

In situ Potentio, Resisto and Dilatometric Measurement of Repeated Hydrogen Absorption in Pd Electrode by Electrochemical Cathodic Loading Method

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ABSTRACT

The physico-chemical properties of hydrogen in Pd have been studied by *in situ* potentio, resisto and dilatometric measurement. A set of potential, resistance ratio and increase of dilation ($\Delta l/l_0$) was recorded simultaneously after the establishment of an equilibrium of hydrogen with Pd lattice. The hydrogen electrode potential is converted to 'equivalent hydrogen pressure', which might signify gaseous pressure in a void or on a surface. The structural phase transition ($\alpha \rightarrow \beta$) occurred during the cathodic discharging of hydrogen and the characteristic values of this phase change are well consistent with those predicted from Pd-H diagram. Hydrogen infusion causes lattice expansion, which resulted in the dilation of Pd electrode. Repeated absorption and desorption cycle deteriorates the mechanical properties, where the hysteresis of R/R_0 vs. hydrogen pressure diagram was appeared depending on the mode of electrolysis (the extent of H/Pd ratio).

INTRODUCTION

Palladium readily absorbs large amounts of hydrogen gas where hydrogen atom exists in interstitial sites. Recently, deuterium loading more than $x = 0.9(\text{PdD}_x)$ results in cold fusion involving D atoms. So far hydrogen infusion into the steels causes hydrogen embrittlement.

A common aspect to these hydrogen-metal related phenomena is the sporadic nature of neutron emission or heat bursts and that of microscopic change of solid, i.e., dislocation generation and motion accompanying crack formation in certain condition. For Pd, the dissolved hydrogen into interstitial sites at first expands the α phase lattice and creates elastic strain fields resulting some deviation from an ideal hydrogen behavior, designated as, electrode potential deviation from Nernst equation. Further insertion of hydrogen occurs an α - β phase transition, where the α and β phases have different partial molar volume. It is apparent that during the α - β phase transition anisotropic each crystal expands independently generating structural defects, i.e. dislocation, slip bands, fault and rifts, which are similar to the characteristics of the heavily cold worked Pd.

In our experiments, where an annealed Pd cathode (9mm ϕ , 10cm long) was used during a long-term deuterium evolution, neutron count rate was observed. In the second experiment (21mm ϕ , 32mm long), initial term electrolysis had no significant count rate of neutron, while high count rate of neutron was appeared for several days after raising current density step by step and after raising temperature¹⁾. Metallographic observation results in two faults, blisters, cross slips and holes on Pd surface. *In situ* measurements of physico-chemical properties of metal-hydrogen system

Material Science Studies

remained open.

It is noted that the materials are encountered by *critical conditions* through the prolonged and high current electrolysis, immediately before sporadic microstructural changes. Since repeated hydrogen absorption and desorption cycles are useful for simulating heavily worked Pd, mechanical and physical properties of Pd under hydrogen absorption and desorption cycles have been *in situ* measured to evaluate the critical conditions in terms of the repetition of the α - β phase transition.

In this study, the electrochemical behavior, dilation and resistance of Pd electrode have been *in situ* measured using a computer controlled potentiostat, dilatometer and miliohm meter under electrochemical cathodic discharging of hydrogen in glycerin and phosphoric acid solution.

EXPERIMENTAL

A set of potential, dilation and resistance of Pd electrode was measured after the establishment of an equilibrium of hydrogen with Pd(2 and 0.8mm ϕ 50mm long). The measurement system was constructed by a computer controlled potentiostat, miliohm meter and dilatometer. The electrolytic cell was the modified three-electrode cell. An electrolyte is the mixture of glycerin and phosphoric acid(2:1 volume ratio). The electrolyte acts as the permeability barrier to hydrogen once introduced into Pd lattice²⁾. The details of experimental procedure are described elsewhere³⁾.

