

Effects of hydrogen self-stress in thin circular-plates with clamped edges

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Received 26 February 2002; received in revised form 27 March 2002; accepted 27 March 2002

Abstract

A description of self-stress produced by hydrogen absorption into thin metallic circular-plates with clamped edges is presented. The plate deflects when the average hydrogen content exceeds a critical value, which depends mainly on the size of the plate, if no external load is applied; the plate distortion exhibits bistable characteristics, i.e. the deflection direction may be either upward or downward. On the other hand, a plate deflects prior to hydrogen insertion while an external force is imposed on it. The self-stresses and their effects on the solubility and diffusivity of hydrogen in plates are discussed as well.

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Keywords: Hydrogen absorbing materials; Metal hydrides; Gas–solid reactions; Diffusion

Effects of self-stress produced by solute atoms on the solubility and diffusivity themselves in solids have been extensively studied in past years [1,2]. However, the available self-stress theories are for infinite (or semi-infinite) size solids or high symmetrical samples, e.g. plates with free-edges or semi-infinite thickness, spheres and cylinders. These theories when applied to actual experiments [3–8] have not given precise physical pictures in previous works [9–19], so treatments of solute self-stress effects in specific situations are important both for understanding the self-stresses and for application of them.

In an earlier work [20], we have discussed effects of self-stress developed during solute atoms diffusion across metallic cylindrical shells. From the viewpoint of physics, diffusion of solute atoms across thin plates with clamped edges (PCE) is a more general situation, e.g. hydrogen permeation across a plate under gas or electrochemical conditions is widely used to measure the diffusion coefficient of hydrogen in materials [21–23]. However, very little attention has been paid to this subject up to now. In this report, we will study self-stress effects in PCEs based on theories on thin plate with large deflections [24] and thermoelasticity [25,26]. Approximations and assumptions are the same as those in previous theories [24–26] except

where noted. Similarly to the earlier work [20], we will concentrate on the situation of hydrogen in homogeneous metallic materials (M), which have been studied most extensively [3–23,27–29].

Considering a circular plate with uniform thickness h and radius r_0 prior to hydrogen insertion as shown in Fig. 1. The cylindrical coordinate system is used in this work, and only the central symmetrical situation is discussed. The origin is taken as the center of the plate midplane; z is the axial coordinate, i.e. the distance from the midplane of plate, the upstream side is $z = -h/2$ and the downstream

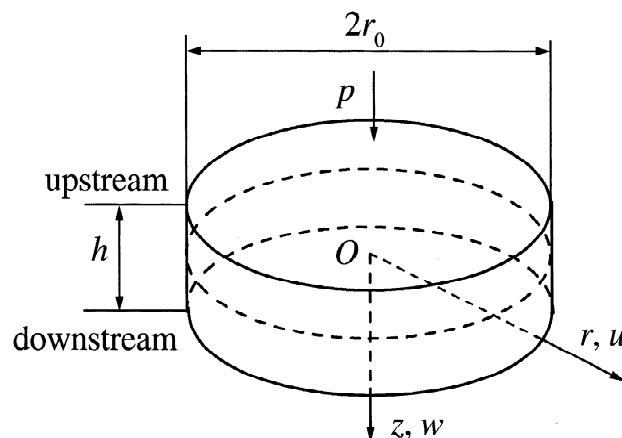


Fig. 1. Schematic picture of thin circular-plate.

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side is $z = h/2$; the deflection of plate midplane along the z -direction is w ; the radial coordinate and displacement are r and u , respectively.

