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# Consequences of lattice expansive strain gradients on hydrogen loading in palladium

A. De Ninno and V. Violante
*ENEA/ERG/FUS, Centro Ricerche Energia Frascati-C.P. 65, 00044 Frascati, Roma, Italy*

A. La Barbera
*ENEA/INN/NUMA, Centro Ricerche Energia Casaccia, Roma, Italy*

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Hydrogen dissolves in metals by occupying interstitial positions and expanding the lattice. It follows that a stress field is generated by the loading process itself. The aim of this paper is to discuss, on the basis of experimental results, whether the stress field is responsible for the force which limits the attainment of high concentrations of hydrogen in massive palladium samples. A calculation of the H/Pd concentration shows that stress-field relaxation aids the hydrogen uptake and our experimental results show that a suitable loading path can improve the final loading ratio. [S0163-1829(97)04329-4]

## I. INTRODUCTION

The Gorsky effect, whose first formulation dates from 1935, is the migration of interstitials in a metal when an external bending is applied to a sample.[1] The deformation field causes the defects to move toward expanded areas, setting up a concentration gradient that causes an additional time-dependent strain. Moreover, the possibility that a self-induced strain field can be generated by the diffusion gradient inside the metal without any external bending has been discussed by Lewis in 1983.[2,3] Lewis and co-workers showed that internal stresses are generated during the insertion and diffusion of hydrogen interstitials and that the consequent strain development results in a force opposing the flux generated by diffusion. They observed a counter-gradient hydrogen flux in a membrane under cathodic discharge.[4] This effect was related to the initial hydrogen content of the membrane, and on the size and the duration of the strain gradient developed during the electrolysis.

During an isothermal loading process, the mobile solute gradient inside the metal is driven by a thermodynamic force, influenced by all the force fields that can affect the free energy of the solute. The diffusion flux is described by the general equation

$$J = -M \cdot c \cdot \mathrm{grad}\mu, \tag{1}$$

where $c$ is the hydrogen concentration, $M$ the mobility [related to $D$, the diffusion coefficient by the Einstein relation $D = c(\partial\mu/\partial c)M$], and $\mu$ is the chemical potential. The stress induced by the hydrogen diffusive flux will cause an inhomogeneous distribution of the solute. Equation (1) will be, in this case,

$$J = -D\left(\nabla c - \frac{c\overline{V}}{RT}\nabla\sigma\right), \tag{2}$$

where $\overline{V}$ is the molar volume of hydrogen in the metal and $\sigma$ the stress field. Kandasamy[5] showed that a suitable strain can stop the diffusion of hydrogen driven by the concentration gradient.

The adsorption isotherms for hydrogen in palladium show that, at room temperature and for a concentration above $c = 0.008$ H/Pd atoms, an $\alpha$ phase with low hydrogen content and an expanded, hydrogen-rich, $\beta$ phase coexist in a solid solution up to a concentration of $c = 0.607$. It is well known that during loading expanded $\beta$ areas grow near the $\alpha$ areas. X-ray measurements[6] show the growth of $\beta$-diffraction peaks near $\alpha$ peaks. In this region of coexistence very strong deformation fields are generated at the border between the two phases, due to the different lattice parameters. This process is highly irreversible because of the energy dissipation involved in the generation of dislocations. The $\alpha$-$\beta$ coexistence region has, in fact, been associated with the hysteretic behavior in the $p,c,T$ diagram.[7] If internal stresses can be removed either by plastic deformation or by dislocation motion, such a stress-free strained crystal will be denoted ''incoherent.'' In the opposite case a deformation field will be associated with the strain and the crystal will be denoted ''coherent.'' The energy related to a structural configuration in the $\alpha$-$\beta$ domain will be very different in the ''coherent'' or ''incoherent'' case. The actual crystal will be a mixture of the two cases depending on the initial metallurgical state.