The electrolysis was performed using three types of galvanostatic pulsed current as shown in Fig.1. A mode electrolysis reveals that a set of pulsed currents(absorption) is applied immediately after accomplishing the preceding set of one(absorption). Thus, repeated hydrogen absorption and possible desorption(during off pulse) is continued until the saturation of hydrogen content takes place. The saturation of hydrogen is easily detected by attaining time independent resistance. In B and C mode electrolysis desorption by pulsed current reversal technique is intervened between one set of pulsed current(absorption) and next one(absorption). The difference of these two modes is in the form of current supply, i.e., galvanostatic pulsed current and potentiostatically controlled constant current. During both mode electrolysis the decision of supplying next pulsed current has been done by diagnosis of complete recovery of resistance.

RESULTS AND DISCUSSION

The formation of microscopic holes and faults on Pd surface was previously explained by the geothermal phenomenon on the earth created by the mantle movement and the heat of the earth¹⁾. This modelistic approach makes possible a reasonable guide line for analysis of a complicated phenomenon. We postulate the microstructural model inside the solid(Fig.2), which improves reproducibility of cold fusion related phenomena, i.e., heat evolution and nuclear products emission. Although the precise description about the model is not shown, an important aspect is cycling 4 sequential processes(some of them yet remain as speculation in this paper), which might be identified by the following measurements of the physical and mechanical properties of Pd⁴⁾.

In the recent experiments⁵⁾, significant changes of the α - β transition behavior of thin Pd film compared with that of bulk Pd suggests that the surface effect play a significant role in obtaining the bulk properties, i.e., resistance and dilation of Pd. Hence, we use rather thick Pd rods to achieve more sensitive measurements to the bulk properties, though much longer electrolysis is required to attain a steady state of diffused hydrogen in thick Pd rod.

Among many metal-hydrogen alloys Pd is particularly known as easily absorbing and desorbing material, which indicates that the formation of a surface layer does not play a significant role as a permeability barrier. However, the transfer of hydro-

Material Science Studies

gen is not determined only by the surface condition, but by the microstructural change of the bulk attributed to the electrochemical loading. Therefore, it is necessary to explain the physical and mechanical characteristics in connection with microstructure of Pd.

Potential, resistance and dilation of Pd under A mode electrolysis

After each increment of a cathodic discharge (Pd: 2 mm ϕ 50mm long, 0.2 and 2mA/cm², pulse duration 500s), the electrode potential changes with time and reaches at the steady state with an equilibrium between hydrogen atmosphere and hydrogen activity of Pd inside. Thus, 'equivalent hydrogen pressure' p_{H_2} : the hydrogen pressure equilibrated with that in Pd metal (e.g., in a void), is expressed as, assuming Nernst equation under the limited condition

$$p_{H_2} = \exp[-(E + E_{SCE})(2F/RT)]$$

where E_{SCE} is the potential of the reference electrode. Figure 3 shows the plot of electrode potential vs. hydrogen concentration of 1st absorption. Although the hydrogen concentration is calculated coulometrically, the absorption efficiency is known to be 1 upto H/Pd ratio 0.6 and 0.8 over H/Pd ratio 0.6. At $x \leq 0.01$ the electrode potential obeys Nernst equation, while it exhibits constant value corresponding to the coexistence of the α and β phases ($0.01 < x < 0.55$). The concentrations of the onset (α_{max}) and the end (β_{min}) of phase transition are well consistent with those predicted from Pd-H phase diagram. The equivalent hydrogen pressure of two phase region is 0.05 atm, which is agreed with that obtained from pressure and composition isotherms of Pd-H. The characteristic values presented in Fig.3, were consistent with those of Pd-H isotherm obtained by gas equilibrium method, which substantiates the correctness of the electrochemical loading method.

It must be kept in mind that electrochemically evolved hydrogen atoms are absorbed readily into Pd lattice because intense driving force, i.e., the gradient of hydrogen concentration under beneath the surface suffices complete infusion of hydrogen, due to the electrochemical overpotential applied. However, it is demonstrated that hydrogen atoms exist homogeneously over the whole electrode, where the attainment of stationary electrode potential is a least diagnosis (computer proceeds next charging step after checking the results of diagnosis).

