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Gorsky Effect Consequences of Lattice Expansive Strain Gradients in Diffusion of Hydrogen in Metals

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ABSTRACT

Among transition metals forming hydrides of a metallic type, palladium and certain palladium alloys have been preferentially utilised as membranes for hydrogen purification — in view of their relative resistances to embrittlement, high solubilities for hydrogen, as derivable from quite comprehensive p - c (n) - T relationships, and accompanying high values of hydrogen diffusion coefficients. As fairly recent points of interest, uphill effects corresponding to temporary localised hydrogen permeation against overall hydrogen concentration gradients have been observed in studies with membranes of Pd, $Pd_{77}Ag_{23}$ and $Pd_{81}Pt_{19}$. These uphill effects have been associated with hydrogen migrations induced by Gorsky Effects resulting from developments of gradients of lattice strain produced by the expansive effects of the permeating hydrogen interstitials. An outline is presented of experimental methods and results of measurements together with some theoretical and technological correlations.

GORSKY EFFECTS IN ANELASTIC STUDIES

Elastic deformations of metallic materials such as occur in the course of bendings of sheets, can create gradients of lattice dimensions [Gorsky, 1935]. Evidences of migrations of substitutional elements or of interstitials, from regions of lattice compression to regions of relative expansion may be broadly classified as Gorsky Effects.

In recent years studies of diffusion of hydrogen in metals have provided several illustrations of Gorsky Effect phenomena [Schaumann *et al*, 1968; Cantelli *et al*, 1970; Völkl, 1972; Völkl and Alefeld, 1976,1979; Mazzolai, 1985]. From a practical experimental standpoint this has been a consequence of the retention of essentially metallic elasticity by several of the transition metals even following incorporations of large concentrations of lattice-expanding and relatively highly mobile hydrogen interstitials. The initial evidence of Gorsky Effect phenomena in metal/hydrogen system was provided from studies of anelastic behaviour such as elastic modulus relaxation [Völkl, 1972; Völkl and Alefeld, 1979] and internal friction [Mazzolai *et al*, 1975, and Mazzolai 1985]. Studies by these techniques have provided measurements of hydrogen diffusion coefficients, perhaps particularly with regard to the relative importance of quantum tunnelling effects at low temperatures [Svare, 1986].

In such techniques however there is a need to assume that contents of hydrogen interstitials remain totally within specimens throughout experiments [Völkl, 1972, Čermák *et al*, 1985]. To ensure that this is true as far as possible, surface coatings have been employed, either of metals with very low solubilities for hydrogen such as copper and gold [Völkl, 1972] or of compounds of elements that inhibit hydrogen desorption or removal by oxidation, such as sulphur, arsenic [*e.g.*, Lewis, 1967] or iodine [Kandasamy *et al*, 1991].

Theoretical Estimations of Stress Gradients Produced by Diffusing Interstitials

Calculation of internal stresses developed during introduction and diffusion of interstitial atoms of finite effective volume, such as V_H in the case of hydrogen, are problems of both theoretical and technological interest in several areas of metallurgical and materials science. It seems now generally recognized [Li, 1978; Larché and Cahn, 1982; Kandasamy, 1988, 1989; Baranowski, 1989] that such stress developments would constitute an opposing factor to the concentration gradients that produced diffusion. For example in regard to a general case of thin sheets of thickness δ, the progression of permeation J_H has been represented [Li, 1978; Kandasamy, 1989; Tong *et al*, 1990] as

$$J_H = - D_H \, \partial c/\partial \delta + (D_H c Y V_H/RT) \, \partial \sigma/\partial \delta \qquad (1)$$

in which D_H is the hydrogen diffusion coefficient and involvements are indicated of hydrogen concentration c, stress σ and elastic constants represented by Y and their dependences on temperature T as well as the effective hydrogen volume V_H. There is a general indication from the form of eqn.1 that the generated stress gradients $\partial\sigma/\partial\delta$ would act to reduce Fickian dependence of permeation on concentration gradients $\partial c/\partial\delta$.

