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TRANSIENT ANALYSIS OF OXYGEN NON-STOICHIOMETRY AND CHEMICALLY INDUCED STRESSES IN PEROVSKITE-TYPE CERAMIC MEMBRANES FOR OXYGEN SEPARATION

Розроблено модель, що встановлює зв’язок між хімічно обумовленими деформаціями у перовскитових оксидах та кисневою нестехіометрією. Використовуючи рівняння Фіка другого роду, початкові та граничні умови при контакті з повітрям та синтетичним газом, а також в непроникній частині мембрани, сформульовано початково-граничну задачу дифузії вакансій кисню у трубчастій мембрані з перовскитової кераміки. Повітря проходить через зовнішню поверхню трубчастої мембрани, газ сосереджений на її внутрішній поверхні. Розглянуто перенос вакансій кисню в інтерфейсі між внутрішньою поверхнею мембрани і оточуючим газом. Представлено граничну задачу для визначення хімічно обумовлених деформацій та напружень в трубчастій перовскітовій мембрані під дією хімічного градієнту кисню. Модель впроваджено в комп’ютерні структурні інструменти для аналізу розподілу хімічно обумовлених напружень в проникних для кисню мембранних системах. Розглянуто чисельний приклад та обговорено перерозподіл у часі нестехіометрії, часткового кисневого тиску та хімічно обумовлених напружень у трубчастій мембрані.

Ключові слова: напруга; перовскіт; керамічна мембрана; відокремлення кисню

Разработана модель, которая устанавливает связь между химически обусловленными деформациями в перовскитоподобных оксидах и кислородной нестехиометрией. Используя уравнение Фика второго рода, начальные и граничные условия при контакте с воздухом и синтетическим газом, а также в непроницаемой части мембраны, сформулирована начально-граничная задача диффузии вакансий кислорода в трубчатой мембране из перовскитоподобной керамики. Воздух проходит через внешнюю поверхность трубчатой мембраны, газ сосредоточен на ее внутренней поверхности. Рассмотрен перенос вакансий кислорода в интерфейсе между внутренней поверхностью мембраны и окружающим газом. Представлена граничная задача для определения химически обусловленных деформаций и напряжений в трубчатой перовскитоподобной мембране под действием химического градиента кислорода. Модель внедрена в компьютерные структурные инструменты для анализа распределения химически обусловленных напряжений в проникающих для кислорода мембранных системах. Рассмотрен численный пример и обсуждено перераспределение во времени нестехиометрии, частичного кислородного давления и химически обусловленных напряжений в трубчатой мембране.

Ключевые слова: напряжение; перовскит; керамическая мембрана; отделение кислорода

A constitutive model that relates the chemically induced strains in perovskite-type oxides to oxygen non-stoichiometry has been developed. The initial/boundary value problem for diffusion of oxygen vacancies in the tubular peovskite-type ceramic membrane has been formulated using Fick’s second law, initial condition and boundary conditions at the air side and syngas side of the membrane, as well as, at the impermeable end of the membrane. Air flows on the outside of the tubular closed end membrane, and reducing atmosphere is introduced on the inside of the tube. The exchange of oxygen vacancies at the interface between the inner membrane surface and surrounding gas phase is considered. The boundary value problem for determination of the chemically induced strains and stresses at the transient state in the tubular perovskite membrane exposed to oxygen chemical potential gradient has been presented. The integrated model has been incorporated into computer-based structural modeling tools for analyzing chemically induced stress distributions in oxygen permeable membrane systems. The numerical example has been considered, and the re-distribution of non-stoichiometry, oxygen partial pressure and chemically induced stresses in the tubular closed end membrane over time has been discussed.

Keywords: Stress; Perovskite; Ceramic membrane; Oxygen separation

Introduction. The price of crude oil is high due to the limited reserves which are estimated to last for only another few decades. In addition, the constantly rising requirements for clean fuels are driving industrials to use natural gas, which offers an interesting energy source when upgraded to higher-value chemicals. Synthesis gas, or syngas $(\mathrm{CO} + \mathrm{H}_2)$, is an intermediate chemical feedstock obtained from methane, the main component of natural gas. It can be further processed to value-added chemicals via methanol synthesis or the well-known Fischer-Tropsch synthesis. Thanks to the constant development of this process, the produced fuel has a high octane index and is very clean since it contains no metals or sulfur. Another possible use for syngas is the production of hydrogen. Combining oxygen separation and reaction in a single unit, as in a membrane-based reactor for the partial oxidation of methane into syngas, is expected to decrease the cost of syngas production by 25–35% compared to present production methods.

