MODELING OF STRUCTURAL AND CHEMICAL CHANGES OF METAL-OXIDE INTERFACES BY VARYING OXYGEN OFFER

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ABSTRACT

Depending on the offered oxygen supply as handy control variable, accumulation or depletion of these special impurity atoms at metal-oxide heterophase boundaries lead to modifications of the atomic structure and chemical composition of the interfaces. The established Kirchheim model, which also explains changes of the macroscopic material behavior, is based on structurally necessary vacancies at terminating close-packed oxide lattice planes that serve as oxygen traps. These point defects are reversibly refillable with excess atoms. Experimental findings on oxygen-controlled alterations of metal-oxide phase boundaries obtained by electron energy loss spectroscopy, quantitative gas volume measurement and the electrochemical hydrogen probe are summarized and valued with regard to the basic modeling assumptions. Thermodynamics data derived from measured isotherms show that this segregation reaction is energetically comparable with the formation of a two-dimensional oxide layer of the metal component at the phase boundary. A kinetics model for palladium-matrix materials is presented. The spatial arrangement of the embedded oxides is characterized by the quantitative image analysis of transmission electron micrographs. The simulation exploits that under practical process conditions in palladium-based nano-dispersion microstructures, diffusion of lattice-dissolved oxygen to the particles, the surfaces of which serve as sinks, is the rate-controlling reaction step of interfacial oxygen segregation.

INTRODUCTION

The strongly increasing research into metal-oxide interfaces during the last decade goes back to their great significance e.g. for dispersion hardening mechanisms, nanotechnology, composite materials, surface coating techniques, micro-electronic and semiconductor applications. These interphase boundaries are often produced by internal reactions, epitactic growth of thin films or diffusion-bonded bicrystals. Enthalpy-driven interfacial segregation of dissolved impurity atoms can affect the material properties considerably. Of particular interest is the accumulation of excess oxygen atoms at metal-oxide phase boundaries since it is controllable by the activity (partial pressure, bulk solubility) of the gas. Although the effect on the material behavior is hitherto not by any means fully understood, this special segregation reaction offers attractive novel scope for semiconductor industry (e.g. MOS) or hydrogen technology (1).

DIRECT EXPERIMENTAL PROOF OF OXYGEN SEGREGATION

To provide evidence of oxygen segregation at metal-oxide interfaces, electron energy loss spectroscopy (EELS) is performed. An EEL spectrum is presented in Fig. 1.
The EELS fine structure near the oxygen K ionization edge is used for the nanoanalysis of the interface (chemical mapping). Unlike the extended energy-loss fine structure (EXELFS, weak oscillations), the electron-loss near-edge structure (ELNES) provides the required unambiguous fingerprints of the bonding state.

The experiments are performed on Ag-MgO samples prepared by internal oxidation of an Ag-3.0 at.% Mg alloy in air at 1173 K. Besides nanoparticles with sizes of few nm, larger MgO precipitates of around 0.1 µm in diameter are formed along grain boundaries (cf. Fig. 2) or as inner oxide films (1), which are used for ELNES analysis (1, 2).

Fig. 2.
HVEM (high voltage transmission electron microscopy) bright-field micrograph of large MgO particles at an Ag grain boundary.

Ag-MgO samples are annealed in pure oxygen and in high vacuum, respectively. The result of the ELNES recording at the interface is given in Fig. 3. Spectrum analysis is performed by comparison to reference standards for MgO and Ag_2O. After degassing in vacuum, oxygen at the interface is in the same bonding state as in MgO (main peak at 539 eV indicated in both diagrams), to which these atoms thus exclusively belong. Annealing in oxygen atmosphere leads to an additional energy shoulder of the ELNES at the labeled position of the main peak (1s-2p electron transition) of Ag_2O at 532 eV, which is emphasized by subtracting the MgO O-K edge from the interface signal according to the spatial difference technique (3): the appearance of a positive and negative extremum at 532 and 539 eV, respectively, reveals the second bonding part that characterizes interfacially segregated excess atoms. The modification of the chemical composition of metal-oxide phase boundaries by varying oxygen offer is thus proven.
Fig. 3. O-K ELNES (background subtracted to isolate intensities) after annealing the Ag-MgO samples in oxygen of 1000 HPa at 673 K and in vacuum at 1163 K.

