

The boundaries and their impact on properties of zirconia electrolyte

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Interfaces and their complexions created in the zirconia 1Ce10ScSZ ceramic electrolyte and altered by three powder types and sintering temperatures were studied via their effect on mechanical behavior and electrical conductivity. Two boundary complexions, which exist and developed between subgrains and grains with sintering temperature were observed. The transition between boundary categories, which was defined as the boundary complexion transition of the second kind, occurs in both very pure 1Ce10ScSZ ceramics and in ceramics of technical purity, powder of which is contaminated with rather large amount of silica and titania. The ceramics contaminated with rather large amount of silica and alumina does not reveal any complexion transitions. Joint analysis of data obtained with electron microscopy and related techniques, mechanical tests for strength, scanning electron fractography and impedance spectroscopy of structural constituents of electrical resistance has given a lot of information on the effect of boundaries and their complexions on properties of electrolyte where mechanical behavior is as important as their conductivity.

Keywords: interfaces, grain boundary complexions, mechanical behavior; impedance spectroscopy, grain conductivity; boundary conductivity; zirconia 1Ce10ScSZ electrolyte; zirconia powders; sintering temperature.

Introduction

In simple polycrystalline electrochemical and structural materials, their interfaces, in general, or in other words, boundaries or boundary complexions between structural constituents are often the only, except matrix, additional structural mean determining their properties. Despite their relatively small volume fraction, the interfaces often play a dominant role in materials properties.

Boundaries between grains and their subgrains (GBs, in general) are thin two-dimensional creatures. They have a different nature and exhibit different phase-like behaviors, in which their structure, chemistry and properties may change continuously or discontinuously at critical values of thermodynamic parameters such, first of all, as temperature and heat treatment time, chemical potential, pressure etc.

A lot of research literature is devoted to the interfaces, their structure and influence on materials properties. Here, the most fresh of them [1—3] are worthy to be mentioned and cited.

As to the interface properties (of grain boundaries mainly) and their influence on materials behavior, the Hall—Petch relation is well-known and widely used [4, 5]. It is linking a grain size and yield strength and was originally

introduced for steels and spreaded later on other metals, as-cast and as-processed. The Hall—Petch relation is describing the dependence of yield strength on size grains metallographically revealed in materials of non-pure systems, in which grain boundary segregation plays a critical role [6 and others]. The Hall—Petch relation predicts that as the grain size decreases, the yield strength increases as $1/\sqrt{d}$ dependence, where d is a grain size. The relationship is so popular that being proposed initially in order to describe the yield strength of ductile material, it is applied now to different phenomena, e. g., brittle strength to explain its dependence on the grain size. A non-typical Hall—Petch behavior, so-called reverse or inverse Hall—Petch relation was demonstrated in many cases. Of course, here, we deal with some mnemonic coincidence of any property dependence on the grain size d as a function of $1/\sqrt{d}$ that reflects sooner, e. g., the strength at brittle intergranular fracture on properties of grain boundary complexions, which themselves depend on grain size thermodynamically because the grain size itself depends on temperature also that results in redistribution of segregations along grain boundaries, i. e., heat treatment, that is usually used as instrument to get various grain size, is altering structure of the grain boundary complexions, and so on.

Except the size properties of boundaries, the segregation ones (grain boundary complexions and their transitions) are probably as the most important. The phenomenon of so-called intercrystalline internal adsorption of dopants diluted in alloy on structural heterogeneity and defects in solids was first proposed by Arkharov in 1945 [6]. The Arkharov's concept of "useful and non-useful", from the point of view of their influence on properties, impurities accumulated along grain boundaries was later elaborated into the "grain boundary engineering" idea in order to develop strong and ductile polycrystals that was first proposed by Watanabe in 1984 [7]. Watanabe has studied the effect of grain boundary structure on intergranular fracture. The theoretical basis of structure-dependent intergranular fracture was considered as low energy grain boundaries, which are very likely are resistant to fracture.

The theories of grain boundary adsorption are based on the McLean model, which assumes that segregation is constrained to a monolayer of atomic sites at the grain boundary [8]. Later models, those are overviewed in [1], acknowledged that thick (multilayer) grain boundary segregation may occur and may be accompanied by structural changes. When multilayer segregation occurs, entirely new structures may manifest at the grain boundary and induce a grain boundary complexion transition. Recent experimental works have demonstrated that such adsorption-based grain boundary complexion transitions are linked to phenomena such as abnormal grain growth in ceramics, activated sintering etc. Furthermore, the authors of the overview [1] underline that there is no generally accepted method of categorizing the many different types of complexion transitions that may occur. Now, it is possible to observe more structural and chemical details of grain boundary complexions using advanced electron microscopy and related techniques, which are able to provide information on both atomic structure and its chemistry.

Many descriptive terms have been used when discussing the grain boundary complexion transitions or simply - structural transitions. In order to develop a categorization scheme, the structure and chemistry of grain boundaries must be

studied experimentally, typically with electron microscopy, and correlated to grain boundary properties to understand a direct correlation between grain boundary features and materials properties.

Grain boundaries may undergo complexion transitions independently of bulk phase transformations, and, thus, grain boundary related properties may change unexpectedly and unpredictably as temperature, pressure or chemical potential is varied. A complexion transition can affect equilibrium properties such as grain boundary energy, activation energy, defect density and adsorbate concentration.

Complexion transitions may also induce discontinuous changes in the non-equilibrium properties of grain boundaries, such as cohesive strength resulting in intergranular fracture or sliding resistance. It is the discontinuity in properties that is the hallmark of a complexion transition, and is the reason why such transitions play a large role in the properties, processing and microstructure development of materials. The effect of a grain boundary transition on these properties is not easy to predict and may be difficult to rationalize on the basis of classical models for grain boundary structure – property relationships.

