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Scattered and linked microcracks in solid oxide fuel cell electrolyte

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Abstract

Scattered and linked microcracks in the electrolyte layer have been analysed in detail in anode supported planar solid oxide fuel cells. The empirical model established allowed critical characteristics of scattered and localised microcracking to be determined using electrolyte microstructural parameters. The model was verified with experimental data obtained for electron beam deposited scandia-stabilised zirconia electrolytes. Suitable annealing and deposition temperatures during fuel cell fabrication could be predicted from the critical temperature difference below which microcracking does not occur.

Key words: Microcracking; Residual stress; Scandia-stabilised zirconia; Electrolyte; Thermal expansion; Solid oxide fuel cell

1. Introduction

Solid oxide fuel cells (SOFC) are a technology to transform the chemical energy of gaseous fuels such as hydrogen, carbon monoxide or methane, directly into electrical and thermal energy at high efficiencies. The electrochemical process in an SOFC brings less environmental hazard than conventional combustion processes. The materials for SOFC should meet specific requirements due to the strong thermal degradation at the high operating temperatures of 650 to 900°C [1, 2]. The problem can be partially solved by decreasing operating temperature. This results in the use of thin electrolyte layers in the order of 5 µm on an anode (or cathode) substrate [3]. Residual stresses

appear in such layered structures due to the thermal expansion mismatch between the different SOFC layers and may lead to microcracking, destroying the cell's mechanical integrity [4, 5]. Generally, the stresses can arise during different stages of SOFC production. Besides differences in thermal expansion coefficients, the existence of thermal or concentration gradients can also give rise to residual stresses [6-9]. Significant degradation, particularly microcracking of SOFC components, as well as of the properties of ceramic materials in general at high temperatures remains an unresolved problem [10]. The analysis of microcracking in fuel cell components, especially in the electrolyte, is an important prerequisite to produce highly reliable SOFC stacks for power generation.

There are three characteristic stages of the electrolyte behaviour upon increasing tensile residual stress [4]. The first stage is characterised by the absence of microcracking. In fact, this is the zone of existence of undamaged material. The second stage is the scattered microcracking where each crack occupies one structural element (SE) and cracks in different SEs are not linked [11-17]. The microcracking process becomes localised at the third stage, meaning each next structural element fails at the tip of the existing crack and linked microcracks are formed. The total number of cracks increases very slowly at this stage. The average microcrack size increases with microcrack density growth, demonstrating a tendency for saturation for localised microcracking, for instance in electron beam deposited 10Sc1CeSZ electrolyte material [4]. However, the microcracking model from [4] has some shortcomings resulting from two rough approximations: (i) a statistical distribution of grain sizes was used instead of a distribution of SE sizes, and (ii) the local failure criterion of SE was based on the strain energy density. In reality, the statistical distribution of SE sizes differs from that of grain sizes for intercrystalline fracture. Failure of an SE (formation of a crack with size equal to SE size) depends on the random flaw inside it and the random fracture toughness of the SE. Such failure is described as statistical and not deterministic in contrast to the failure description which follows from the criterion based on the strain energy density. Besides, the above model describes only scattered microcracking. As a whole, nevertheless,

the problem of electrolyte microcracking is far from a complete solution.

The goal of this article is a more detailed analysis of scattered and linked microcracks in SOFC electrolyte materials, the development of an empirical model of scattered and localised microcracking, and the verification of the model using experimental data obtained for a 10Sc1CeSZ electrolyte.

2. Experimental

Experimental data on elastic moduli, Poisson ratios, coefficients of thermal expansion (CTE), thicknesses of electrolyte and anode layers as well as the difference ΔT between annealing and deposition temperatures were derived from half-cell (anode-electrolyte system) experiments [4] and then used for the further calculations presented here. The composition of the electrolyte material of the half-cells was 10 mol.% Sc_2O_3 –1 mol.% CeO_2 –89 mol.% ZrO_2 (10Sc1CeSZ). The elastic modulus, the Poisson ratio and the thermal expansion coefficient of electrolyte material are 200 GPa, 0.31 and $1 \times 10^{-5} \text{ K}^{-1}$, respectively [4]. The anode layer consisted of a mixture of 40 wt.% NiO and 60 wt.% 10Sc1CeSZ. The anode material was prepared as disk-shaped samples with a diameter of 22.5 mm and with a thickness of 1 mm. Electron beam deposition (EBD) was used for producing electrolyte films deposited on the porous, non-reduced anode substrates. The electrolyte was deposited at different temperatures in the range from 600 to 900°C. Details of half-cell fabrication have been presented in [4]. Then the half-cells were annealed at 1173, 1178, 1473, 1548 and 1633 K for 2 h. Heating the half-cell to a temperature higher than the deposition temperature induces equibiaxial tensile stress in the electrolyte. The thermal stresses in half-cells during annealing were determined on the basis of a method presented in [18, 19]. In fact, the thermal stresses result in a certain mechanical loading of the electrolyte dependent on the temperature difference.

Flat sections of grain boundaries (facets) are the structural elements in the case of intercrystalline fracture. The statistical distribution of SE sizes was determined using microstructure

images obtained by scanning electron microscopy (SEM). The micrographs were recorded from the free surface of the electrolyte layer of the half-cell. The image processing and microcrack measurements were performed manually using Image-Pro Plus Software, due to the difficulties of reliably recognising microcracks with automated software. The size and number of scattered and linked microcracks were also measured from the images. The number of links was measured for linked microcracks. Then the statistical distribution of microcrack sizes as well as average microcrack size were determined for different annealing temperatures of half-cells. The microcrack density was calculated as

$$f_f = \frac{1}{A} \sum_{i=1}^{N_A} c_i^2, \quad (1)$$

where c_i is the effective length of the i th microcrack, and N_A is the number of microcracks on the scanned area A (in our case $A = 45000 \mu\text{m}^2$).

3. Microcracking model

For ceramic materials the nucleuses of fracture are pre-existing flaws inside structural elements. The microcracking process includes the activation of potential microcrack sites (pre-existing flaws inside SEs), and then the growth of the microcracks up to metastable barriers (boundaries of SEs) [20]. The microcracks are thought to be nucleated at grain boundary junctions or vertices where local stress concentrations occur [21]. In the case of intercrystalline fracture they typically run over one grain boundary facet until halting at another grain boundary junction [22, 23].

The process of successive nucleation of microcracks occupying a single SE can be described using the parameter of microcrack density. Electrolyte microcracking exhibits a so-called 2D case when microcracks are formed through a thin layer [24, 25]. The electrolyte is under equibiaxial residual stress, meaning that the microcrack orientation is not important. For the 2D case the microcrack density is

$$f_f = n_c \langle c^2 \rangle = n_c \int c^2 f_c(c) dc, \quad (2)$$

where n_c is the number of microcracks per area unit, c is the microcrack size, $f_c(c)$ is the density of the statistical distribution of microcrack sizes (pointed parentheses denote averaging over all microcracks).