The results of this equilibrium check can also be seen as evidence that the time dependence of resistance, as obtained by interrupting discharging is still for 30h within the uncertainty of the experiment. Figure 4 shows whole potential and resistance plot vs. H/Pd ratio, where intervening was indicated by an arrow.

On the other hand, hydrogen infusion causes lattice expansion, which resulted in the dilatation ($\Delta l/l_0$) of Pd. The plot of the dilatation vs. H/Pd ratio in the α region is shown in Fig.5, which is measured simultaneously with the case of Fig.3. The dilatation of Pd is almost in proportional to an increase in H/Pd ratio, whose slope, the molar volume of hydrogen is obtained as $V_H = 1.64 \text{ cm}^3(\text{mol H})^{-1}$ with the $V_{Pd} = 8.87 \text{ cm}^3\text{mol}^{-1}$. The result coincides with the literature value $V_H = 1.77 - 0.873 \text{ cm}^3(\text{mol H})^{-1}$ (6).

The plot of the dilatation in more than the α region is shown in Fig.6 with respect to $x > 0.06$. The β phase has a larger lattice constant than the α phase, though the dilatation is smaller in the $\alpha + \beta$ phase than in the α phase. Assuming that the lattice constant of Pd is $a(0) = 3.890 \text{ \AA}$, $a(\alpha_{max}) = 3.893 \text{ \AA}$ and $a(\beta_{min}) = 3.929 \text{ \AA}$ can be obtained. The values coincide with the reported ones: $a(\alpha_{max}) = 3.894 \text{ \AA}$ and $a(\beta_{min}) = 4.025 \text{ \AA}$ (7). When the β phase is attained, large dilatation can again be exhibited linearly to the H/Pd ratio upto 0.8.

Repeated absorption and desorption of hydrogen in Pd ($x < 0.02$) under B mode electrolysis

Repeated absorption and desorption of hydrogen (Pd: 0.8mm ϕ 50mm long, 0.2mA/cm², 7000s) was performed using B mode ($x < 0.02$) electrolysis, where the H/Pd ratio of

Material Science Studies

absorption was controlled upto the on-set of the α - β transition: α_{\max} . In this case hydrogen infusion does not heavily deteriorate the mechanical properties of desorption cycle, since the diffusion of hydrogen proceeds rapidly and without hysteresis to the α phase. The results of 1st to 5th cycle absorption and desorption show that the electrode potential obeys the Nernst equation while the potential shifts to less noble direction as the cycle number is increased. The plots of the potential vs. H/Pd ratio of 5 to 11th cycle show steep straight lines, thus the on-set of phase transition proceeds with much smaller H/Pd ratio. It is noted that the potential, that is, ultimate hydrogen pressure of the α - β coexistence is increased accompanying the evolution of the potential fluctuations. These features of a large number of cycle indicate that even the low level of discharging accumulate the mechanical effect(stress and/or stimulating hydrogen association) as evidenced by the increased, as well as, unstable hydrogen pressure.

The dilation vs. H/Pd ratio of absorption is shown in Fig.7, where the slopes of 2nd to 4th cycle increase progressively; most of the slopes after 5th cycle tend to converge into one line. For all the cycles except 1st cycle, the induction period of the dilation is appeared, whereupon the α single phase exists. Inspecting the dilation vs. H/Pd diagrams and taking into account of error of experiment, it is reasonable to assume that the dilation($\Delta l/l_0$) is comprised of the linear term of lattice expansion and the complementary term as,

$$\Delta l/l_0 = a \cdot x + b \quad a: \text{constant}$$

where the first term of the right hand corresponds to the change of dilation due to lattice expansion and the second term is attributable to sporadic dilation(discontinuous to H/Pd ratio and time): the plastic strain appears over work hardening region on a single crystal. Although it is questionable that the Pd rod under repeated absorption and desorption behaves like a heavily strained crystal, we often observe such sporadic and stepwise dilation under the electrochemical loading. It is highly possible to evaluate the progress of the critical condition in terms of the amplitude and/or frequency of the second term⁴⁾.