The radial and tangential strains are [26]

$$\varepsilon_r = \frac{du}{dr} + \frac{1}{2} \varphi^2 + \frac{d\varphi}{dr} z, \quad (1)$$

and

$$\varepsilon_\theta = \frac{u}{r} + \frac{\varphi}{r} z, \quad (2)$$

respectively, where $\varphi = -dw/dr$. The radial and tangential stresses are [26]

$$\sigma_r = \frac{E}{1-\nu^2} \left[\frac{du}{dr} + \frac{1}{2} \varphi^2 + \nu \frac{u}{r} + \left(\frac{d\varphi}{dr} + \nu \frac{\varphi}{r} \right) z - (1+\nu)\alpha n_H \right], \quad (3)$$

and

$$\sigma_\theta = \frac{E}{1-\nu^2} \left[\nu \frac{du}{dr} + \frac{\nu}{2} \varphi^2 + \frac{u}{r} + \left(\nu \frac{d\varphi}{dr} + \frac{\varphi}{r} \right) z - (1+\nu)\alpha n_H \right], \quad (4)$$

respectively, where E is Young's modulus, $E = (1 \sim 2) \times 10^{11}$ Pa; ν is Poisson's ratio, $\nu = 0.3 \sim 0.4$; n_H is the atomic ratio of hydrogen to metal (H/M); α is the expansion coefficient caused by hydrogen insertion and it is a dimensionless quantity, $\alpha = V_H C_0 / 3$; V_H is the partial molar volume of H in M, $V_H = 1.7 \text{ cm}^3 \text{ mol}^{-1}$ for f.c.c. metals or alloys while $n_H < 0.75$ [30,31]; C_0 is the concentration of H in M corresponding to $n_H = 1$, $C_0 = 0.1 \sim 0.15 \text{ mol H cm}^{-3}$. The total stress is

$$\sigma = \sigma_r + \sigma_\theta. \quad (5)$$

For a clamped edge, the deflection and slope normal to the edge boundary are zero, i.e. $w = \varphi = 0$ at $r = r_0$; and the central symmetrical condition of deflection gives $\varphi = 0$ at $r = 0$. The clamped edge prohibits relative displacements of the contour in the midplane along the radial direction, i.e. $u = 0$ at $r = 0$ and r_0 .

For simplicity, we will deal with the stress problem using the variational method. The total strain energy is taken to be [24]

$$\Pi = U + V \quad (6)$$

with the strain energy induced by self-stress

$$\begin{aligned} U &= \frac{1}{2} \iiint (\sigma_r \varepsilon_r + \sigma_\theta \varepsilon_\theta) r \, dr \, d\theta \, dz \\ &= \pi D_M \int_0^{r_0} \left[r \left(\frac{d\varphi}{dr} \right)^2 + \frac{\varphi^2}{r} \right] dr \\ &\quad - \pi \int_0^{r_0} M_H \left(r \frac{d\varphi}{dr} + \varphi \right) dr \end{aligned}$$

$$\begin{aligned} &+ \frac{\pi E h}{1-\nu^2} \int_0^{r_0} \left[\left(\frac{u}{r} + \frac{du}{dr} + \frac{\varphi^2}{2} \right)^2 r - (1-\nu) u \varphi^2 \right] dr \\ &- \pi \int_0^{r_0} N_H \left(u + \frac{du}{dr} r + \frac{\varphi^2}{2} r \right) dr, \end{aligned} \quad (7)$$

where D_M is the bending rigidity of the plate per unit of length, $D_M = Eh^3/12(1-\nu^2)$; M_H is the hydrogen moment pure unit of length, $M_H = [\alpha E/(1-\nu)] \int n_H z \, dz$; N_H is the hydrogen membrane force per unit of length, $N_H = [\alpha E/(1-\nu)] \int n_H \, dz = \alpha h E \bar{n}_H / (1-\nu)$; \bar{n}_H is the average hydrogen content in plate. In the deduction of Eq. (7), above boundary conditions are used. The strain energy induced by the external pressure p (strictly speaking, p should be the pressure difference between the two sides of the PCE) on the plate is

$$V = -2\pi p \int_0^{r_0} w r \, dr. \quad (8)$$

The variation of total energy requires

$$\delta \Pi = 0. \quad (9)$$

Taking the approximation solutions [24]