GORSKY EFFECTS INDUCED BY DIFFUSION - ELASTIC EFFECT STRAIN GRADIENTS OF HYDROGEN INTERSTITIALS

In the initial studies of the Gorsky Effect in metal/hydrogen systems summarised above, the initiating strain gradient has been induced by mechanical stresses [*e.g.*, Völkl, 1972]. However, over latter years the possibility of Gorsky Effect initiation by elastic bendings alternatively produced by the lattice expanding effects of the hydrogen interstitials themselves has been increasingly recognized [Lewis *et al*, 1983; Čermák *et al*, 1985]. Elastic bending phenomena have indeed been independently utilised for determinations of hydrogen diffusion coefficients by a designated [Čermák and Kufudakis, 1976] Diffusion-Elastic technique involving measurements of the uniaxial bendings of strips of metal sheet produced by introductions (and removals) of hydrogen through one face with the other face covered by an effectively hydrogen impervious coating.

As a similar consequence to that of suddenly applied mechanical stressing, strain gradients corresponding to the Diffusion-Elastic Effect could be expected to produce Gorsky transfers of hydrogen across the membrane, which in this case would be opposed to the direction of hydrogen flux attributable to a hydrogen concentration gradient [Čermák *et al*, 1985]. In this case, however, the actual corresponding elastic deformations (bendings) will develop time dependently associated with gradients of the lattice expansions produced by the hydrogen interstitials — which contribute positive bending moments when located in the outer half of the cross section (thickness) of the membrane (*cf.* Fig.5) and could be particularly large in the course of development and advance of a hydride phase transition [Kufudakis *et al*, 1982; Sakamoto *et al*, 1991].

Uphill Diffusion Associated with Gorsky Effects

Gorsky Effects arising in courses of studies summarised in sections above could be described as occurring in closed-surface and part-closed-surface systems respectively. More recently Gorsky Effects have been advanced as being responsible for uphill effects observed in studies of hydrogen permeation through membranes of Pd, $Pd_{81}Pt_{19}$ and $Pd_{77}Ag_{23}$ in the forms of sheets [Bucur and Lewis, 1990] and tubes, in open surface systems in which both upstream and downstream surfaces have been active catalytically for hydrogen permeation.

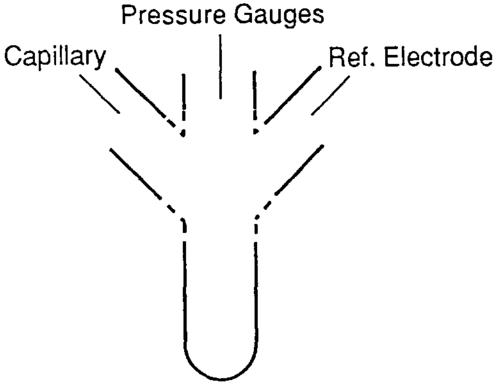

Fig. 1. Diagrammatic representation of alternative arrangements of tubular membranes

In the studies with membranes in the form of tubes with one closed and rounded end (Fig.1) which have constituted a majority of studies of uphill effects [Lewis *et al*, 1983; Kandasamy *et al*, 1991] both inner and outer surfaces had generally been catalytically activated by palladium black. Experimental variant arrangements with these tubes are indicated in Fig.1 where they were either: a) connected to a vacuum line and pressure gauges, b) filled with an electrolyte solution with an inserted reference electrode [Barton and Lewis, 1961; Lewis *et al*, 1976; Sakamoto *et al*, 1991] and c) filled with water extending into an attached capillary [Kandasamy *et al*, 1991] to allow measurements of internal volume changes with cathetometric observations. In regard to outer surface conditions studies have been made where both input and removal of hydrogen have been effected both by electrolysis [Lewis *et al*, 1983; Kandasamy *et al*, 1991] and by pressure control of contacting gaseous atmospheres [Lewis *et al*, 1987; Tong and Lewis, 1991].

