



# Multi-layer problems in time-lag measurements applied on metal–hydrogen systems

H. Züchner\*, L. Opara, H. Barlag

*Institute of Physical Chemistry, University of Münster, Schloßplatz 4+7, D-48149 Münster, Germany*

## Abstract

Time-lag techniques are powerful tools to determine diffusion coefficients of hydrogen in metals. The quality and reliability of time-lag measurements depends strongly on an exact consideration of the experimentally established boundary conditions in the mathematical evaluation of the measured time-lag curves. This also means that a change of inner and/or outer boundary conditions can lead to another type of time-lag experiment with a different solution for the diffusion equation. In numerous cases the metal foil is coated by surface layers possessing hydrogen solubilities and diffusivities different from that of the enclosed metal. The surface layers determine the boundary conditions at the interface between the metal and the surface layer. In these cases solutions of the diffusion equation for multi-layer problems have to be found. Complete analytical solutions normally do not exist; however, numerical calculations allow to solve the problems reliably. We present results from those calculations for double (AB) and triple (ABA) layer systems for cases where A or B controls the time-lag, but also for the situations in between these two extreme cases. The simulation also describes the transition from one type of time-lag experiment to another one. © 1999 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

The principle of time-lag techniques to study hydrogen diffusion in metals is to measure the time delay of the response signal (hydrogen concentration, concentration gradient (flux) or total amount) at the measuring side of a metal/alloy foil of defined thickness after exciting the entrance side by a well-defined change of hydrogen concentration. The concentration change at the entrance side as well as the monitoring of the concentration as a function of time at the detection side can be done electrochemically [1] or gas volumetrically [2]. The diffusion coefficient, the most interesting physical property, is obtained from the concentration (flux, amount)–time curve by measuring characteristic diffusion times (break-through time  $t_b$  or time-lag  $t_L$ ). The relationship between these diffusion times and the diffusion coefficients results from the solution of the diffusion equation (second Fick's law) [1–3]:

$$t_b = \tau_b s^2 / D \quad \text{or} \quad t_L = \tau_L s^2 / D.$$

An exact consideration of the initial and the boundary conditions really established in the experiment is impera-

tively necessary to determine correct and well-defined diffusion quantities. One source of error in the analysis of time-lag experiments results from an insufficient establishment and/or incorrect consideration of the outer boundary conditions. A second and main source of error is the neglect of surface layers (such as oxide layers), which normally cause additional (inner or system-controlled) boundary conditions because they exhibit hydrogen solubilities and diffusivities quite different from that of the pure metal of interest.

In the present investigation we have calculated numerically characteristic diffusion times for various time lag methods applied on samples wearing a thin surface layer on the entrance side or/and on the detection side, in order to demonstrate the strong influence of such layers on the effective diffusion times, and especially on the relationship between these times and physically meaningful diffusion coefficients.

## 2. Numerical simulations of time-lag diffusion problems

### 2.1. Principle of numerical calculations and special requirements

An algorithm analogous to the Richardson method [4],

\*Corresponding author.

described in detail elsewhere [5,6], has been applied. The main idea of the numerical evaluation is to introduce dimensionless variables for the sample thickness  $s$ , the time  $t$ , and the diffusion coefficient  $D$  and to express the diffusion process as well as the different boundary conditions in terms of simple differences of the number of particles in adjacent volume elements. A good approximation for getting reliable characteristic diffusion times can only be reached if a large number of layer and time increments are defined. The number of volume elements and time intervals is generally restricted by the storage capacity, calculation accuracy and computation times. We carried out the simulations using a personal computer with 32 MB RAM equipped with an Intel Pentium Pro 200 MHz processor. The whole sample is divided into 2000 volume elements. Since the thicknesses of the surface layers are kept constant at 2% of the complete sample thickness, the number of surface layer elements is fixed at a value of 40. This was found sufficient for the determination of diffusion times with high reliability. It is assumed that the interfaces between the surface layer and the metal are infinitesimally small and that the thermodynamic hydrogen solubility equilibrium between the two adjacent layers is completely established. Additionally, the initial and boundary conditions at the outer sides of the metal foil are ideally fixed. The surface layers and the metal are completely homogeneous.