In the last decades, researchers have developed mixed ionic and electronic conductors suitable as membranes for the partial oxidation of methane into syngas. Perovskites are the most promising candidates among the materials in question. The general structure of the perovskite mineral is $\mathrm{AB\,X}_3$ where A and B are cations, and X oxygen anion. Perovskite materials are classified as ceramics and can be doped, i.e. a fraction of the A-site and/or the B-site cations can be replaced by another metal. A driving force which has to be provided for oxygen ions to permeate through the perovskite-type ceramic membrane is a chemical potential gradient (i.e. oxygen partial pressure gradient). The feature of interest for oxygen separation from air and for the conversion of methane into syngas is the concentration of charged defects in the perovskite-type ceramics, such as of oxygen vacancies. Using doping, oxygen vacancies can be created in the perovskite lattice. At low temperature they remain ordered but at high temperature, typically more than $600\,^{\circ}\mathrm{C}$, they become available for transport, providing a path for the migration of the oxygen anions from one side of the membrane (air side) with the high oxygen partial pressure to the other side (syngas side) with the low oxygen partial pressure.

The oxygen flux in membrane reactor at the steady state is proportional to the oxygen vacancies concentration difference across the membrane. The general formula for the perovskite-type ceramic in question can be now rewritten as $\mathrm{AB\,X}_{3-\Delta}$ where the creation of lattice oxygen vacancies is indicated by the deviation from oxygen stoichiometry, $3-\Delta$, and by the oxygen non-stoichiometry, Δ, which is a function of composition, temperature and oxygen partial pressure.

It was established experimentally that the membrane materials under consideration belong to perovskite ceramics in which not only thermal expansion, but also another component, called chemical expansion, contributes to the overall observed expansion at high temperature [1, 2]. Thus, the chemical expansion observed in these perovskites at high temperature occurs in addition to the thermal expansion.

Under the operating conditions, the membrane, placed in the oxygen partial pressure gradient, is in a gradient of oxygen vacancies activity. Oxygen vacancies migrate in the opposite direction compared to the oxygen ions, namely from the syngas side of the membrane to its air side. The oxygen activity in a membrane generally occurs in both interface regions and in the bulk of the material. It is therefore of particular interest for practical applications to know whether the oxygen flux is limited by bulk diffusion or by a surface exchange process for a certain perovskite. The rate and mechanism of the diffusion of oxygen depends on the defect chemistry of the oxide, the oxygen partial pressure gradient and geometry of membrane. Therefore, membrane is subject to chemically induced straining caused by the gradient in concentration of oxygen vacancies in the material. This induces stresses that could ultimately cause fracture of membrane. The chemically induced stresses depend on the variation of oxygen non-stoichiometry through the membrane under the operating conditions, the amount of chemical expansion for the given degree of oxygen non-stoichiometry and the geometry of membrane system. Thus, chemical expansion of perovskite can cause the membrane degradation over time and the lifetime reduction of catalytic membrane reactor.

A small amount of studies on the effect of surface exchange process at the interface between gas and membrane on the oxygen transport and stress evolution in ceramic oxygen ion-conducted membranes are available in literature [3, 4]. The present paper is related to the further investigations in this direction. In this way, we do not consider the degradation of perovskite-type ceramic membranes induced by the thermal gradients and creep deformation.

Basic equations. The chemical expansion can be considered as a lattice expansion that occurs in the perovskites $\mathrm{AB\,X}_{3-\Delta}$ upon an increase in oxygen non-stoichiometry, accompanied by reduction of the B site cations with decreasing oxygen partial pressure $\mathrm{P}_{\mathrm{O}_2}$. It can be defined at the constant temperature *T* as follows

$$\varepsilon^{ch} = \left.\frac{(a-a_0)}{a_0}\right|_{T=const}, \tag{1}$$

where a is the current lattice parameter, and a_0 is the lattice parameter at the reference state. This phenomenon can be explained taking into account that the perovskites under discussion must contain a high concentration of oxygen vacancies, and a decrease in the oxygen content of the perovskite will lead to expansion of the unit cell due to the weakening of the ionic bonds caused by removal of mobile charged species. Lowering the oxygen partial pressure will also lead to increasing chemical expansion. Note that chemical expansion is not limited to perovskite ceramics, but it can be considered as a general phenomenon concerning all mixed–valence materials that compensate for the reduction of cations by creating anion vacancies. Chemical expansion of the numerous membrane materials was determined either on the macroscopic samples by dilatometry in controlled atmospheres or by high temperature neutron and X-ray diffraction with subsequent calculation of lattice parameters using the Rietveld analysis. It was found that the chemical expansion of perovskite-type membrane materials can reach values up to 0.4%.

