

The "Uphill" Diffusion of Hydrogen

STRAIN-GRADIENT-INDUCED EFFECTS IN PALLADIUM ALLOY MEMBRANES

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Certain unexpected effects observed during developments and reductions of pressures of hydrogen gas inside tubular membranes of palladium alloys now seem to be self-consistently interpretable in terms of lattice-strain-induced temporary "uphill" hydrogen diffusion processes.

There has been increasing appreciation over recent years of the importance of the studies reported by Gorsky in the 1930s concerning the influences of strain gradients on the processes of diffusion in metals (1-3). These strain gradients can, for example, be produced by mechanical bending. As a particular case of strain induced diffusion, evidence has been obtained from anelastic effects—such as elastic after effects and internal friction—that hydrogen contained in interstitial lattice sites can, as a consequence of bending deformations, preferentially diffuse from regions of relatively compressed interstitial sites, to regions of relatively expanded lattice sites.

Diffusion-Elastic Effects

As an alternative origin to mechanical stressing, elastic deformation of metal specimens can result from inhomogeneously distributed regions of lattice expansion and contraction. Thus, for example, bendings of specimens can be attributed to preferentially higher levels of hydrogen occupation of the available interstitial positions within one of the halves of the thickness of sheets, or the walls of tubes, when these are acting as hydrogen diffusion membranes (4, 5).

Such bending effects originating from interstitial incorporation and diffusion of hydrogen have been classified as Diffusion-Elastic effects (4, 5). They are allied to the strain effects resulting from surface deposition processes which were originally noted by

Stoney and reported some eighty years ago (6).

Diffusion-Elastic effects have been studied as a means of determining hydrogen diffusion coefficients in several metals and alloys, including platinum, palladium and the palladium-platinum series of alloys (4, 5).

Over the past two decades the measurements of anelastic processes such as elastic after-effects and internal friction (elastic energy dissipation) associated with the Gorsky Effect have also been utilised to determine values of hydrogen diffusion coefficients in metals and alloys (2, 3) including (7) the alloy composition Pd₇₇Ag₂₃, widely utilised commercially for hydrogen diffusion membranes (8-10). Problems of the occurrence of simultaneous inducement of Gorsky Effects in the course of measurements of hydrogen diffusion coefficients by the Diffusion-Elastic technique have recently been discussed (5).

Concentration Gradient Opposed Effects

Latterly, effects that were initially somewhat unexpected have been observed in the course of studies of developments and reductions of hydrogen gas pressures within tubular shaped membranes of certain palladium alloys at temperatures of 0 to 50°C; these would now seem to have their origins in combinations of Gorsky and Diffusion-Elastic Effects (11-13).

Two alloy compositions have been studied to date, these being Pd₈₁Pt₁₉ from the palladium-platinum series (11, 13) and Pd₇₇Ag₂₃ from the

widely studied palladium-silver series (14).

These particular compositions from the palladium-platinum and palladium-silver alloy series, respectively, correspond to contents of the alloying element (platinum or silver) near those for which critical* temperatures $T_c(\alpha, \beta)$ —of isothermal (p - n) relationships between equilibrium hydrogen pressure p and hydrogen content n (atomic ratio of hydrogen to metal atoms)—have been reduced to about 25°C from a value close to 300°C in the case of the pure palladium-hydrogen system (15, 16).

Preparatory to observations of the effects, initial conditions of virtually constant pressures of hydrogen gas were established within the tubular membrane—and this hydrogen gas was in equilibrium with the evenly distributed hydrogen contents of the tube wall.

A subsequent increase of the hydrogen content of the outer surface of the wall by electrolytic cathodisation, corresponding, for example, to A in Figure 1, has been found to produce the originally somewhat surprising results of initial decreases of the hydrogen pressure within the tube. Conversely, sudden decreases of the hydrogen content of the outer surface of the wall of the tube have been found to produce initial increases of the hydrogen pressure in the tube. Very importantly however, such effects were so small that they were hardly perceptible **unless** the surface of the inner wall of the tube was highly catalytically active for equilibration with the hydrogen gas contained within the tube. Experiments have indicated that such a sufficiently high surface activity could be satisfactorily achieved by electrolytically coating the inner wall of the tube with palladium black (11-14).