For scattered microcracking, when there are no microcracks occupying a few structural elements (one microcrack corresponds to one structural element), the density of microcrack size distribution is given by an expression similar to that obtained in [26], taking into account the statistical distribution of SE sizes and random fracture toughness of the SEs:

$$f_c(c) = \frac{f_{SE}(c) \int_{K_{\min}(c)}^{K_{\max}(c)} f_K(K) F(\sigma_i, c, K) dK}{\int_{l_{\min}}^{l_{\max}} f_{SE}(l) \left[\int_{K_{\min}}^{K_{\max}(l)} f_K(K) F(\sigma_i, l, K) dK \right] dl}, \quad (3)$$

where $f_{SE}(l)$ is the density of statistical distribution of SE sizes, $f_K(K)$ is the density of the statistical distribution of the SE fracture toughness K , $F(\sigma_i, l, K)$ is the probability of SE failure as a function of stress σ_i acting in the SE with size l and fracture toughness K (the probability that SE with size l and fracture toughness K is fractured at σ_i), l_{\min} is the minimum fractured SE size (for the case of ideal log-normal distribution $l_{\min}=0$, however in reality $l_{\min}>0$), l_{\max} is the maximum SE size (there are no structural elements with size larger than l_{\max}), K_{\min} is the minimum SE fracture toughness (statistical distribution of K can be approximated as log-normal and the ideal case is $K_{\min}=0$, however in reality $K_{\min}>0$), $K_{\max}(l) = Y_1 \sigma_i \sqrt{\pi l}$ is the maximum fracture toughness possible for SE with size l at stress σ_i , and Y_1 is a dimensionless geometrical factor for pre-existing flaws inside structural elements (typically $Y_1 = \sqrt{2}/\pi$ for penny-shaped flaws). The denominator in (3) supplies the normalization of the distribution density function.

The statistical distribution of SE sizes is typically log-normal [4, 26]:

$$f_{SE}(l) = \frac{1}{l\sqrt{2\pi D_{SE}}} \exp\left(-\frac{(\ln l - \mu_{SE})^2}{2D_{SE}}\right), \quad (4)$$

μ_{SE} is the mathematical expectation of $\ln l$; D_{SE} is the dispersion of the distribution. A real specimen contains a finite number of structural elements. Therefore, if SE sizes obey the logarithmic normal distribution, SE with size larger than l_{\max} cannot exist in the specimen. The number of SEs with size larger than l_{\max} can be determined as $N_{SE} p$, where N_{SE} is the number of SEs in the representative elementary volume of the electrolyte, and p is the probability of existence of structural element with size larger than l_{\max} :

$$p = \int_{l_{\max}}^{\infty} f_{SE}(l) dl. \quad (5)$$

From a physical point of view, the size l_{\max} can be defined as that size for which the number of SE with size larger than l_{\max} equals 1. In fact, this results in absence of such SE in the specimen. In such a way, l_{\max} can be estimated from the following equation:

$$N_{SE} \int_{l_{\max}}^{\infty} f_{SE}(l) dl = 1. \quad (6)$$

If there is a large technical defect in the material, the size of such defect could be taken as l_{\max} . In this case the parameter D_{SE} should be recalculated using (6), using the size of such defect in the place of l_{\max} .

Statistical distributions of fracture toughness K and grain size l_g can also be presented by Eq. (4) in which μ_{SE} and D_{SE} should be replaced by μ_K and D_K , respectively, for fracture toughness, and with μ_g and D_g , respectively, for grain size. Note that

$$D_{SE} = \ln(1 + s_{SE}^2 / \langle l \rangle^2), \quad (7a)$$

$$\mu_{SE} = \ln \langle l \rangle - D_{SE} / 2, \quad (7b)$$

$$D_K = \ln(1 + s_K^2 / \langle K \rangle^2), \quad (7c)$$

$$\mu_K = \ln \langle K \rangle - D_K / 2, \quad (7d)$$

$$D_g = \ln(1 + s_g^2 / \langle l_g \rangle^2), \quad (7e)$$

$$\mu_g = \ln \langle l_g \rangle - D_g / 2, \quad (7f)$$

where $\langle l \rangle$ is the average size of the SE, s_{SE} is the standard deviation of SE size, $\langle K \rangle$ is the mean fracture toughness of SE, s_K is the standard deviation of SE fracture toughness, $\langle l_g \rangle$ is the mean grain size, and s_g is the standard deviation of grain size. By analogy with the three-sigma rule for normal distribution, in case of log-normal distribution, the minimum SE fracture toughness can be determined as

$$K_{\min} = \exp(\mu_K - 3D_K^{1/2}) \quad (8)$$

where $D_K^{1/2}$ stands for sigma.

The probability of structural element failure has a Weibull-like distribution

$$F(\sigma_i, l, K) = \begin{cases} 0, & K \geq Y_1 \sigma_i \sqrt{\pi l} \\ 1 - \exp\left[-\frac{V(l)}{V_0} \left(\frac{\sigma_i^m - \sigma_{th}(l)^m}{\sigma_0^m}\right)\right], & K < Y_1 \sigma_i \sqrt{\pi l} \end{cases} \quad (9)$$

where $\sigma_0 = \frac{K}{Y_1 \sqrt{\pi a_0}}$, $\sigma_{th}(l) = \frac{K}{Y_1 \sqrt{\pi l}}$, $V_0 = 1/n_{c0}$, $V(l) = bhl$, m is the Weibull exponent, a_0 is the minimum size of pre-existing flaws inside an SE, n_{c0} is the number of pre-existing flaws inside an SE per volume unit, b is the through-thickness height of the SE, and h is the effective thickness of the grain boundary or interface. The existence of cracked structural elements results in an increase of the stress σ_i acting in the SE in comparison with the applied stress σ_a . Stress redistribution between the intact SE and the effective continuum consisting of undamaged and cracked structural elements can be taken into account using the ratio of elastic moduli E_0 and E of undamaged and damaged materials, respectively, i.e. [27]

$$\sigma_a = \sigma_i \frac{E}{E_0} \quad (10)$$

The dependence of the elastic modulus on the microcrack density for the 2D case is [24]:

$$E = E_0 \exp(-\pi f_f / 4). \quad (11)$$

Statistical consideration results in

$$\frac{n_c}{n_g} = m_{SE} \int_{l_{\min}}^{l_{\max}} f_{SE}(l) \left[\int_{K_{\min}}^{K_{\max}(l)} f_K(K) F(\sigma_i, l, K) dK \right] dl, \quad (12)$$

where $m_{SE} = n_{SE} / n_g$ is the number of SEs per single grain, n_{SE} is the number of SEs per area unit for the 2D case, and n_g is the number of grains per area unit. Note that in the 2D case:

$$n_g = \left(\frac{\pi}{4} \int_0^{l_{\max}} l_g^2 f_g(l_g) dl_g \right)^{-1}, \quad (13)$$

where l_g is the grain size, and $f_g(l_g)$ is the density of statistical distribution of grain sizes [4].