Uphill Effects with Tubular Membranes Consequent on Outer Surface Introductions and Removals of Hydrogen by Electrolysis

Figure 2 illustrates examples of hydrogen pressure changes within tubular membranes following commencements of a sequence of cathodisation and anodisation of the outer surface. Initially the inside of the tube had been evacuated. On subsequent cathodisation the changes of

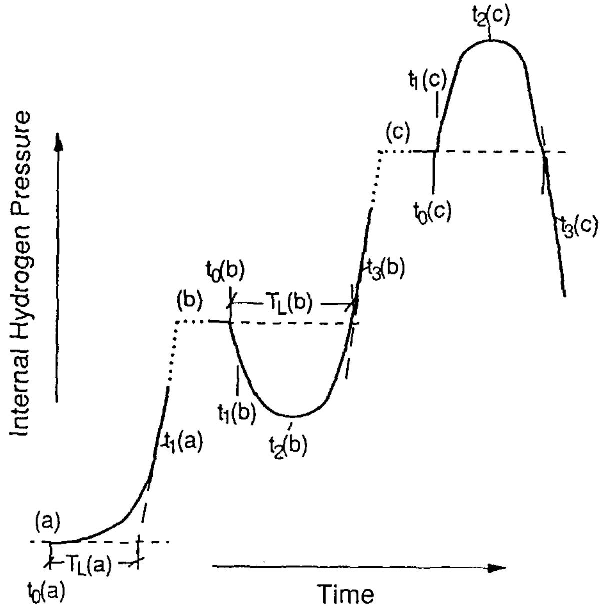

Fig. 2. Time dependences of hydrogen pressure within tubular membranes following outer surface cathodisations for initial pressures of $p_0 \approx 0$ ($n_0 \approx 0$) at t_0(a); $p_0 > 0$ ($n_0 > 0$) at t_0(b) and outer surface anodisation for initial pressure $p_0 > 0$ ($n_0 > 0$) at t_0(c)

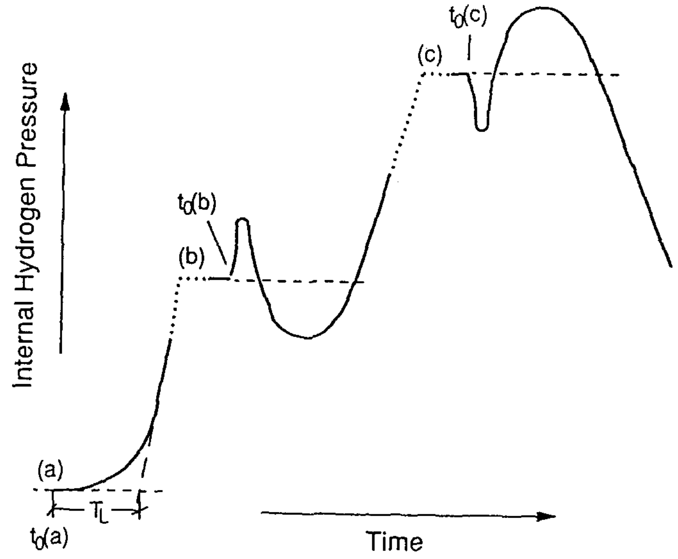

Fig. 3. Time dependences of hydrogen pressure within tubular membranes following introductions of gaseous hydrogen to the outer surface for initial pressures of $p_0 \approx 0$ ($n_0 \approx 0$) at t_0(a); $p_0 > 0$ ($n_0 > 0$) at t_0(b) and outer surface volume evacuation for initial pressure $p_0 > 0$ ($n_0 > 0$) at t_0(c)

pressure inside the tube exhibited an anticipated delay before a gradual development of a region of virtually constant rate of pressure increase. However if an initial quasi static equilibrium pressure of hydrogen had been present in the tube following an interruption of electrolysis [Lewis *et al*, 1983; Kandasamy *et al*, 1991], then pressures in the tube have shown an initial decrease on resumption of outer surface cathodisation or an initial increase on anodisation.