### 2.2. Time-lag quantities for single layer problems

For single-layer problems complete analytical solutions of the diffusion equation for the different types of time-lag methods are available and well known. Numerical calculations yield, of course, identical results, if the boundary conditions are considered properly.

Diffusion coefficients can be determined by measuring or calculating  $t_b$  or  $t_L$  [1]. In some cases, for instance in single-layer problems, the diffusion coefficients can also

be obtained by a fit of the experimental curve with the complete mathematical solution of the concentration (gradient)–time curve. In more complicated cases of multilayer problems this is hardly possible because analytical solutions rarely exist (an exception is discussed in Ref. [7]).

Table 1 summarizes the reduced break-through times  $\tau_b$ <sup>1</sup> obtained from theoretical simulations for single-layer solutions for various time-lag problems with different boundary conditions.

### 2.3. Double- and triple-layer diffusion problems

#### 2.3.1. Dependence on the hydrogen solubility ratio $L_{surf}/L_{me}$

First, it is assumed that the diffusion coefficient in the surface layer is identical to that in the metal. Since the thickness of the surface layer is fixed (2% of the foil thickness) the diffusion resistance  $R$  of the surface layer is small compared to that of the complete foil ( $R_{surf}/R_{me} \approx 4 \times 10^{-4}$ ).

Fig. 1a shows the effect of hydrogen solubility of the surface layer  $L_{surf}$  at the entrance side on the break-through time  $\tau_{b,me} = t_b / (s_{me}^2 / D_{me})$ . Fig. 1b shows the effect resulting from a surface layer on the detection side, Fig. 1c refers to the case where both sides are coated with a thin surface layer. Table 2 summarizes the  $\tau_{b,me}$  values for the extreme solubility ratios at different time-lag methods. The marked values indicate that in these cases the outer conditions are effective as established in the experiment, in all other cases a changeover of the method is observed due to the influence of the inner boundary conditions. The hydrogen solubility of the surface layer  $L_{surf}$  which is different from that in the metal  $L_{me}$  affects the permeation

<sup>1</sup>In this paper we concentrate only on the break-through times  $\tau_b$ . Corresponding calculations and discussions about the time-lag  $\tau_L$  are published elsewhere [6].

Table 1  
Reduced break-through times  $\tau_b$  obtained from theoretical simulations for single layer solutions for different time-lag methods

Name of method	Initial conditions $t = 0$	Boundary conditions		Measuring signal	$\tau_b$
		$x = 0$	$x = s$		
Concentration pulse non-permeation (cp–np)	$0 \leq x \leq s$ $c(x,0) = f(x)$	$t > 0$ $\left(\frac{\partial c}{\partial x}\right)_{x=0,s} = 0$		$c = f(t)$	0.0505
Constant concentration non-permeation (cc–np)	$0 \leq x \leq s$ $c(x,0) = c_0$	$t > 0$ $c(0,t) = c_0 + \Delta c$	$t \geq 0$ $\left(\frac{\partial c}{\partial x}\right)_{x=s} = 0$	$c = f(t)$	0.0765
Constant concentration permeation (cc–p)	$0 \leq x \leq s$ $c(x,0) = c_0$	$t > 0$ $c(0,t) = c_0 + \Delta c$	$t \geq 0$ $c(s,t) = c_0$	$\frac{dc}{dx} = f(t)$	0.0505
Constant gradient permeation (cg–p)	$0 \leq x \leq s$ $c(x,0) = c_0$	$j(0,t) = D \frac{c_\infty}{s}$ $= \text{const}$	$t \geq 0$ $c(s,t) = c_0$	$\frac{dc}{dx} = f(t)$	0.0765

