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Effects of self-induced stress in tubular membranes during hydrogen diffusion

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Abstract

Various effects induced by self-stress during hydrogen diffusion across metallic tubular membranes are discussed. The up-hill diffusion in the initial time of permeation, the time course of inner pressure change, the steady distributions of hydrogen concentration and residual stress in membranes, and the acceleration of permeation rate on interruption of hydrogen charging are properly interpreted. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Migration of hydrogen interstitials in metals or alloys has been mainly focused on the behavior under effects of elastic lattice strain resulting from lattice deformation, which can be produced either by external mechanical forces [1–3] or by internal stresses due to lattice-dilating interstitials [4,5]. As far as the internal stress is concerned, Lewis and co-workers, and some other researchers have shown experimentally that it results in a hydrogen flux opposing that generated by the overall gradient of concentration, this feature has been referred to as ‘up-hill diffusion’ (UHD) [6–19]. It is verified that self-stress leads to a misestimation of diffusion coefficient using the time-lag method [6–16]. Afterwards, some theoretical efforts have been made to explain the UHD and steady-state distribution of hydrogen in solids [19–29]. On the whole, it appears that the theoretical interpretations are perfect except some controversies on the problem of the steady-state distribution of interstitial in solids [19–22,25–28]. However, we have found that previous theories about UHD [19–28] contain fatal mistakes. The widely used expression of self-stress produced in metallic membranes is for plates with free edges and is only valid in some limited situations such as those in Ref. [30]. But this theory has been improperly extended to thin cylindrical shells [19–

28], which makes the calculated self-stresses and induced effects differ prominently from the actual ones, and causes some controversies on the understanding of experimental phenomena. At the same time, there were serious errors in numerical calculations in some works because the predicted phenomena (e.g. UHD; the non-linear distribution of hydrogen concentration) cannot take place by their model [23–25]. In this report, we will propose a theory to discuss the self-stress and the induced effects for hydrogen diffusion across tubular membranes, and interpret the experimental results in a simplified and unified manner.

2. Model

According to Refs. [4,5,19,20,31,32], the chemical potential of hydrogen interstitials in a metallic lattice (M) under a stress σ for infinite dilute solid-solution can be expressed as:

$$\mu_{\text{H}}(n_{\text{H}}, \sigma) = \mu_{\text{H}}^0 + RT \ln n_{\text{H}} - V_{\text{H}} \sigma \quad (1)$$

where μ_{H}^0 denotes the chemical potential of hydrogen under the reference state; n_{H} is the atomic ratio of H/M; V_{H} is the partial molar volume of H in M. Referring to Baranowski [33] and Fukai [34], $V_{\text{H}} = 1.7 \text{ cm}^3 \text{ mol}^{-1}$ while $n_{\text{H}} < 0.75$.

Considering hydrogen diffusion across a thin tubular membrane, the induced stress should be treated by the

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theory of thermoelastic stresses in shells with the thermal expansion coefficient being replaced by the corresponding expansion coefficient caused by hydrogen insertion [35]. For simplicity, we deal with it by using the theory of thermal stresses in long and hollow cylinders [36] with thin walls, thus it can be treated as a linear and one-dimensional problem. The self-stress for homogeneous materials (e.g. Pd and Pd-based alloys as used experimentally [6–19]) is:

$$\sigma = \frac{2V_{\text{H}}EC_0}{3(1-\nu)}(\bar{n}_{\text{H}} - n_{\text{H}}) \quad (2)$$

with the average H atomic ratio:

$$\bar{n}_{\text{H}} = \frac{1}{L} \int_0^L n_{\text{H}} dz \quad (3)$$

where E is Young's modulus, $E = (1 \sim 2) \times 10^{11}$ Pa; ν is Poisson's ratio, $\nu = 0.3 \sim 0.4$; C_0 is the concentration of H in M corresponding to $n_{\text{H}} = 1$, $C_0 = 0.1 \sim 0.15$ mol H cm^{-3} ; L is the membrane thickness; z is the coordinate along the thickness direction, the upstream side is $z = 0$ (outer surface) and the downstream side is $z = L$ (inner surface). σ is composed of two principal stresses and they are along the axial and tangential directions of the cylinder, respectively. By comparison with the expression for plates with free edges [19–28], the resultant moment term in σ vanishes in Eq. (2) because the zero moment condition does not exist in cylinder shells. The hydrogen flux has the form [4,5]:

$$J(z, t) = -DC_0(1 + u_{\sigma}n_{\text{H}}) \frac{\partial n_{\text{H}}}{\partial z} \quad (4)$$

with

$$u_{\sigma} = \frac{2V_{\text{H}}^2EC_0}{3(1-\nu)RT} \quad (5)$$

where D is the Fick's diffusion coefficient of H in M when $n_{\text{H}} \rightarrow 0$; u_{σ} is the self-stress factor and it is a dimensionless material constant, $u_{\sigma} = 13 \sim 33$ at room temperature utilizing the parameters aforementioned. Eq. (4) is similar to the flux expression under self-stress in solid cylinders, spheres or plates with symmetrical boundary conditions (or infinite thickness) [4,5]. The flux is dependent on the local concentration n_{H} , the non-local non-Fickian component that appeared in previous theories [19–28] vanishes in this case. Applying the mass balance condition to the flux expression, gives one:

$$C_0 \frac{\partial n_{\text{H}}}{\partial t} = - \frac{\partial J(z, t)}{\partial z} \quad (6)$$

The boundary conditions depend on the experimental technique applied. In this report, we concentrate on the electrolyte/membrane/gas situation [6–10], i.e. the outer surface of the tube is in contact with an aqueous solution

pre-saturated with H_2 and a galvanostatic charging current density J_0 is applied. The boundary condition is:

$$J(0, t) = J_0 \quad (7)$$

The H_2 gas is introduced into the tube and the inner wall surface is active to satisfy the boundary condition [19,27,28]:

$$\mu_{\text{H}}(n_{\text{H}}, \sigma) = \mu_{\text{H}}(n_{\text{H}}^*, 0) = \frac{1}{2} \mu_{\text{H}_2} \quad (8)$$

where n_{H}^* is the H/M ratio at the inner surface in correspondence to the imposed hydrogen pressure p under the stress-free condition, μ_{H_2} is the chemical potential of H_2 gas. The pressure change in the tube is:

$$\Delta p = p - p_0 = \frac{RTA}{2V} \int J(L, t) dt \quad (9)$$

where p_0 is the initial hydrogen pressure, A is the area of the tube wall involved in the diffusion process, V is the volume into which the diffused hydrogen is collected and the other parameters have their usual meanings. The factor 2 in the denominator accounts for the presence of two hydrogen atoms per hydrogen molecule.

3. Results

In this section, we first discuss the UHD phenomena, the inner pressure changes and the characteristic parameters of UHD in the initial periods of hydrogen absorption. Then other problems occurred in the steady diffusion and after the interruption of steady diffusion are studied.

3.1. Up-hill diffusion

Fig. 1 shows an example of numerical results based on Eqs. (1)–(9) with parameters shown in the caption; the numerical details are similar to those in Ref. [30]. It is found that the hydrogen pressure decreases in the initial period as observed experimentally [6–20], but the UHD is not caused by the non-local non-Fickian component in expression of J as proposed earlier [19,20,23–25]. It arises from the decrease of $\mu_{\text{H}}(z, t)$ with $z \lesssim L$ due to the dilation of lattice. This situation is also indicated by the accompanied distributions of hydrogen concentration and stress in Fig. 1(b) and (c). According to earlier theories [19–28], the bending of plate make the lattices near the inner surface bear the compressive stress and the chemical potential increases, so the inner pressure should increase initially as also anticipated by Baranowski [37]. On the other hand, the H/M ratio increases at the downstream as shown in Fig. 1(b) but does not decrease initially as predicted by previous theories [21,23,24,27] or changes as deduced from experimental results [9,12,13,17,18].