The results of the resistance ratio(R/R_0) vs. H/Pd ratio of absorption shows a monotonic increase with an increase of H/Pd ratio, where the effect of cycle number lies within the maximum experimental error. The resistance behavior suggests that hydrogen is readily mobile: irrespective of the dilation varied with the number of cycles and the appearance of the induction period.

Repeated absorption and desorption of hydrogen in Pd ($x < 0.8$) under C mode electrolysis

The same repeated absorption and desorption of hydrogen was performed using C mode($x < 0.8$) electrolysis(Pd:0.8mm ϕ 50mm long, 7000s) where the electric charge of absorption is more than that of hydrogen required to attain H/Pd ratio 1.0. It is known that the efficiency of absorption of hydrogen drops over H/Pd c.a. 0.6. We promote to examine the exact value of efficiency at various charging conditions.

Table 1 summarizes the comparison of repeated absorption and desorption cycle between B($x < 0.02$) and C($x < 0.8$) mode electrolysis. For example the resistance behavior for B mode electrolysis shows no distinct dependence on the cycle number, while the resistance ratio vs. H/Pd ratio under C mode electrolysis exhibits totally different dependence on the cycle number: the resistance ratio shows a steady increase and attains a flatten regime at $R/R_0 = 1.7$ with an increase of H/Pd ratio. During a few number of cycle the H/Pd ratio to reach the flatten regime shifts towards higher content.

One of the important characteristics of the repeated absorption experiments is seen in R/R_0 vs. hydrogen pressure diagram, where one of typical data is shown in Fig.8. The comparison of these data shows that larger hysteresis of absorption and desorption cycle is attributable to deterioration of the mechanical property^{4,8)}.

Material Science Studies

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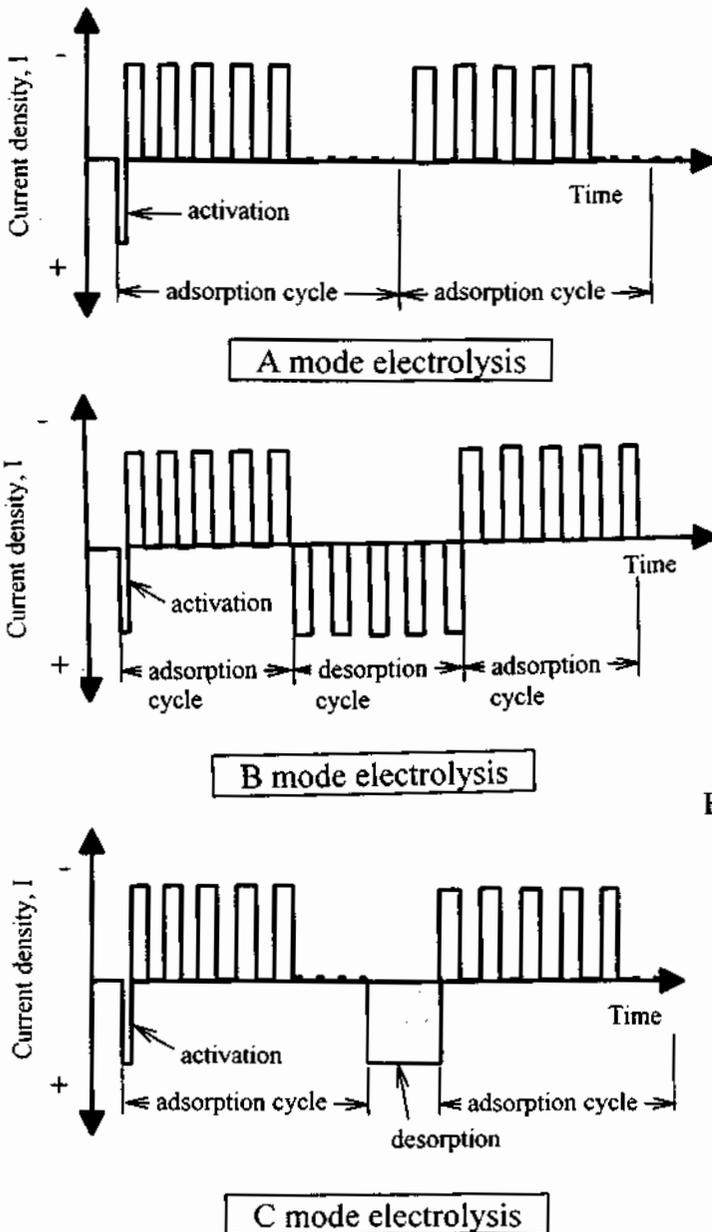