Next, a constitutive theory within the framework of solid mechanics for initially isotropic oxygen-deficient membrane materials and for isothermal processes at small strains and with multiaxial stress state is considered.

The total strain tensor $\varepsilon_{ij}\ (i, j=1,2,3)$ can be written as the sum:

$$\varepsilon_{ij} = \varepsilon_{ij}^{e} + \varepsilon_{ij}^{ch}, \tag{2}$$

where ε_{ij}^{e} is the elastic strain tensor, and ε_{ij}^{ch} is the chemically induced strain tensor. Last magnitude can be defined as

$$\varepsilon_{ij}^{ch} = A\left(\Delta-\Delta_0\right)\delta_{ij}, \tag{3}$$

where Δ_0 is the oxygen non-stoichiometry at the reference state, *A* is the chemical expansion coefficient, δ_{ij} is the Kronecker delta, and

$$\delta_{ij} = \begin{cases} 1 & \text{if } i = j; \\ 0 & \text{if } i \neq j. \end{cases}.$$

The components of the stress tensor $\sigma_{ij}\ (i, j=1,2,3)$ are related to the elastic components of the strain tensor according to the generalized Hooke's law:

$$\sigma_{ij} = C_{ijkl}\,\varepsilon_{kl}^{e} \tag{4}$$

with the elastic material parameter tensor $C_{ijkl}\ (i, j, k, l=1,2,3)$ given for the isotropic membrane material as follows

$$C_{ijkl} = \frac{E}{2\left(1-\nu^2\right)}\left[\left(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}\right)\left(1-\nu\right)+2\nu\delta_{ij}\delta_{kl}\right], \tag{5}$$

where an Einstein summation for repeating indexes in tensors is used, E is the Young's modulus, and ν is the Poisson's ratio.

Let us consider a hollow-tube reactor for the conversion of methane into syngas. Oxygen permeable membrane system consists of a tubular closed end membrane of inner radius a and outer radius b connected at the other end AB (Fig. 1) by sealing with a support material. The membrane system (Fig. 1) includes a cylindrical part AMNB and a spherical one MCDN of the constant thickness $h=b-a$. Lert l be a length of the membrane system.

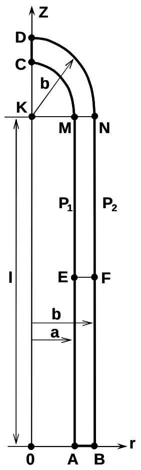

Fig. 1 – Schematic of oxygen transport membrane system

Air flows on the outside of the tube, and reducing atmosphere is introduced on the inside of the tube. In general, the transport of oxygen ions through the perovskite-type ceramic membrane can occur through the combination of interstitial oxygen ions migration in its rock-salt layers and lattice oxygen ions migration through oxygen vacancies in its perovskite layers according to the following chemical reactions:

$$0{,}5\mathrm{O}_2 \Leftrightarrow \mathrm{O}_i'' + 2h \quad (6) \qquad \text{and} \qquad \mathrm{O}_\mathrm{O}^x + 2h \Leftrightarrow \mathrm{V}_\mathrm{O}^{\cdot\cdot} + 0{,}5\mathrm{O}_2 . \quad (7)$$

Although many types of defects may occur, the crystal structure is usually dominated by only one defect type. In the following, we pay our attention to the migration of the oxygen ions via oxygen vacancies from one side of the membrane (air side) with the high oxygen partial pressure $\mathrm{P}_{\mathrm{O}_2} = P_2$ to the other side (syngas side) with the low oxygen partial pressure $\mathrm{P}_{\mathrm{O}_2} = P_1 \ (P_2 > P_1)$. Under operating conditions the oxygen activity in a membrane occurs in the bulk of the material and in both interface regions. Oxygen vacancies considered as the mobile ionic defects migrate in the opposite direction compared to the oxygen anions, namely from the syngas side of the membrane to its air side.