The difficulty in experimentally measuring grain boundary energy has led researchers to measure other properties that are strongly correlated with grain boundary complexion transitions, such as grain boundary mobility and diffusivity. Discontinuities in these properties are indirect indicators of complexion transitions, in which an increase in mass transport kinetics accompanies increases in the structural or chemical width of the grain boundary.

In principle, grain boundary complexion transitions may impact many other grain boundary properties as well, including electrical, thermal, optical, magnetic ones etc. The role of complexions in affecting these various properties has not been thoroughly investigated, although there is some evidence that complexion transitions are correlated with marked changes in these properties.

We are interested in the knowledge on solid oxygen ion conductors. Grain boundary transitions in multi-component systems remain largely unexplored, even though they represent the majority of engineering materials. It might be explained by that simple situation that necessary "experiments are timeconsuming and challenging, but grain boundary complexion diagrams overlaid onto bulk phase diagrams will be most useful if it is known how each complexion transition affects grain boundary properties of interest, such as diffusivity, conductivity and mechanical strength" [1].

Thermally induced grain boundary complexions, e. g., by heat treatment or sintering at different temperatures, may alter fundamental grain boundary properties, which ultimately affects the performance of a bulk polycrystalline material. While the role of complexions in affecting diffusional transport during materials processing is reasonably well studied, their impact on diffusion-dependent properties such as ionic conductivity remains somewhat unexplored. It is necessary to keep in our minds that using temperature as the instrument in order to produce materials consisting of different size of grains and the same state of their boundaries is practically impossible.

Despite decades of research, efforts to identify grain boundary complexion transitions in pure materials via high resolution transmission electron microscopy (HRTEM) and computer simulations have been largely unsuccessful. Only a few references related to the topic could be found. One of

them is concerning silica-rich intergranular films those have been observed in zirconia utilized as ion conducting electrolytes [9]. These films have been demonstrated to reduce oxygen ion conduction. However, it was supposed also that similar films may enhance cation conduction. Other examples say [1] that intergranular films in ZnO introduce barriers to electrical conductivity that produces a non-linear current – voltage response. The electrical properties of individual grain boundaries in MnZn ferrites containing no solute segregation, CaO segregation and intergranular films have been characterized. The grain boundaries with no solute segregation display the highest conductivity, while the segregated boundaries exhibit the lowest conductivity.

We are dealing with zirconia ceramic electrolyte. The data on scandia stabilized zirconia electrolyte are obtained by comparing mainly three types of 1Ce10ScSZ powder. Their formal composition is 1 mol. % CeO₂ — 10 mol. % Sc₂O₃ — 89 mol. % ZrO₂. Powders have different purity, i. e., are differing with sets of dopants and their distribution across particles, and other morphological features [10]. They have different ability to sintering. Their ceramics have very different both mechanical behavior at room temperature and oxygen ionic conductivity in temperature interval 400—800 °C [11, 12]. Any visible correlation between traditional properties was not observed yet.

The goal of the work was, using solid electrolyte 1Ce10ScSZ made of different types of 1Ce10ScSZ powders and sintered at different temperatures in 1250—1550 °C, to study features of its mechanical behavior related to grain boundaries, which could be revealed with biaxial bend loading and scanning electron fractography, and grain boundary electrical conductivity to be revealed with impedance spectroscopy at 600 °C. In such a way, the rather wide spectrum of samples those are different by their interfaces — grain boundary complexions was studied and compared. 600 °C is chosen as the temperature of SOFC operation that is under development.

Materials and methods

Ceramics 10Sc1CeSZ (1 mol. % CeO₂ — 10 mol. % Sc₂O₃ — 89 mol. % ZrO₂) were made of three types of powder with formally the same chemical composition, but using different initial raw materials and synthesis conditions resulting in different morphology, impurities composition and distribution.

The typification of powders has its origin in their morphological and chemical properties, properties of their agglomerates, ability to be sintered and mechanical behavior of their ceramics consolidated with uniaxial and cold isostatic pressing. The properties listed were obtained at comparative studies. The Type I powder (developed by V. Vereshchak and produced at Vilnohirsk Mining & Metallurgical Plant and Zirconia Ukraine Ltd., Ukraine) was made by co-precipitation technique; the Type II powder delivered by Daiichi Kigenso Kagaku Kogyo, DKKK, Japan, was produced, as we could know, by the hydrothermal synthesis, and the Type III powder delivered by Praxair, USA, was made by spray-pyrolysis.

The structural and mechanical properties of these powders, the methods of manufacturing as well as the comparative results were reported earlier [10—12]. Here, we remind that the Type I powder is agglomerated in ~2,5 μ semisoft-semirigid creatures of 11 ± 2 nm particles; the Type II is practically non-agglomerated and consist of soft 73 ± 20 nm particles, and the Type III is

agglomerated in $\sim 1,3 \mu$ rigid ceramic creatures, which are as fragments of well-sintered ceramics.

The powders were milled in alcohol for 24 h using ZrO_2 ceramic balls and left to dry in air. Afterwards, 10Sc1CeSZ powders were uniaxially pressed at 30 MPa into discs of 20 mm in diameter and 1,5–2 mm thick. 10Sc1CeSZ samples were sintered in the temperature range of 1250–1550 °C for 1,5 h in air using VK 1600, Linn High Term furnace (Germany). Strength of the as-sintered samples was measured with biaxial bend loading technique. The fracture surfaces of the samples were observed with the scanning electron microscope (SEM, Superprobe-733, JEOL).

Materials and methods of their characterization are described in details in [10–12]. Here, we would like to remind that the initial carriers of dopants, contaminants or impurities are surfaces of initial particles and their agglomerates. During sintering they are redistributing between grains and their boundaries forming grain boundary complexions, which are transforming in the courses at their heat treatment at sintering. As to features of chemical composition of samples, the concentration of impurities in the bulk made of the Type I and the Type III powders is around 0,01 wt. %. The Type II is much purer; it contains only 0,001 wt. % of impurities. Regarding the nature of the contaminants, the Type I is contaminated mainly with silica (0,05%) and alumina ($<0,025\%$) while in the Type III mainly silica (0,05%) and titania ($<0,14\%$) are present. Additional minor contamination in the form of K, Na, Ca, and Fe was also found in Types I and III powders. From the point of surface-bulk distribution obtained with secondary ion mass spectroscopy, in the Type II, the surface of particles is enriched with Sc and Al; in the Type III, Sc and Si are mostly present on the surface. In the Type I, the surface is depleted with Sc; while Sc and Si are mostly localized in the bulk of the particles.