Unlike MgO, Ag₂O is only weakly bound ($\Delta E = -0.24$ eV, cf. Fig. 4): differentiation from free oxygen dissolved in silver is, therefore, impossible by ELNES alone due to the limited energy resolution of the spectrometer. However, the free enthalpy of segregation can be derived from isotherms measured volumetrically (see next section).

Fig. 4. Bonding energies of oxygen in Ag₂O and MgO.

MEASUREMENT OF SEGREGATION ISOTHERMS

Assuming thermodynamic equilibrium between oxygen atoms dissolved in the matrix metal (atomic ratio $c_O$) and segregated at the interface (coverage $\Theta = N_O/N_{tot}$, $N_O$ and $N_{tot}$ respectively denote the number of oxygen atoms at the phase boundary and its maximum value), the Langmuir-type McLean isotherm can be derived (1):

$$\Theta = \frac{c_O e^{-\frac{\Delta G_{seg}}{RT}}}{1 + c_O e^{-\frac{\Delta G_{seg}}{RT}}} = \frac{K_{seg} c_O}{1 + K_{seg} c_O}, \quad \Delta G_{seg} = \Delta H_{seg} - T \Delta S_{seg}$$

$R$ and $T$ are the universal gas constant and the absolute temperature. $\Delta G_{seg}$, $\Delta H_{seg}$ and $\Delta S_{seg}$ denote the (effective) free enthalpy, the enthalpy and the entropy of segregation, respectively, which are correlated by the given Gibbs-Helmholtz equation. The segregation coefficient $K_{seg}$ is defined as follows:
\[
K_{\text{seg}} = K_0 \exp\left(\frac{-\Delta H_{\text{seg}}}{RT}\right), \quad K_0 = \exp\left(\frac{\Delta S_{\text{seg}}}{R}\right)
\]  

(2)

If the degree of interfacial coverage \(\Theta\) is kept constant, usually \(\Theta=\frac{1}{2}\), the segregation isosters can be derived from measured isotherms by applying the Clausius-Clapeyron equation (1). The isosteric heat of segregation is easily accessible by experiment:

\[
\Delta H_{\text{seg}} = R \frac{\delta \ln c_O}{\delta (T^{-1})}\bigg|_{\Theta=\text{const}}
\]  

(3)

Ag-MgO sheets (80×0.8 mm\(^2\)) of 150 \(\mu\)m thickness are prepared by complete internal oxidation of Ag-Mg alloys in air at 1173 K. Figure 5 shows a typical TEM image of the distribution of the nanosized MgO precipitations (see previous section).

Quantitative volumetric measurements, i.e. sorption of oxygen at various temperatures and constant partial pressures up to the equilibrium state followed by isothermal desorption with gas volume determination, are performed in an ultrahigh vacuum equipment using resistance heating of the samples (1, 4). For reference, pure Ag sheets are treated the same way. Figure 6 presents the results. The Ag-MgO material containing 10.9 at.% Mg emits around twice the oxygen release of the 3.0 at.% Mg sheet, which expresses the interface areas: \((10.9/3)^{\frac{2}{3}}=2.36\). Figure 7 gives an isosteric plot at \(\Theta=\frac{1}{2}\).

**Fig. 5.**
TEM (transmission electron microscope) bright-field image of internally oxidized Ag-3.0 at.% Mg material.

**Fig. 6.** Sorption-desorption experiment (\(N_o\) is the number of oxygen atoms per m\(^3\) Ag) and derived isotherms for Ag-MgO with 3.0 at.% Mg at 673, 773 and 873 K.
The segregation isotherms in the right-hand diagram of Fig. 6 are quantitatively fitted by a two-site McLean model that explains the deviations from Eq. (1):

\[
\begin{align*}
\Theta &= \delta \frac{c_0 \exp \left( -\frac{\Delta G_{\text{seg},1}}{R T} \right)}{1 + c_0 \exp \left( -\frac{\Delta G_{\text{seg},1}}{R T} \right)} + (1 - \delta) \frac{c_0 \exp \left( -\frac{\Delta G_{\text{seg},2}}{R T} \right)}{1 + c_0 \exp \left( -\frac{\Delta G_{\text{seg},2}}{R T} \right)} \quad (4)
\end{align*}
\]

