 \times 10^{-4}$  S.cm<sup>-1</sup>) is also close to the value of zirconia single crystals in monoclinic + tetragonal form  $(1.16 \times 10^{-4}$  S.cm<sup>-1</sup>) and lower than the values of zirconia single crystals in tetragonal form  $(13.3 \times 10^{-4}$  S.cm<sup>-1</sup>)
- 2) the samples of composites with composition 3
  - the conduction activation energy  $(0.86 \div 0.99)$  eV is similar to that of zirconia single crystals in tetragonal + cubic form (0.95 eV) and zirconia single crystals in cubic form (1.06 eV)
  - the conductivity at 850 K  $(0.7 \times 10^{-4} \div 2.4 \times 10^{-4}$  S.cm<sup>-1</sup>) is lower than that of tetragonal + cubic zirconia single

crystals  $(31.4 \times 10^{-4}$  S.cm<sup>-1</sup>) and cubic zirconia single crystals  $(35 \times 10^{-4}$  S.cm<sup>-1</sup>)

- the conductivity at 850 K is up to two orders lower than the conductivity of the best conducting yttria stabilized zirconia ceramics  $(104 \times 10^{-4}$  S.cm<sup>-1</sup>), the conduction activation energy of composites is higher than that of cubic zirconia ceramics.

#### 4. Conclusions

The microstructure of Al<sub>2</sub>O<sub>3</sub> – (Y<sub>2</sub>O<sub>3</sub>) ZrO<sub>2</sub> eutectic composites is cellular. It contains the eutectic colonies elongated in the growth direction. ZrO<sub>2</sub> fibers in colonies are short and mostly they deviate from the growth direction. As a result, the conduction activation energy in direction perpendicular to the growth direction is only slightly higher than that in direction parallel to the growth direction. The activation energy slightly rises with the distance from the seed, probably due to a non-homogeneous distribution of yttria along the composite after directional solidification. The small amount of monoclinic ZrO<sub>2</sub> causes an extra semicircle in impedance

spectra, which is well resolved by impedance analysis. In hypereutectic composites, zirconia dendrites are present. At higher growth rates and lower contents of yttria, the  $\text{Al}_2\text{O}_3$  phase tends to facet the crystallization front, and faceted colonies are formed. In a close neighborhood of facets, zirconia fibers are relatively well directionally ordered, but their length does not exceed 20  $\mu\text{m}$ . In hypoeutectic composites, cellular dendrites of  $\text{Al}_2\text{O}_3$  and faceted eutectic colonies (also at low growth rates) appear. Conductivities of all samples of compositions 2 and 3 (with medium and high yttria content, respectively) are very close each other, at 850 K. Although the conduction activation energies of composites are close to those of zirconia single crystals and ceramics with similar phase composition, the conductivity of composites at higher temperatures is significantly lower.

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