The electrical impedance of the samples was measured as a function of AC frequency using a Solartron 1260 impedance/gain-phase analyzer within the frequency range of 10^{-2} – 10^6 Hz at 600 °C in air. For these measurements, the silver paste electrodes were deposited onto the sample surface and sintered.

The resulting impedance diagrams described and analyzed in [13] were modelled by means of electrical equivalent circuits (EC), which consisted of two or three parallel RC-circuits (depending on the number of the impedance semicircles) and a resistor connected in series. As a result, the model parameters such as the resistances and capacitances of the grains and grain boundaries, Ohmic resistances, and the parameters (α , Θ and β), which reflect the deviation of the impedance spectra from the Debye representation, were obtained.

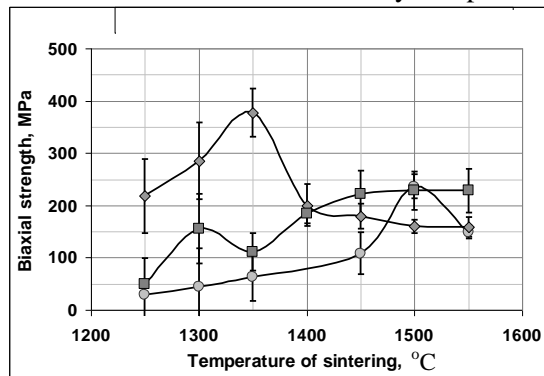
Results and their discussion

Mechanical Behavior

Fracture mechanisms and strength of 1Ce10ScSZ electrolyte at room temperature are described in details in [10–13]. In order to do easier following discussion, the dependence of biaxial bend strength of ceramics made of all the three types of powder is shown in fig. 1.

Concerning the fractographical visualization of interfaces via their behavior under mechanical stresses at loading or their interaction with brittle cracks, it became possible to determine that they are brittle interpartial and intergranular (intergrain) fracture, and an alteration of cleavage plane and cracking at

boundary crossing that could form so-called river patterns. This picture is altering with sintering temperature that results from the boundary complexions Fig. 1. The biaxial bending strength of uniaxially pressed ceramics made of three Types of 10Sc1CeSZ powders studied vs. temperature of sintering. IPMS (\circ) — Type I, DKKK (\diamond) — Type II, and Praxair (\square) — Type III [11].



transitions that might be defined as the transition of the second kind that is, in fact, the transition between boundary complexions, between subgrain boundary and grain boundary ones. The first kind of the transition is the boundary complexion transition, which occurs within the same category of boundaries, e. g., intergranular one that is traditionally discussed. The second kind is the transition between categories of boundaries, e. g., from subgrain category to grain one. It may occur, i. e., at refinement of grains with a heat treatment removing impurities or unwanted structural elements from the grain. As result, the grains are refined from the subgrain boundaries, contaminations are redistributed within the grains or removed from them onto their boundaries. In such a way, the boundaries of subgrains disappear in much extent, and the grain boundaries remain in their new state. It may happen at some critical temperature interval. As a final result, material properties may alter at this temperature of heat treatment / sintering abruptly. The authors are succeeded in observing these phenomena relating fracture behavior, fracture mechanism especially, and electrical conductivity that will be shown below.

We have to note that the boundaries in the Type I ceramics do not reveal themselves in fractures practically at all with the microscopes available as it is possible to see in fig. 2, *a, b*. Though, the thermally etched surfaces of its samples evidence that some internal boundaries are there (fig. 3, *a*).

The Type II ceramics allow observing subgrains, which have been as initial particles before the sintering, and have united and created grains in a course of sintering. These grain creatures are well-visible already in samples sintered at 1250 °C for 1,5 hour (fig. 2, *c—e*). The fractographical situation here is similar to that is observed at brittle fracture of deformed polycrystalline metals like Mo, W, Cr where two categories of boundaries may be observed simultaneously, namely boundaries of big initial grains and boundaries of small grains, which are as subgrains, which have arisen in material during plastic deformation. At 1300 °C, the Type II particles are consolidated already well enough (fig. 2, *c*). The sites of their joining, interparticle boundaries, are strong, stronger than of particle body; particles fail with the cleavage fracture mechanism mainly. Increasing sintering temperature only for 50 to 1350 °C, results in dramatic increase of densification and new details in the fracture, so-called fragmentation that itself is fragmenting a large cleavage surfaces that is result of nano- and microcracking along boundaries of particles (fig. 2, *d*). Their joint effect is the maximal possible strengthening with particle boundaries that might be renamed

as subgrain ones. The strength may reach above 400 MPa (fig. 1). Thermally etched surfaces reveal two categories of structure: subgrains and grains, both