$$u(\rho) = r_0 b_0^2 \rho (1-\rho)(a_0 + a_1 \rho), \quad (10)$$

and

$$w(\rho) = r_0 b_0 (1-\rho^2)^2, \quad (11)$$

where $\rho = r/r_0$ is the reduced radial coordinate, these two solutions satisfy the above boundary conditions. Introducing them into Eqs. (6)–(8) and applying them to the variation of Π with respect to a_0 , a_1 and b_0 in the first approximation that n_H is independent of r , we give $a_0 = 1.421 - 0.706\nu$, $a_1 = -1.881 + 0.309\nu$ and

$$\left[\left(\frac{h}{r_0} \right)^2 - \frac{3}{8} (1+\nu) \alpha \bar{n}_H \right] b_0 + c b_0^3 = \frac{p r_0 h^2}{64D} \quad (12)$$

with $c = 0.425 + 0.241\nu - 0.158\nu^2$. If $\bar{n}_H = 0$, this equation simplifies to the central deflection of thin circular-plate under external load [24]. On the other hand, if $p = 0$, the solution reduces to

$$b_0 = \begin{cases} 0, & \bar{n}_H \leq n_{H,C}^0 \\ \pm b'_0 \sqrt{\alpha(\bar{n}_H - n_{H,C}^0)}, & \bar{n}_H \geq n_{H,C}^0 \end{cases} \quad (13)$$

with

$$n_{H,C}^0 = \frac{8}{3(1+\nu)\alpha} \left(\frac{h}{r_0} \right)^2, \quad (14)$$

and $b'_0 = [3(1+\nu)/8c]^{1/2}$. $b'_0 = 1.004 \sim 1.028$ for $\nu = 0.3 \sim 0.4$, namely, $b'_0 = 1$ in an approximation. The first root of Eq. (13) is a trivial solution, which means that the plate does not bend while hydrogen is inserting into it, and this state is unstable when $\bar{n}_H > n_{H,C}^0$. The last two

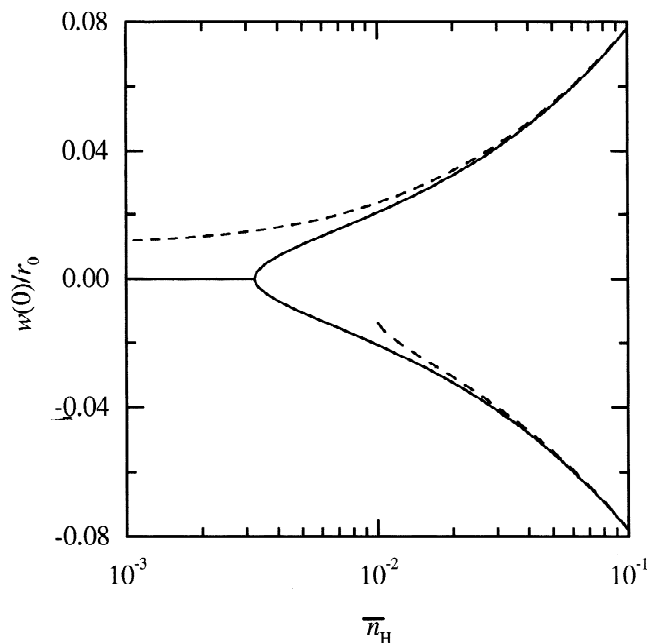


Fig. 2. Central deflections of plate at different hydrogen contents. The parameters: $\nu = 0.38$, $h/r_0 = 10^{-2}$ and $\alpha = 0.06$. Solid and dashed curves are for results of $p/E = 0$ and 10^{-7} , respectively.