The best-fit set of curves with \( \delta = \frac{1}{3}, \Delta G_{\text{seg},1} = -100 \text{ kJ/mol} \) and \( \Delta G_{\text{seg},2} = -66 \text{ kJ/mol} \) is drawn in. The isosteric Clausius-Clapeyron plot in Fig. 7 provides \( \Delta H_{\text{seg}}(\Theta = \frac{1}{2}) \approx -70 \text{ kJ/mol} \) for the exothermic chemisorption process. With reference to the ELNES study and the discussion of Fig. 4, it is emphasized that the values of \( \Delta G_{\text{seg},2} \) characterizing most of the segregation sites, and of \( \Delta H_{\text{seg}} \) are comparable to the concerning quantities for the precipitation of Ag₂O from a supersaturated solid solution of oxygen in silver: \( \Delta G_{\text{pr}} \approx -50 \text{ kJ/mol} \) at 673 to 873 K, \( \Delta H_{\text{pr}} \approx -78.34 \text{ kJ/mol} \). The two different segregation energies, which represent a heterogeneous interface, may result from different interface bonding states of the polar \{111\} and the non-polar \{001\} lattice planes forming the truncated MgO octahedra, their corners, edges and faces (very small particles of only few nm in size) or from misfit dislocations incorporated into the phase boundary with standoff (shift) on the metal side (1, 4).

**ATOMISTIC KIRCHHEIM SEGREGATION MODEL**

The experimental findings summarized above support the structural vacancy model of interfacial oxygen segregation at metal-oxide interfaces postulated by Kirchheim (5): excess oxygen is bound oxidically to the nobler matrix metal \( \text{Me}^{(i)} \) at the phase boundary. With the stoichiometry factor \( \mu \) (Ag: \( \mu = \frac{1}{2} \), Pd: \( \mu = 1 \)), the equation of the process-modeling chemical reaction is as follows:

\[
\text{Me}^{(i)} + \frac{1}{2} \text{O}_2 \rightarrow \text{Me}^{(i)}\text{O}_\mu
\]  

(5)

Thus, desorption takes place at oxygen partial pressures below the decomposition pressure of this two-dimensional oxide leaving vacancies on the terminating oxygen layer of the metal-oxide interface. Figure 8 introduces an illustrative sketch of this
atomistic Kirchheim segregation model of structurally necessary vacancies at terminal close-packed oxide lattice planes (Me\(^{(2)}\) is the oxide-forming metal), which can be filled with excess oxygen, O(seg). Segregated and in Me\(^{(2)}\)O\(_{v}\) (\(v\) is the stoichiometry factor) oxidically bound atoms, O(ox), in the fully occupied final oxygen layer then form a kind of mixed state in a sense that both are indistinguishable on subsequent desorption: the \(^{18}\)O isotope experiment, i.e. annealing of an initially vacuum-degassed sample in \(^{18}\)O atmosphere followed by recorded quantitative desorption, reveals statistical \(^{18}\)O-\(^{16}\)O exchange at the interface for Ag-MgO and Pd-MgO specimens.

From a series of TEM images, the specific interface area per volume of the internally oxidized Ag-3.0 at.% Mg material is found to be \(2 \cdot 10^7\) m\(^2\) Ag-MgO/m\(^3\) Ag. The density of the segregation sites for oxygen at the phase boundary is thus around \(2 \cdot 10^{18}\) to \(3 \cdot 10^{18}\mbox{ m}^{-2}\). This estimation corresponds to a saturation coverage of about one-quarter of a monolayer. However, considering that, according to the Kirchheim model, only the terminating eight close-packed polar \(\{111\}\) lattice planes of the truncated MgO octahedra with an atomic density of \(1.3 \cdot 10^{19}\mbox{ m}^{-2}\) should offer segregation sites for excess oxygen in the form of structural vacancies (see Fig. 9), the measured isotherms nearly result in the predicted degree of coverage of half a monolayer.

**KINETICS MODEL OF OXYGEN SEGREGATION**

For describing the surface processes and the adsorption and desorption reactions in an overall kinetics model of the oxygen segregation at internal metal-oxide interfaces, a boundary condition of the third kind in Fick's second law of diffusion and a generalized Elovich equation can be applied, respectively (1). In this section, a practically important special case is considered: the matrix metal palladium. Pd-oxide materials are, for instance, technically relevant to metal-oxide-semiconductor (MOS) devices. The low decomposition pressure of PdO makes sorption treatments at modest temperatures (exothermic chemisorption) under sufficiently high partial pressures of oxygen impossible.
Segregation of Oxygen at Pd-MgO Interfaces