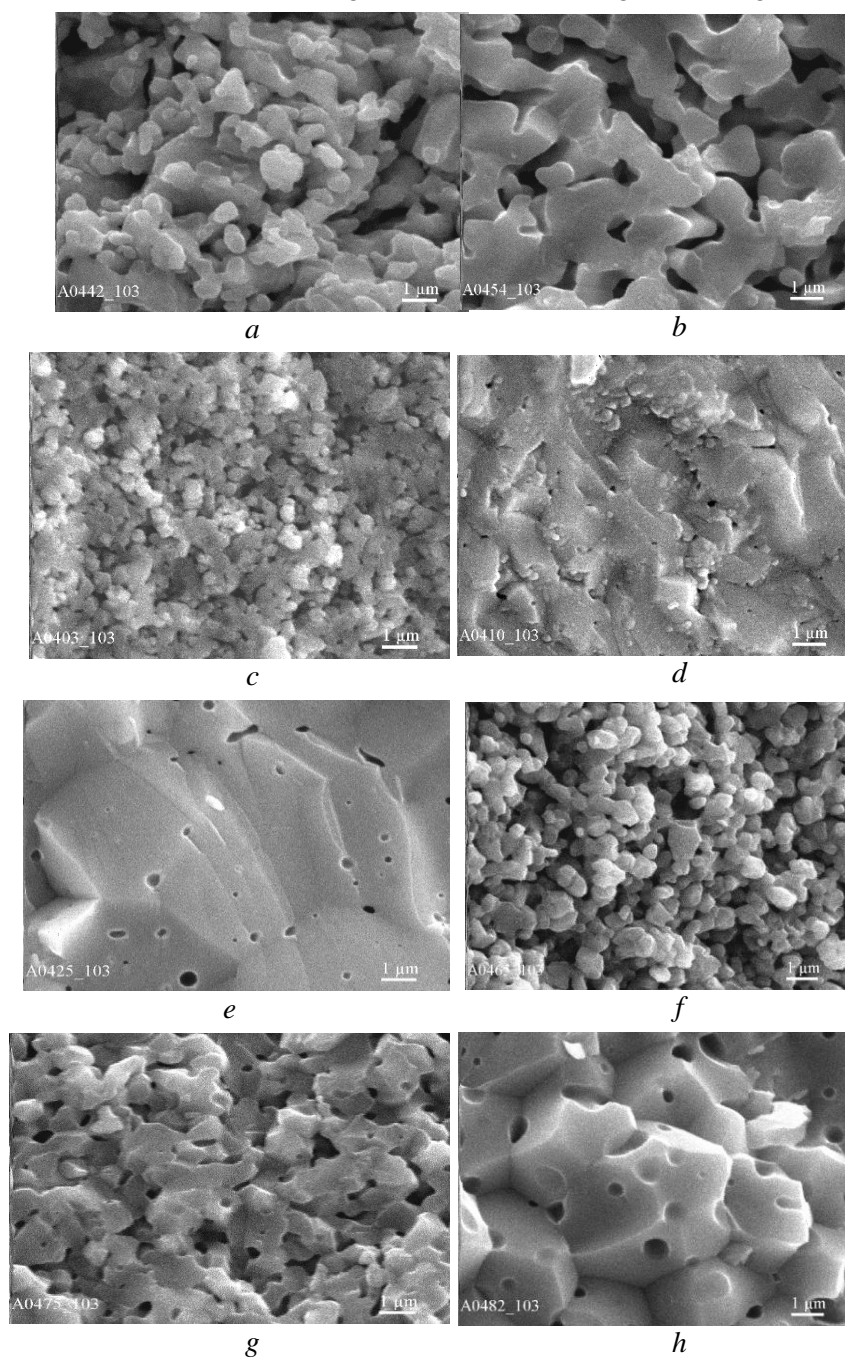


Fig. 2. SEM images of fracture surfaces of the electrolytes sintered of different type powders and at different temperatures. The type I: *a* — 1400 °C; *b* — 1550 °C; the type II: *c* — 1250 °C; *d–t* — 1350 °C; *e* — 1550 °C; the type III: *f* — 1350 °C; *g* — 1450 °C; *h* — 1550 °C [11–14].

of which are clearly distinguished in samples sintered at 1350 and 1450 °C (fig. 3, *b–c*).

At sintering temperatures above 1350 °C, the cracking resulted from an interaction of cleavage crack with the particle / subgrain boundaries is disappearing. We observe the typical picture of cleavage fracture of brittle

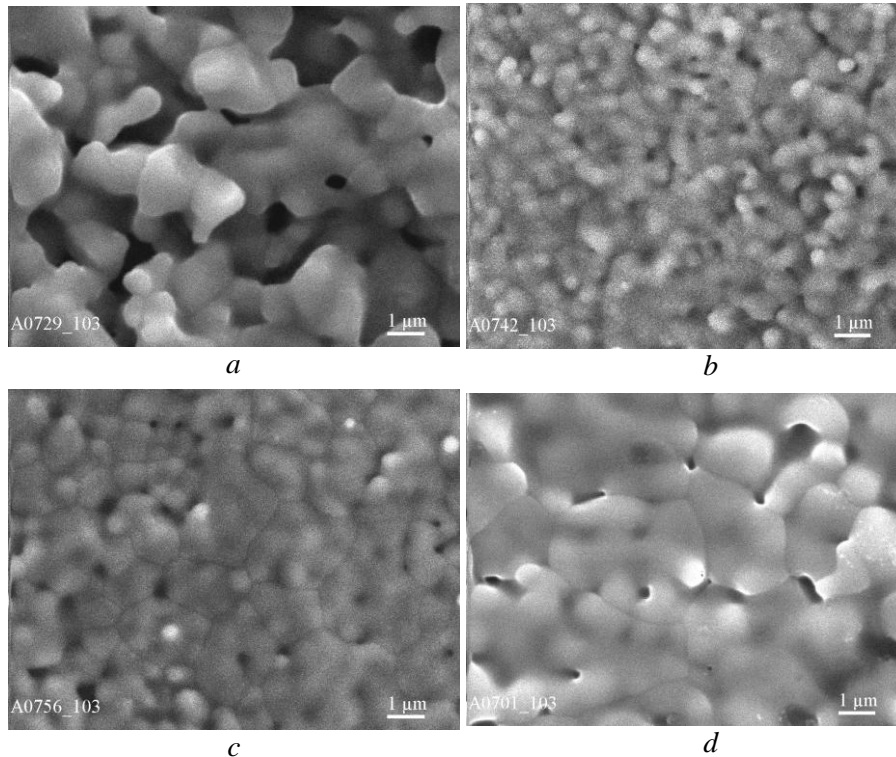


Fig. 3. SEM images of thermally etched surfaces of the electrolytes sintered of different type powders. The type I: *a* — 1550 °C; the type II: *b* — 1350 °C; *c* — 1450 °C; the type III: *d* — 1550 °C.

polycrystalline material decorated by river patterns and crack slopes on each grain boundary (fig. 2, *e*). As result, the strengthening effect by boundaries decreases abruptly and strength drops to ~200 MPa at 1400 °C (fig. 1). It is necessary to underline that material become slightly denser but significantly weaker because a number of strengthening elements decreases abnormally. Further increase of sintering temperature results in logical growing grain size and decreasing strength.