solutions have the same amplitude but opposite sign, which indicates that the plate may deflect to the upstream or downstream side as shown in Fig. 2, i.e. it is a bistable system. Eq. (13) and Fig. 2 illustrate that the buckling of the plate requires a critical average H/M ratio $n_{H,C}^0$, which is 3.22×10^{-3} in Fig. 2. The value of $n_{H,C}^0$ depends mainly on the expansion coefficient α and the ratio of thickness to radius h/r_0 as indicated by Eq. (14). It is qualitatively consistent with $n_{H,C}^0 = [1.22/(1 - \nu^2)\alpha](h/r_0)^2$, deduced from the theory of buckling of circular-plate under lateral loads [24]. When $\bar{n}_H \gg n_{H,C}^0$, $w(0)/r_0 \approx \pm(\alpha\bar{n}_H)^{1/2}$, which is similar to the relation obtained previously [32].

The above discussion is suited to the electrolyte/plate/electrolyte situation [4–8,21,22], in which no external load is applied to the plate. In the gas/plate/gas [23] or gas/plate/electrolyte situation, the pressure difference between the two sides of plate makes the PCE deflect initially before bending caused by hydrogen insertion. The corresponding solutions of Eq. (12) are complex so we do not show them here. Similar to Eq. (13), there are only one solution when $\bar{n}_H < n_{H,C}$; two solutions occur when $\bar{n}_H \geq n_{H,C}$ as shown in Fig. 2. The critical hydrogen content under a pressure difference p is

$$n_{H,C} = n_{H,C}^0 \left\{ 1 + \left[c(1 - \nu^2) \left(\frac{3}{4} \right)^5 \left(\frac{r_0}{h} \right)^8 \left(\frac{p}{E} \right)^2 \right]^{1/3} \right\}, \tag{15}$$

which is 0.01 in Fig. 2. It is easily seen that $n_{H,C}$ is proportional to p as expectation. In this case, the deflection is preferred to be along the original direction except for

external disturbance. When \bar{n}_H is large enough, the contribution to the deflection caused by the external pressure decreases and w approaches that without pressure difference as shown in Fig. 2. In actual cases, the deflection direction is determined by the specific situations such as the hydrogen charging and discharging processes, and the initial and boundary conditions.

The stress can be obtained from Eqs. (3)–(5), (10) and (11), and expressions of a_0 , a_1 and b_0 , we choose the solution for plate protruding to the downstream direction ($w > 0$) while $p = 0$

$$\sigma = -\frac{2E}{1 - \nu} \times \begin{cases} \alpha n_H & \bar{n}_H \leq n_{H,C}^0 \\ \alpha n_H - b_0^2 f(\rho) + 4b_0(2\rho^2 - 1)z/r_0, & \bar{n}_H \geq n_{H,C}^0 \end{cases} \tag{16}$$

with $f(\rho) = a_0 + 3(a_1 - a_0)\rho/2 - 2a_1\rho^2 + 4\rho^2(1 - \rho^2)^2$. An example is shown in Fig. 3, it is for a plate in equilibrium with environment and the hydrogen content should be 0.01 under the stress-free condition. The self-stress exhibits complex behavior than that in plate with free edges [9–12,17–19] or in long cylindrical shells [20] while $\bar{n}_H \geq n_{H,C}^0$. The bend of plate and mechanical constraint together make the self-stresses differ in different regions, the maximum value appears in the upstream region near edges. The overall stress are compressive except at the central region near the upstream side as