Then the microcrack density can be expressed from (2), (3), and (12) as:

$$f_f = \frac{4m_{SE} \int_{l_{\min}}^{l_{\max}} c^2 f_{SE}(c) \left[\int_{K_{\min}}^{K_{\max}(c)} f_K(K) F(\sigma_i, c, K) dK \right] dc}{\pi \int_0^{l_{\max}} l_g^2 f_g(l_g) dl_g}. \quad (14)$$

Other model equations are:

$$\langle c \rangle = \frac{\int_{l_{\min}}^{l_{\max}} c f_{SE}(c) \left[\int_{K_{\min}}^{K_{\max}(c)} f_K(K) F(\sigma_i, c, K) dK \right] dc}{\int_{l_{\min}}^{l_{\max}} f_{SE}(l) \left[\int_{K_{\min}}^{K_{\max}(l)} f_K(K) F(\sigma_i, l, K) dK \right] dl}, \quad (15)$$

$$s_c^2 = \frac{\int_{l_{\min}}^{l_{\max}} c^2 f_{SE}(c) \left[\int_{K_{\min}}^{K_{\max}(c)} f_K(K) F(\sigma_i, c, K) dK \right] dc}{\int_{l_{\min}}^{l_{\max}} f_{SE}(l) \left[\int_{K_{\min}}^{K_{\max}(l)} f_K(K) F(\sigma_i, l, K) dK \right] dl} - \langle c \rangle^2, \quad (16)$$

$$q = \frac{\sigma_a^2}{2E} = \frac{\sigma_a^2}{2E_0} \exp(\pi f_f / 4), \quad (17)$$

where $\langle c \rangle$ is the average microcrack size, s_c is the standard deviation of the microcrack size, and

q is the strain energy density.

For scattered microcracking it is possible to calculate n_c/n_g , f_f , σ_a , q , and $\langle c \rangle$ parameters for different σ_i at given values of $\langle l \rangle$, s_{SE} , l_{\max} , $\langle K \rangle$, s_K , E_0 , $\langle l_g \rangle$, s_g , m_{SE} , bhn_{c0} , a_0 , and m . In the stress range from $\sigma_i = 0$ to $\sigma_i = \sigma_{i0} = K_{\min} / (Y_1 \sqrt{\pi l_{\max}})$ microcracking can be considered as negligible when, in fact, $n_c/n_g = 0$, $f_f = 0$, $\sigma_a = \sigma_i$, and $q = \sigma_i^2 / (2E_0)$. In the stress range from $\sigma_i = \sigma_{i0}$ to $\sigma_i = \sigma_{ic}$ there is scattered microcracking when σ_{ic} corresponds to the maximum of $q(\sigma_i)$ dependence. Note that $n_c/n_g = (n_c/n_g)_c$, $f_f = f_{ic}$, and $\langle c \rangle = \langle c \rangle_c$ at $\sigma_i = \sigma_{ic}$. At $\sigma_i > \sigma_{ic}$ the linked microcracks begin to form. When analyzing this stage, one should distinguish between cases of uniaxial and equibiaxial tension in the layer. Typically, only one linked microcrack transforming into a main crack is formed under uniaxial tension [12]. In this case the first linked microcrack is oriented perpendicular to the loading direction, promoting further cracking to be localised only in the cross section where it resides. In our case (equibiaxial tension), many linked microcracks are formed since the microcrack orientation relative to loading direction is not important. These microcracks form a saturated structure which remains unchanged upon further increase in σ_i .

The number of one-link microcracks (single cracks) through the layer per area unit formed at $\sigma_i = \sigma_{ic}$ is $n_g (n_c/n_g)_c$. Each such crack can be presented as a point in coordinates $K_{eff} - c$ (Fig. 1A) where K_{eff} is the effective critical stress intensity factor for the crack, and c is the microcrack size (Fig. 1B). In general, the stress intensity factor of a crack can be presented as $K_I = Y \sigma_a \sqrt{\pi c}$ where $Y = Y_2 Y_h / Y_g$, $Y_2 = 1/\sqrt{2}$ is the geometrical factor for simple straight through crack, Y_h is the factor accounting for additional stress concentration due to other surrounding microcracks ($Y_h = 1$ for isolated microcrack, $Y_h > 1$ for $f_f > 0$), and Y_g is the factor accounting for the complex geometry of linked microcracks ($Y_g \geq 1$). It is assumed that $Y_h = E_0 / E = \exp(\pi f_f / 4)$, leading to

$Y_h \sigma_a = \sigma_i$. In general case the factor Y_g is not determined analytically. Thus, it is reasonable to include Y_g into the critical stress intensity factor considering some effective critical stress intensity factor and effective stress intensity factor $Y_2 \sigma_i \sqrt{\pi c}$. When the effective stress intensity factor of a given crack is equal to or more than K_{eff} , the crack grows. In the contrary case, the crack size remains unchanged.

At $\sigma_i = \sigma_{ic}$ an ensemble of single cracks with mean crack size $\langle c \rangle_c$ exists which do not grow. Then K_{eff} of these microcracks is located on the right side of curve 1 (Fig. 1A) determined as

$\frac{1}{\pi Y_2^2} \left(\frac{K_{eff}}{\sigma_{ic}} \right)^2$. Curve 1 describes the minimum possible value of K_{eff} for a given crack size c . It is obvious that the maximum possible value of K_{eff} also exists for the same crack size. The growth of a one-link microcrack occurs as a failure of adjacent SEs which can have different orientation with the angle θ relative to the original crack ($\theta_{min} \leq \theta \leq \theta_{max}$ where $\theta_{min} = 0$ and $\theta_{max} > 0$) (Fig. 1A).

The normal stress causing the failure of the adjacent SE is $\sigma_{\theta\theta} = \frac{K_{eff}(\theta)}{\sqrt{2\pi r}} \left(\frac{3}{4} \cos \frac{\theta}{2} + \frac{1}{4} \cos \frac{3\theta}{2} \right)$ where r is the distance from the crack tip [28]. Suggesting $\sigma_{\theta\theta}$ is the same for different θ ,

$K_{eff}(\theta_{max})/K_{eff}(\theta_{min})$ can be obtained as $\left(\frac{3}{4} \cos \frac{\theta_{max}}{2} + \frac{1}{4} \cos \frac{3\theta_{max}}{2} \right)^{-1}$ and $K_{eff}(\theta_{max})/K_{eff}(\theta_{min}) > 1$

is always valid. The angle θ_{max} can be estimated from analysis of the microstructure. The ratio

$K_{eff}(\theta_{max})/K_{eff}(\theta_{min})$ can help to estimate the stress $\sigma_i = \sigma_{i_{max}} = \sigma_{ic} \left(\frac{3}{4} \cos \frac{\theta_{max}}{2} + \frac{1}{4} \cos \frac{3\theta_{max}}{2} \right)^{-1}$

when the effective stress intensity factor equals the maximum possible value of K_{eff} for any size of

one-link cracks. Then the curve 3 determined as $\frac{1}{\pi Y_2^2} \left(\frac{K_{eff}}{\sigma_{i_{max}}} \right)^2$ describes the maximum possible

value of K_{eff} for a given crack size c (Fig. 1A). At $\sigma_i = \sigma_{ic}$ the ensemble of single cracks can be presented as points located between curves 1 and 3 where K_{eff} values are uniformly distributed at a

fixed c .

For the stress $\sigma_{ic} < \sigma_i \leq \sigma_{imax}$ the effective stress intensity factor of a crack with fixed c can be depicted using curve 2 (Fig. 1A). Curve 2 is determined as $\frac{1}{\pi Y_2^2} \left(\frac{K_{eff}}{\sigma_i} \right)^2$. If point P, representing a crack in Fig. 1a, coincides with curve 2, then the corresponding crack begins to grow. The size of the crack and its number of links increase (arrow "up"), and the effective critical stress intensity factor of the crack also increases due to the growing complexity of linked crack geometry (arrow "right"). As a result, the grown crack will be represented by the point P', located to the right of curve 2. This crack stops growing until the moment when curve 2 reaches point P' at the new larger value of σ_i . In fact, curve 2 describes the minimum possible value of K_{eff} at the stress $\sigma_{ic} < \sigma_i \leq \sigma_{imax}$ for a given crack size c .