As to the Type III ceramics, their feature is that they fail with brittle interpartial and intergranular fractures mainly (fig. 2, *f*, *h*), and partially with cleavage in sintered at 1450 °C samples (fig. 2, *g*), in vicinity of which the transition from interpartial to intergranular fracture occurs where the strengths of particle bodies for cleavage and interpartial joining is probably equal. In vicinity of this transition temperature, that is near the inflection point on temperature dependence of grain size growth, its activation energy is altering from 1,01 to 4,21 eV [12]. The grains and their subgrains are clearly visible on thermally etched surfaces of samples (fig. 3, *d*).

Thus, the Type III ceramics manifest the second kind of the complex transition also, but the transition from particle boundaries to grain ones is complicated by that fact that it occurs in the material, subgrain boundaries of which is contaminated heavily by SiO₂ and TiO₂. And, if the complex

transition in the Type II ceramics occurs at a cleavage fracture mechanism mainly (fig. 2, *c—e*), the transition in the Type III ceramics occurs at a fracture mechanism, the brittle crack of which is spreading along boundaries of particles at lower sintering temperatures and grains at higher temperatures (fig. 2, *f, h*). Only at temperature of the transition, that is around 1450 °C, samples fail with mixed mode — interpartial / intergranular and cleavage — manifesting that the strength of the particle / grain bulk and their boundaries are practically equal and the complexion transition of the second kind becomes possible (fig. 2, *g*). The porosity, which is developing along grain boundaries, is only facilitating the transition in spite of the comparatively high intergranular strength (fig. 1).

Electrical conductivity

The impedance spectroscopy allows distinguishing the contribution of each structural constituent into overall resistance of the material. It is traditionally applied for characterization of SOFC materials. This non-destructive method is studying the system response to the application of a periodic small amplitude alternating current signal. These measurements are carried out at different frequencies. Analysis of the system response contains information about the interfaces, their structure and reactions taking place there.

The resistance of a sample for alternating current is composed of a real and an imaginary parts. If the real part is plotted on the X-axis and the imaginary part is plotted on the Y-axis of a chart, we get a Nyquist plot that is typically depicted by a few semicircles as it is shown in fig. 4, *a* obtained for ceramics made of the Type I powder. The semicircles reflects the bulk (intragranular) response (grain, G), intergranular response (grain boundary, GB) and the intercept on the real axis in the high frequency range represented the total Ohmic resistance.

The detailed discussion of the impedance spectroscopy data on materials of our interest obtained at 600 °C is given in [14].

The Type I ceramics

As it is seen in fig. 4, *a*, the impedance spectra of the Type I samples show two or even three semicircles with the two intercepts on the real axis at higher frequencies corresponding to the total Ohmic and polarization resistances, respectively. The third semicircle in the low frequency range (<1 Hz) is due to the electrode effects and was observed only for the samples sintered at relatively low temperatures, 1250—1300 °C that had low mechanical strength and were highly porous leading to high Ohmic resistances. The second intercept at the intermediate frequencies of 50—100 Hz is related to the blocking of charge carries due to the internal surfaces of the specimens also denoted as intergranular response (grain boundary, GB). The first semicircle at high frequencies (with the peak frequency of 200—398 kHz was assigned to the bulk (intragranular) response (grain, G) and the intercept on the real axis in the high frequency range represented the total Ohmic resistance.

The grain boundary resistance of the Type I samples is about 30 Ω·cm (fig. 4, *b*) that does not depend on the sintering temperature. The porosity of the samples decreases from 37 to 21% with increasing sintering temperature from 1300 to 1550 °C [11—13], causing increase in the electrical conductivity of the

samples. The results of the secondary ion mass spectroscopy showed [11] that the surface layer of Type I particles has a large amount of contaminants — Al_{3+} , Si_{4+} and K_+ , which are known as elements decreasing the ionic conductivity.

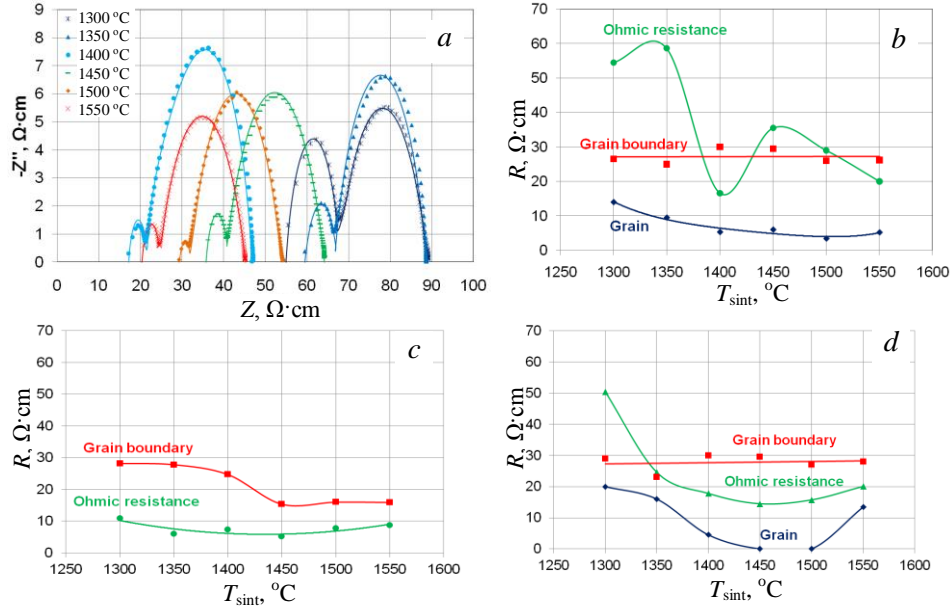


Fig. 4. Representative impedance spectra of type I samples (a), and grain, grain boundary and Ohmic resistances of type I (b), type II (c), and type III (d) samples in regard to their sintering temperature (°C): 1 — dots — experimental data, lines — model approximation.