The transport of oxygen vacancies is considered in the coordinate system (r,θ,z) under condition of symmetry about the axis z (Fig. 1). Here r is the radial coordinate, θ corresponds to the circumferential direction, and z is the axial coordinate.

The diffusion equation for the oxygen non-stoichiometry has a form:

$$\frac{\partial\Delta}{\partial t} = D\left(\frac{\partial^2\Delta}{\partial r^2} + \frac{1}{r}\frac{\partial\Delta}{\partial r} + \frac{\partial^2\Delta}{\partial z^2}\right), \qquad (8)$$

where D is the chemical diffusion coefficient. At the reference state, the membrane is in equilibrium with air with a corresponding oxygen non-stoichiometry Δ_0. In the following, reducing atmosphere is introduced at the inner surface of the membrane. The exchange of oxygen vacancies between the inner membrane surface and surrounding gas phase occurs involving a number of reactions and processes including adsorption/dissociation, charge transfer, surface diffusion and incorporation. The oxygen non-stoichiometry at the inner surface of the membrane at the equilibrium is given as Δ_1.

The initial condition to the diffusion equation (8) can be accepted in a form

$$\Delta = \Delta_0 \ \text{at} \ t = 0 . \qquad (9)$$

The boundary conditions to Eq. (8) can be written as follows

$$\Delta = \Delta_0 \ \text{on the outside of the membrane} \qquad (10)$$

$$D\frac{\partial\Delta}{\partial r} = \beta(\Delta - \Delta_1) \ \text{on the inside of the membrane} \qquad (11)$$

and

$$\frac{\partial\Delta}{\partial z} = 0 \ \text{at the end AB of the tube.} \qquad (12)$$

Here β is the chemical surface exchange coefficient.

Thus, the initial/boundary value problem for transport of oxygen vacancies in membranes for oxygen separation is given by Eq. (8) together with Eqs (9)-(12). This initial/boundary value problem under consideration can be reduced to the following variational equation

$$\int_V \delta\Delta \frac{\partial\Delta}{\partial t}\mathrm{d}V + \int_V \delta\Delta_{,i} D_{ij} \Delta_{,j}\mathrm{d}V = \int_S \delta\Delta\,\beta\left(\Delta_1 - \Delta\right)\mathrm{d}S , \qquad (13)$$

where V is a volume of the system under study, S is the inner surface of the membrane where the boundary condition (11) takes place, $\delta\Delta$ is an allowable virtual oxygen non-stoichiometry, the coma indicates a partial derivative with respect to the given index, $D_{ij}\ (i, j = 1,2,3)$ is the diffusivity tensor written for the isotropic material as follows

$$D_{ij} = D\delta_{ij} . \qquad (14)$$

The boundary value problem for the analysis of the chemical strains and stresses can be reduced to the variational problem of minimizing the following functional:

$$L(u, w) = \int_V C_{klmn}\left(\varepsilon_{kl} - \varepsilon_{kl}^{ch}\right)\left(\varepsilon_{mn} - \varepsilon_{mn}^{ch}\right)\mathrm{d}V . \qquad (15)$$

Here the total strains are related to the displacements u and w by the kinematic equations, such as

$$\varepsilon_r = \frac{\partial u}{\partial r}, \ \varepsilon_\theta = \frac{u}{r}, \ \varepsilon_z = \frac{\partial w}{\partial z}, \ \gamma_{rz} = \frac{\partial u}{\partial z} + \frac{\partial w}{\partial r} \qquad (16)$$

and the chemically induced strains are defined by Eq. (3).

Three different approaches were used in the present study in order to find a solution to the uncoupled problem formulated above. First, closed-form analytical solutions [3, 4] for the oxygen non-stoichiometry and chemical stresses under an assumption of the plane strain have been used. The second approach is related to the in-housed developed software [5, 6]. The third approach is based on ANSYS software [7]. It was established that results derived by three different approaches correlate well with each other.

Example. The tubular membrane system (Fig. 1) with parameters given in Table 1 is considered. The results of the analyses obtained using equations and three different approaches discussed in the previous section will be presented below.