Calculations performed for a cylindrical geometry for cathodic charging of hydrogen in palladium show that the maximum shear stress is obtained on the surface at the beginning of the diffusion process. The effect of gradient stress is not trivial. From Eq. (2) it follows that a zero flux requires $\Delta\sigma/\Delta c = RT/c\overline{V}$; and for $c = c_0$ it follows that the minimum strain field value is $\Delta\sigma = RT/\overline{V} = 1.49$ GPa at room temperature ($\overline{V} = 1.68$ cm$^3$/mol). This value is comparable to the yield strength of the metal, i.e., to the threshold above which plastic deformation occurs (see Table I) and is less than the strain near a dislocation. Thus, the loading path is very important to design the concentration profile inside the metal. If special care is used during the electrochemical loading the maximum ratio will be at least the minimum $\beta$-phase value even if high current densities are used.[6]

## II. HYDROGEN LOADING IN PALLADIUM: EXPERIMENTAL RESULTS

The crossing of the coexistence phase allows strain gradient growth and the addition of stress energy to the system.

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TABLE I. The measured yield stress for palladium hydride.

| | | Yield stress 0.02% (MPa) | Young modulus (GPa) |
|---|---|---|---|
| Cold worked | Sample 1 $c=0.712$ | 270±1 | 132.1±6.9 |
| | Sample 2 $c=0.628$ | 278±1 | 125.2±5.1 |
| Temperature treated (1000 °C) | Sample 1 $c=0.697$ | 150±1 | 105.2±14.7 |
| | Sample 2 $c=0.50$ | 145±1 | 107.4±5.6 |
| Temperature treated (1000 °C) Precharged in $H_2$ | Sample 1 $c=0.718$ | 99±1 | 102.4±19.4 |
| | Sample 2 $c=0.712$ | 104.±1 | 111.3±2.3 |

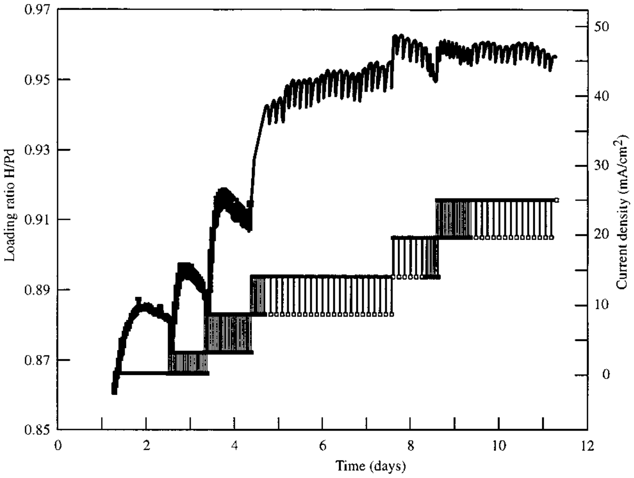

FIG. 2. A further increase in the concentration value is obtained allowing the lattice to relax the stored stress fields temporarily decreasing the electrochemical action on the electrode surface.

The phase transition is, in this sense, irreversible and not reproducible from the experimental standpoint. A gradual reduction of such irreversibility through the reduction of the hysteresis loop in the $p$-$c$-$T$ curve is obtained by increasing the temperature up to the critical value $T_c=310$ °C.

Palladium 14×10 mm sheets 150 $\mu$m thick were subjected to cathodic discharge in the LiOH solution. The hydrogen concentration was monitored by measuring the variation of electrical resistance with a lock-in amplifier based system. The ratio $R(c)/R(c=0)$ (denoted in the following as $R/R_0$) is related to the concentration $c$,[8,9] so it is possible to follow the concentration in real time during the electrolysis. Samples were temperature treated in vacuum for 30 min at 900 °C. We compare the maximum loading reached for two different procedures: (a) the sheet was charged in electrolysis; (b) the sheet was precharged in $H_2$ gas. The loading procedure for the precharged samples is the following: the palladium sheets were heated to 400 °C under vacuum and then a hydrogen pressure of 40 atm was set up. A very slow cooling to room temperature, keeping the pressure constant, was performed and, after a suitable time, the vessel was evacuated. This path allows one to circumvent the coexistence phase and avoid the growth of a high stress field at the border of the $\alpha$-$\beta$ phases. The comparison of the experimental results (Fig. 1) shows that higher loading ratios are reached in the latter case (see figure caption). This result allows us to conclude that the existance of an high stress field in the lattice increases the difficulty in obtaining high concentrations.