The number of through microcracks per grain increases visibly with a growth in σ_i during localised microcracking, although the rate of this increase is significantly lower than at the stage of scattered microcracking [4]. Such an increase in the number of cracks can occur only through the failure of structural elements outside the zone of existing crack influence. Thus, the new cracks are one-link and have a size smaller than a certain size c_t . Since the distribution of microcrack sizes changes proportionally with growth in σ_i , that is, there is no noticeable increase in the number of microcracks with small sizes, it is logical to assume that new cracks are added instead of those that have become linked microcracks (dark grey area in Fig. 1A) and these are moved to the area of larger sizes. Then at $\sigma_i > \sigma_{ic}$

$$\frac{n_c}{n_g} = \begin{cases} \left(\frac{n_c}{n_g} \right)_c \left[1 + f_t \left(\frac{\sigma_i - \sigma_{ic}}{\sigma_{imax} - \sigma_{ic}} \right) \right], & \sigma_{ic} < \sigma_i \leq \sigma_{imax} \\ \left(\frac{n_c}{n_g} \right)_c [1 + f_t], & \sigma_i > \sigma_{imax} \end{cases} \quad (18)$$

where $f_t = \int_0^{c_t} f_c(c) dc$, $f_c(c)$ is the density of microcrack size distribution (3) at $\sigma_i = \sigma_{ic}$. The

parameter c_t can be assessed as $\frac{1}{\pi} \left(\frac{K_{\text{mod}}}{Y_1 \sigma_{ic}} \right)^2$, where $K_{\text{mod}} = \exp(\mu_K - D_K)$ is the value of K that appears most often.

It is obvious that the linked microcracks cannot have infinite size with σ_i growth. Moreover, the ultimate size of a microcrack in a thin layer is much smaller than the size of the layer in the direction perpendicular to its thickness. The ultimate average size of the linked microcracks can be estimated from the average area per single crack at $\sigma_i = \sigma_{ic}$. Supposing that the area is bounded by a circle, the ultimate average size is

$$\langle c \rangle_u = 2 \left[\pi n_g \left(n_c / n_g \right)_c \right]^{1/2} \quad (19)$$

The minimum possible value of K_{eff} for the crack with size $\langle c \rangle_c$ at $\sigma_i = \sigma_{ic}$ is

$$K_{cc} = Y_2 \sigma_{ic} \sqrt{\pi \langle c \rangle_c} \quad (20)$$

Then, the minimal possible value of K_{eff} for the crack with size $\langle c \rangle$ at $\sigma_{ic} < \sigma_i \leq \sigma_{i\text{max}}$ is

$$K_{ci} = Y_2 \sigma_i \sqrt{\pi \langle c \rangle} \quad (21)$$

The following dimensionless parameter can be introduced

$$Y_{g\text{min}}(\sigma_i) = \frac{K_{ci}}{K_{cc}} = \frac{\sigma_i}{\sigma_{ic}} \sqrt{\frac{\langle c \rangle}{\langle c \rangle_c}} \quad (22)$$

Note that $Y_{g\text{min}}(\sigma_{ic}) = 1$ (open circle in Fig. 2A). Since the average microcrack size cannot be greater than $\langle c \rangle_u$, the points corresponding to the values of $Y_{g\text{min}}(\sigma_i)$ cannot also lie to the left of the upper dashed line emerging from the coordinate origin in Fig. 2A. The equation of this line is

$$y(\sigma_i) = \frac{\sigma_i}{\sigma_{ic}} \sqrt{\frac{\langle c \rangle_u}{\langle c \rangle_c}} \quad (23)$$

The dimensionless parameter $Y_{g\text{min}}(\sigma_i)$ increases from 1 at $\sigma_i = \sigma_{ic}$ to approach the line $y(\sigma_i)$ with growth in σ_i . In a first approximation, $Y_{g\text{min}}(\sigma_i)$ can be expressed as a linear function

$$Y_{g\text{min}}(\sigma_i) = 1 + k_g (\sigma_i - \sigma_{ic}) \quad (24)$$

for $\sigma_i > \sigma_{ic}$ up to intersection with the line $y(\sigma_i)$ at σ_t . At $\sigma_i > \sigma_t$ (after the intersection) $Y_{g\min}(\sigma_i)$ coincides with $y(\sigma_i)$ (Fig. 2A). The k_g value will be determined below. Then the average microcrack size at $\sigma_{ic} < \sigma_i \leq \sigma_{imax}$ is

$$\langle c \rangle = \begin{cases} \langle c \rangle_c \left(\frac{\sigma_{ic}}{\sigma_i} \right)^2 [1 + k_g (\sigma_i - \sigma_{ic})]^2, & \sigma_{ic} < \sigma_i \leq \sigma_t \\ \langle c \rangle_u, & \sigma_i > \sigma_t \end{cases} \quad (25)$$

Equation (25) is only an approximation linked with the approximate expressions (23) and (24) for $Y_{g\min}(\sigma_i)$. In reality, the dependence $\langle c \rangle$ on σ_i ($\sigma_{ic} < \sigma_i \leq \sigma_{imax}$) is a smooth curve approaching both parts of (25). In order to determine the microcrack size distribution, two parameters, $\langle c \rangle$ and s_c , need to be known. It was found that for localised microcracking [4]

$$s_c = k_s \langle c \rangle \quad (26)$$

where k_s is the constant.

The ratio $k_s = s_c / \langle c \rangle$ is presented in Fig. 2B as a function of σ_i . The problem is that $s_c / \langle c \rangle$ at $\sigma_i = \sigma_{ic}$ (open circle) is not equal to k_s . In fact, there is a sharp change of microcrack size distribution near $\sigma_i = \sigma_{ic}$ when a drastic increase of s_c occurs with a slight change in $\langle c \rangle$. It is obvious that this is due to a widening of the microcrack size distribution resulting from linked microcrack formation. In first approximation one can consider the log-normal distribution $f'_c(c)$ with $\langle c \rangle = \langle c \rangle_c$ and maximum crack size $c_{\max c} = l_{\max} + \langle l \rangle$ due to the first linked microcrack formation. Then the parameter k_s can be determined from equations such as (6) taking into account expressions like (7a) and (7b):

$$N_c \int_{c_{\max c}}^{\infty} f'_c(c) dc = N_c [1 - F_c(c_{\max c})] = 1 \quad (27)$$

where

$$F_c(c_{\max c}) = \frac{1}{2} \operatorname{erfc} \left(-\frac{k_{mc}}{\sqrt{2}} \right) \quad (28)$$

$$k_{mc} = \frac{\ln \left[\frac{c_{\max c} (1 + k_s^2)^{1/2}}{\langle c \rangle_c} \right]}{[\ln(1 + k_s^2)]^{1/2}} \quad (29)$$

and N_c is the number of microcracks in the representative unit volume of the electrolyte.