Series of studies of such effects have now been carried out with membranes of $Pd_{81}Pt_{19}$ [Lewis *et al*, 1983; Baranowski and Lewis, 1989; Kandasamy *et al*, 1991] and $Pd_{77}Ag_{23}$ [Tong and Lewis, 1990] alloys and also with Pd [Tong *et al*, 1990] in which the relative magnitudes of the effects, in terms of maximum uphill pressure decreases and their durations have been recorded over ranges of values of initial pressure as will be discussed further below.

Correlating studies also have been made in which equivalent changes of hydrogen pressures within the tubular membranes have been alternatively derived from measurements of appropriate components of electrode potential [Lewis *et al*, 1983; Sakamoto *et al*, 1991; Tong and Kandasamy, to be published].

Uphill Effect Observations with Outer Surface Hydrogen Content Changes Effected by Alterations of Contacting Gaseous Atmospheres

Studies with tubular membranes also have been carried out in which introductions into and removals of hydrogen from outer surfaces have been effected by sudden alterations (corresponding to mechanical stressing) of a surrounding gaseous atmosphere [Lewis *et al*, 1987, 1988; Kandasamy *et al*, 1990; Tong and Lewis, 1990, 1991]. Figure 3 illustrates examples of subsequent changes of internal pressure from initial quasi static values in such cases. By comparison with the ‘electrolytic’ sequences of example (Fig.2), it may be seen in the case of experiments with an initially hydrogen- containing wall, that there are additional features of initial increases of tube internal pressure following outer surface hydrogen pressure application — and decreases of internal pressure following removals of the external pressure before the respective 'uphill' periods.

From results of experiments in which argon was used as the medium of both initial and supplementary pressures, and when no hydrogen was already present in the membrane wall, purely internal tube volume changes have been discounted [Tong and Lewis, 1991; Lewis and Tong, 1992] as being solely accountable for these additional effects — which have now seemed satisfactorily attributable to further Gorsky Effect hydrogen transfers resulting from the mechanically induced strain gradients in the tube walls.

Summary of Current Information and Conclusions Concerning Origins of Uphill Effects

Recently an alternative explanation has been proposed [Mällo and Krozer, 1991] of results of a preliminary report of external pressure induced uphill effects [Lewis *et al*, 1987]. This has suggested that a Gorsky Effect explanation was of secondary importance as the explanation of initial uphill hydrogen flux into the membrane inner surface in comparison to reductions of hydrogen chemical potential due to lattice expansions at the inner surface corresponding to those produced by hydrogen entry at the outer surface. This explanation is not however in satisfactory balance with more extensive recent results [Kandasamy *et al*, 1990; Tong and Lewis, 1990, 1991; Lewis and Tong, 1992] which have now characterised the Gorsky Effect involvement in initial increases of internal pressure produced in the types of experiment illustrated in Fig.3.

In the more recently reported studies with tubular membranes, direct evidence of distensions of the tube walls (analogous to bending distortions of strips in specifically diffusion-elastic studies [Kufudakis *et al*, 1982, 1989]) have been evidenced by measurements of internal volume change (*cf.* Fig.1) deduced by a water displacement technique [Kandasamy *et al*, 1991; Tong and Lewis, to be published]. Other control experiments, in which surfaces have been temporarily deactivated, have, however, also provided evidence against the possibility that the uphill effects could be wholly attributable to such internal volume changes — and, complementarily, have emphasised the requirement of high catalytic activities of surfaces for the clearest possible exhibitions of the effects [Tong and Lewis, 1991; Kandasamy *et al*, 1991; *cf.* also Lewis *et al*, 1983; Tong and Lewis, 1990].