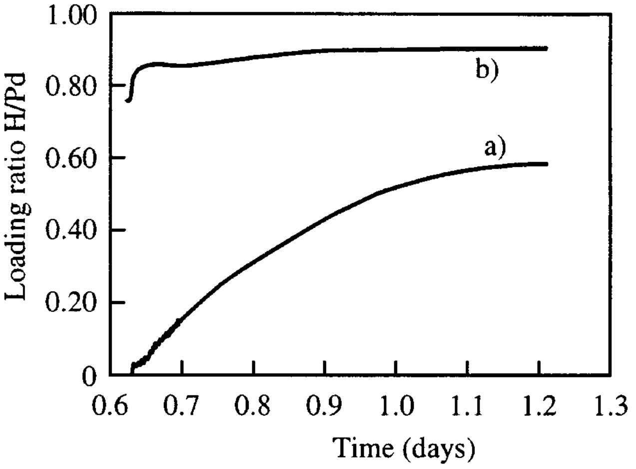

FIG. 1. Concentration behavior vs time. (a) Pd sheet charged in electrolysis, $I=10$ mA. (b) Pd sheet precharged in $H_2$ gas and then in electrolysis with $I=10$ mA.

A further increase of the concentration can be reached if the stress is allowed to relax. In Fig. 2 it can be observed that changing the current level between two values causes the loading ratio to increase. Moreover, the yield stress value can also influence the loading dynamics: the relaxation of stresses through plastic deformation can remove incoherent states, as defined above. We measured the yield stress for palladium hydride as shown in Table I. Samples were rods 4 mm in diameter and 100 mm in length. Those subjected to the precharging procedure showed 50% lower yield stress. Higher values were obtained for cold worked samples, where the dislocation number is higher: the high number of dislocations strongly decreases the sample plasticity. We also observed experimentally (Fig. 3) an ondulatory behavior of the average concentration in massive samples in an advanced $\beta$-phase. The oscillations occur spontaneously even if the experimental parameters are unchanged. The period of these oscillations does not seem to correlate with any electrolytical parameter. In the next paragraph we will show that this phenomenon can be related to sample plasticity and its ability to relax mechanical stresses.

## III. STRESS FIELD EFFECT EVALUATION: A SOLUTION FOR THE DIFFUSIVE FLUX

Diffusion under isothermal conditions is a flux generated by a thermodynamic force producing a bias on the random walk of particles. Let $\mu$ be the chemical potential of the diffusing solute: the thermodynamic force producing the flux is grad $\mu$ [Eq. (1)]. The chemical potential of the hydrogen isotopes in a metal lattice (e.g., palladium) is composed of several contributions: concentration, electronic, configura-

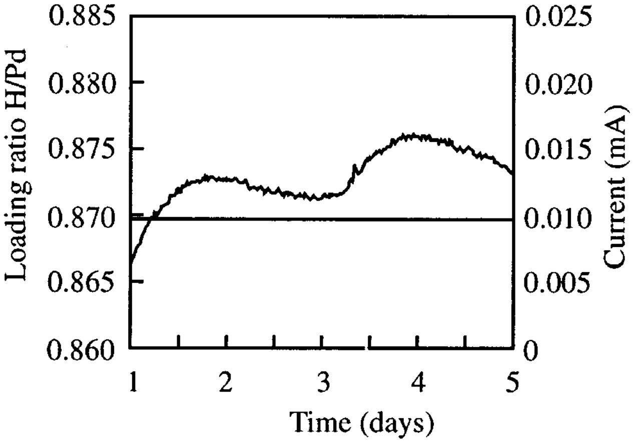

FIG. 3. Spontaneous oscillation of the electrode concentration observed for a fixed ($I = 10$ mA) value of the current.

tional. However, such a thermodynamic function is modified by all the force fields that can modify the free energy of the solute itself.