It is seen (Fig. 2) that the oxygen non-stoichiometry at the inner surface of a membrane increases with increasing time while the same magnitude at the its outer surface has a constant value. It is interesting to note that due to the influence of the surface exchange processes at the interface between membrane and gas, the values of the non-stoichiometry at the inner surface of the present membrane are always smaller than the value Δ_1. For example, it can be seen from Fig. 2 that those value at the instant of 400 s is found to be 0.249 which is smaller than Δ_1 =0.260. Therefore, it is necessary to use the value of 0.249 in the calculations of the oxygen flux in a steady state instead of 0.260 for oxygen non-stoichiometry at the inner surface.

Oxygen can permeate through a perovskite-type ceramic membrane under oxygen partial pressure gradient. Oxygen partial pressure in a perovskite-type membrane is a function of oxygen nonstoichiometry and temperature. In a membrane under consideration it relates to oxygen non-stoichiometry by the following semi-empiric equation [4]:

$$P_{O_2} = \left[K\left(\frac{3}{\Delta}-1\right)\right]^{\frac{1}{n}}, \qquad (17)$$

where K and n are the temperature dependent material constants. Eq. (17) was obtained starting from the point defect model. Model predictions based on Eq. (17) agree well with the experimental data for five perovskite-type ceramics found in the literature. For the $La_{0.5}Sr_{0.5}CoO_{3-\Delta}$ perovskite membrane at the temperature of $800\,^\circ C$ the values of the material constants are $K = 4.19\cdot10^{-2}$ bar^n and $n = 0.118$.

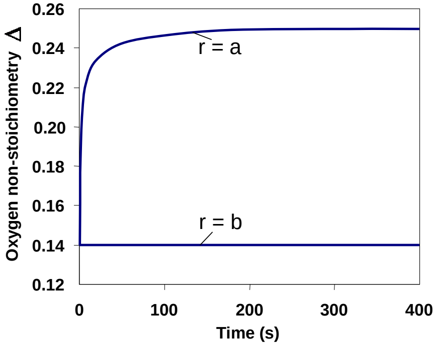

Fig. 2 – Time variation of the oxygen non-stoichiometry at the inner and outer surfaces of membrane in its middle part

From the calculated oxygen non-stoichiometry distributions, the oxygen partial pressure data were calculated using Eq. (17). It is easy to see (Fig. 3) that oxygen partial pressure in the middle part of a membrane in a transient state is a nonlinear function of the radial coordinate. On the other hand, the oxygen partial pressure in a steady state at about 400 s is approximately a linear function of the radial coordinate (Fig. 3). It is also seen (Fig. 4) that oxygen partial pressure on the inside of a membrane decreases with increasing time while the same magnitude on the outside of a membrane has a constant value $P_2 = 0.21$ bar. Note that the values of oxygen partial pressure at the inner surface of the membrane are always larger than the value $P_1 = 10^{-4}$ bar. For example, it is not difficult to see from Fig. 4 that those value in a steady state at the instant of 400 s is found to be $1.75\cdot10^{-4}$ bar. Therefore, it is necessary to use the value of $1.75\cdot10^{-4}$ bar for oxygen partial pressure at the inner surface of a membrane in a steady state instead of $P_1 = 10^{-4}$ bar for oxygen partial pressure in a surrounded gas atmosphere.

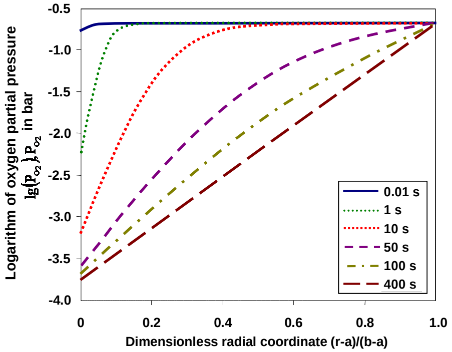

Fig. 3 – Time re-distribution of oxygen partial pressure in the radial direction of membrane in its middle part

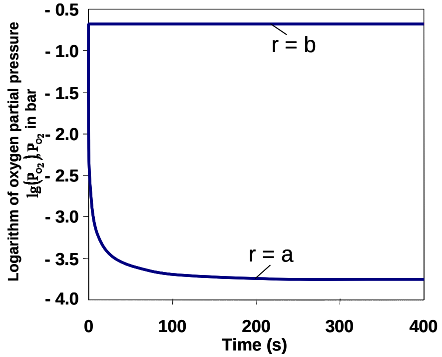

Fig. 4 – Time variation of oxygen partial pressure at the inner and outer surfaces of membrane in its middle part

Figs. 5-9 illustrate the changing of the chemically induced stresses with time in the radial direction of membrane under consideration in its middle part.