Thin Pd and Pd-MgO sheets of 100 to 150 µm in thickness by 80 mm in length and 0.8 mm in width are used for the following experiments. The Pd-MgO samples are prepared by complete internal oxidation of a Pd-1.1 at.% Mg alloy in air at 1273 K. Perfect magnesia octahedra with terminating {111} lattice planes (cube-on-cube orientation relationship: also valid for the truncated octahedra of MgO in Ag, see above) are formed. From a series of 41 TEM images of the Pd-MgO material (cf. Fig. 12), the distribution of the surface area of the oxide particles is determined yielding \( A_{if}/V_{MgO}=7 \times 10^7 \text{ m}^{-1} \). Here, \( A_{if} \) and \( V_{MgO} \) denote the total of the interface area and the MgO volume, respectively. Considering the lattice parameters \( a_{MgO}=0.4213 \text{ nm} \) and \( a_{Pd-Mg}=0.38907 \text{ nm} \), \( V_{MgO}/V_{Pd}=(a_{MgO}/a_{Pd-Mg})^3 \cdot c_{Mg} \) amounts to 1.40 vol.%, where \( V_{Pd} \) stands for the sample volume. Therefore, the specific interface area per volume, \( A_{if}/V_{Pd}=(A_{if}/V_{MgO}) \cdot (V_{MgO}/V_{Pd}) \), equals \( 1 \times 10^6 \text{ m}^{-1} \). Here, \( c_{Mg} \) denotes the magnesium content: \( c_{Mg}=1.1 \text{ at.\%} \). According to the Kirchheim segregation model of structural vacancies (see previous section), half of the \( O^2- \) ions of the (111) \( \text{MgO} \) planes (total interfacial atom density: \( 1.3 \times 10^{19} \text{ m}^2 \)) corresponds to the segregation sites available to excess oxygen atoms, \( 6.5 \times 10^{18} \text{ m}^{-2} (N_{tot \text{ per volume unit}}) \). Multiplication by \( A_{if}/V_{Pd} \) yields \( 6.5 \times 10^{24} \text{ m}^{-3} \).

As explained before, oxygen segregation at Pd-MgO interfaces predominantly occurs during cooling of these specimens after sorption annealing in an oxygen-containing atmosphere by diffusion of lattice-dissolved atoms from the bulk to the phase boundaries. Interfacial accumulation of excess oxygen can thus be suppressed by quenching the samples in liquid nitrogen (1, 4), which is insoluble in palladium up to a temperature of 1673 K. This astonishing effect is demonstrated by Fig. 10:

![Fig. 10. Sieverts plot (on the left) of the total oxygen amount (expressed in at.\%) absorbed in Pd and Pd-MgO (1.1 at.\% Mg) during sorption at 1123 K, [Je]; (6). Diffusion coefficient of hydrogen measured at 316 K as a function of its concentration in Pd-MgO (1.1 at.\% Mg, 100 µm thick specimen) after annealing in air at 1273 K and cooling in air at room temperature (denotation: sample 1) or quenching in liquid nitrogen (diagram on the right-hand side).](image)

In the diagram on the left-hand side, it can be seen that for both Pd and Pd-MgO after annealing at 1123 K under various oxygen pressures the amount of absorbed gas is the same within the measuring accuracy of almost 20 % and agrees well with the
solubility data from the literature drawn in as straight line (6). However, by using hydrogen as a probe for interfacial oxygen (1, 4, 5, 7, 8), it is proved that during slow cooling of the samples e.g. in air at room temperature accumulation of oxygen at the Pd-MgO phase boundaries takes place, whereas segregation does not occur after quenching the same sheet in liquid nitrogen because this freezes oxygen into the bulk (cf. Fig. 10, right-hand side). The determination of the hydrogen diffusivity at 316 K, predestined for the Pd-MgO samples because of the high hydrogen permeability of palladium, is carried out in an electrochemical double cell (9). In accordance with the Kirchheim model of structural vacancies, the concentration of irreversible hydrogen traps, $^{irr}c_H$, which is obtained as the H-trap concentration difference between the first and second run (i.e. repeated measurement after removing weakly bound hydrogen stemming from the first cycle by anodic polarization) taken at the detection limit ($3 \cdot 10^{-13} \text{ m}^2/\text{s}$), if necessary by means of data extrapolation (cf. Fig. 11, on the left), corresponds to twice the amount of segregated oxygen given as coverage $\Theta$. This discovered effect becomes more applicationally interesting in the framework of modern hydrogen technology e.g. for energy storage. Both segregated and oxidically bound oxygen atoms in the interface layer serve as traps for the observed subsequent hydrogen accumulation, which does not occur after removing the excess oxygen from the phase boundary, for instance, by annealing of the samples in vacuum or vapor of the alloying metal (here: Mg, i.e. low oxygen partial pressure) before hydrogen sorption. Within the Kirchheim model (cf. Fig. 8), hydrogen segregation at the oxygen-covered metal-oxide interfaces is modeled by $\text{Me}^{(2)}$ hydroxide formation as follows (1, 5, 8):