It follows from the definition of microcrack size variance s_{ci}^2 for $\sigma_i > \sigma_{ic}$ that:

$$\langle c^2 \rangle = \langle c \rangle^2 + s_c^2 = \langle c \rangle^2 (1 + k_s^2) \quad (30)$$

Using (2), (18), and (30) one can obtain the equation for the microcrack density:

$$f_f = \begin{cases} \langle c \rangle^2 (1 + k_s^2) n_g \left(\frac{n_c}{n_g} \right)_c \left[1 + f_t \left(\frac{\sigma_i - \sigma_{ic}}{\sigma_{i\max} - \sigma_{ic}} \right) \right], & \sigma_{ic} < \sigma_i \leq \sigma_{i\max} \\ \langle c \rangle_u^2 (1 + k_s^2) n_g \left(\frac{n_c}{n_g} \right)_c [1 + f_t], & \sigma_i > \sigma_{i\max} \end{cases} \quad (31)$$

Then the applied stress σ_a and strain energy density q can be calculated using (10), (11), (17).

The k_g value can be estimated from the condition that the strain energy density $q(\sigma_i)$ has a maximum at $\sigma_i = \sigma_{ic}$, i.e.

$$\left. \frac{dq}{d\sigma_i} \right|_{\sigma_{ic}} = 0 \quad (32)$$

Then from (10), (17), (25), (31) one can obtain:

$$k_g = \frac{1}{\sigma_{ic}} \left[1 + \frac{2}{\pi f'_{ic}} + \frac{1}{4} \frac{f_t}{(1 - \sigma_{i\max} / \sigma_{ic})} \right] \quad (33)$$

where $f'_{ic} = \langle c \rangle_c^2 (1 + k_s^2) n_g \left(\frac{n_c}{n_g} \right)_c$.

Using (10), (11), (17), (18), (25), (31) it is possible to calculate n_c / n_g , f_f , σ_a , q , $\langle c \rangle$ at given values of θ_{\max} , $\langle l \rangle$, l_{\max} , $\langle K \rangle$, s_K , E_0 , $\langle l_g \rangle$, s_g and at calculated parameters of σ_{ic} , $(n_c / n_g)_c$, f_{ic} , $\langle c \rangle_c$ for localised microcracking ($\sigma_i > \sigma_{ic}$). The average number of links in linked microcrack can be estimated as:

$$n_l = \langle c \rangle / \langle l \rangle. \quad (34)$$

4. Results and discussion

The annealing at various temperatures above deposition temperature creates equibiaxial tensile stress in the electrolyte. The stress depends on the difference in temperature, ΔT , between annealing and deposition temperatures. Such annealing is one of the possible approaches to characterise the mechanical properties of EBD electrolyte films. Electron microscopy investigation of the electrolyte surface after annealing allows the statistical distribution of SE sizes, the size and number of scattered and linked microcracks, average microcrack size, the number of links for linked microcracks, and the microcrack density to be determined. The surfaces of an EBD 10Sc1CeSZ electrolyte film after deposition at 873 K, 1023 K, 1173 K and annealing at 1473 K, corresponding to temperature differences of 300 K, 450 K, and 600 K, are shown in Fig. 3. At such temperature difference, thermal tensile stress results in intensive microcracking in the electrolyte layer. Many linked microcracks are observed.

The distributions of microcrack sizes and the number of links are presented in Fig. 4 for three different ΔT of 300, 450, and 600 K. The ΔT increase leads to a growth in the average value and standard deviation of the microcrack size (Fig. 4 A, C, E). However, these parameters differ a little for 450 and 600 K (Table 1). The logarithmic normal distribution is a good approximation for the experimentally determined microcrack size distribution. The obtained results on microcrack size distribution are similar to those presented in [4]. Average value and standard deviation of the number of links increases when ΔT grows from 300 to 450 K (Fig. 4 B, D). Little change of these parameters is observed for further ΔT increase from 450 to 600 K (Table 1). In reality, the average number of links must grow with ΔT increase. The observed decrease of the parameter can be probably associated with some inaccuracy of its measurement. In fact, a sufficiently large number of links in linked microcracks is an indicator of their complex geometry.

The input parameters for microcracking modelling now need to be determined. The statistical distribution of the size of grain boundary flat portions (SEs) in the electrolyte is shown in Fig. 5. According to the experimental data, the average SE size is 5.65 μm and the standard deviation is 1.65 μm . The experimental distribution of SE size can be approximated with sufficient accuracy by a logarithmic normal distribution with parameters $\mu_{SE}=1.691$ and $D_{SE}=0.082$. The orientation angle θ_{SE} of the structural elements was also investigated (Fig. 6). It can be seen that the statistical distribution of θ_{SE} is approximately uniform (Fig. 6A) meaning that the electrolyte microstructure is isotropic. Pairs of adjacent structural elements were considered as potential two-link microcracks.

The angles θ between the elements named as SE1 and SE2 were measured (Fig. 6B). This statistical distribution is difficult to be described analytically. The experimental value of θ corresponding to the maximum density of the distribution is approximately equal to 67° . This angle value can be used as an estimate of θ_{\max} because the crack deflection at angles of around 90° and especially $>90^\circ$ is unlikely. The parameter $m_{SE} = n_{SE} / n_g = 3.1$ was determined from analysis of the electrolyte microstructure. The parameters $\langle l_g \rangle = 6.64 \mu\text{m}$, $s_g = 1.53 \mu\text{m}$, $E_0 = 200 \text{ GPa}$, and $l_{\max} = 17 \mu\text{m}$ are given in [4].

The range of SE fracture toughness of 0.242 to 0.282 $\text{MPa}\cdot\text{m}^{1/2}$ can be found from the specific energy γ presented in [4], taking into account a corrected geometrical factor of the structural element. Thus, we obtain: $\langle K \rangle = 0.262 \text{ MPa}\cdot\text{m}^{1/2}$ and $s_K = 0.020 \text{ MPa}\cdot\text{m}^{1/2}$. The values of bhn_{c_0} , a_0 , and m have little effect on the microcracking parameters. The Weibull exponent m for structural elements was adopted to equal 3.8 [29].

The minimum size of pre-existing flaws inside SE parameters a_0 and bhn_{c_0} were adopted to be 0.3 μm and 1100 μm^{-1} , respectively. The minimum size a_0 should be less than the size of the smallest SE existing in the electrolyte ($\sim 1 \mu\text{m}$). The parameter bhn_{c_0} can be estimated from the

assumption that any SE should contain at least one pre-existing flaw. Then, one can derive $n_{c0} \geq 1/V_{SE}^{(\min)}$, where $V_{SE}^{(\min)} \sim 10^{-5} \mu\text{m}^3$ is the volume of the smallest SE existing in the electrolyte. Such small value of the volume results from the small through-thickness height of SE $b=10 \mu\text{m}$ (electrolyte thickness) [4] and very small effective grain boundary thickness of $h \sim 1 \text{ nm}$. The input parameters for modelling the microcracking are summarised in Table 2.

Using the input parameters and (10), (11), (12), (14), (15), (17) it is possible to calculate n_c/n_g , f_f , σ_a , q , and $\langle c \rangle$ values for different σ_i for scattered microcracking. In the stress range from $\sigma_i = 0$ to σ_{i0} the following holds $n_c/n_g = 0$, $f_f = 0$, $\sigma_a = \sigma_i$, and $q = \sigma_i^2 / (2E_0)$. The critical parameters of scattered microcracking are presented in Table 3. Using the input parameters, the critical parameters of scattered microcracking, and (10), (11), (17), (18), (25), (31) the dependences of n_c/n_g , f_f , σ_a , q , $\langle c \rangle$ on σ_i were calculated for localised microcracking. Specific parameters of localised microcracking are presented in Table 4. The dependencies of the calculated parameters on σ_i for scattered ($\sigma_{i0} < \sigma_i \leq \sigma_{ic}$) and localised ($\sigma_{ic} < \sigma_i \leq \sigma_{imax}$) microcracking are shown in Fig. 7.