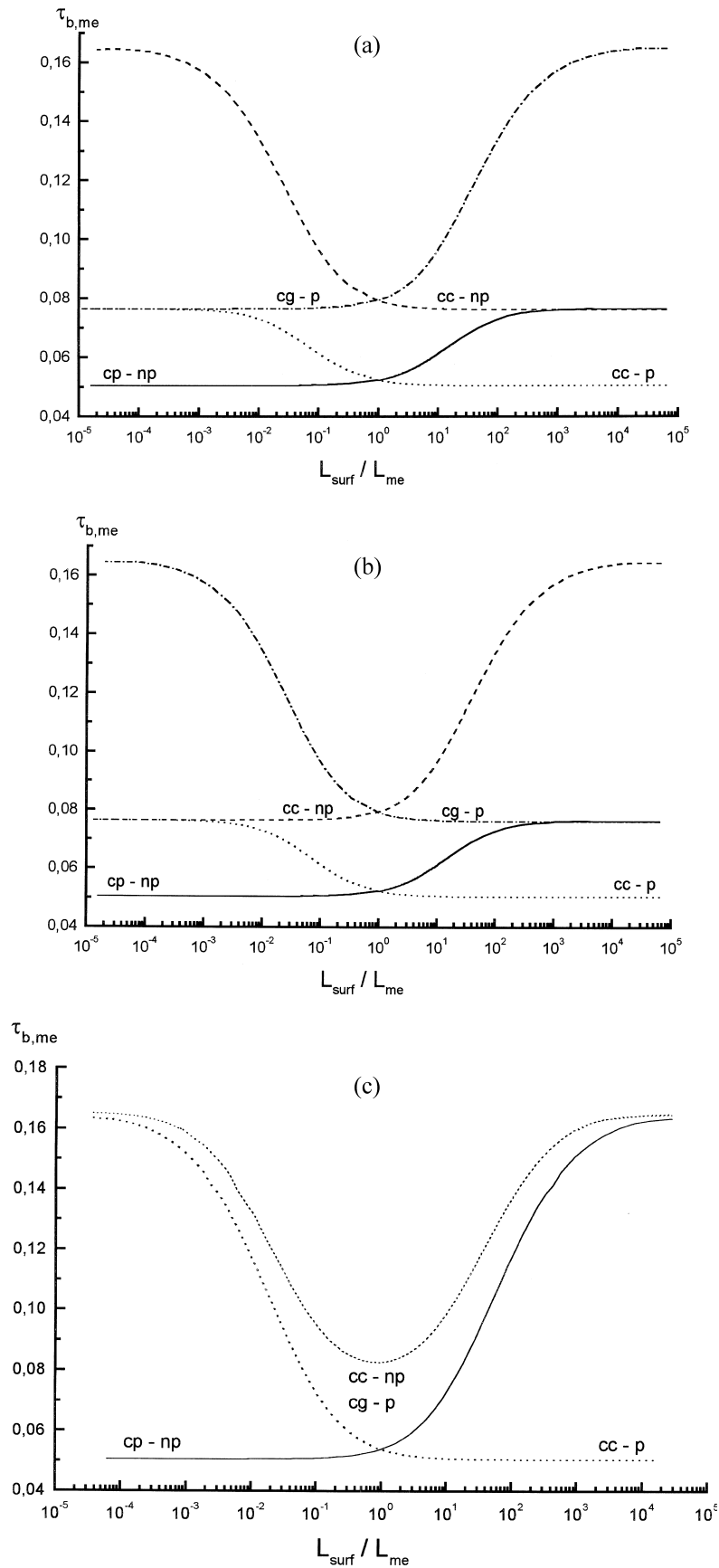


Fig. 1. Reduced break-through times for double- and triple-layer problems as a function of hydrogen solubility ratios for different time-lag methods with  $D_{surf} = D_{me}$ : (a) surface layer on entrance side; (b) on detection side; (c) on entrance and detection side.