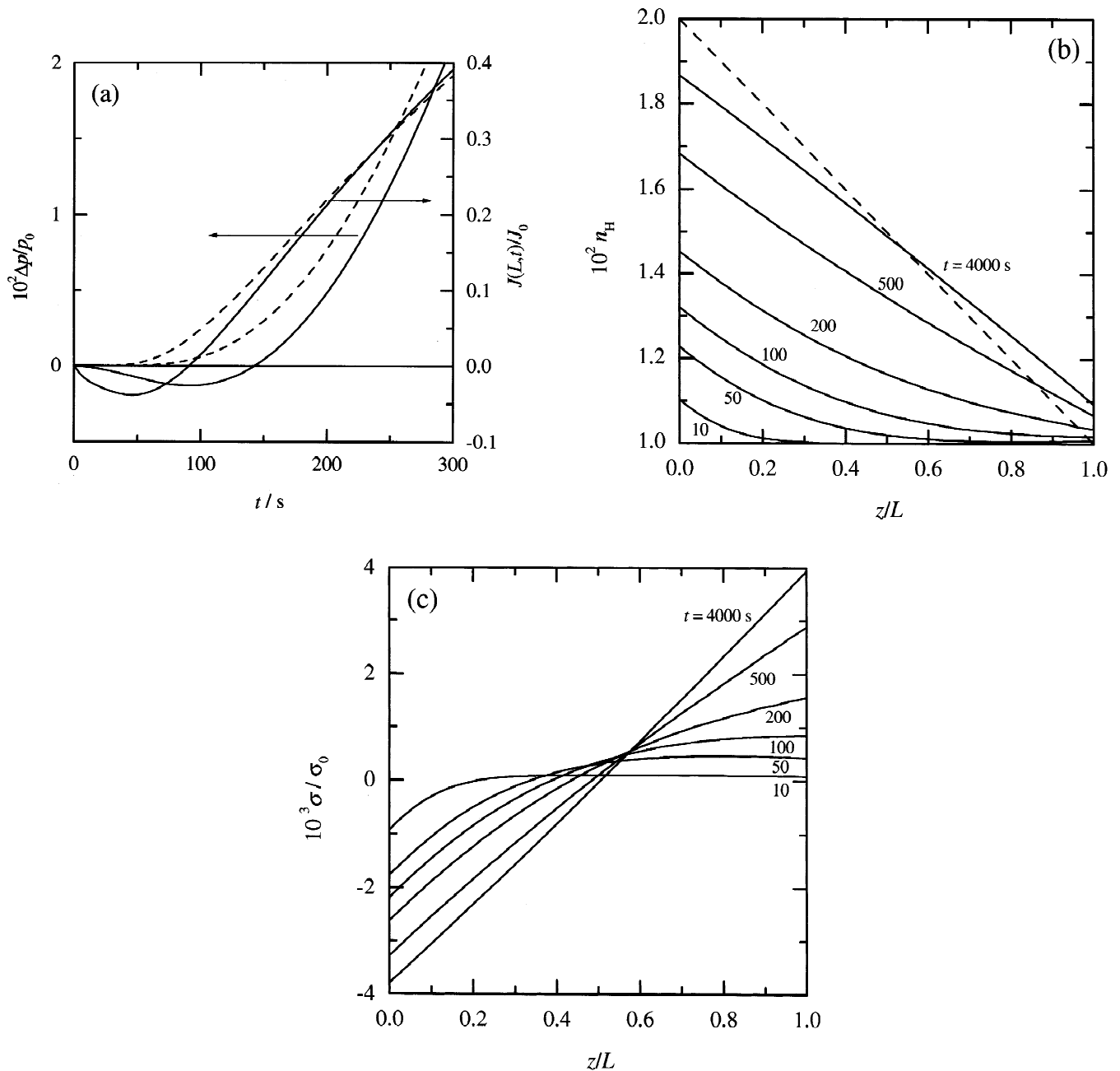


Fig. 1. Numerical results for hydrogen diffusion across a tubular membrane under a galvanostatic condition. (a) Pressure change in the tube and the corresponding permeation flux; the solid curve is for $u_\sigma = 20$ and the dashed curve is for $u_\sigma = 0$ (stress-free situation). (b) Hydrogen concentration distributions at different times, the dashed line is the linear profile under the stress-free condition. (c) Profiles of the relative residual self-stress σ/σ_0 at different times, where $\sigma_0 = 2V_H EC_0/3(1-\nu)$. The parameters: $J_0 = 10^{-8}$ mol H cm $^{-2}$ s $^{-1}$, $C_0 = 0.1$ mol H cm $^{-3}$, $D = 10^{-7}$ cm 2 s $^{-1}$, $L = 10^{-2}$ cm, $A = 10$ cm 2 , $p_0 = 10^4$ Pa, $u_\sigma = 20$, $T = 298.15$ K, $V = 24.465$ cm 3 (corresponding to $N_0 = 10^{-4}$ mol H $_2$). The initial condition is $n_H = n_{H,0} = 0.01$ and $J_0 = 0$ at $t < 0$.

Baranowski [19] has observed that the inner pressure decreases by $t^{3/2}$ in the initial period of hydrogen charging and he gave a theoretical explanation based on the improper stress expression and boundary conditions. In the following, we will derive a similar relation based on our model.

In the initial time intervals, before the Fickian diffusion

wave break-through, the average H/M ratio in the membrane is:

$$\bar{n}_H = n_{H,0} + \frac{J_0 t}{C_0 L} \quad (10)$$

where $n_{H,0}$ is the initial constant value of n_H . In the first

order approximation, $n_H = n_{H,0}$ at $z = L$, inserting Eq. (10) into Eq. (2) gives the stress on the downstream side:

$$\sigma(L, t) = \frac{2V_H E J_0 t}{3(1 - \nu)L} \quad (11)$$

Introducing Eq. (1) into Eq. (8) gives:

$$\begin{aligned} n_H^* &= n_{H,0} \exp\left(-\frac{V_H \sigma}{RT}\right) \\ &\approx n_{H,0} \left(1 - \frac{V_H \sigma}{RT}\right) \end{aligned} \quad (12)$$

