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Properties of Aged Metal Tritides

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Abstract

The interaction of tritium with metals is made complex by two phenomena. The first is that the beta decay in the metal produces ^3He . The helium moves to form bubbles. This report will show that the growth of the bubbles produces a two-stage swelling of the metal that comes first from the appearance of the helium and second from the relaxation of the lattice disorder.

The second phenomena is the steady state ion and free radical concentration in the tritium over gas that interacts with impurities on the metal surface. This report will show that the reaction rates are much faster than for normal hydrogen cleaning.

Introduction

Hydrogen (H) in palladium (Pd) has been the object of much study because of its convenient experimental range of temperature and pressure and because of its relatively simple metallurgy. The early work has been reviewed by T. B. Flanagan [1] and by E. Wicke and H. Brodowsky [2]. H_2 dissociates at the Pd surface and moves into octahedral sites in the face-centered cubic Pd lattice. Up to a concentration of $\text{H}=0.008$ Pd, the loading pressure increases as the α phase grows by filling the center of every other unit cell. After $\text{H}=0.008$, the α plus β phase grows by filling the octahedral sites closest to the already-filled sites to form clusters, rather than by filling intermediate cell centers. In the process, the electrons from the hydrogen are actually filling the 4d band of Pd, which leaves nearly free protons in the octahedral sites with no resultant increase in pressure. Thus, the protons can come to the

surface under a rather small potential change.

When the concentration reaches a H/Pd ratio of about 0.6, the 4d band fills up, and increasing the H concentration becomes more difficult. It requires higher pressures. Thus, the so-called pure β phase results from electronic filling of the d band, and not from a continued filling of the octahedral sites. The electronic environment controls the onset of the β phase.

Hydrogen isotopes in Pd have an inverse isotope effect, as manifest in the higher transition temperature for PdD than for PdH. Thus, H rather than deuterium (D) is energetically more favorable in the octahedral site, and tritium is least favorable. Pd is convenient for storing tritium because one can easily remove the tritium, thus forming a tritium pump.

However, two factors can inhibit the operation of the pump:

- As the tritide ages, the tritium decays to ^3He .
- Impurities in the system, such as carbon, can migrate to the Pd surface and inhibit the dissociation of the hydrogen isotopes.

This report deals with these two phenomena:

- Growth of ^3He
- Carbon as a specific impurity

The helium ingrowth forms very high pressure bubbles. These ^3He bubbles put strain on the lattice, which causes the Pd to swell. This report also shows that the carbon in the bulk Pd diffuses very slowly, and that the surface carbon exists in a dynamic equilibrium with tritiated methane (CT_4) in the tritium gas overpressure.

Helium Growth

At nearly room temperature, $\text{PdT}_{0.6}$ can be maintained for long periods of time. As it ages, tritium (T) atoms emit a β^- and transmute to a $^3\text{He}^+$ in the lattice that quickly neutralizes the positive charge. The neutral ^3He is too big for the octahedral site and pushes the nearest Pd atoms out of their equilibrium positions. The size of the helium atom depends on the local pressure exerted on it. Some evidence indicates that the metal atoms distort the helium electron cloud. For certain ^3He sizes, it is

energetically favorable to push one of the Pd atoms into the next octahedral site and distort two unit cells. Such a situation is shown in Figure 1. The cross-hatched area represents the additional volume, ΔV , as a result of the helium atom. If one takes V as the volume of the Pd unit cell, one can relate ΔV to the local pressure, P , through the bulk modulus B as

$$-\Delta V/V = P/B \quad (1)$$

where for Pd, $B = 1.8 \times 10^{12}$ dynes/cm². A sample calculation was done for a 2.7 Angstrom (Å) diameter helium atom where $\Delta V/V = 0.138$. The resulting pressure for a uniform displacement of nearest neighbors is $P = 2.5 \times 10^{10}$ Pa or 0.25 Megabar (Mbar). If one allows a Pd atom to be pushed into the next octahedral site, as in Figure 1b., the corner atoms move in, which reduces the volume increase in the two unit cells. The move is energetically less expensive, which leads to a local pressure of 0.21 Mbar. As one decreases the diameter of the hard sphere, it becomes energetically favorable for a uniform motion of the nearest neighbors.