The unrelaxed stress, due to the lattice expansion during hydrogen loading in palladium, represents the dominant force field modifying the solute chemical potential. The effect of strain on the chemical potential of an interstitial solute is approximately related to the chemical potential $\mu(0)$ of the solute at the same concentration in a zero stress body as

$$\mu = \mu(0) - \overline{V}\sigma_h, \tag{3}$$

where $\overline{V}$ is the partial molar volume of the solute and $\sigma_h$ is the trace of the stress tensor. Here we are interested in having an approximate evaluation of the stress field effect on the equilibrium value of the loading ratio $\overline{C} = D(H)/Pd$ obtained in palladium membrane cathodes under electrolysis in order to have a better understanding of the experimental results. As mentioned above, the hydrogen diffusion can generate stress due to the concentration gradient, however, a fraction of such a stress is relaxed by the deformation of the body, therefore if $\eta$ is the fraction of the relaxed stress the constitutive flux equation (2) can be rewritten as

$$J = -D\left(\mathrm{grad}C - (1-\eta)\,\frac{CV}{RT}\,\mathrm{grad}\sigma_h\right). \tag{4}$$

Equation (4) leads to the following mass balance equation for hydrogen diffusing through the palladium membrane for non-steady-state conditions:

$$\frac{\partial C}{\partial t} = D\,\frac{\partial^2 C}{\partial x^2} - (1-\eta)\,\frac{D\overline{V}}{RT}\,\frac{\partial C}{\partial x}\,\frac{\partial \sigma_h}{\partial x} - (1-\eta)\,\frac{D\overline{V}}{RT}\,C\,\frac{\partial^2 \sigma_h}{\partial x^2}. \tag{5}$$

The trace of the stress tensor can be approximated by the stress ($\sigma$)-strain ($\varepsilon$) relationship:[10]

$$\sigma(\overline{C}) = E\varepsilon(\overline{C}), \tag{6}$$

where $E$ is Young's modulus ($\cong 1.15 \times 10^6$ Kg/cm$^2$ for Pd).

If we assume a homogeneous initial concentration of the $\beta$-phase ($\overline{C} \cong 0.7$), obtained, for instance, with the gas-loading technique described above, we can use the Schirer-Morosin[10] relationship to obtain an approximate correlation between the strain and loading ratio:

$$\varepsilon(\overline{C}) = [1 + 0.044(\overline{C} - C_\beta)]. \tag{7}$$

Substituting Eqs. (6) and (7) into Eq. (4) and by introducing the dimensionless quantities

$$\overline{C} = \frac{C}{C_0}, \quad \overline{x} = \frac{x}{L}, \quad \tau = \frac{L^2}{D}, \quad \overline{\sigma} = \frac{\sigma_h}{RT/\overline{V}}, \tag{8}$$

where $C_0$ is the palladium atom concentration and $L$ the membrane thickness, it follows that

$$\frac{\partial \overline{C}}{\partial \tau} = \frac{\partial^2 \overline{C}}{\partial x^2} - (1-\eta)\,\frac{\overline{V}}{RT}\,0.0044E\left(\frac{\partial \overline{C}}{\partial \overline{x}}\right)^2 - (1-\eta)\,\frac{\overline{V}}{RT}\,0.044E\overline{C}\,\frac{\partial^2 \overline{C}}{\partial \overline{x}^2}. \tag{9}$$