The causes of the respective effects have been identified (11-14) with outward bendings of

*The critical temperature $T_c(\alpha, \beta)$ corresponds to the lowest temperature at which courses of absorptions and desorptions of hydrogen do not, in principle, involve regions of hydrogen concentration over which there is hysteresis of pressure-composition and other relationships associated with $\alpha \rightleftharpoons \beta$ phase transitions and accompanying deformation effects (12, 15, 16).

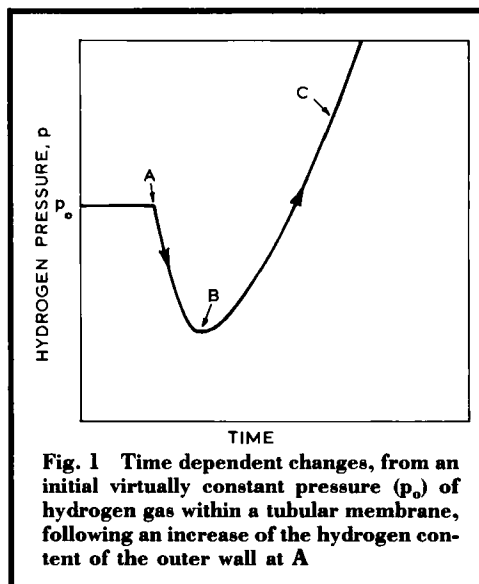


Fig. 1 Time dependent changes, from an initial virtually constant pressure (p_0) of hydrogen gas within a tubular membrane, following an increase of the hydrogen content of the outer wall at A

the tube wall resulting from expansions of the outer part of the tube wall produced by absorption of hydrogen as illustrated diagrammatically in Figure 2—and with inward bendings produced on hydrogen removal, by electrolytic anodisation, from the outer wall. The condition of outward bending of the wall of the tube produces a Gorsky Effect diffusion of hydrogen from within regions close to the inner wall towards the outer wall, as indicated in Figure 3. It has been a general finding that the relative magnitudes of the effects are related to the

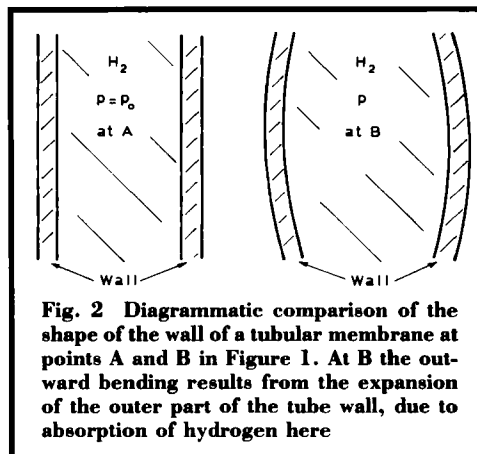


Fig. 2 Diagrammatic comparison of the shape of the wall of a tubular membrane at points A and B in Figure 1. At B the outward bending results from the expansion of the outer part of the tube wall, due to absorption of hydrogen here

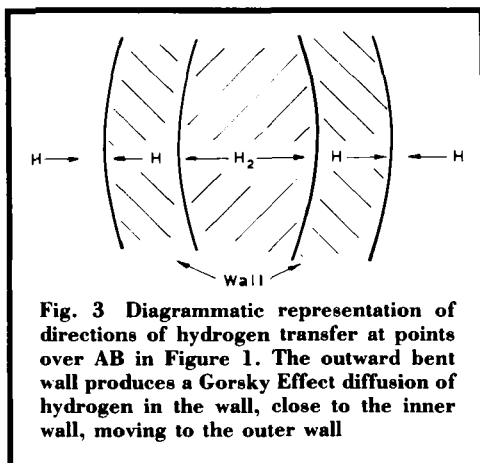


Fig. 3 Diagrammatic representation of directions of hydrogen transfer at points over AB in Figure 1. The outward bent wall produces a Gorsky Effect diffusion of hydrogen in the wall, close to the inner wall, moving to the outer wall

initial hydrogen content, as may be calculated in situ from the known forms of the p-n relationships of the particular alloys (11, 14).