Theoretical calculations of this effect all involve approximations of the real size and shape of the helium atom in the lattice. A model for the formation of a helium bubble starting with a few atoms was postulated by Wilson *et al* for a nickel lattice [3]. If one uses their He-Ni interaction potential, nickel atoms are pushed out non-uniformly to form a denser nickel region on one side of the helium

Figure 1 - a. Positions of hydrogen atoms in α and β phases.
 b. Helium pushes Pd into adjacent octahedral site.

cluster as the number of helium atoms increases beyond 5. It appears to take only a few helium atoms in a cluster to act as a sink for further helium atoms formed within a 70Å radius. Those formed within 50 to 70Å of a free surface escape to the surface. When the cluster becomes larger, one uses the Embedded Atom Method, of Daw and Beskes [4], to calculate energies of the cluster

without having to know the pairwise interactions.

Another method of describing bubble growth that uses elastic stress analyses has been explored in a series of papers by Wolfer and co-workers [5]. The condition for dislocation loop punching in a material of shear modulus, G , is $P = G/6$. In the material under consideration, loop

punching in a uniform elastic lattice can begin at $P=0.14$ Mbar. The effect of loop punching can be observed in Wolfer's Monte Carlo calculation, shown in Figure 2, with 369 helium atoms in the bubble and 8,787 atoms in a nickel lattice [6]. The displaced lattice atoms are moved one Burgers vector into an octahedral site. In a strain-free lattice, the loop gets larger to relieve the local stress in the lattice. The way the loop is formed and the distance it moves depends on the initial conditions of the bubble and the degree of other disorder in the lattice. The disorder can maintain higher pressures in the bubbles.

Figure 2 - Lattice distortion calculated from helium bubble growth (from Wolfer et al [6]).

Abell and Attalla showed that a distribution of densities in the helium bubbles can be determined from the second moment of the ^3He Nuclear Magnetic Resonance (NMR) line shape [7]. The spin-lattice relaxation (T_1) was measured as a function of temperature for samples of 1, 2, 4,

and 8 years. Below a certain temperature, depending on the age of the sample, the time dependence of the magnetization data could be described with a sum of two exponentials:

- One corresponding to the solid phase
- One corresponding to the liquid phase

The analysis leads to a fraction $f_L(T)$ of bubbles at each temperature in the liquid state, shown in Figure 3, as

$$f_L(T) = \int_0^{\rho_m(T)} G(\rho) d\rho \quad (2)$$

where $\rho_m(T)$ is the melting density at temperature T . Then $G(\rho)$ at $\rho = \rho_m$ is

$$G(\rho)_{\rho=\rho_m} = \frac{df_L(T)}{dT} / \frac{d\rho_m}{dT} \quad (3)$$

The quantity $d\rho_m/dT$ is determined from the helium melting curve of Loubeyre *et al* [8]. It is shown in Figure 4 as tangents to the melting curve. The ^3He density in the two-year-old samples studied by Abell and Attalla ranged from 0.16 to 0.26 molecules per cubic centimeter (moles/cm^3). Applying the equation of state for helium bubbles derived by Wolfer [9], at $T = 300$ K, one gets

$$P = \rho kT (0.943 + 21.22\rho + 154.4\rho^2 + 2330\rho^3) \quad (4)$$

where P is in pascal and $k = 8.317 \times 10^6$ (pascal cm^3)/mole in Table 1.

TABLE 1 - Density Variation in Two-Year-Old Samples	
Density	Pressure
0.26	2.4×10^{10}
0.24	1.7×10^{10}
0.22	1.3×10^{10}
0.20	0.9×10^{10}
0.18	0.6×10^{10}
0.16	0.4×10^{10}

Figure 3 - Fraction of helium in liquid state (from Abell [10])

Age: ■ 0.55 year

◆ 2 years

▲ 4 years

● 8 years

Figure 4 - Tangents to the helium melting curve.

One can see that pressures above and below the loop punching indicate a considerable variation in the stress fields in the sample. Initially, the pressure can be very high, but later the Pd lattice relaxes. Preliminary experiments [7] with one- and two-year-old samples indicated that the mean helium density in the bubbles did not decrease with time. More careful analysis by Abell, with aged samples of 0.5, 2, 4, and 8 years, indicated that the mean helium density does decrease with time [10]. By using equation 3, one can obtain from Figures 3 and 4 the quantity $G(\rho_m)$ where ρ_m is $\rho(T)$ at $T=T_m$, the melting temperature. The four curves in Figure 5 show that the distribution of densities spreads as the mean density decreases. The dotted line for the eight-year-old sample shows a correction for thermal expansion in the lattice in changing ρ_m to $\rho(300\text{ K})$ that turns out to be small.

Values for the mean. density from Equation 5 are given in Table 2.

$$\langle \rho \rangle = \frac{\int \rho G(\rho) d\rho}{\int G(\rho) d\rho} \quad (5)$$

Figure 5 - Distribution of densities in helium bubbles as a function of age.