$$\text{Me}^{(2)}O_v + \frac{\nu}{\mu} \text{Me}^{(1)}O_\mu + \nu H_2 \rightarrow \text{Me}^{(2)}(\text{OH})_{2v} + \frac{\nu}{\mu} \text{Me}^{(1)} \quad (6)$$

For cooling the Pd-MgO material in ambient air at room temperature (sample 1), the diagram on the right-hand side of Fig. 10 provides $^{irr}c_H \approx 6.6 \cdot 10^{-3}$ at.% and so $\Theta \approx 35 \%$. As oxygen segregation is, according to Eq. (5), energetically similar to the formation of a two-dimensional PdO layer at the interface, $\Delta G_{\text{seg}}$ in Eq. (1) can be estimated by $\Delta G_{\text{pr}} = -95.1 \text{ kJ/mol} + 21.8 \text{ J/(mol K)} \cdot T$, the free enthalpy of PdO precipitation in the Pd matrix. Thus, by applying the Kirchheim model and considering the $A_{\text{pr}}/V_{\text{Pd}}$ ratio, this approximation explains the result of the volumetric gas volume determination (cf. Fig. 10, on the left) as the difference in absorbed oxygen between Pd and Pd-MgO then ranges from 10 to 15 %. However, the electrochemical measurement of the Pd-MgO sample quenched in liquid nitrogen (cf. Fig. 10, right-hand side), which yields $^{irr}c_H = 0$, points phenomenologically to a modification as $\Theta \approx 12 \%$ corresponds to $^{irr}c_H \approx 2.4 \cdot 10^{-3}$ at.%. With an experimental error of $^{irr}c_H \approx 1 \cdot 10^{-3}$ at.% or $\Theta \approx 6 \%$, leaving the entropy term unchanged, $\Delta H_{\text{seg}}$ amounts to around $-86 \text{ kJ/mol}$ (exothermic chemisorption): this is about 10 % lower than $\Delta H_{\text{pr}}$, in agreement with the findings for the Ag-MgO material.

On the left, Fig. 11 refers to Pd-MgO annealed in pure oxygen and cooled slowly in the same atmosphere after suddenly cutting off the heater current (sample 2). Now, one obtains $^{irr}c_H \approx 1.8 \cdot 10^{-2}$ at.% and therefore $\Theta \approx 95 \%$. Assuming that no additional oxygen penetrates into the sheets during cooling and taking into account the coverage $\Theta$ under annealing conditions, 5 and 20 % (see above), and the concerning solubility data (6), sample 1 and 2 correspond to an amount $f_o$ of segregated oxygen of around 10 and 25 % (see Fig. 11, on the right), with respect to the initial bulk concentration, and final-state equilibrium temperatures of about 1000 and 750 K, respectively.
Fig. 11. Diffusion coefficient (316 K) of hydrogen as a function of its concentration in Pd-MgO (1.1 at.% Mg, 150 µm thick sheet) after annealing in pure oxygen at 1123 K and 200 HPa and cooling in ambient atmosphere (sample 2, on the left). Cooling curves of both evaluated specimens (right-hand side diagram).

The considerable increase in the diffused oxygen fraction from sample 1 to 2 can be attributed to the different rates of cooling shown in the right-hand side diagram of Fig. 11. The given cooling curves, i.e. course of the specimen temperature as a function of time after cutting off the heater current, are recorded by an infrared pyrometer. These experimental findings support a diffusion-controlled process of oxygen segregation at the internal Pd-MgO interfaces and motivate the kinetics model established in the next section.