Changes of Tube Volume

Of course bendings of the tube wall also produce changes of the total internal volume of the tube and associated "dead space". However direct measurements of actual volume changes in complementary water displacement studies (14) have shown equivalent calculated changes

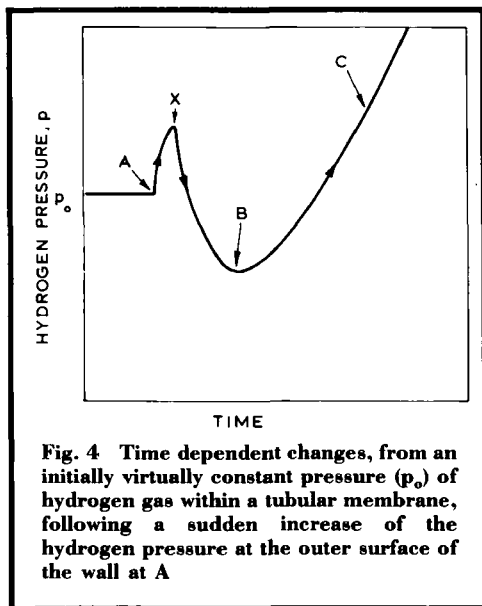


Fig. 4 Time dependent changes, from an initially virtually constant pressure (p_0) of hydrogen gas within a tubular membrane, following a sudden increase of the hydrogen pressure at the outer surface of the wall at A

of pressure to be very much smaller than the observed pressure changes, for similar hydrogen contents of the tube wall and with highly catalytically-active inner surfaces of the wall. Such pressure changes, calculated from the actual volume changes, are more in keeping with the limited pressure changes observed when the inner surface of the wall is only poorly active for the hydrogen gas pressure to be in step with changes of the chemical potential on the inner wall—as reflected both by values of hydrogen pressures in contact with active surfaces and by electrode potential measurements (11, 14). Also it has been found from water displacement studies that minima in pressure-time relationships, such as at B in Figure 1, do not correspond precisely to maximum extents of bending, which usually continue to increase over regions such as BC in Figure 1.

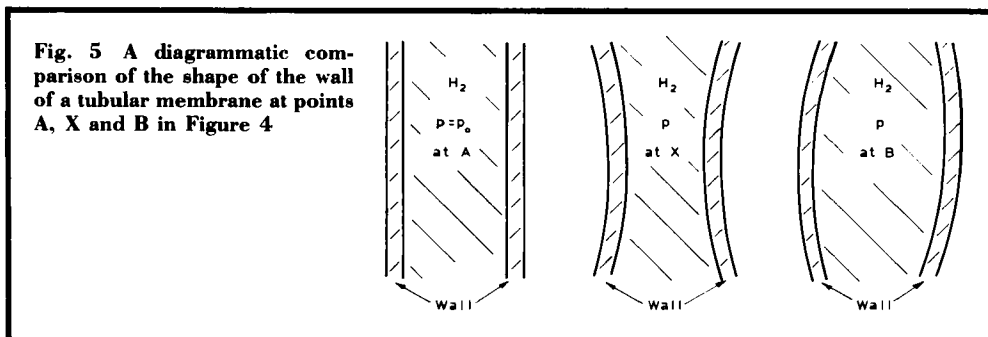
Effects of Outer Wall Changes of Hydrogen Pressure

As already mentioned above, the form of the initial changes of hydrogen pressure with time in Figure 1 is characteristic of the effects recorded when the hydrogen content at the outer surface of the tubes has been increased by electrolytic cathodisation.