Substituting σ by Eq. (11), we have:

$$n_{H,0} - n_H^* = \frac{u_\sigma n_{H,0} J_0}{C_0 L} t \quad (13)$$

The right hand side of this equation is a linear function of time, the corresponding flux is [38]:

$$J_\sigma(L, t) = -2J_0 u_\sigma n_{H,0} \left(\frac{Dt}{\pi L^2}\right)^{1/2} \quad (14)$$

Utilizing Eq. (9), we get:

$$\frac{\Delta p}{p_0} = -\alpha t^{3/2} \quad (15)$$

where

$$\alpha = \frac{2u_\sigma n_{H,0} I_0}{3N_0 L} \left(\frac{D}{\pi}\right)^{1/2} \quad (16)$$

Here α is a dimensionless constant, $I_0 = AJ_0$ is the applied current; N_0 is the molar number of H_2 in the tube. By comparison of the present predictions with the data from Ref. [19], we find they are consistent qualitatively with each other.

A similar method can be used to discuss the situations of a gas/membrane/gas experiment [11–16], where the boundary condition of Eq. (7) should be replaced by Eq. (8), and the pressure change in the tube should be proportional to $t^{1/2}$ [38].

Another characteristic parameter of UHD is the maximum reduction of initial pressure, $-\Delta p_{\max}$, at time t_{\max} as shown by the pressure minimum in Fig. 1(a). It is easily understood that $-\Delta p_{\max}$ and t_{\max} are proportional to u_σ . Here, we discuss these parameters changing with $n_{H,0}$. At the time t_{\max} , the stress-induced flux J_σ cancels out the concentration flux J_C , where J_C under the galvanostatic charging condition is [39]:

$$J_C(L, \tau) = 2J_0 \operatorname{erf} c\left(\frac{1}{2\sqrt{\tau}}\right) \quad (17)$$

with $\tau = Dt/L^2$ while $\tau < 0.32$, where τ is the reduced diffusion time. Combining Eqs. (14) and (17) gives an equation used to solve τ_{\max} :

$$\operatorname{erf} c\left(\frac{1}{2\sqrt{\tau_{\max}}}\right) = u_\sigma n_{H,0} \left(\frac{\tau_{\max}}{\pi}\right)^{1/2} \quad (18)$$