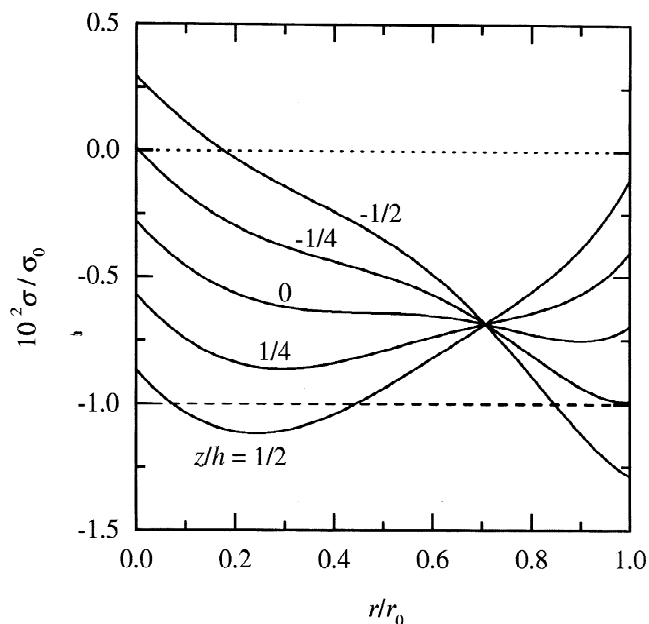


Fig. 3. Profiles of self-stress in plate in the equilibrium state. The parameters are the same as those in Fig. 2 except the stress-free hydrogen content is $n_H = 10^{-2}$, $p = 0$. The dashed and dotted lines are for the plate without deflection and plate with free edges, respectively.

shown in Fig. 3. At the same time, the deflection of plate makes the amplitude of average stress less than the value without deflection as illustrated in Fig. 3. Another interesting feature is that the stresses all have the same value at $\rho = 1/\sqrt{2}$ as indicated by Eq. (16) and Fig. 3.

Self-stresses also affect the distribution of hydrogen content in the plate. The average hydrogen content is 8.73×10^{-3} in Fig. 3 which is less than the stress-free value of 0.01 but greater than the un-deflected value 8.19×10^{-3} . These results indicate that hydrogen contents obtained using PCEs in diffusion experiments differ from those under stress-free conditions. Similarly, other mechanical constraints on samples also affect the isothermal behavior of solute in solids by the same mechanism. However, this effect has been neglected in previous studies.

Another problem is the diffusion flux in the plate, similar to earlier works [1,2,13,14,20], the hydrogen flux has two components

$$j = j_C + j_\sigma, \quad (17)$$

where j_C and j_σ are fluxes induced by gradients of concentration and stress, respectively. In the first order approximation ($h/r_0 \ll 1$), the concentration gradient exists only in the thickness direction, we have

$$j_C = -DC_0 \frac{\partial n_H}{\partial z}, \quad (18)$$

and the stress-induced flux

$$\begin{aligned} j_\sigma &= \frac{DC_0 V_H n_H}{RT} \frac{\partial \sigma_H}{\partial z} \\ &= DC_0 u_\sigma n_H \left[\frac{1}{2\alpha r} \frac{d}{dr}(\varphi r) - \frac{\partial n_H}{\partial z} \right] \end{aligned} \quad (19)$$

with

$$u_\sigma = \frac{2V_H^2 EC_0}{3(1-\nu)RT}, \quad (20)$$

where D is the Fick's diffusion coefficient of H in M when $n_H \rightarrow 0$; u_σ is the self-stress factor and is a dimensionless material constant, $u_\sigma = 13 \sim 33$ at room temperature utilizing the parameters aforementioned; other symbols have their usual meanings. The first term in the bracket of Eq. (19) is zero after integrating with respect to the circular surface using the above boundary conditions. Therefore, the average current density is

$$\bar{j} = -DC_0(1 + u_\sigma n_H) \frac{\partial n_H}{\partial z}, \quad (21)$$

which is the same as that in earlier works [1,2,20]. This equation indicates that the average flux has the same expression either for solid spheres, cylinders and plates with semi-infinite thickness [1,2], or cylindrical and spherical shells and PCEs in a first order approximation.