The dependence of microcrack density f_f on σ_i is shown in Fig. 7A. There are four ranges of σ_i corresponding to ‘no’ ($0 \leq \sigma_i \leq \sigma_{i0}$), ‘scattered’ ($\sigma_{i0} < \sigma_i \leq \sigma_{ic}$), and ‘localised microcracking’ ($\sigma_{ic} < \sigma_i \leq \sigma_{imax}$), and microcracking saturation ($\sigma_i > \sigma_{imax}$). The microcrack density equals zero in the first range. It grows in the second and third range. The linear part of the dependence towards the end of the third range is only due to the use of the approximate expressions (23) and (24) for $Y_{g\min}(\sigma_i)$. Then the density remains constant in the fourth range.

The dependence of ratio n_c/n_g on σ_i is shown in Fig. 7B. The ratio equals to zero in the first range, growing in the second and third ranges. In the fourth range the ratio remains constant. The dependence of applied stress σ_a on σ_i is shown in Fig. 7C. In the first range $\sigma_a = \sigma_i$ ($0 \leq \sigma_i \leq \sigma_{i0}$). The dependence $\sigma_a(\sigma_i)$ has a maximum in the second range ($\sigma_{i0} < \sigma_i \leq \sigma_{ic}$). An

irregular curve is seen in the third range ($\sigma_{ic} < \sigma_i \leq \sigma_{imax}$). However, this irregular curve is only a result of the approximate expressions (23) and (24) for $Y_{gmin}(\sigma_i)$. The real curve is monotonous, approaching both parts of the approximated irregular curve. The monotonously increasing linear part lies in the fourth range ($\sigma_i > \sigma_{imax}$).

The dependence of strain energy density $q(\sigma_i)$ is similar to $\sigma_a(\sigma_i)$ (Fig. 7D). However, the quadratic dependence $q(\sigma_i)$ prevails in the first range. The maximum of the dependence is located on the boundary between the second and third ranges. An increasing part of the dependence can be observed at the end of the third range. The real curve corresponding to $q(\sigma_i)$ in the third range is smooth, approaching both parts of the approximated irregular curve. The monotonously increasing part is in the fourth range.

The dependence of $\langle c \rangle$ on σ_i is shown in Fig. 7E. Note that no dependence exists in the first range since here no microcracking occurs. The monotonously decreasing dependence lies in the second range. The minimum of the dependence is located at the boundary between the second and third ranges. The approximated irregular curve is shown in the third range. Then the average microcrack size remains constant in the fourth range.

The average number of links in linked microcracks $n_l(\sigma_i)$ is presented in Fig. 7F. No dependence is seen in the first range since no microcracking occurs. In the second stage n_l equals 1 because only one-link microcracks are supposed to exist in the range $\sigma_{i0} < \sigma_i \leq \sigma_{ic}$. The approximated irregular curve corresponding to $n_l(\sigma_i)$ defines the third range. The average number of links remains constant in the fourth range.

The solid circles denote experimental data. The microcrack density f_f , ratio n_c/n_g , average microcrack size $\langle c \rangle$, and average number of links n_l were measured from microcrack structure images. The corresponding values of σ_a are thermal residual stresses in the electrolyte at a given ΔT . These were calculated using the corresponding f_f measured in this work, the initial data

presented in [4], and the method described in [30]. The values of σ_i and q were determined using (10), (11) and (17), respectively. One can see that the calculated dependencies are in good agreement with the experimental data in Figs. 7A-E. Regarding Fig. 7F, it is obvious that the calculated lines show the trend of $n_i(\sigma_i)$ correctly. However, the calculated dependence underestimates the experimental values although it is located within the confidence range.

For given microstructural parameters the above modelling allows the key parameters of microcracking, including microcracking onset stress σ_{i0} and corresponding applied stress σ_a , to be determined. The critical difference ΔT between annealing and deposition temperatures can be estimated from the applied stress corresponding to σ_{i0} . Note that there is no microcracking for the temperature difference lower than the critical one. In such a way, it is possible to predict the safe technological regimes (appropriate annealing and deposition temperatures) during fuel cell fabrication to avoid the appearance of microcracks. It is evident that the critical temperature difference depends on the electrolyte microstructure. If there is opportunity to adjust microstructural parameters of the electrolyte, the possibility also enables us to affect annealing and deposition temperatures. Therefore, the modelling described in this paper along with the method of residual stress calculation described in [30] permits to elaborate the most effective technology of the anode supported planar SOFC fabrication. For example, the temperature difference of 150 K can be calculated from the stress at onset of microcracking (63 MPa) in the layered system (half-cell) 10Sc1CeSZ, with a 10 μm thick electrolyte and 40 wt.% NiO - 60 wt.% 10Sc1CeSZ 990 μm thick anode. It means that the difference between annealing and deposition temperatures during fuel cell fabrication should be less than this value to avoid microcrack appearance in the electrolyte. Since the annealing temperature (cathode sintering temperature, 1473 K) is in fact fixed, the deposition temperature should be varied. Note that the difference of 150 K is not so high as to restrict the choice of manufacturing technology.

The above model can be used to define recommended technological regimes for arbitrary anode/electrolyte systems in order to avoid electrolyte microcracking. The procedure consists of the

following steps: (1) determination of input parameters for the calculation; (2) calculation of the stress of microcracking onset using the above model; (3) evaluation of the temperature difference which corresponds to microcrack appearance using the calculation procedure from [30]; (4) determination of the recommended deposition temperature from a given annealing temperature (sintering temperature of cathode) and the calculated temperature difference. The input parameters include (i) the specific material information for the selected anode and electrolyte, and (ii) geometrical characteristics of the layered system. The specific material information should contain elastic properties, coefficients of thermal expansion, SE sizes, and the fracture toughness of the electrolyte. The determination of this data set is a certain challenge. For example, it is necessary to know how the deposition regime affects SE size distribution in the electrolyte. The geometrical characteristics of the layered system are the layer thicknesses. With regard to the model limitations, note that the above model is applicable for quite thin electrolyte layers when the thickness of electrolyte is comparable with the SE size within it. The difference between deposition and annealing temperatures should be less than the calculated temperature difference which is also dependent on layer thicknesses.

5. Conclusions

A detailed analysis of scattered and linked microcracks in solid oxide fuel cell electrolytes was performed. An empirical model of scattered and localised microcracking was elaborated and verified using experimental data obtained for a 10Sc1CeSZ electrolyte. The modelling allows microcracking onset stress, applied stress, microcrack density, and average microcrack size to be determined knowing electrolyte microstructural parameters. The model is able to be used in study of through thickness microcracks inside thin ceramic layers. However, it is not applicable for interfaces between different layers.

The critical difference ΔT between annealing and deposition temperatures can be estimated and used to predict appropriate annealing and deposition temperatures during fuel cell fabrication. It

is possible to elaborate the most effective technology of fabrication of anode supported planar SOFC cells based on a combination of the model and residual stress calculations.