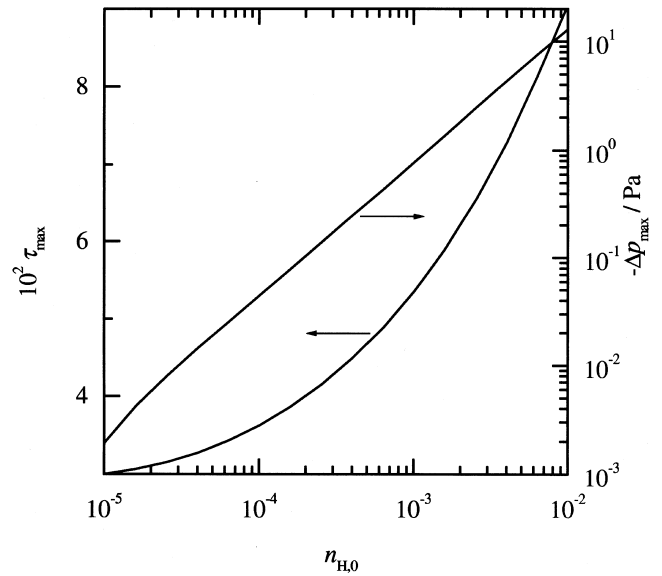


Fig. 2. Changes of τ_{\max} and $-\Delta p_{\max}$ with initial hydrogen concentration $n_{H,0}$. The other parameters are the same as those in Fig. 1.

Numerical results of τ_{\max} and $-\Delta p_{\max}$ based on Eqs. (1)–(9) are shown in Fig. 2. We find the time τ_{\max} increases monotonically with $n_{H,0}$ as verified experimentally [6–8,12,13]. At the same time, it is found from Eq. (18) that τ_{\max} is independent of the applied current, of course, this conclusion is only effective when J_0 is so small that $D(1 + u_\sigma n_H)$ almost does not change with z . The corresponding $-\Delta p_{\max}$ also increases with $n_{H,0}$ as shown in Fig. 2 and observed experimentally [6–8,12,13].

3.2. Steady diffusion and interruption of steady diffusion

An interesting and arising controversial problem is the profiles of hydrogen concentration and self-stress in the steady-state diffusion [4,19–22,25–28]. From Fig. 1(b) and Eq. (4), we find that the steady concentration distribution protrudes somewhat. This is due to the fact that the apparent diffusion coefficient $D(1 + u_\sigma n_H)$ decreases with z , and the concentration profile is not a linear function as in the case of a free plate [4,19,20,27,28]. Because of the presence of self-stress as shown in Fig. 1(c), n_H in the upstream (downstream) half region is less (greater) than that in the stress free situation. Finally, the residual stress does not vanish; this is quite different from the situation of free-edge plates [4,19,20,27,28].

Another striking feature of self-stress effects is the acceleration of permeation flux on the interruption of the charging current [17,18]. This situation is demonstrated in Fig. 3, where we find that the permeation flux and hence the change of inner pressure following the charging current being stopped are greater than those in the steady-state, and this trend of pressure change is the same as that in experiments [17,18]. Some researchers proposed that the non-linear profile of hydrogen concentration is the reason