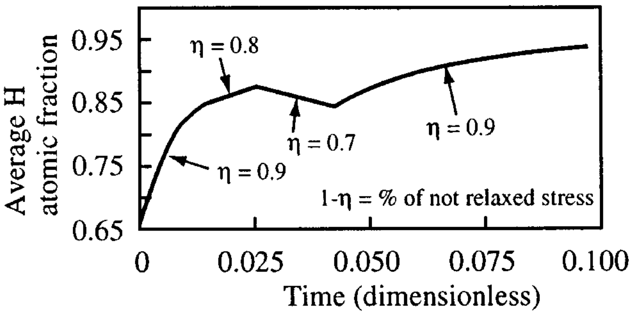

FIG. 4. Stress field effect on $H$ loading in palladium. $\eta$ is the percentage of relaxed stress.

Equation (9) describes the hydrogen concentration evolution taking into account the stress field induced by the hydrogen concentration gradient.

Figure 4 shows the effect of the stress relaxation on the average concentration. It has been obtained by solving Eq. (9) assuming a percentage of relaxed stress ranging from 70 to 90 %. The spontaneous oscillations of the concentration that we observed in several samples with constant electrolysis conditions (cf. Fig 3) are well reproduced assuming that only a fraction of the stresses stored during the loading procedure is relaxed because of the metallurgical state of the palladium.

## IV. CONCLUSIONS

The experimental data analysis shows that the self-induced strain field arising from very steep concentration gradients can be responsible for the well-known difficulty in obtaining reproducible high loading samples. Several authors have reported the difficulty in maintaining a loaded sample for long times in electrolysis at high concentrations. We saw in Eq. (2) that, when the stress field force term is added to the linear diffusive term a counter-gradient force arises moving the solute toward the high concentration surface of the electrodes thus balancing the gradient itself. Furthermore, possible damage induced by the loading process itself can modify the material during the experiment in an unpredictable way, resulting in poor reproducibility. We have observed experimentally that a different loading process can improve the final ratio.

Preliminary measurements on the yield stress also show that there is a connection between the loading procedure and the sample plasticity (Table I). The experimental results lead one to believe that the removal of the self-strain allows one to obtain, in a reproducible way, a very high (close to $c=1$) loading of hydrogen in palladium, with an electrolytical procedure even with very low current density at room temperature. Our computer simulations have shown that stress field relaxation favors the loading. Our difficulty in keeping high loading for long times is due to the change in the percentage of relaxed stresses. Thus it is essential to characterize the palladium before each loading cycle to determine the metallurgical parameter values compatible with achieving and maintaining high loading ratios.

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[1] H. Wipf, J. Less-Common Met. **49**, 291 (1976).

[2] F. A. Lewis, J. P. Magennis, S. G. McKee, and P. J. M. Ssebuwufu, Nature (London) **306**, 673 (1983).

[3] F. A. Lewis, B. Baranowski, and K. Kandasamy, J. Less-Common Met. **134**, L27 (1987).

[4] F. A. Lewis, X.q. Tong, K. Kandasamy, R. V. Bucur, and Y. Sakamoto, Electrochim. Acta **218**, 57 (1993).

[5] K. Kandasamy, Int. J. Hydrogen Energy **20**, 455 (1995).

[6] R. Felici, L. Bertalot, A. De Ninno, A. La Barbera, and V. Violante, Rev. Sci. Instrum. **66**, 3344 (1995).

[7] F. A. Lewis, Int. J. Hydrogen Energy **20**, 587 (1995).

[8] A. W. Szafranski, B. Baranowski, Phys. Status Solidi A **9**, 435 (1972).

[9] G. Bambakidis, R. J. Smith, and D. A. Otterson, Phys. Rev. **117**, 1044 (1969).

[10] J. E. Schirer and B. Morosin, Phys. Rev. B **12**, 117 (1975).