The grain resistance of the Type I samples is equal to 14 and 9,5 $\Omega \cdot \text{cm}$ at 1300 and 1350 °C sintering temperatures, respectively, and further temperature increase to 1400—1500 °C decreases it to ~5 $\Omega \cdot \text{cm}$. In contrast to Types II and III, the initial agglomerates in the Type I powder are not uniform, which averts densification of Type I samples (fig. 2, a, b). These results are inversely proportional to the resistance R_1 of the grain size d ($R_1 = f(1/d)$) at $T_{\text{sint}} = 1300$ —1350 °C and maintain almost constant resistance at higher sintering temperatures.

The Type II ceramics

All Type II 10Sc1CeSZ electrolytes have only one semicircle indicating the grain boundary resistance (GB) in the frequency range of 50—79 Hz (fig. 4, c). Furthermore, the Type II samples have the highest total ionic conductivity due to near zero grain resistance. The grain boundary resistance of the samples obtained at 1300—1350 °C is about 30 $\Omega \cdot \text{cm}$, slightly decreases at 1400 °C, and drops twice as much at 1450—1500 °C.

The Ohmic resistance of these samples show a parabolic behavior: it decreases from 11 $\Omega \cdot \text{cm}$ at 1300 °C to ~6 $\Omega \cdot \text{cm}$ at the intermediate sintering temperatures and then increases again to the initial values at sintering temperature of 1550 °C. As result of the high purity of the Type II powder (<10⁻³ wt. % of impurities) [11] a considerable grain growth during the sintering process is observed. Such behavior can be explained by the weak influence of the initial boundaries of the particles (subgrains) on a grain recrystallization during the

sintering process. Due to this, identification of the grain edges (subgrains) is very complicated and the structure fragmentation totally disappears at the sintering temperatures above 1400 °C. We assume, that the absence of the grain response (explained by the extremely low impurities content and the decrease of the grain boundary resistance of the samples sintered at the temperatures above 1450 °C) is determined by the grain boundaries improvement, for instance, homogenization of the impurities and structural changes of the grain boundaries.

The Type III ceramics

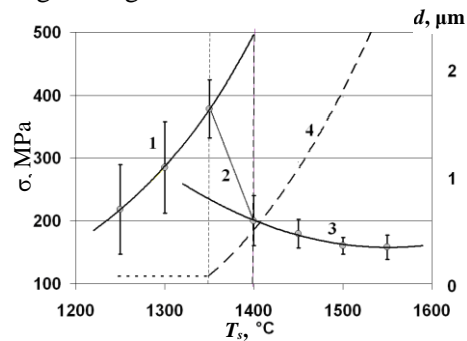
As it is shown in fig. 4, *d*, the Type III samples sintered at 1300—1400 and 1550 °C have two semicircles responsible for the grain boundary (63—316 Hz) and the grain bulk (316—794 Hz) resistances. All other Type III samples demonstrate only one semicircle related to the grain boundary response (126—158 Hz). Here, the grain boundary resistance (30 Ω·cm) is similar to the Type I ceramics and is independent on the sintering temperature. However, taking into account significant densification and porosity decreases from 37% at $T_{\text{sint}} = 1300$ °C to ~0% at $T_{\text{sint}} = 1550$ °C [12—13], the grain boundary resistance is increasing. This can be explained by the electrical conductivity decrease relevant to the Al³⁺, Si⁴⁺, and K⁺ doping ions found on particle surfaces in this and Type I powders at the first stage of sintering, and the porosity localization along grain boundaries at the second sintering stage. The grain bulk and the Ohmic resistances of the ceramics are decreasing with increasing sintering temperatures up to 1450—1500 °C, however, they are increasing at $T_{\text{sint}} = 1550$ °C. Unlike Type I, the Type III powder consists of equiaxial agglomerates that together with interpartial admixtures accelerate the sintering. An improved contact between the grains at $T_{\text{sint}} = 1450—1500$ °C decreases the grain bulk and the Ohmic resistances (0 and 15 Ω·cm), respectively. The increase of the grain bulk resistance to 13,5 and Ohmic resistance to 20,2 Ω·cm at $T_{\text{sint}} = 1550$ °C is related to the intragranular porosity increase.

It was unexpected, that the electrical resistance responsible for interfaces in the samples made of all three powders sintered at temperatures up 1300—1400 °C is practically the same and equal to ~30 Ω·cm. Only at further increase of sintering temperature, the changes of a intergranular resistance related to the sintering temperature are observed.

In pure the Type II material, the grain boundary resistance drops abruptly by half. The relevant changes are observed in mechanical strength that drops abruptly by more than half. The nanocracks related to subgrain boundaries disappear as relevant fractographical mark of the interaction between the cleavage cracks and the subgranular interfaces [10—13]. These complex properties may indicate that in the Type II electrolyte, the sintering at 1350—1400 °C results in a full dissolution of initial particle boundaries, which play a role of subgrain boundaries and are observed as a fractographical fragmentation of grains fracture with cleavage (fig. 2, *d*) and high subgrain boundary resistance (fig. 4, *b*).