However alterations of the hydrogen content of the outer surface of the wall also can be the result of an increase in hydrogen pressure at catalytically active outer surfaces.

In such cases an additional effect has been observed (13, 14) of rapid time dependent increases of pressure within the tube as represented for example by AX in Figure 4.

Comparisons of results of complementary experiments, in which the effects of analogous changes of pressure on both inner and outer surfaces of the tube wall were studied with argon in place of hydrogen, have again shown that pressure changes resulting solely from volume changes are too small to account for the magnitudes of pressure changes, such as over AX, recorded with highly catalytically active palladium-black-coated inner and outer wall surfaces. Therefore such latter effects have again seemed to be established as having an



essentially similar explanation in terms of strain-induced hydrogen diffusion processes.

In these cases the force of the initial increase of pressure is responsible for an inward bending of the tube wall, illustrated diagrammatically in Figure 5, which will induce a Gorsky Effect transport of hydrogen within the wall, from regions near the outer surface towards regions near the inner surface. The accompanying increases of hydrogen content and hydrogen chemical potential at the inner surface will be reflected in a compensating overall transfer of hydrogen to the gas phase and a complementary increase of pressure. Subsequently, however, as absorption of hydrogen into the outer wall proceeds, this again produces an expansion of volume which gradually reverses the direction of bending of the wall and leads to a similar sequence of events and explanations over X, B, C, in Figure 4 as those referring to the sequence A, B, C in Figure 1 described above.

Some Implications of the Studies

Explanations in terms of Gorsky and Diffusion-Elastic Effect strain-induced diffusion processes would appear not only to be consistent with the more recently examined effects in the temperature range 0 to 50°C, but also to be relevant to the interpretation of some earlier observations with palladium bielectrodes (17) and tubular gas diffusion membranes (18) at higher temperatures and pressures, which were reported before the possibilities of significant strain induced influences were as widely appreciated. A further important consequence of the recognition of the influences of these uphill

hydrogen diffusion effects is an appreciation that their existence can lead to marked prolongations (11-14) of the adoptions of quasi-steady-state rates of hydrogen permeation through membranes—and so to significant errors in calculations of hydrogen diffusion coefficients from estimates of breakthrough times made from these measurements. Such errors can then in turn give rise to rather important discordancies in trends of relationships between hydrogen diffusion coefficients and hydrogen contents (7, 11-19). For example in the case of the Pd₇₇Ag₂₃ alloy, there have been experimental indications (17) of initial decreases of hydrogen diffusion coefficient, D, with increasing hydrogen content, n, rather than continuous increases of D with n which the uphill diffusion effects (11-14) would now seem to suggest to be a stronger possibility. From a thermodynamic standpoint an interesting aspect of the recent studies has been the findings that the lattice strain effects would appear to be responsible not only for uphill diffusion against overall hydrogen concentration gradients but also against overall gradients of hydrogen chemical potential (11, 12, 14).