Fig.1 Patterns of current density-time

Material Science Studies

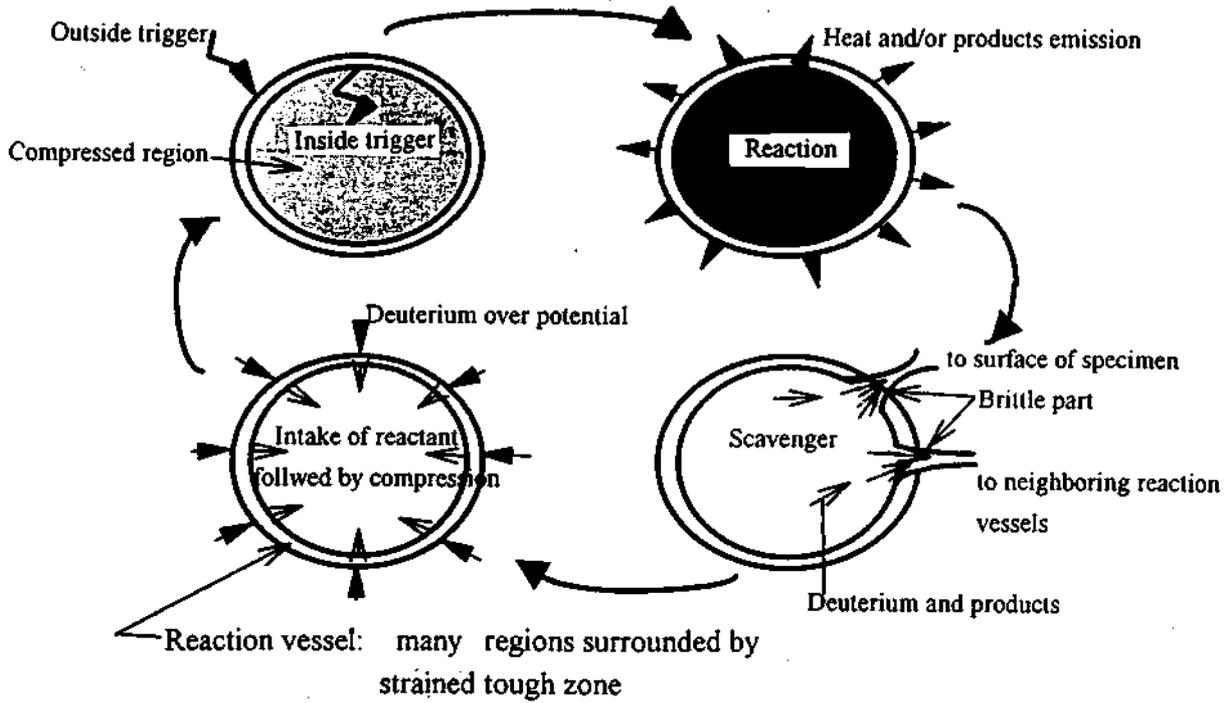


Fig.2 Cold fusion reaction in condensed matter(Pd-D)