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Glossary

10Sc1CeSZ	Scandia Ceria Stabilised Zirconia (10 mol.% Sc ₂ O ₃ –1 mol.% CeO ₂ –89 mol.% ZrO ₂)
CTE	Coefficient of Thermal Expansion
EBD	Electron Beam Deposition
LC	Linked Crack
SC	Single Crack
SE	Structural Element
SEM	Scanning Electron Microscopy
SOFC	Solid Oxide Fuel Cell

List of variables

Latin letters

<i>A</i>	scanned area
<i>a</i> ₀	minimum size of pre-existing flaws inside an SE
<i>b</i>	through-thickness height of the SE
<i>c</i>	microcrack size

c_i	effective length of the i th microcrack
$\langle c \rangle$	average microcrack size
$\langle c \rangle_c$	average microcrack size at $\sigma_i = \sigma_{ic}$
$\langle c \rangle_u$	ultimate average size of microcrack
$c_{\max c}$	maximum crack size due to the first linked microcrack formation
D_g	dispersion of the grain size distribution
D_K	dispersion of fracture toughness distribution
D_{SE}	dispersion of SE size distribution
E	elastic modulus of damaged material
E_0	elastic modulus of undamaged material
$F(\sigma_i, l, K)$	probability of SE failure as a function of stress, SE size and fracture toughness
$f_c(c)$	density of the statistical distribution of microcrack sizes
f_f	microcrack density
f_{ic}	microcrack density at $\sigma_i = \sigma_{ic}$
$f_K(K)$	density of the statistical distribution of SE fracture toughness
$f_{SE}(l)$	density of statistical distribution of SE sizes
h	effective thickness of the grain boundary or interface
K	SE fracture toughness
K_{cc}	minimum possible value of K_{eff} for the crack with size $\langle c \rangle_c$ at $\sigma_i = \sigma_{ic}$
K_{ci}	minimum possible value of K_{eff} for the crack with size $\langle c \rangle$ at $\sigma_{ic} < \sigma_i \leq \sigma_{i\max}$
K_{eff}	effective critical stress intensity factor for the crack

K_{\max}	maximum fracture toughness possible for SE with size l at stress σ_i
K_{\min}	minimum SE fracture toughness
K_{mod}	value of K that appears most often
$\langle K \rangle$	mean fracture toughness of SE
l	SE size
l_g	grain size
l_{\max}	maximum SE size
l_{\min}	minimum fractured SE size
$\langle l \rangle$	average size of the SE
$\langle l_g \rangle$	mean grain size
m	Weibull exponent
m_{SE}	number of SEs per single grain
N_A	number of microcracks on the scanned area
N_c	number of microcracks in the representative unit volume of the electrolyte
n_c	number of microcracks per area unit
n_{c0}	number of pre-existing flaws inside an SE per volume unit
n_g	number of grains per area unit
n_l	average number of links in linked microcrack
N_{SE}	number of SEs in the representative elementary volume of the electrolyte
n_{SE}	number of SEs per area unit
p	probability of existence of structural element with size larger than l_{\max}
q	strain energy density
s_c	standard deviation of microcrack size

s_g	standard deviation of grain size
s_K	standard deviation of SE fracture toughness
s_{SE}	standard deviation of SE size
$V_{SE}^{(\min)}$	volume of the smallest SE existing in the electrolyte
Y_1	dimensionless geometrical factor for pre-existing flaws inside structural elements
Y_2	geometrical factor for simple straight through crack
Y_g	factor accounting for the complex geometry of linked microcracks
Y_h	factor accounting for additional stress concentration due to other surrounding microcracks
<i>Greek letters</i>	
γ	specific energy of the new surface creation
ΔT	difference in temperature between annealing and deposition temperatures
θ	orientation angle of next link of crack relative to original crack
θ_{SE}	orientation angle of the structural elements
μ_{SE}	mathematical expectation of $\ln l$
μ_K	mathematical expectation of $\ln K$
μ_g	mathematical expectation of $\ln l_g$
σ_a	applied stress
σ_i	stress acting in the SE
σ_{i0}	stress of microcracking onset
σ_{ic}	stress corresponding to maximum of $q(\sigma_i)$ dependence
$\sigma_{i\max}$	stress corresponding to maximum effective stress intensity factor

References

1. A.J. Jacobson, Materials for solid oxide fuel cells, *Chem. Mater.* 22 (2009) 660-674.
2. J.M. Ralph, A.C. Schoeler, M. Krumpelt, Materials for lower temperature solid oxide fuel cells, *J. Mater. Sci.* 36 (2001) 1161-1172.
3. J. Will, A. Mitterdorfer, C. Kleinlogel, D. Perednis, L.J. Gauckler, Fabrication of thin electrolytes for second-generation solid oxide fuel cells, *Solid State Ionics* 131 (2000) 79-96.
4. M. Lugovy, V. Slyunyayev, R. Steinberger-Wilckens, Microcracking in electron beam deposited scandia-stabilised zirconia electrolyte, *J. Power Sources* 194 (2009) 950-960.
5. S. Shuying, F. Zhengxiu, S. Jianda, Evolutions of residual stress and microstructure in ZrO₂ thin films deposited at different temperature and rates, *Thin Solid Films* 445 (2003) 59-62.
6. T.R. Armstrong, J.W. Stevenson, L.R. Pederson, P.E. Raney, Dimensional instability of doped lanthanum chromite, *J. Electrochem. Soc.* 143 (1996) 2919-2925.
7. A. Atkinson, Chemically-induced stresses in gadolinium-doped ceria solid oxide fuel cell electrolytes, *Solid State Ionics* 95 (1997) 249-258.
8. K.P. Recknagle, R.E. Williford, L.A. Chick, D.R. Rector, M.A. Khaleel, Three-dimensional thermo-fluid electrochemical modeling of planar SOFC stacks, *J. Power Sources* 113 (2003) 109-114.
9. P. Singh, N.Q. Minh, Solid oxide fuel cells: technology status, *Int. J. Appl. Ceram. Technol.* 1 (2004) 5-15.
10. O. Yamamoto, Solid oxide fuel cells: fundamental aspects and prospects, *Electrochim. Acta* 45 (2000) 2423-2435.
11. A.S. Drachinskii, N.I. Lugovoi, V.N. Slyunyaev, Simulation of microcracking in inhomogeneous structures in the ductile-brittle transition range, *Met. Phys. Adv. Tech.* 15 (1995) 243-251.