The density of the helium is decreased by a relaxation of the lattice with the Pd atoms being displaced until they reach the surface or some other void. Thus, the swelling of the lattice takes place in two steps, as shown in Table 3.

The growth rate of ^3He in the metal lattice is 3.3% per year, and the presence of a helium atom in the unit cell increases the cell size by 13%, as

TABLE 2 - Determination of Mean He Density in Bubbles (moles/cm ³)				
Time	0.55 Year	2 Years	4 Years	8 Years
$\langle G(\rho) \rangle$	109.9	119.8	119.1	117.2
$\langle \rho G(\rho) \rangle$	228.1	225.7	189.4	175.6
$\langle \rho \rangle$	0.207	0.188	0.159	0.150

TABLE 3 - Swelling as a Percentage of Age

Time	66 Days	0.55 Yr.	2 Yr.	4 Yr.	8 Yr.	12 Yr.
He Growth	0.24%	0.7%	2.6%	5.6%	10.7%	16.0%
Relax Ratio		1.00%	1.1%	1.3%	1.38%	1.46%
Total	0.24%	0.7%	2.9%	6.9%	14.4%	23.4%

represented in Figure 1 by the cross-hatched area. A 12.3 year half life for tritium results in 2.4% ^3He atoms appearing in the $\text{PdT}_{0.6}$ per year, which produces 0.55 Pd atomic volume per helium [6]. This growth represents a linear volume increase of 1.34% per year, which is shown as He growth in Table 3. The initial increase in volume is obtained by squeezing Pd into interstitial sites. The second step in the volume increase occurs on a different time scale as the interstitial Pd diffuses to a free surface. A measure of this change in volume is given in the relaxation ratio. This ratio is obtained from the inverse of the densities given in line 3 of Table 2 where the denominator is the 0.55-year density. The effect of this second step is shown by dotted lines in Figure 6 where 50 and 100% of the sample volume have the same expansion rate as the helium bubbles. About 60% is consistent with the NMR data.

Impurities

Impurities that bond strongly to hydrogen gas isotopes would thermodynamically prefer to be in gas than on a metal surface. Thus,

Figure 6 - Two stage swelling as helium bubbles grow.

hydrogen gas is used in cleaning metal surfaces. Elements such as Chlorine (Cl) and Sulfur (S) go almost completely into the gas from the surface. Carbon is an intermediate case. In a gas where ions and free radicals are present, the cleaning effect is even stronger.

The effect of carbon in stainless steel and Pd rich systems was demonstrated in experiments on methane in tritium by McConville and Menke [11]. Figure 7 shows the

stainless steel mixing container used in the deuterium-tritium (DT) reaction rate experiments. It has a volume of 300 cm^3 and an area of 200 cm^2 .

Figure 7 - Diagram of mixing cell (from McConville et al [12]).

The container was vacuum-baked and electropolished by Quantum Mechanics, Inc. to remove protium and to bind carbon in carbides. During the exchange experiments, it was found that a carbon source that existed in the experiment [12] as tritiated methane, appeared in the tritium-deuterium mixture. The source was the stainless steel sheath on the Platinum Resistance Thermometer (PRT) inserted in the mixing chamber. The effective area of the sheath was estimated to be 8 cm^2 . The initial growth rate was estimated to be approximately 0.03% per hour from the slope at $t=0$ in Figure 8. Given the volume of the mixing cell and the effective area of the PRT, the removal rate is $2 \times 10^{14}/\text{cm}^2$ per second. Assuming that a monolayer on the metal surface is $1.3 \times 10^{15}/\text{cm}^2$, impurity concentrations of the order of a monolayer are removed rapidly,

compared to molecular H_2 cleaning with a removal rate of $3 \times 10^{10}/\text{cm}^2$ per second. Therefore, systems to be used in tritium service can be more effectively cleaned with a final flush of freshly prepared tritium.

Figure 8 - Initial growth of CT_4 in Tritium.

In Figure 8, the methane ingrowth slows with time. Further experiments were performed with initial concentrations of 1.5 and 3.0% of CT_4 in the tritium. The CT_4 concentration was observed to decrease with time, as shown in Figure 9. The linear reduction in the region between 2×10^3 to 10^4 minutes leads to a relative concentration of $\text{CT}_4 \approx 0.2\%$ in about 1.1×10^5 minutes or about 9 weeks. The mixture was stored in the mixing chamber for 18 months, and the steady state CT_4 was measured at 0.2% . The work in Reference 11 shows that the β decay produces methane fragments that result in free carbon plating out on the surface. The T_3^+ ion, formed by β decay in the gas, can react with free carbon on the surface and form CT_3 . That returns

carbon gas where it recombines with T to form the steady state CT_4 . The steady state value depends on the metal surface and the affinity of carbon for that surface.