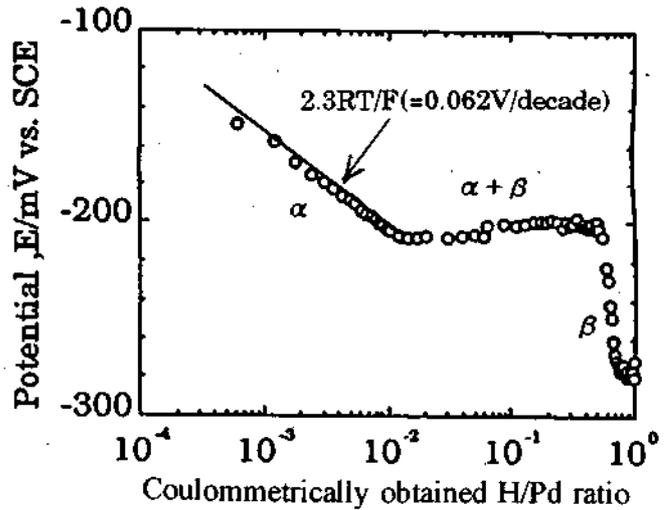


Fig.3 Potential vs. logarithm of H/Pd ratio at 40 °C .

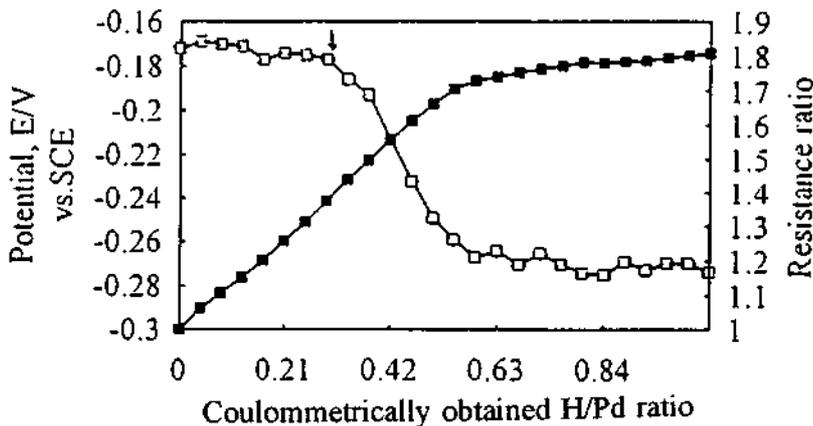


Fig.4 A mode potential, resistance ratio vs. H/Pd plots, 40 °C after 30h holding(at arrow) Pd was again electrolyzed.