Considering an influence of sintering temperature on the structural parameters and mechanical behavior of 10Sc1CeSZ electrolyte we might conclude [12] that the sintering temperature of 1300—1400 °C is critical for the Type II material. Namely at this temperatures, the activation energies of grain

growth and densification, strengthening or weakening occur. Namely in vicinity of 1300—1400 °C, the strength of the Type II electrolyte is decreased abruptly that is a result of replacement of basic strengthening constituent of the material Fig. 5. The generalized schematic representation of a Type II ceramics strengthening-weakening with sintering temperature that results from relative structural element altering: 1 — subgrain strengthening; 2 — transition from subgrain strengthening to grain weakening; 3 — grain growth weakening; 4 — size of effective structural element.



when subgrains, which boundaries were improved with increasing temperature up to ~1375 °C and dissolved with a further increasing temperature up to ~1400 °C, are replaced abruptly by grains. It should be emphasized here that the grain size does not reveal any evident deviations from the exponential growth that might cause such dramatic changes of the mechanical strength and its decrease from more than 400 to 150 MPa. Schematically, the results of the contradictory processes are shown in fig. 5, where the transition between strengthening elements and their sizes are given also.

The data on the impedance spectroscopy and SEM also indicate two different stages of the traditionally determined boundary or intergranular resistance. During the first stage, till the 1300—1400 °C critical temperatures, the boundary resistance in 10Sc1CeSZ is ~30 Ω·cm that is independent on contaminants and other properties of powder used for the electrolyte production. The improvement of the interpartial or subgranular boundaries is reflected in a rapid growth of the electrolyte strength to more than 400 MPa at biaxial bend. High electrical resistance (~30 Ω·cm) of these boundaries points out a weak influence on temperature at this stage of sintering.

During the second stage, at temperatures above 1300—1400 °C, the situation is changed radically. Here, the grains, the boundary structure of which became rather perfect in order to be easy distinguished fractographically via as both disorientation like in pure the Type II electrolyte and admixture segregation additionally like in Types I and III electrolytes. The intergranular constituent of the resistance may be decreased with both abrupt decrease of a specific boundary surface like it happens in Type II electrolyte, and promoting chemical composition of a small amount of impurities segregating along grain boundaries.

In ceramic electrolytes containing a large number of contaminants, the grain boundary response has an unexpected behavior. The temperature increase and the adequate growth of the grain size that depends on amount of admixtures, which are either constraining grain growth like in the Type I electrolyte, or promoting grain growth like in the Type III electrolyte, do not reflect measurably in neither increase, neither decrease of the grain boundary resistance in spite of they influence significantly on the mechanical behavior. At the level of 30 Ω·cm, the difference in neither chemical composition of admixtures and their amounts, nor in their distribution across structure of initial powder particles [11].

It is known that a deviation from the Debye's model indicates a greater degree of structural heterogeneity [14]. The application of the Havriliak—Negami model [15] to the single semicircle may be as an evidence of continuous solid microstructure, where the grain and grain boundary phases cannot be distinguished, i. e., both the bulk of the grains and the intergranular layers have the same chemical composition that may explain the existence of the only one semicircle in a complex plane of Type II 10Sc1CeSZ electrolyte impedance. Thus, the solid phase of the Type II electrolyte is as single-phase in contrast to the Types I and III where there is the grain bulk and the phase of the intergranular layers of different origins.

Conclusions

The heat (temperature-time) treatment via sintering and the powder typification are the suitable and convenient thermodynamical and chemical tools for the boundary engineering with “useful or non-useful” admixtures to control the boundary complexions and their transitions in sintered materials such as scandia stabilized zirconia electrolyte. Using this approach, the most full variety of structural parameters such as porosity, subgrain and grain size growth and redistribution of admixtures across structural constituents and their boundaries, and altering their states have become available for the study. Joint analysis of data obtained with electron microscopy and related techniques, mechanical tests for strength, scanning electron fractography and impedance spectroscopy of structural constituents of electrical resistance is giving much more reliable information on the effect of boundaries and their complexions on properties of materials especially such as ceramic electrolytes where mechanical behavior is as important as their conductivity.

In the electrolyte made of three types of 1Ce10ScSZ powder, two kinds of boundary complexions, subgranular and granular, were observed. They are developing in both very pure and of technical purity materials with sintering temperature. Moreover, the transitions between complexions, those might be defined as the boundary complexion of the second kind, occur.

The first kind of the boundary complexion transition means usually the transition within the same category of boundaries, e. g., of subgrains or their grains. The second one is the transition between categories, e. g., from subgrains to their grains when the mechanical behavior and the boundary resistance become to be determined by grain boundaries, of course, jointly with the grain bulks.

The second kind of the boundary complexion transition caused by sintering in temperature interval 1250—1550 °C occurs in both very pure 1Ce10ScSZ ceramics (the Type II), boundaries of which are contaminated with small amounts of Sc and Al, and in 1Ce10ScSZ of technical purity (the Type III), powder of which is contaminated with large amounts of silica (0,05%) and titania (<0,14%).

The Type I ceramics made of powder contaminated with silica (0,05%) and alumina (<0,025%) does not reveal any notable changes in properties those might be related to the boundary complexion transitions in the temperature interval of the sintering studied. The Type I ceramics does not reveal nor fracture mechanism change, it fails with cleavage only, nor boundary resistance change. The dependence of the grain size on sintering temperature of the Type I ceramics in Arrhenius coordinates has the inflection at ~1450 °C.

The boundary complexion transition in the Type II ceramics reveals itself as the transition from subgrain strengthening to grain weakening, which manifests the abrupt drop of strength resulting from any interaction of cracks with intragranular (subgrain) interfaces accompanied by cleaning the cleavage picture from any marks of cracking at interfaces. It occurs in samples sintered in the narrow temperature interval 1350—1400 °C where the dependence of the grain size on sintering temperature in Arrhenius coordinates has the inflection.

The boundary complexion transition in the Type III ceramics reveals itself as the transition from the brittle interpartial fracture to the brittle intergranular one except a mixed with cleavage intergranular fracture at temperature 1450 °C where the dependence of the grain size on sintering temperature in Arrhenius coordinates has the inflection too.