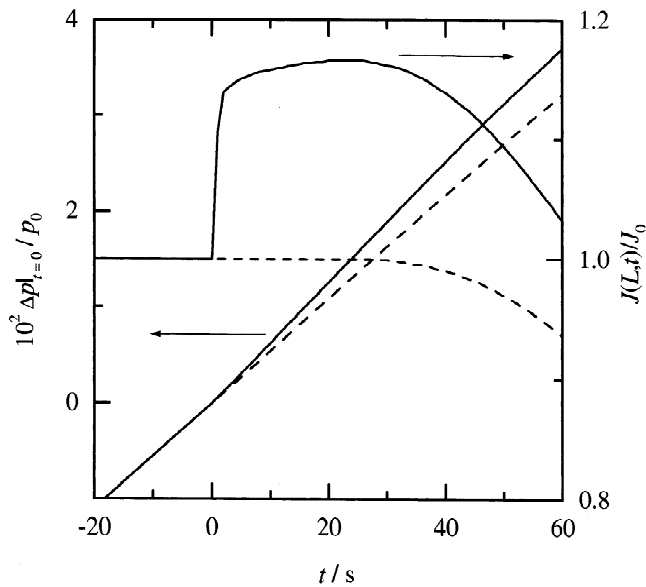


Fig. 3. Changes of hydrogen pressure in the tube and the corresponding hydrogen permeation flux while the charging current is stopped at $t = 0$. The dashed curve is for the stress-free situation. Other parameters are the same as those in Fig. 1.

for this behavior [17,18]. In fact, the acceleration effect is also induced by the similar reason of UHD although these two phenomena appear contrary to each other, i.e. the contraction of lattices near surfaces induced by the hydrogen desorption makes the desorption rate accelerate. This is also the reason of UHD that appears in the hydrogen desorption process.

4. Discussion

In this work, we use a model for cylinder shells with infinite length, which differs from the finite length model by the boundary effect. In the thin-shell theory [40], the boundary effect is confined to the axial length of $\pi\sqrt{r_0L}$ (r_0 is the radius of tube). For the parameters used in experiments [6–19], $r_0 = 4$ mm and $L = 0.2 \sim 0.4$ mm, so $\pi\sqrt{r_0L} = 2.81 \sim 3.97$ mm, which is much less than the tube length 40–80 mm. Therefore, the boundary effect can be neglected in a first order approximation. Another related problem is the deformation of membrane in the hydrogen absorption process. The tube dilates in the radial and axial directions uniformly except near the tube ends in the axial length of $\pi\sqrt{r_0L}$. This geometric picture differs from that of the bending of a plate with free-edges.

Different from our model, Mällo and Krozer [29] have demonstrated the UHD behavior by considering the tube as a sphere shell but not the cylinder shell. On the ground that their work has more numerical details than analytical treatments, our conclusions are more straightforward, abundant and convincing than theirs.

In this report, we have dealt only with the electrolyte/membrane/gas situation. For the gas/membrane/gas situation, the main effects are the same as here except for the occurrence of some additional influences [11–16]. On the other hand, we have dealt only with the stress effect in the hydrogen absorption process, the effect in the hydrogen desorption process can be obtained in a similar manner. Finally, this report only provides a simple description of self-stress induced phenomena. Details of these applications and comparison with experimental results based on the thermodynamic and kinetic parameters in metal (alloy)–hydrogen systems will be given in a forthcoming more extended work.