It is seen (Fig. 5) that the radial stresses are compressive for all moments of time up to the steady state at the about 400 s at each point of a membrane except for the outer and inner of its surface. It is clear also that the radial stress is always equal to zero at the outer and inner surfaces that satisfy the boundary conditions. The radial stresses in the interior of a membrane except the region near the outer surface during the final period of the diffusion, decrease monotonically with time.

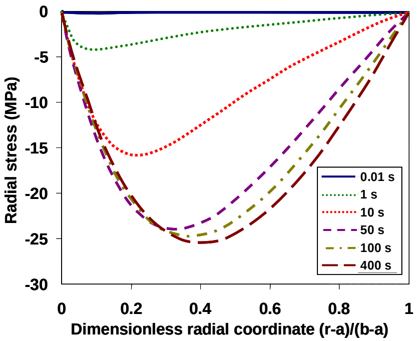

Fig. 5 – Time changing of the radial stress across the thickness of membrane in its middle part

The tangential and axial stresses (Figs. 6 and 7) are compressive in the region of a membrane near the inner surface and tensile in the region near the outer surface. The absolute values of the tangential and axial stresses at the inner surface of a membrane state increase with time except the final period of the oxygen diffusion before the steady state. On the other hand, tensile stresses at the outer surface increase monotonically with time up to the steady state. It is clear (Figs. 6 and 7) that the absolute value of the maximum level of the tangential and axial stresses corresponds to a compressive stress.

Table – **Parameters for the** $La_{0.5}Sr_{0.5}CoO_{3-\Delta}$ **perovstite membrane at the temperature of 800 °C [7]**

Description	Value
Elastic modulus, GPa	86
Poisson's ratio	0.25
Chemical diffusion coefficient, m^2/s	$3.10\cdot10^{-9}$
Chemical surface exchange coefficient, m/s	$3.12\cdot10^{-5}$
Chemical expansion coefficient	0.035
Oxygen non-stoichiometry at the inner surface of membrane at equilibrium	0.260
Oxygen non-stoichiometry at the outer surface of membrane	0.144
Oxygen non-stoichiometry at the initial instant of time	0.144
Oxygen partial pressure in air, bar	0.21
Oxygen partial pressure under reduced atmosphere, bar	10^{-4}
Radius of the inner surface of membrane, m	$2.00\cdot10^{-3}$
Radius of the outer surface of membrane, m	$3.25\cdot10^{-3}$
Length of membrane, m	0.3

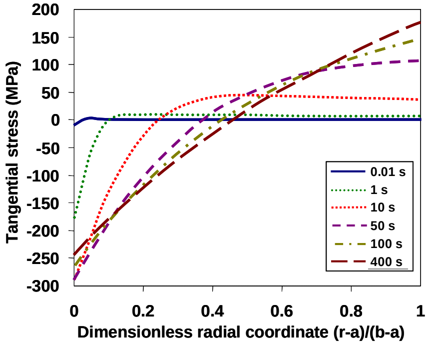

Fig. 6 – Time re-distribution of the tangential stress in the radial direction of membrane in its middle part

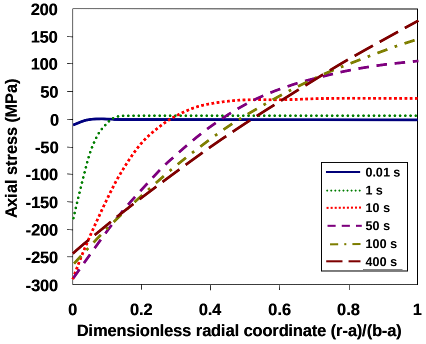

Fig. 7 – Time changing of the axial stress across the thickness of membrane in its middle part

Perovskites are brittle materials with different strength limits under tension and compression. Obviously that the cracking at the points of a membrane with the high compressive stresses can occur when the von Mises stress at these points exceeds the strength limit of the perovskite under compression. The von Mises stress can be found as

$$\sigma_i = \frac{1}{\sqrt{2}}\sqrt{(\sigma_r-\sigma_\theta)^2+(\sigma_z-\sigma_\theta)^2+(\sigma_r-\sigma_z)^2+6\tau_{rz}^2}\ . \qquad (18)$$

The changing of the von Mises stress over time in the middle part of a membrane is shown in Fig. 8.