Table 2

Reduced break-through times for double- and triple-layer problems for extreme solubility ratios for different time-lag methods

Method	$\tau_{b,me}$ values					
	entrance side		detection side		both sides	(triple layer)
	$L_{surf}/L_{me} \ll 1$	$L_{surf}/L_{me} \gg 1$	$L_{surf}/L_{me} \ll 1$	$L_{surf}/L_{me} \gg 1$	$L_{surf}/L_{me} \ll 1$	$L_{surf}/L_{me} \gg 1$
cp–np	<b>0.0505</b>	0.0765	<b>0.0505</b>	0.0765	<b>0.0505</b>	1/6
cc–np	1/6	<b>0.0765</b>	<b>0.0765</b>	1/6	1/6	1/6
cc–p	0.0765	<b>0.0505</b>	0.0765	<b>0.0505</b>	1/6	<b>0.0505</b>
cg–p	<b>0.0765</b>	1/6	1/6	<b>0.0765</b>	1/6	1/6

flux and, therefore, controls the inner boundary conditions at the interface between the surface layer and the metal. Such an additional boundary condition has been considered in the calculation, while in evaluation of real time-lag experiments it is often neglected.

If the *entrance* side is covered with a layer (see Fig. 1a) having *small* hydrogen solubility (compared to that in the metal) the cp–np, but also the cg–p method are not influenced, while the cc–np and cc–p methods run into solutions for  $\tau_{b,me}$  which correspond to the cg–np and cg–p methods, respectively. A surface layer with a *high* hydrogen solubility at the entrance side is advantageous for the cc–p and cc–np methods, which require a constant concentration. The surface layer represents a hydrogen reservoir, thus the cp–np method changes over to the cc–np method.

A surface layer with a *small* solubility<sup>2</sup> on the *detection* side (see Fig. 1b) supports the condition of an impermeable surface. Thus, a surface layer on the detection side affects the cp–np and the cc–np methods positively, while the cc–p method, for instance, runs into the solution for the cc–np method. In contrast, a surface layer with a *high* hydrogen solubility on the detection side supports a boundary condition of an ideally permeable surface ( $c(t) = c_o = \text{const.}$ ), thus showing no influence on the cc–p and cg–p time-lag methods. The cp–np and cc–np methods, however, require an impermeable surface<sup>3</sup>. In this case the interface is completely permeable, the outer surface is impermeable. The measuring signal, for instance, in the cc–np method, changes from the concentration to the total permeating amount, thus  $\tau_{b,me}$  is nothing else but  $\tau_{L,me} (= 1/6)$  for the cc–p method, the solution of which is  $\tau_L = 1/6$ .

If both sides of the foil are coated with thin and identical surface layers (see Fig. 1c) the dependence of the break-through time on the solubility can be discussed similarly to the double-layer problem, even if the influence of the

surface layers in triple-layer samples has to be considered twice. This fact complicates the situation considerably.

Fig. 1, as well as the overview given in Table 2 make clear that the cp–np method is obviously the best method, even when the metal foils are covered with surface layers of small hydrogen solubilities. This is the normal and most interesting case from a technological point of view.

For surface layers with hydrogen solubilities higher than that of the enclosed metal (for instance, Pd layers which are used as protective films against oxidation) the application of the cc–p method is more advantageous. In all other cases, ignoring the influence of surface layers can lead to errors in the determination of about 50 up to 210%, provided that the diffusion resistance of surface layers can be neglected. In these cases double-layer problems can be understood on the basis of single-layer solutions with (sometimes) altered boundary conditions.

### 2.3.2. Dependence on the ratio of diffusion resistances

In the simplest case the diffusion coefficient in the surface layer is higher than that in the metal. Calculations for the solubility dependence of  $\tau_{b,me}$  values for  $D_{surf}/D_{me} = 10^2$  ( $R_{surf}/R_{me} = 4 \times 10^{-6}$ ) are shown in Fig. 2, together with the relations for  $D_{surf}/D_{me} = 1$  (for comparison). The higher diffusion coefficient in the surface layer shifts the  $\tau_{b,me}$  curves for the cc–np and cc–p method by two orders of magnitude to smaller solubility ratios if the entrance side is covered (Fig. 2a). If the detection side has a surface layer, an analogous shift is obtained for the cg–p and cc–p methods (Fig. 2b). In general, in these cases the higher diffusion coefficient in the surface layer reduces the ‘negative’ influence of a small solubility in the surface layer as discussed before on  $\tau_{b,me}$ . This is also true for the triple layer problem (Fig. 2c). From the shift of the curves one must conclude, that neither the solubility nor the diffusion coefficient, but both of them, namely the permeation coefficient, determines the inner boundary condition. The cp–np method is the only one not affected at all by a higher diffusion coefficient in the surface layer on the entrance and/or detection side.