These more recent studies have centred around information independently derived of p-c (n)-T data relevant to the membrane compositions (so far Pd, $Pd_{81}Pt_{19}$ and $Pd_{77}Ag_{23}$) so as to be able to relate the course of observed effects to the hydrogen contents, of both the substrate wall of the membrane and of each of its surfaces. Another objective has been to utilise possibilities of interconvertibility of measurements of equilibrium hydrogen pressure and of electrode potential (*cf.* Fig.1) [Sakamoto *et al*, 1991; Bucur and Lewis, 1990]. Considerable attention has also been directed to observations of analogous converse effects of initial increases of quasi-static internal hydrogen pressures produced on removals of hydrogen from external surfaces either (*cf.* Fig.2) by anodisation [Kandasamy *et al*, 1991] or (*cf.* Fig.3) by evacuation [Kandasamy and Tong, to be published].

Experiments with both $Pd_{81}Pt_{19}$ and $Pd_{77}Ag_{23}$ alloys have shown very marked dependences of the magnitudes (maximum reduction of pressure) and durations of the uphill effects on the initial hydrogen content n (n=atomic ratio of hydrogen to metal atoms, H/Me) of the membrane. The recent studies with the $Pd_{77}Ag_{23}$ alloy have been of particular interest in view of the substantial depth of information available for the Pd/Ag/H system (Küssner, 1966; Wicke *et al*, 1978; Lewis, 1990], and the common employment of the particular $Pd_{77}Ag_{23}$ alloy composition as a hydrogen purification membrane. Experiments have so far been possible over a wide range of initial hydrogen contents n_0 at conveniently accessible pressures at temperatures close to ambient. Examples of results of such experiments with introductions of hydrogen by electrolytic cathodisation into outer surfaces of $Pd_{77}Ag_{23}$ tubular membranes are shown in Fig.4b together with p-n relationships at the same temperature in Fig.4a [Kandasamy *et al*, 1990; Tong and Lewis, 1990,1991]. It may be seen that magnitudes of the uphill effects initially increase with increasing values of n_0 but then show a decrease for the same initial conditions of reintroduction of outer surface hydrogen — although with a continued increase in the initial rate of decrease of pressure with time.

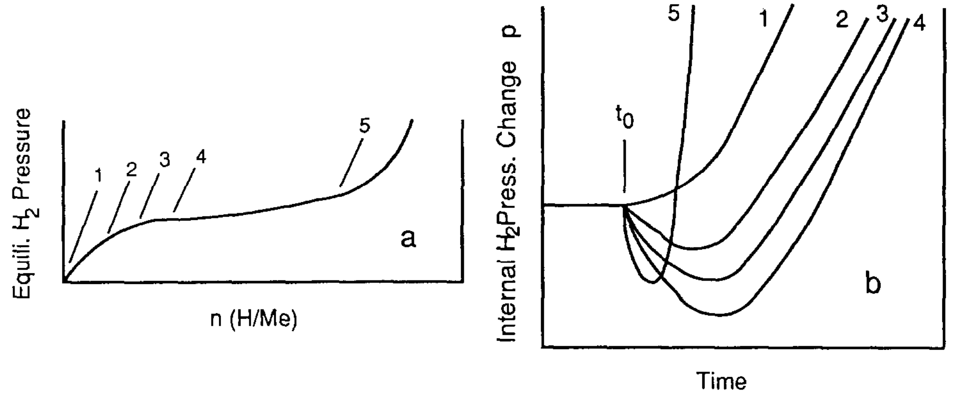

Fig. 4. Incremental changes of hydrogen pressure within a $Pd_{77}Ag_{23}$ tubular membrane following onsets of the same conditions of cathodisation at t_0 with initial quasi-static pressure p_0 for curves 1-5 in Fig.4b corresponding to the values of equilibrium pressures indicated as points 1-5 on the p-n relationship in Fig.4a