On the other hand, the possible membrane cracking can occur at the points of the membrane with the high tensile stresses when the first principal stress at these points exceeds the strength limit of the perovskite under tension. The distribution of the first principal stress across the thickness of the membrane in its middle part over time is shown in Fig. 9.

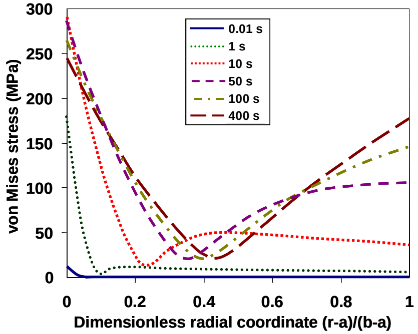

Fig. 8 – Time re-distribution of the von Mises stress in the radial direction of membrane in its middle part

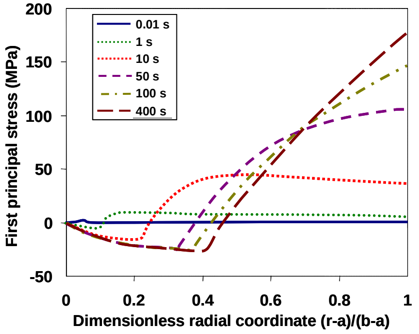

Fig. 9 – Time changing of the first principal stress across the thickness of membrane in its middle part

In general, it can be concluded that the cracking on the inside of a membrane under study can occur at the instant of 27 s when the von Mises equivalent stress exceeds the strength limit of the perovskite ceramic under compression, as well as, the cracking on the outside of a membrane can occur at the instant of 215 s when the first principal stress exceeds the strength limit of the perovskite under tension.

Conclusion. The creation of oxygen vacancies in the perovskite-type oxide is indicated by the oxygen non-stoichiometry, which is a function of composition, temperature and oxygen partial pressure. At low temperature oxygen vacancies remain ordered but at high temperature, typically more than 600 °C, they become available for transport from one side of the membrane (syngas side) with the low oxygen partial pressure to the other side (air side) with the high oxygen partial pressure. In general, the transport kinetics of oxygen vacancies depends on both bulk diffusion and surface exchange processes at the interface between membrane and surrounded gas atmosphere. A decrease in the oxygen content of the perovskite ceramic is leading to expansion of the unit cell (chemical expansion) due to the weakening of the ionic bonds caused by removal of mobile charged species. Lowering the oxygen partial pressure is also leading to increasing chemical expansion. This induces stresses that could ultimately cause fracture of membrane. The chemically induced stresses depend on the variation of oxygen non-stoichiometry through the membrane under the operating conditions, the amount of chemical expansion for the given degree of oxygen non-stoichiometry and the geometry of membrane system

In the constitutive model, proposed in this work, attention has been primarily directed towards understanding the relation between chemically induced strains and oxygen non-stoichiometry in transient state in the perovskite-type oxides. In the following, the formulations of the two uncoupled two-dimensional mathematical problems (for oxygen vacancies transport and stress analysis) for the tubular perovskite-type closed end membrane have been considered. First, the initial/ boundary value problem of oxygen transport via oxygen vacancies under the driving force of oxygen chemical potential gradient has been formulated in order to find the oxygen non-stoichiometry in membrane as a function of the coordinates and time. In this way, Fick's second law written for oxygen non-stoichiometry has been used. Time dependent boundary condition for oxygen non-stoichiometry related to surface exchange processes at the interface between the inner surface of the tubular membrane and surrounded reduced atmosphere has been considered. Second, the structural boundary value problem for the determination of the chemically induced stresses in membrane as a function of the coordinates and time has been formulated. Three different approaches were used in the present study in order to find a solution to these uncoupled problems. Simulations have been performed to analyze the relationships between oxygen non-stoichiometry, oxygen partial pressure, bulk diffusion, surface exchange processes, chemical expansion and chemically induced stresses in transient state under the operation conditions in the tubular closed end membrane made of the $\mathrm{La_{0.5}Sr_{0.5}CoO_{3-\Delta}}$ perovstite at the temperature of $800\,^{\circ}\mathrm{C}$ in air.

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