Material Science Studies

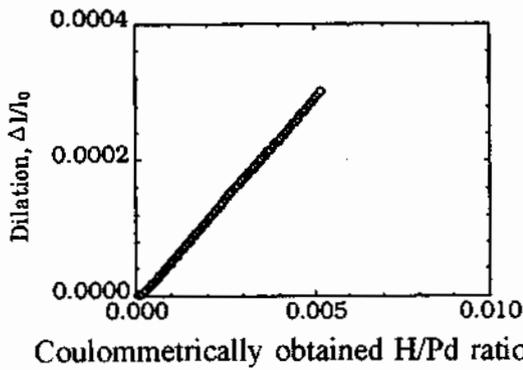


Fig 5 Dilation($\Delta l/l_0$) vs. H/Pd ratio($x < 0.005$).
40 °C , 0.2mA, 500s

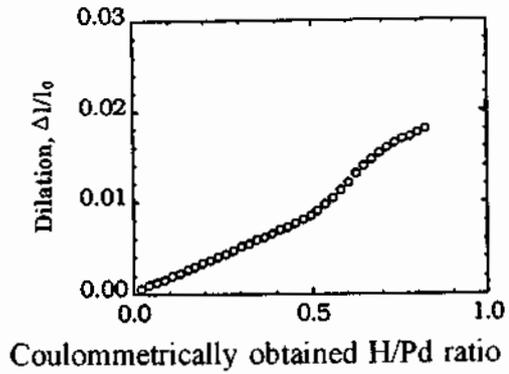
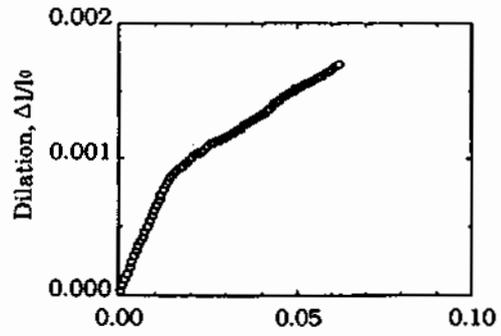


Fig 6 Dilation($\Delta l/l_0$) vs. H/Pd ($x < 0.06$ and < 0.8)
top 40 °C , 0.5mA, 2000s,
bottom 40 °C , 5mA, 7000s

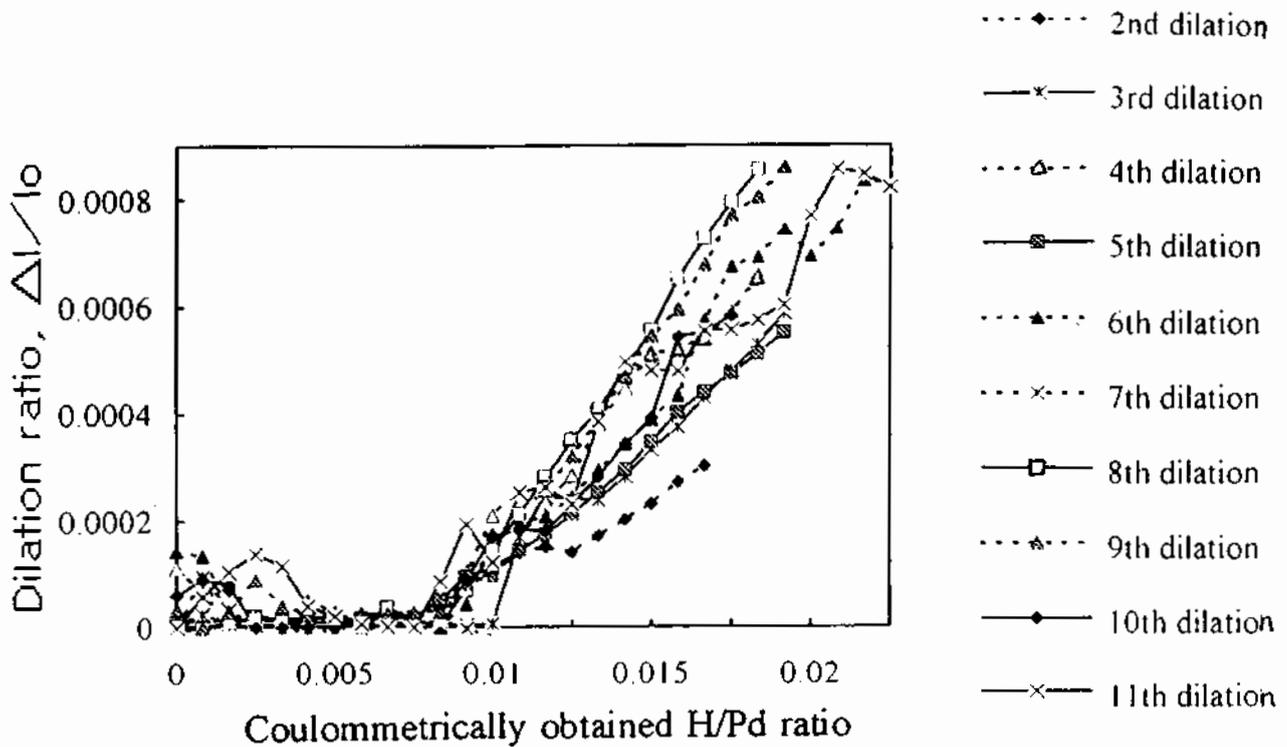


Fig.7 Effect of number of cycle on B mode dilation($\Delta l/l_0$)
vs. H/Pd ratio($x < 0.02$) diagram.