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References

- [1] J. Völkl, Ber. Bunsenges. Phys. Chem. 76 (1972) 797.
- [2] J. Völkl, G. Alefeld, Z. Phys. Chem. (N.F.) 114 (1979) 129.
- [3] H. Wipf, J. Less-Common Metals 49 (1976) 291.
- [4] J.C.M. Li, Metall. Trans. A 9 (1978) 1353.
- [5] F.C. Larché, J.W. Cahn, Acta Metall. 30 (1982) 1835.
- [6] F.A. Lewis, J.P. Magennis, S.G. McKee, P.J.M. Seebuufu, Nature 306 (1983) 673.
- [7] X.Q. Tong, K. Kandasamy, F.A. Lewis, Scripta Metall. 24 (1990) 1923.
- [8] X.Q. Tong, R.V. Bucur, K. Kandasamy, F.A. Lewis, Z. Phys. Chem. (N.F.) 181 (1993) 225.
- [9] K. Kandasamy, F.A. Lewis, J.P. Magennis, S.G. McKee, X.Q. Tong, Z. Phys. Chem. (N.F.) 171 (1991) 213.
- [10] Y. Sakamoto, X.Q. Tong, F.A. Lewis, Scripta Metall. Mater. 25 (1991) 1629.
- [11] F.A. Lewis, B. Baranowski, K. Kandasamy, J. Less-Common Metals 134 (1987) L27.
- [12] X.Q. Tong, F.A. Lewis, J. Less-Common Metals 169 (1991) 157.
- [13] X.Q. Tong, R.-A. McNicholl, K. Kandasamy, F.A. Lewis, Int. J. Hydrogen Energy 17 (1992) 777.
- [14] K. Kandasamy, X.Q. Tong, F.A. Lewis, J. Phys.: Condens. Mater. 4 (1992) L439.
- [15] D. Dudek, B. Baranowski, Polish J. Chem. 69 (1995) 1196.
- [16] D. Dudek, B. Baranowski, Z. Phys. Chem. (N.F.) 206 (1998) 21.
- [17] F.A. Lewis, X.Q. Tong, K. Kandasamy, Int. J. Hydrogen Energy 18 (1993) 481.
- [18] X.Q. Tong, F.A. Lewis, Int. J. Hydrogen Energy 20 (1995) 641.
- [19] B. Baranowski, J. Less-Common Metals 154 (1989) 329.
- [20] B. Baranowski, in: S. Sieniutycz, P. Salaman (Eds.), Advances in Thermodynamics, Flow, Diffusion and Processes, Vol. 6, Taylor and Francis, New York, 1992, p. 168.
- [21] K. Kandasamy, Scripta Metall. 22 (1988) 479.
- [22] K. Kandasamy, Int. J. Hydrogen Energy 20 (1995) 455.
- [23] K. Kandasamy, F.A. Lewis, Defect Diffus. Forum 150–152 (1997) 56.

- [24] K. Kandasamy, F.A. Lewis, *Int. J. Hydrogen Energy* 24 (1999) 763.
- [25] A.M. Simon, Z.J. Grzywna, *Acta Metall. Mater.* 40 (1992) 3465.
- [26] A.M. Simon, *Int. J. Hydrogen Energy* 22 (1997) 27.
- [27] W.S. Zhang, X.W. Zhang, Z.L. Zhang, *J. Alloys Comp.* 302 (2000) 258.
- [28] W.S. Zhang, X.W. Zhang, Z.L. Zhang, *Phys. Rev. B* 62 (2000) 8884.
- [29] A. Mällo, A. Krozer, *J. Less-Common Metals* 167 (1991) 305.
- [30] W.S. Zhang, Z.L. Zhang, X.W. Zhang, *J. Electroanal. Chem.* 474 (1999) 130.
- [31] H.A. Wried, R.A. Oriani, *Acta Metall.* 18 (1970) 753.
- [32] R. Kirchheim, *Acta Metall.* 34 (1986) 37.
- [33] B. Baranowski, S. Majchrzak, T.B. Flanagan, *J. Phys. F.: Met. Phys.* 1 (1971) 258.
- [34] Y. Fukai (Ed.), *The Metal–Hydrogen System, Basic Bulk Properties*, Springer–Verlag, Berlin, 1993, p. 95.
- [35] J.L. Nowinski, *Theory of Thermoelasticity with Applications*, Sijthoff & Noordhoff International Publishers, Alphen aan den Rijn, Netherlands, 1978, Chapter 15.
- [36] S. Timoshenko, in: *Strength of Materials, Part II, Advanced Theory and Problems*, D. Van Nostrand Company, Inc, Princeton, New Jersey, 1956, p. 228.
- [37] B. Baranowski, Private Communication.
- [38] J. Crank (Ed.), *The Mathematics of Diffusion*, Clarendon, Oxford, 1975, p. 33.
- [39] C. Montella, *J. Electroanal. Chem.* 465 (1999) 37.
- [40] S. Timoshenko, S. Woinowsky-Krieger, *Theory of Plates and Shells*, McGraw–Hill, New York, 1959, Chapter 15.