12. G. Gogotsi, M. Lugovy, Local stochastic analysis of microcracking and non-elastic behavior of ceramics, *Theor. Appl. Fract. Mech.* 36 (2001) 115-123.
13. G.A. Gogotsi, N.I. Lugovoi, V.N. Slyunyaev, Statistical evaluation of microcracking of inelastic ceramics, *Strength Mater.* 34 (2002) 349-358.
14. N.I. Lugovoi, V.N. Slyunyaev, Limiting state of two-phase composites under uniaxial tension, *Mater. Sci.* 31 (1995) 716-724.
15. M. Lugovy, N. Orlovskaya, K. Berroth, J. Kuebler, Microstructural engineering of ceramic-matrix layered composites: Effect of grain-size dispersion on single-phase ceramic strength, *Compos. Sci. Technol.* 59 (1999) 283-289.
16. Y.N. Podrezov, N.I. Lugovoi, V.N. Slyunyaev, Statistical aspects of micro-inhomogeneous material cleavage, *Met. Phys. Adv. Tech.* 15 (1995) 651-664.
17. Y.N. Podrezov, N.I. Lugovoy, V.N. Slyunyaev, N.V. Minakov, Statistical failure model of materials with micro-inhomogeneity, *Theor. Appl. Fract. Mech.* 26 (1997) 35-40.
18. M. Lugovy, V. Slyunyayev, V. Subbotin, N. Orlovskaya, G. Gogotsi, Crack arrest in Si_3N_4 -based layered composites with residual stress, *Compos. Sci. Technol.* 64 (2004) 1947-1957.
19. M. Lugovy, V. Slyunyayev, N. Orlovskaya, G. Blugan, J. Kuebler, M. Lewis, Apparent fracture toughness of Si_3N_4 -based laminates with residual compressive or tensile stresses in surface layers, *Acta Mater.* 53 (2005) 289–296.
20. F.E. Buresch, The role of microcracking on fracture toughness of brittle composites, ECF2, Darmstadt 1978, 256-268.
21. V. Tvergaard, J.W. Hutchinson, Microcracking in ceramics induced by thermal expansion or elastic anisotropy, *J. Am. Ceram. Soc.* 71 (1988) 157-166.
22. M. Ruehle, A.G. Evans, R.M. McMeeking, P.G. Charalambides, J.W. Hutchinson, Microcrack toughening in alumina/zirconia, *Acta Metall.* 35 (1987) 2701-2710.

23. J.W. Hutchinson, Mechanisms of toughening in ceramics, *Theoretical and Applied Mechanics*, P. Germain, M. Piau, D. Caillerie (Editors), Elsevier Science Publishers B.V. (North-Holland), IUTAM, 1989, 139-144.
24. R.L. Salganik, Mechanics of solids with large number of cracks, *Izv. AN SSSR (Mekhanika tverdogo tela)* N 4 (1973) 149–158 (in Russian).
25. A. Karimi, Y. Wang, T. Cselle, M. Morstein, Fracture mechanisms in nanoscale layered hard thin films, *Thin Solid Films* 420–421 (2002) 275–280.
26. M. Lugovy, V. Slyunyayev, S. Yarmolenko, J. Sankar, T. Graule, J. Kuebler, D. Nicholson, N. Orlovskaya A further insight into spherical indentation: Ring crack formation in a brittle $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ perovskite, *Acta Mater.* 59 (2011) 4425-4436.
27. B. Schultrich, Mechanical properties of brittle materials, in: *Modern theories and experimental evidence*. Akademie der Wissenschaften der DDR, Zentralinstitut für Festkörperphysik und Werkstofforschung, N 32, 1986, s. 229–266.
28. A.T. Zehnder, Linear Elastic Stress Analysis of 2D Cracks. In: *Fracture Mechanics. Lecture Notes in Applied and Computational Mechanics*, vol 62, 2012, Springer, Dordrecht.
29. E. Maire, D.S. Wilkinson, J.D. Embury, R. Fougères, Role of damage on the flow and fracture of particulate reinforced alloys and metal matrix composites, *Acta Mater.* 45 (1997) 5261-5274.
30. M. Lugovy, V. Slyunyayev, M. Brodnikovskyy, R. Steinberger-Wilckens, Residual stress distribution in solid oxide fuel cells: anode-electrolyte and anode-electrolyte-cathode systems, *Energy* 2019 (submitted).

Table 1. Microcracking characteristics at different ΔT .

ΔT , K	f_f	σ_a , MPa	$\langle c \rangle$, μm	s_c , μm	$\langle n_l \rangle$	s_n	c_{min} , μm	c_{max} , μm	n_c/n_g
300	0.53	75.34	13.37	7.37	3.83	2.07	3.87	41.96	0.082
305	0.58	72.98	14.25	7.78	3.49	1.64	3.66	57.11	0.08
375	1.19	51.91	18.41	10.06	5.67	3.32	3.8	64.5	0.099
450	2.07	29.82	24.59	12.82	6.47	3.94	4.84	74.86	0.098
460	2.12	29.07	24.04	12.9	5.53	3.2	5.4	80.74	0.104
600	2.69	23.86	25.07	14.22	5.06	2.69	5.26	86.35	0.118

Table 2. Input parameters for modelling.

$\langle l \rangle, \mu\text{m}$	5.65	$\langle K \rangle, \text{MPa}\cdot\text{m}^{1/2}$	0.262	$\langle l_g \rangle, \mu\text{m}$	6.64	$bhn_{c0}, \mu\text{m}^{-1}$	1100
$s_{SE}, \mu\text{m}$	1.65	$s_K, \text{MPa}\cdot\text{m}^{1/2}$	0.020	$s_g, \mu\text{m}$	1.53	$a_0, \mu\text{m}$	0.3
$\theta_{\max}, ^\circ$	67	E_0, GPa	200	m_{SE}	3.1	m	3.8

Table 3. The critical parameters of scattered microcracking.

σ_{i0} , MPa	σ_{ic} , MPa	$(n_c/n_g)_c$	f_{ic}	$\langle c \rangle_c$, μm
63	104	0.078	0.21	9.85

Table 4. Specific parameters of localised microcracking.

$\sigma_{i\max}$, MPa	c_t , μm	k_g , MPa^{-1}	k_s	$\langle c \rangle_u$, μm
180	9.81	0.0308	0.54	24.42

Figure Captions

Fig. 1. Schematic of linked microcrack growth (A) and size measurement of structural element (SE), single crack (SC), and linked crack (LC) (B): 1 –minimum effective fracture toughness for microcracks with different sizes corresponding to σ_{ic} ; 2 –minimum effective fracture toughness for microcracks with different sizes corresponding to σ_i ; 3 –ultimate effective fracture toughness for microcracks with different sizes corresponding to σ_{imax} .

Fig. 2. Dependencies of Y_{gmin} (A) and $s_c / \langle c \rangle$ (B) on σ_i for different ranges of σ_i corresponding to: 1 – no microcracking; 2 – scattered microcracking; 3 – localised microcracking; 4 – microcracking saturation. The open circles correspond to $\sigma_i = \sigma_{ic}$. The solid circles denote experimental data.

Fig. 3. Microcracks in electrolyte corresponding to: $\Delta T = 300$ K (A); $\Delta T = 450$ K (B); $\Delta T = 600$ K (C).

Fig. 4. Statistical distribution of microcrack size (A, C, E) and the number of microcrack links (B, D, F) at $\Delta T = 300$ K (A, B), $\Delta T = 450$ K (C, D), and $\Delta T = 600$ K (E, F). The curves show corresponding log-normal distributions.

Fig. 5. Statistical distribution of SE size. The curve shows the corresponding log-normal distribution.

Fig. 6. Statistical distributions of SE orientation angle θ_{SE} (A) and the angle θ between two adjacent SEs (B). The dashed line presents the density of uniform distribution in the range from 0 to 180° .

Fig. 7. Dependencies of microcracking parameters on the stress acting in the SE for different ranges of the stress corresponding to: 1 – no microcracking; 2 – scattered microcracking; 3 – localised microcracking; 4 – microcracking saturation. A – microcrack density; B – ratio of the number of microcracks per area unit to the number of grains per area unit; C – applied stress; D – strain energy density; E – average microcrack size; F - average number of links in linked microcrack. The open

diamonds, triangles and circles correspond to microcracking onset, maximum of applied stress and maximum of strain energy density, respectively. The solid circles denote experimental data. The grey and black lines present the calculated dependencies before and after maximum of strain energy density is reached, respectively.