The impedance spectroscopy study confirms also that the 1Ce10ScSZ electrolyte is largely heterogeneous, and its degree of heterogeneity is determined by not only the type of the powder, but its sintering temperature. In many cases, the electrical resistance of the polycrystalline electrolyte samples is determined by the grain bulk and their intergranular layers. In some cases, like in the Type II electrolyte, the polycrystalline electrolyte exists as a single phase one where ionic conductivities of grain bulk and their boundaries are similar. This results in the electrical response with the only one semicircle characterizing the resistance of the boundary complexion.

It is surprising that the resistance of intergranular phase is near 30 Ω·cm in all samples made of the Type I and Type III powders sintered at all temperatures studied, and does not depend on the type and the amount of admixtures (either SiO₂ and Al₂O₃ in the Type I, either SiO₂ and TiO₂ in the Type III, either the third oxides (the total number of Si, Al, Ti, Fe oxides is ~0,01%) in the Type II at sintering temperatures below ~1375 °C) and their distribution across the grains, grain size and general porosity.

Only in the Type II electrolyte sintered at temperatures above ~1375 °C, the boundary resistance is abruptly decreasing from ~30 to 17 Ω·cm. Namely, in withinity of this temperature, the activation energy of numerous thermoactivated processes of powder consolidation is changed, the grain bulk is purifying from the subgrain boundaries as fractography evidences. The mechanical strength decreases here abruptly from 400 to 150 MPa as result of abrupt replacement of the effective strengthening structural element from subgrain for grain and, thereby, abrupt decrease of their number.

As to the grain bulk resistance, it can be concluded that in Type I electrolyte, it decreases continuously from 14 to 6 Ω·cm with porosity decrease at 1300—1450 °C and does not depend on structural evolution considering the cleavage fracture mechanism that may evidence continuous altering in the grain bulks and their boundaries with no any transitions, at least at temperatures in the interval studied. In Type II electrolyte, the grain body resistance cannot be detected indicating that the electrochemical properties of the grain bodies and their boundaries are the same, and the material looks like a single phase one. In Type III electrolyte, the resistance decreases from 20 to 5 Ω·cm at decreasing porosity and interpartial fracture mechanism at 1300—1400 °C; it becomes almost zero at mixed fracture mechanisms containing cleavage (1450—1500 °C), and increases to 13 Ω·cm during the recrystallizing grain growth.

Acknowledgement

The authors are gratefully acknowledged the National Academy of Science of Ukraine, Projects "Structural Fundamentals of Materials for Zirconia Ceramic Fuel Cells", and "SOFC structural optimization based on consideration of interdiffusion at manufacturing and operation"; the European FP7 and FP6 Projects: NANOMAT-EPC N608906 "Deployment of Socially Beneficial Nano- and Material Technologies in European Partnership Countries", and N020089 "Demonstration of SOFC stack technology for operation at 600 °C (SOFC600)"; NATO, the "Science for Peace" project N980878 "Solid Oxide Fuel Cells for Energy Security" for their financial support.

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Межі та їхній вплив на властивості цирконієвих електролітів

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Межі та їхні комплекси в керамічному електроліті 1Ce10ScSZ, які були утворені і змінювані застосуванням трьох типів вихідних порошків і різних режимів спікання, вивчені через їхній вплив на механічну поведінку та електропровідність. Спільний аналіз даних, отриманих методами електронної мікроскопії та іншими, пов'язаними із нею, методами механічних випробувань на міцність, скануючої електронної фрактографії та імпедансної спектроскопії структурних складових електричного опору, надав багато інформації щодо впливу меж та їхніх комплексів на властивості електроліту, для якого механічна поведінка є настільки важливою, як і його провідність. Спостережено корелятивний вплив меж, які визначаються вихідними типами порошків та температурою їхнього спікання, на механічну поведінку і електричну провідність електроліту. Визначено два типи межевих комплексів, які існують і розвиваються між субзернами та зернами з ростом температури спікання. Перехід між цими категоріями меж, що було названо переходом межевих комплексів другого роду, відбувається як в хімічно чистій кераміці 1Ce10ScSZ, так і в кераміці технічної чистоти, порошки якої збагачені досить значною кількістю оксидів кремнію та титану. В кераміці 1Ce10ScSZ з великим вмістом оксидів кремнію та алюмінію помітних переходів не виявлено.

Ключові слова: межі, межеві комплекси, механічна поведінка, імпедансна спектроскопія, провідність зерна, провідність межі, цирконієвий електроліт 1Ce10ScSZ, цирконієві порошки, температура спікання.

Границы и их влияние на свойства циркониевых электролитов

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Образованные в керамическом электролите 1Ce10ScSZ границы и их комплексы, измененные посредством контроля температуры спекания с использованием исходных порошков трёх типов, исследовали, анализируя их влияние на механическое поведение и электропроводность. Комплексная обработка данных, полученных методами электронной микроскопии и другими, связанными с ней, методами механических испытаний на прочность, сканирующей электронной фрактографии, а также импедансной спектроскопией структурных составляющих электрического сопротивления, предоставила информацию о влиянии границ и их соединений на свойства электролита, для которого механическое поведение также важно, как и его проводимость. Наблюдалась корреляция между влиянием границ, определенных исходными порошками трёх типов и температурой их спекания, на механическое поведение и электрическую проводимость электролита 1Ce10ScSZ. Найдено две комбинации граничных комплексов, которые существуют и улучшаются с ростом температуры спекания между субзернами и зёрнами. Переход между видами граничных комплексов, который был определен как переход второго рода, происходит как в химически чистой керамике 1Ce10ScSZ, так и в керамике технической чистоты из порошков, обогащенных оксидами кремния и титана. В керамике 1Ce10ScSZ содержащей значительные количества оксидов кремния и алюминия, переходы не обнаружены.

Ключевые слова: границы, граничные комплексы, импедансная спектроскопия, проводимость зерна, проводимость границы, циркониевый электролит 1Ce10ScSZ, циркониевые порошки, температура спекания.