Another feature of hydrogen permeation in plates is the up-hill diffusion (UHD) behavior similar to that in cylin-

drical shells [3] as observed experimentally [4–8]. Analogous to the discussion in cylindrical shells [20], we will concentrate on the stress at the downstream while hydrogen is introduced at the upstream. Because stresses change with r , we consider only the average value. From Eqs. (3)–(5) and (16), and using the above boundary conditions, we get

$$\begin{aligned} \bar{\sigma} &= \frac{2E}{(1-\nu)r_0^2} \int \left[\frac{1}{2} \varphi^2 - 2\alpha n_H \right] r \, dr \\ &= \frac{2E}{(1-\nu)} \left(\frac{b_0^2}{3} - \alpha n_H \right) \\ &\approx \frac{\sigma_0}{3} (\bar{n}_H - n_{H,C}^0 - 3n_H), \end{aligned} \quad (22)$$

with $\sigma_0 = 2V_H EC_0 / 3(1-\nu)$. Prior to the concentration (or current) step at the upstream side, $n_H = n_{H,0} = \bar{n}_H$ when $t < 0$; and $n_H \approx n_{H,0}$ at the downstream side in the initial period of hydrogen charging before the Fickian diffusion wave break through, so the average stress change at the downstream is

$$\bar{\sigma} - \bar{\sigma}|_{t=0} = \frac{\sigma_0}{3} (\bar{n}_H - n_{H,0}). \quad (23)$$

Using the formula [1,2,13,14,20,33,34]

$$\mu_H(n_H, \sigma) = \mu_H^0 + RT \ln n_H - V_H \sigma, \quad (24)$$

where μ_H^0 denotes the chemical potential of hydrogen under the reference state, we get the average chemical potential change at the downstream

$$\bar{\mu}_H - \bar{\mu}_H|_{t=0} = \frac{V_H \sigma_0}{3} (n_{H,0} - \bar{n}_H). \quad (25)$$

Because $n_{H,0} < \bar{n}_H$ in the absorption process and $\bar{\mu}_H|_{t=0}$ equals the chemical potential of hydrogen outside the plate (electrolyte or gas), so this equation indicates that the hydrogen will be absorbed into the plate at the downstream in the initial period of hydrogen charging. Similarly, the UHD behavior in the discharging process can be understood by the same mechanism.

It must be pointed out that the stress is only a local function of n_H and the UHD cannot take place while $\bar{n}_H < n_{H,C}^0$. This is the reason why a critical value of hydrogen content is required to observe the UHD phenomena in experiments [4–7]. At the same time, we mainly discuss self-stress effects for $p = 0$; otherwise, the stress effects are complex since the external and internal stresses together influence the solubility and diffusivity of hydrogen in PCEs if $p \neq 0$.

In this work, we suppose n_H is independent of r , this is the first order approximations. The accurate results must be solved numerically based on Airy's stress function as done in Ref. [26] and considering the interaction between stress and hydrogen content distributions. On the other hand, our treatment and conclusion are confined to dilute solutions. Phase transformations and plastic deformations that occur

in concentrated solutions need to consider the plasticity and other physical processes. Detailed treatments on the PCE problem will be given in a forthcoming more extended work.

Finally, although our work is focused on metal (alloy)–hydrogen systems, the present conclusions can be extended to stress problems of general interstitial or substitutional solutions (e.g. N in Fe), or to some type of point defects in solids.

Acknowledgements

This work was supported by NSFC No. 10145006 and 20103009 and the President's Innovation Foundation in Chinese Academy of Sciences.