Material Science Studies

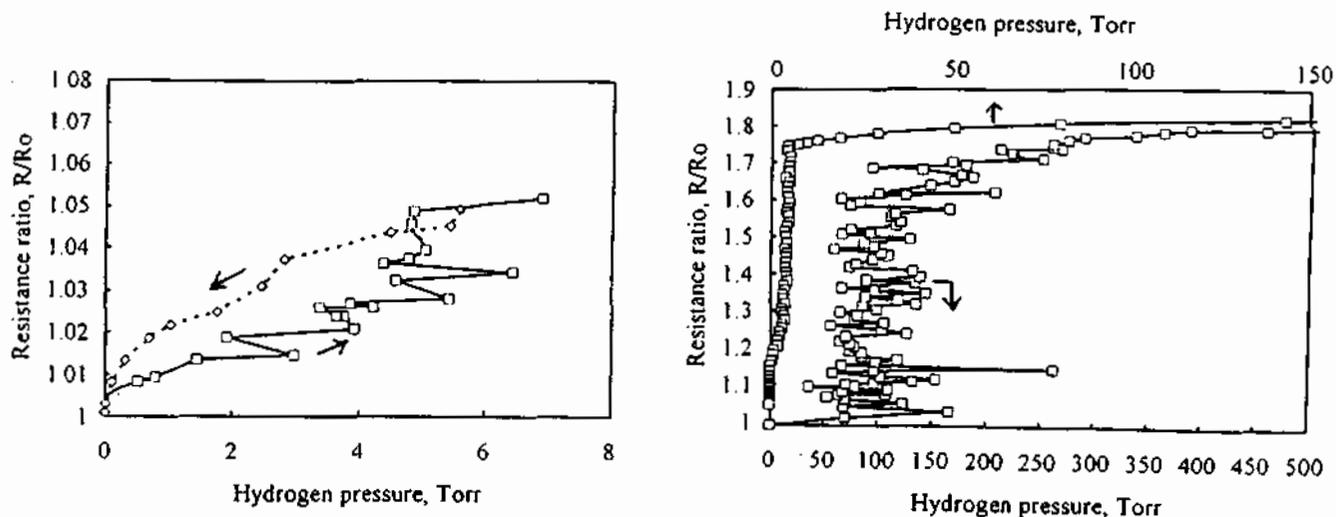


Fig 8 Comparison of R/Ro-hydrogen pressure diagrams, left H/Pd ratio<0.02, right H/Pd ratio<0.8

Table1 Comparison of absorption cycle effect on E, R/Ro and $\Delta l/l_0$ -H/Pd ratio diagrams; B mode <0.02, C mode <0.8

Electrolysis cond.		Potential	Resistance ratio	Dilation, elongation	Hydrogen pressure
Mode	H/Pd ratio	E-log(H/Pd)	(R/Ro)-H/Pd	($\Delta l/l_0$)-H/Pd	Torr-log(H/Pd)
B	<0.02 (c. d. 0.2 mA/cm ²)	1st-5th Nernstian	1st, 2nd: early	1st to 3rd increased	small hysteresis
		6th-11th deviation from Nernstian	jump, other cycle no hysteresis	slope, 4th to 11th no cycle effect	
C	<0.8 (c. d. 0.2 & 2mA/cm ²)	Data scattered but much deviated from Nernstian	large hysteresis	Data not available	large hysteresis

note; Desorption cycle was mostly found to be orderly effective or less effective on these diagrams compared with adsorption ones. Mode C data of desorption cycle was not available because of its form of electrolysis mode.