A quite different behavior is obtained if the diffusion coefficient of the surface layer becomes small compared to that of the metal. In Fig. 3 the results are shown for a more extreme case with  $D_{surf}/D_{me} = 10^{-6}$  ( $R_{surf}/R_{me} = 4 \times 10^2$ ), which implies that the surface layer should determine the

<sup>2</sup>It has to be emphasized, that a small hydrogen solubility in the surface can lead in a real experiment to a strong reduction or even disappearance of the measuring signal. The theoretical simulations are quite more sensitive. The dynamic measuring or calculation range covers several orders of magnitude.

<sup>3</sup>An impermeable surface means that there is no flux, nevertheless, the concentration and its changes at the surface are still measurable.

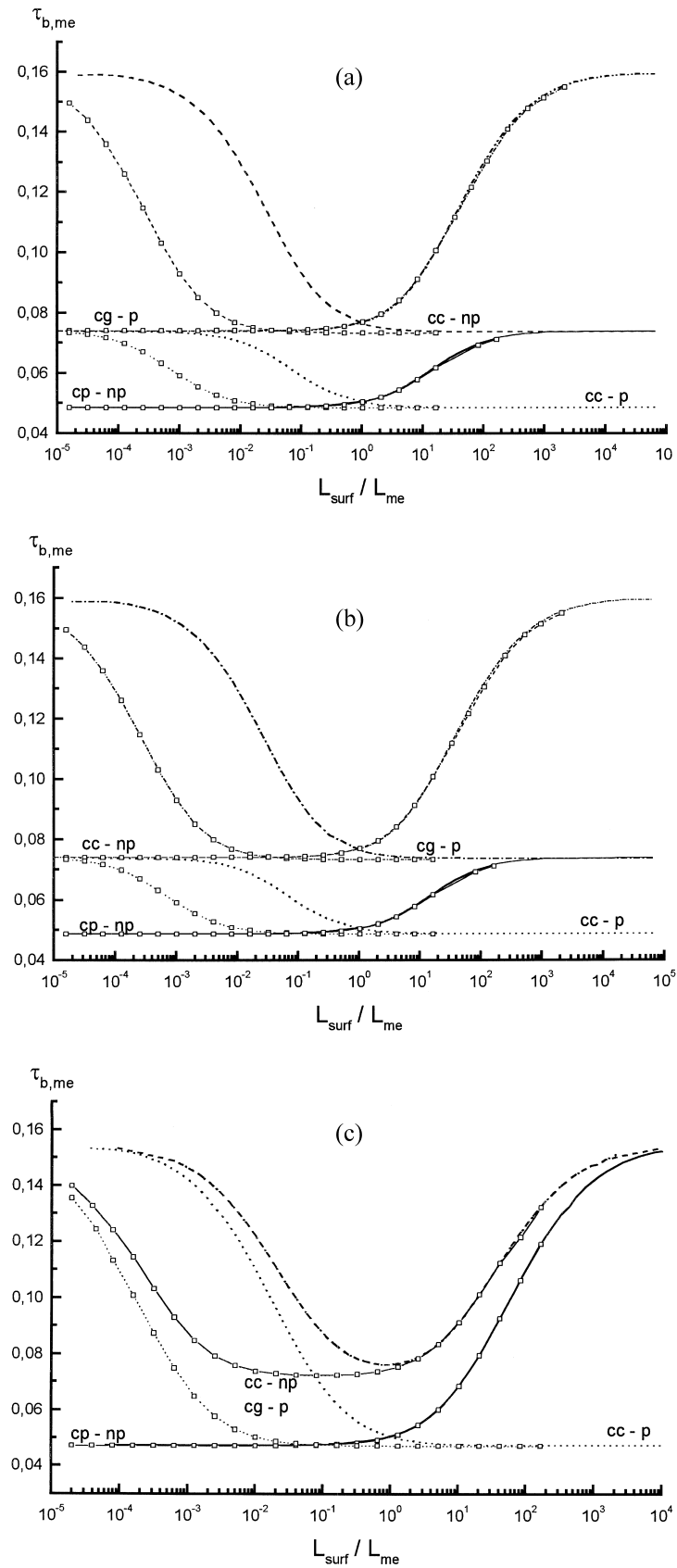


Fig. 2. Reduced break-through times for double- and triple-layer problems as a function of hydrogen solubility ratios for different time-lag methods with  $D_{surf} = D_{me}$  (—) and  $D_{surf}/D_{me} = 10^2$  ( $\square$ ); (a) surface layer on entrance side; (b) on detection side; (c) on entrance and detection side.

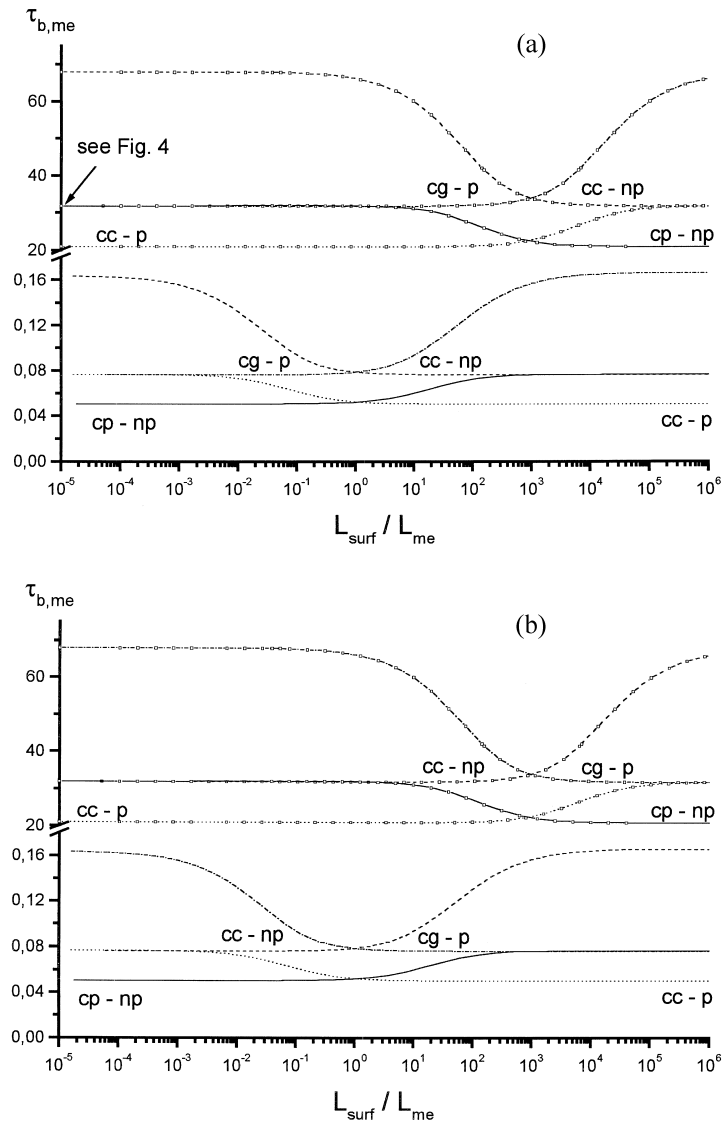


Fig. 3. Reduced break-through times for double-layer problems as a function of hydrogen solubility ratios for different time-lag methods with  $D_{\text{surf}} = D_{\text{me}}$  (—) and  $D_{\text{surf}}/D_{\text{me}} = 10^{-6}$  (---); (a) surface layer on entrance side and (b) on detection side.