The SLE Kinetics Model of Oxygen Segregation at internal Pd-Oxide Interfaces

On the left, Fig. 12 presents a typical TEM image of Pd-MgO material produced by complete internal oxidation of a Pd-1.1 at.% Mg alloy in air at 1273K. A series of 41 such photographs, containing a total number of around 1600 precipitates, is evaluated by image analysis. The diffusion distances of lattice-dissolved oxygen atoms from the bulk to the Pd-MgO interfaces are determined, neglecting the perspective of these projection images: the result is shown on the right of Fig. 12. A fine scan forming a network of a total of about 375000 quadratic fields each 385 nm² in area is carried out over the entire region under investigation. Where the center of such an element lies outside a MgO precipitate (around 360000), its smallest distance from the surface of an oxide particle is determined. On all sides of each TEM image, a 150 nm wide edge zone, the mapped surrounding area of which is not representative of the sample material, is excluded. Whereas the matrix regions within the rim are not considered, the particles are included in the evaluation of the remaining bulk elements.

The diagram on the right of Fig. 12 serves as the basis for deducing a diffusion-controlled segregation kinetics model designed for the matrix metal palladium, where diffusion of oxygen is slow. The idea of this simulation is sketched in the following (1, 10). The distribution of the bulk diffusion distances measured is divided into independent substitute length elements, SLE. The oxygen amount \(N_{O,i}\) (expressed in %, cf. Fig. 12: \(\sum N_{O,i}=100\%\)) assigned to the SLE \(i\) is calculated by integration of the polynomial fit curve indicated in the diagram. The length \(l_i\) of such a SLE is then taken as half the length of a corresponding one-dimensional rod.
Fig. 12. TEM bright field image of the internally oxidized Pd-1.1 at.% Mg alloy and deduced distribution of the diffusion distances from matrix positions to the nearest MgO particle, given as relative frequency $N_{\text{rel}}$, with definition of the substitute length elements (SLE) according to the indicated polynomial fit.

In a first-order approximation, infinite sink absorption capacity is assumed. Thus, by solving Fick’s second law, the total fraction of oxygen segregated isothermally at time $t$ from the bulk to the interfaces, $f_O$ (expressed in % with respect to the initial matrix concentration), is given as the sum of the contributions of all $i_0$ SLE’s used ($i_0=13$ for the chosen classification in the right-hand side diagram of Fig. 12), $f_{O,i}$, times $N_{O,i}$:

$$f_O = \sum_{i=1}^{i_0} f_{O,i} \cdot N_{O,i} = \sum_{i=1}^{i_0} N_{O,i} \cdot \left\{ 1 - \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2} \exp \left[ -\left(2j+1\right)^2 \frac{D_O t}{4l^2} \right] \right\}$$  (7)

Here, $i$, $i_0$ and $j$ are respectively positive and non-negative integers. $D_O$ denotes the diffusion coefficient of oxygen in palladium (containing the oxide precipitations). Its concentration dependence can be neglected since the oxygen solubility is rather low.

**Results of the SLE Diffusion Model for the Kinetics of Oxygen Segregation**

On the left, Fig. 13 presents tempering curves (i.e. diffusion-controlled course of atom accumulation at modest temperatures) predicted by the SLE kinetics model of oxygen segregation at internal Pd-oxide interfaces. From this diagram, 423 K is derived to be a suitable tempering temperature. As quenching in liquid nitrogen is necessary to ensure a well-defined initial state, for the sake of experimental simplicity oxygen sorption annealing should be performed in air. In this case, the limiting temperatures are 1073 K (no surface PdO oxide) and 1800 K (melting temperature of palladium: 1828 K) yielding an initial coverage of 25 and 0.5 % and oxygen concentrations of 0.030 and 0.015 at.% respectively. For appropriately low tempering temperatures (e.g. 423 and 473 K), the equilibrium coverage equals 100 %. Thus, $f_O$ ranges from around 20 to 60 % (cf. Fig. 13, left-hand side) if sorption occurs in air between 1073 and 1800 K. A comparison drawn with simpler simulations confirms that the SLE model has better regard to the short diffusion distances and provides a realistic approach to this complex diffusion process (10). Literature data for the diffusion coefficient of oxygen in palladium (1, 4), extrapolated to lower temperatures, are used in the computations.
Fig. 13. Results of the simulation of oxygen kinetics at internal Pd-MgO interfaces according to Eq. (7) and Fig. 12 (right-hand side diagram), i.e. the substitute length elements (SLE) model. The amount of segregated oxygen is respectively expressed as fraction $f_O$ with respect to the initial bulk concentration.

Also, the marked increase in the diffused oxygen fraction from sample 1 to 2, which arises from the different cooling rates of both specimens, is in good agreement with the outcome of the SLE model. This can be read from the diagram on the right-hand side of Fig. 13.

REFERENCES