The more recent findings have confirmed that the uphill effects are dependent on the initial hydrogen content of the wall as represented by the pressure in equilibrium with the inner surface. They have also indicated in combination with the form of plots of changes of inner volume with time [Kandasamy *et al*, 1991] that the effects are dependent on the size and duration of the strain gradient developed in the course of electrolysis. Within a background of development of more quantitatively precise relationships [Kandasamy, 1988, 1989; Baranowski, 1989] the permeation rate, J_δ, across a membrane of thickness, δ, has therefore been suggested to be broadly represented by a relation of the form [Kandasamy *et al*, 1991; Sakamoto *et al*, 1991]

$$J_\delta = - D \{\text{grad } n - f(n_0, \text{grad } \varepsilon)\} \qquad (2)$$

which has the same general form as eqn.1 except that in this case the parameter of strain ε is used instead of stress σ as being more physically representative from a Gorsky Effect standpoint. This relation thus reflects a combination of diffusional processes underlying the main features of the effects illustrated in Figs.2 and 4 and analogous data obtained with $Pd_{81}Pt_{19}$ alloys [Baranowski and Lewis, 1989; Kandasamy *et al*, 1991]. As examples, diagrammatic representations are shown in Fig.5 of stages of changes of profiles of hydrogen content n across the thickness δ of a membrane wall (containing an initial hydrogen content n_0 at t_0(b)) following further introductions of hydrogen at the outer surface — complementary with the alterations of internal hydrogen pressure indicated in Fig.2 at times t_1(b), t_2(b) and t_3(c). Thus for times t_1(b) and t_2(b) in Figs.2 and 5, initial increases of hydrogen content within the outer half of the cross section produce elastic bending corresponding to a continuously altering Diffusion-Elastic strain gradient (Kufudakis *et al*, 1982; Kandasamy *et al*, 1991). This strain gradient, in turn, will engender a Gorsky Effect transfer of hydrogen (Čermák *et al*, 1985) from regions of the wall near the <u>inner</u> surface, to an extent dependent on n_0, and a corresponding thermodynamically equilibrating reduction of hydrogen pressure within a tubular membrane (Lewis *et al*, 1983,1989; Kandasamy *et al*, 1991). The strain gradient contribution due to the extent of bending will however begin to decrease as the concentration gradient driven hydrogen increasingly enters the inner half of the tube wall cross section and finally the breakthrough of the concentration gradient driven diffusion front will lead to an overall positive downhill hydrogen permeation by time t_3(b) in Fig.2. The existence of a continued non-linear concentration gradient shown for t_3(b) in Fig.5 in the final steady state, corresponding with a complementary residual strain gradient, has been indicated by an initial increased rate of pressure change, on reduction of this gradient by interruption of electrolysis [Kandasamy *et al*, 1991, and to be published].

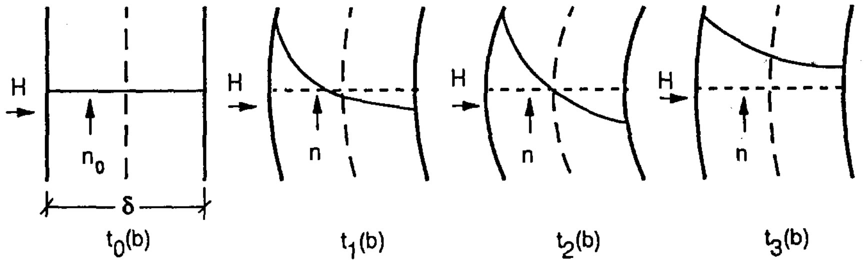

Fig. 5. Hydrogen concentration profiles across sections of the wall of a membrane containing a hydrogen content $n_0 > 0$ corresponding to indicated stages of pressure-time plots in Fig.2

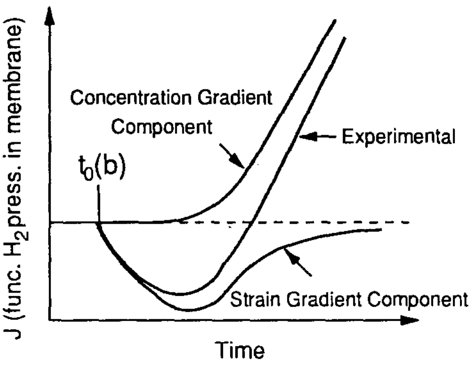

Fig. 6. Estimated separate contributions complementary with Fig.5 of components corresponding to terms in eqn.2 to pressure changes following t_0(b) in Fig.2

Separate and combined time dependent concentration gradient and strain gradient contributions to the actual measured incremental changes of hydrogen pressure within a tubular membrane, over the sequence of changes outlined above, are represented in Fig.6.