diffusion resistance. If one ignores this and references the break-through time to the metal (as done intentionally in the calculations presented in Fig. 3) strong deviations for  $\tau_{b,me}$  from the curves with  $D_{\text{surf}}/D_{\text{me}} = 1$  will occur. This means that time-lag curves are no longer evaluable in terms of diffusion data in the metal. If the break-through time is referenced to the diffusion resistance of the surface layer, results for  $\tau_{b,surf} = t_b / (s_{\text{surf}}^2 / D_{\text{surf}})$  are obtained which can be explained in the same manner as discussed before for  $\tau_{b,me}$  (see Fig. 1): in this case the thin surface layer works as the metal layer and vice versa. In Fig. 4,  $\tau_{b,me}$  and  $\tau_{b,surf}$  are shown as a function of  $D_{\text{surf}}/D_{\text{me}}$  for the cp–np method, if the entrance side is coated with a surface layer,  $L_{\text{surf}}/L_{\text{me}} = 10^{-5}$  and  $s_{\text{surf}}/s_{\text{me}} = 2/98$ .

The arrows in Figs. 3a and 4 indicate the solution for this arbitrarily chosen case. (Analogous relations can be found for all the other methods and different conditions.)

Fig. 4 clearly demonstrates that a time-lag experiment carried out under these conditions only allows to determine diffusion data for the surface layer. Since the metal layer works as a ‘surface layer’ at the detection side with a high hydrogen solubility for the thin but diffusion-controlling surface layer, the solution for  $\tau_b$  changes from 0.0505 to 0.0765 as indicated in Table 2.

### 3. Conclusions

Today’s computers allow us to simulate time-lag diffusion problems of hydrogen in double- and triple-layer samples, even for extreme solubility and diffusivity ratios. The calculations presented in this paper demonstrate the strong influence of inner boundary conditions on the solutions of the diffusion equation which are due to a

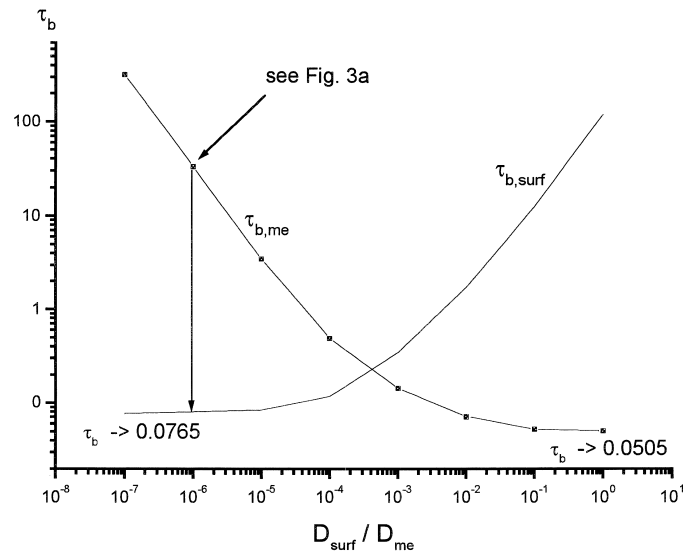


Fig. 4.  $\tau_{b,me}$  and  $\tau_{b,surf}$  as a function of the ratio of diffusion coefficients for the cp–np method, if the entrance side is coated with a surface layer,  $L_{surf}/L_{me} = 10^{-5}$  and  $s_{surf}/s_{me} = 2/98$ .

hydrogen solubility and diffusivity behavior of surface layers different from that of the metal. Only a precise consideration of the outer and inner conditions allows a physically meaningful evaluation of time-lag experiments.

An important aspect for the application of time-lag methods in studying hydrogen diffusion in metals is to ensure that the pure metal layer itself is the only diffusion-controlling layer in every time-lag experiment. This can be checked experimentally by verifying the parabolic thickness dependence of  $t_b$ .

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