Figure 9 - Decrease in carbon content in tritium gas.

Another material used in tritium pumps is palladium (Pd), in the form of powder, to increase the surface area. However, carbon on the surface of the Pd impedes the efficiency of the pump. A bulk measure of carbon in the powder was found to be 40 ppm. A simple calculation of volume to surface shows that if all the carbon were on the surface of 1 micron (μ) diameter spheres, 1 surface atom in 60 would be carbon. The question arises, "If the carbon were in the bulk, how long would it take to diffuse to the surface?"

To our knowledge, there are no measurements of the diffusion of carbon in Pd. It appears to be very difficult to get carbon to enter bulk Pd. In high temperature preparation, carbon tends to come out of the bulk as the

Pd powder is cooled. Since diffusion of carbon in nickel and iron is known to be slow, it can be compared to Pd. At room temperature, the diffusion coefficient of carbon in iron is of the order of 10^{-17} $cm^2/second$. (There is a second iron phase in which the diffusion is much slower). Figure 10 shows a "Doneness parameter" for one micron particles. In 68 years, half the carbon would come to the surface at the rate of a carbon atom every two minutes per square centimeter of surface. In a tritium environment, all the carbon present on the surface would enter the gas as CT_4 .

Figure 10 - "Doneness parameter" with 1 μ particles for 3 diffusion constants.

To see if the carbon transformed and appeared in tritium over gas, three lots of material were stored for different periods of time in stainless steel containers. In these three samples, the ratio of Pd to stainless steel surface was large. In the first sample, 4.5×10^{20} tritium molecules and 1.5×10^{18} carbon atoms were in the Pd powder. After a year, with some temperature cycling about room temperature, about 0.1% CT_4 was in

the gas, which represented about 8% of the powder surface area. A second larger sample, with 1.3×10^{31} surface sites, produced 1.1% CT_4 in the gas, which represented about 10% of the surface sites. A third sample, with about half the surface, was stored for 3.5 years. In that sample, 2.7% methane appeared in the 63 STP cm^3 of tritium in the system. In this sample, the carbon in the methane represented about 6% of the surface sites. In each sample, the carbon was removed from about the same amount of surface per gram. That amount was about 20% of what was measured in the "bulk" determination on the first sample. Since the gas accommodates 2.7% methane in the Pd rich system, the samples that had only 1.1 and 0.1% in the gas removed all the surface carbon into the gas. The efficiency of the process depends on the surface geometry in the powder.

Discussion

Tritium in two-phase, gas-solid systems presents a complicated picture for two reasons:

- In the solid, the ^3He is formed in the β decay, which is trapped in the lattice.
- A steady state population of ions and free radicals in the gas interacts with the metal surface.

The growth of helium bubbles produces disorder in the lattice by sweeping up decay products into a nucleation site from a 70Å radius.

The disorder, in the form of dislocation loops or more complicated forms, varies the lattice force fields acting on the bubbles, which allows the helium density in the bubbles to vary. This variation was measured in the NMR experiments of Abell and Attalla. The change in the density variation with time is a measure of the lattice relaxation as the Pd in octahedral sites find their way into normal lattice positions. This change in volume has a different time scale from the helium growth, which leads to the nonlinear effect seen in Figure 6. The whole lattice does not grow at the same rate as the bubbles. To simplify, this growth rate can be characterized with a single parameter. This unknown parameter can be compared to the NMR points in Figure 6, which gives it a value of about 0.6.

The amount of helium a metal lattice can hold depends on the type of lattice and electronic properties of the particular metal. In Pd, the metal begins to fracture as the ^3He content approaches 0.5, which allows helium to communicate between bubbles and, finally, with the surface [5]. Then a large portion comes out at once.

Methane is a very common impurity in tritium stored in metal containers because the carbon from surfaces would rather reside in the gas as CT_4 , at impurity levels less than about 0.1%, through a series of complex ion-molecule reactions. The amount of CT_4 in the gas depends on the affinity of the metal for tritium. The present methane experiments showed

that, in the Pd rich systems, an order of magnitude more of CT_4 can be in the gas than in a stainless system. Given the geometry and the surface carbon concentration of the Pd rich systems, for systems with less than 2.5% methane in the gas, all the carbon is removed from the surface. From indirect evidence, any carbon in the bulk Pd would be very slow to come out. Thus, in Pd rich systems with a "bulk" carbon impurity content of 40 ppm, all of the surface carbon should reside in the over gas after a few months of storage.

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