Acknowledgements

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References

- 1 W. S. Gorsky, *Phys. Z. Sowjetunion*, 1935, **8**, 457
- 2 J. Völkl and G. Alefeld, *Z. Phys. Chem. Neue Folge*, 1979, **114**, 123
- 3 F. M. Mazzolai, *Op. cit.*, (Ref. 2), 1985, **145**, 199
- 4 A. Kufudakis, J. Čermák and F. A. Lewis, *Surf. Technol.*, 1982, **16**, 59
- 5 J. Čermák, G. Gardarská, A. Kufudakis and P. Lejček, *Op. cit.*, (Ref. 2), 1985, **145**, 239
- 6 G. G. Stoney, *Proc. R. Soc., London*, 1909, **82**, 172
- 7 F. M. Mazzolai, M. Nuovo and F. A. Lewis, *Scr. Metall.*, 1975, **9**, 617
- 8 A. G. Knapton, *Platinum Metals Rev.*, 1977, **21**, (2), 44
- 9 G. J. Grashoff, C. E. Pilkington and C. W. Corti, *Platinum Metals Rev.*, 1983, **27**, (4), 157
- 10 J. E. Philpott, *Platinum Metals Rev.*, 1985, **29**, (1), 12
- 11 F. A. Lewis, J. P. Magennis, S. G. McKee and P. J. M. Ssebuwufu, *Nature*, 1983, **306**, 673
- 12 F. A. Lewis, *Op. cit.*, (Ref. 2), 1985, **146**, 171
- 13 F. A. Lewis, B. Baranowski and K. Kandasamy, *J. Less-Common Met.*, 1987, **134**, L27
- 14 K. Kandasamy and F. A. Lewis, to be published
- 15 E. Wicke, H. Brodowsky and H. Züchner, *Top. Appl. Phys.*, 1978, **29**, 73
- 16 F. A. Lewis, *Platinum Metals Rev.*, 1982, **26**, (3), 121
- 17 A. Küssner, *Z. Naturforsch. A*, 1966, **21**, (4), 515
- 18 R. G. Hickman, *J. Less-Common Met.*, 1969, **19**, (4), 369
- 19 M. Nuovo, F. M. Mazzolai and F. A. Lewis, *J. Less-Common Met.*, 1976, **49**, (1, 2), 37

Temperature Measurement Conference

Over one hundred delegates from some fifteen countries attended the third international symposium on Thermal and Temperature Measurement in Science and Industry, sponsored by the Institute of Measurement and Control and the International Measurement Confederation (IMEKO), which was held in Sheffield during September, 1987. This triennial event attracted speakers from national research organisations and major industrial companies. The conference began with a keynote lecture by Dr. T. J. Quinn, Deputy Director of the Bureau International des Poids et Mesures, on the International Temperature Scale. This paper first reviewed the history of the topic, then it outlined the proposals of the Conférence Générale des Poids et Mesures (CGPM) for the new scale, ITS-90, which is expected to be adopted worldwide in 1990 or 1991. The major proposal is that ITS-90 should be defined in terms of platinum resistance thermometry from -272.65°C (half a degree above absolute zero) to the silver point, 961.93°C , and in terms of radiation pyrometry above this temperature. Values for the various fixed (temperature) points, such as the freezing point of tin, silver, gold and platinum, will be modified in keeping with recent advances made in their accurate determination.

Progress on the determination of some of the thermodynamic temperatures of the fixed points, especially in the cryogenic range, was reported in detail. Some temperature determinations near absolute zero were described; for example the melting point of helium and the triple point of deuterium were established using techniques such as rhodium-iron resistance

thermometry and electrical radio-frequency noise thermometry. This last method utilises superconductive quantum interference devices (SQUID's). Papers on high temperature determinations were concerned mainly with radiation pyrometric methods and emissivity values, the source of their largest error.

Practical temperature measurement and heat-flows were also discussed. Measurements made in hostile environments, such as those found in industrial combustion chambers, showed that the robustness and simplicity of thermocouples made them difficult to improve upon. Acoustic methods are being developed for use in dusty and corrosive environments, and results are reproducible enough for commercial exploitation to be considered for the future. Single-crystal fibre optic devices incorporating an iridium coated tip have been evaluated industrially, and gave accurate readings provided there was no contamination of the fibre surface. A novel method of measurement by a laser technique known as coherent anti-Stokes Raman spectroscopy (CARS) was described, but at present the accuracy is insufficient for it to be considered as a practical alternative to other methods of temperature measurement. The great reliance of these newer products on microprocessor technology brought out a point of relative accuracy; random and systematic errors in the measurement system may erode the improved resolution of temperature which would otherwise be achieved.

The conference papers showed that the platinum metals continue to play a vital role in the field of temperature and thermal measurement.

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