References

- [1] J.C.M. Li, *Metall. Trans. A9* (1978) 1353.
- [2] F.C. Larché, J.W. Cahn, *Acta Metall.* 30 (1982) 1835.
- [3] F.A. Lewis, J.P. Magennis, S.G. McKee, P.J.M. Seebuufu, *Nature* 306 (1983) 673.
- [4] Y. Sakamoto, H. Tanaka, F.A. Lewis, X.Q. Tong, *Int. J. Hydrogen Energy* 17 (1992) 965.
- [5] Y. Sakamoto, H. Tanaka, F.A. Lewis, X.Q. Tong, *Z. Phys. Chem. (N.F.)* 181 (1993) 219.
- [6] Y. Sakamoto, H. Tanaka, F. Sakamoto, F.A. Lewis, X.Q. Tong, *Int. J. Hydrogen Energy* 20 (1995) 35.
- [7] Y. Sakamoto, H. Tanaka, F.A. Lewis, X.Q. Tong, K. Kandasamy, *Int. J. Hydrogen Energy* 21 (1996) 1025.
- [8] H. Tanaka, Y. Sakamoto, F.A. Lewis, X.Q. Tong, *Defect Diffus. Forum* 141–142 (1997) 85.
- [9] K. Kandasamy, *Scripta Metall.* 22 (1988) 479.
- [10] K. Kandasamy, *Int. J. Hydrogen Energy* 20 (1995) 455.
- [11] K. Kandasamy, F.A. Lewis, *Defect. Diffus. Forum* 150–152 (1997) 56.
- [12] K. Kandasamy, F.A. Lewis, *Int. J. Hydrogen Energy* 24 (1999) 763.
- [13] B. Baranowski, *J. Less-Common Met.* 154 (1989) 329.
- [14] B. Baranowski, in: S. Sieniutycz, P. Salaman (Eds.), *Advances in Thermodynamics*, Vol. 6, Taylor and Francis, New York, 1992, p. 168.
- [15] A.M. Simon, Z.J. Grzywna, *Acta Metall. Mater.* 40 (1992) 3465.
- [16] A.M. Simon, *Int. J. Hydrogen Energy* 22 (1997) 27.
- [17] W.S. Zhang, X.W. Zhang, Z.L. Zhang, *J. Alloys Comp.* 302 (2000) 258.
- [18] W.S. Zhang, X.W. Zhang, Z.L. Zhang, *Phys. Rev. B* 62 (2000) 8884.
- [19] D. Dudek, *J. Alloys Comp.* 329 (2002) 1.
- [20] W.S. Zhang, Z.L. Zhang, X.W. Zhang, *J. Alloys Comp.* 336 (2002) 170.
- [21] B.G. Pound, in: J.O.M. Bockris, R.E. White (Eds.), *Modern Aspects of Electrochemistry*, Vol. 25, Plenum, New York, 1993, p. 63.
- [22] P.K. Subramanian, in: J.O.M. Bockris, B.E. Conway, E. Yeager, R.E. White (Eds.), *Comprehensive Treatise of Electrochemistry*, Vol. 4, Plenum, New York, 1981, p. 41.
- [23] B.D. Kay, C.H.F. Peden, D.W. Goodman, *Phys. Rev. B* 34 (1986) 817.
- [24] S. Timoshenko, S. Woinowsky-Krieger, *Theory of Plates and Shells*, McGraw-Hill, New York, 1959, Chapters 2, 3, 12 and 13.
- [25] B.O. Boley, J.H. Weiner, *Theory of Thermal Stresses*, Wiley, New York, 1960, Chapters 12 and 13.
- [26] J.L. Nowinski, *Theory of Thermoelasticity with Applications*, Sijthoff and Noordhoff International Publishers, Alphen aan den Rijn, Netherlands, 1978, Chapter 15.
- [27] J. Völkl, *Ber. Bunsenges. Phys. Chem.* 76 (1972) 797.
- [28] J. Völkl, G. Alefeld, *Z. Phys. Chem. (N.F.)* 114 (1979) 129.
- [29] H. Wipf, *J. Less-Common Met.* 49 (1976) 291.
- [30] B. Baranowski, S. Majchrzak, T.B. Flanagan, *J. Phys. F.: Met. Phys.* 1 (1971) 258.
- [31] Y. Fukai, *The Metal–Hydrogen System, Basic Bulk Properties*, Springer-Verlag, Berlin, 1993, p. 95.
- [32] D. Fort, I.R. Harris, *J. Less-Common Met.* 45 (1976) 247.
- [33] H.A. Wried, R.A. Oriani, *Acta Metall.* 18 (1970) 753.
- [34] R. Kirchheim, *Acta Metall.* 34 (1986) 37.