SOME GENERAL CONCLUSIONS AND PROPOSITIONS CONCERNING THE ROLE OF GORSKY EFFECTS IN PROCESSES OF HYDROGEN DIFFUSION AND PERMEATION

In broad accordance with applicabilities of relationships of the forms of eqns. 1 and 2 — more recent experimental studies concerning permeations of volume-expanding interstitials such as hydrogen, have increasingly emphasised the probabilities of Gorsky Effect migrations in response to the strain gradients of lattice expansion produced in conjunction with the conjoint developments of concentration gradients.

The form of eqns.1 and 2 provide broad indications of how magnitudes of Gorsky Effects can be expected to relate to the experimental factors of concentration of interstitials, strain gradients and diffusion coefficients. It is to be appreciated however that less easily defined factors such as specimen geometry, lattice defects and catalytic activities of surfaces can have equally important relevance. Recently reported experiments also have indicated probabilities that following impositions of mechanical stress, subsequent Gorsky Effect migrations of lattice-expanding hydrogen can produce additional extensions of the concentration gradient differences created mechanically [Tong and Lewis, 1991].

However, under conditions of developments of concentration gradients by hydrogen entry (or exit) through surfaces of membranes, complementary Diffusion-Elastic strain-gradient-induced Gorsky Effect transfers of hydrogen will operate in directions opposed to the concentration gradient driven flux as outlined above. The observed temporary uphill permeation effects (in open systems with surfaces sufficiently catalytically active for measurements of surface hydrogen contents to be diagnostic of processes taking place within the solid membrane) — could now seem to be reliably assessed as providing particularly direct evidence of Gorsky Effect operation.

An increased understanding of interrelationships which can exist between diffusional processes in the solid substrate in conjunction with appropriate considerations of surface activation procedures and a knowledge of the hydrogen pressure-composition (p-n) relationships of the material of the membrane such as palladium and palladium alloys have thus now provided possibilities of a range of experimental variables in studies of open surface systems by alternative methods and controls of hydrogen introductions and removals, under conditions of both physically and chemically produced stressing [Li, 1978; Baranowski, 1989].

From the standpoint of determinations of hydrogen diffusion coefficients, D_H, in metal/hydrogen systems — it now seems a clear possibility that Diffusion-Elastic effect induced prolongation of Gorsky Effect related relaxation processes could have an important influence in regard to uncertainties [Völkl and Alefeld, 1976, 1979] in measurements of D_H obtained by anelastic techniques over ranges of hydrogen content adjacent to regions of phase transition. It has also been recognized [Lewis et al, 1983, 1988; Sakamoto *et al*, 1991] in regard to values of D_H obtained from estimations of 'breakthrough times' derived from experimental results of the types illustrated in Figs.2 and 3 — that extensions of the actual breakthrough times as consequences of uphill effects can result in calculations of misleadingly low values of D_H over regions of onset and criticality with respect to phase transitions, which can, in turn, lead to misleading trends of changes of D_H with hydrogen content.

From a technological viewpoint, considerations of these factors can have bearing on the most appropriate modes of operation of diffusion membranes utilised for hydrogen purification and allied purposes [Gryaznov, 1986] in regard for example to choices of temperature and pressure differentials. A still more widely important technical outcome of lattice strain gradient induced Gorsky Effects, could be in regard to the problems of hydrogen embrittlement, where localised accumulations of hydrogen around dislocations and other defects can induce further 'uphill gettering' of hydrogen from regions of an even very low hydrogen content matrix [Wipf, 1976] and produce incipient conditions of fracture initiation and progression [Daw and Baskes, 1984; Lewis, 1990].

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