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Journal of Alloys and Compounds 356–357 (2003) 36–40

Journal of ALLOYS AND COMPOUNDS

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Aging effects on palladium pressure–composition isotherms during tritium storage

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Received 26 August 2002; accepted 15 November 2002

Abstract

Aging effects on palladium pressure–composition isotherms have been studied for tritium storage up to 9 years. Storage properties are remarkably well preserved during aging, and only small modifications of *P–c* isotherms are observed: a decrease of plateau pressures, and shifts of α and β single phase regions towards greater stoichiometries. For the plateau pressures, the main changes are observed during the first half of the aging period (≈5 years) while phenomena slow down quickly to become almost negligible during further aging. By contrast, the displacements of α and β single phase solubilities are more continuous. These observations can all be correlated to the evolution of the (micro)structural properties. For instance, the ^{3}He generated by tritium decay and retained in the metallic lattice tends to segregate into bubbles, where it has only a weak influence on the structure and consequently on the storage properties. The bubble formation has been demonstrated by transmission electron microscopy (TEM) observations, and the global conservation of structural properties has been established by X-ray and neutron diffraction and by X-ray absorption.

Keywords: Palladium; Tritium; Pressure–composition isotherms; Aging; ^{3}He

1. Introduction

Metals and intermetallic compounds which react to form reversible hydrides with equilibrium pressures under 1 atm offer several advantages for storing and processing tritium: safety, high density storage, delivery of high purity tritium (^{3}He-free), etc. Among these materials, palladium is of particular interest because of its resistance to oxidation and poisoning, its fast kinetic of absorption and desorption, and its ability for retaining the ^{3}He generated in the matrix for at least 16 years [1].

The ^{3}He trapped in the metal induces large structural and microstructural changes in the host lattice leading to modifications of tritium storage properties with aging time, as can be seen from the evolution of Pressure–composition isotherms. Literature reports these evolutions of *P–c* isotherms for bulk Pd aged for 1 or 2 years under tritium [2,3] and for Pd on kieselguhr aged for 5 years [4].

In this paper, the evolution of *P–c* isotherms for bulk Pd are followed for 9 years. The modifications of thermodynamical properties deduced from these observations are correlated to changes in structural and microstructural properties established in previous studies by X-ray and neutron diffraction, by X-ray absorption [5] and by transmission electron microscopy (TEM) [6], in agreement with the self-trapping theory [7].

2. Experimental

The palladium powder used in this study was purchased from Comptoir Lyon Alemand Louyot. The powder was produced by precipitation from solution and consists of particles of 14 μm mean diameter. Samples were constituted by 5 to 20 g of powder placed in a tight sample holder and were activated by five cycles of absorption–desorption with deuterium before loading.

All samples were loaded with an amount of tritium

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doi:10.1016/S0925-8388(03)00097-5

estimated volumetrically during loading and more accurately measured by calorimetry at the end. Samples were aged at room temperature during a period ranging from 2 to 9 years. Before *P–c* measurements, the pressure over the sample was measured and the gas was analyzed by mass spectrometry to quantify the ^{3}He released during aging (usually about 5%).

As the initial tritium content in Pd may be different from one sample to another (depending on the final loading pressure), the aging state was characterized by the ^{3}He content in the Pd samples expressed as the atomic ratio He/Pd (instead of considering only the aging time). The ^{3}He content was first estimated from the initial tritium stoichiometry and the aging time by applying the radioactive decay law and finally measured by thermal desorption after all the other characterizations.

P–c isotherms were measured using a volumetric method at 25 and 40 °C, which are the commonly employed temperatures for our tritium storage devices. As the gas provided contained a few % of D, H and ^{3}He (generally between 1 and 2% of H and D and less than 1% of ^{3}He), gas analyses were periodically performed, by mass spectrometry, during *P–c* measurements to estimate the amounts of D and H absorbed–desorbed and to obtain the partial pressures of H, D and T from the total equilibrium pressure. In the following, *P–c* isotherms are given as the partial pressure of H, D and T (noted PHDT) vs. the total stoichiometry of H, D and T in palladium (noted HDT/Pd). This allowed an easier comparison between the different *P–c* isotherms as H and D contents can vary a few % from one experiment to another. After an absorption/desorption measurement, the tritium content obtained by calculations from the volumetric method was checked by calorimetry.

The main experimental error was due to the calorimetry which determined the initial (and the final) tritium content. The error varied from 2 to 3 mg of tritium, resulting in an error of stoichiometry from 0.005 to 0.014 depending on the weight of Pd in the sample. The error of the pressures was estimated to be 5 mbar for pressures under 1 bar and 10 mbar for pressures over 1 bar. The temperature error was about ±1 °C.

3. Results and discussion

Figs. 1 and 2 show *P–c* isotherms at 25 and 40 °C measured after different aging times. The first observation is that storage properties are remarkably well preserved during aging even for high ^{3}He content, especially in comparison to other well known storage materials such as $LaNi_5$ [8]. However, small changes have occurred during aging: a decrease of plateau pressures, an increase of plateau slopes and shifts of the α and β single phase regions towards larger tritium contents.

The main evolution of plateau pressures (at 25 and 40 °C) is observed during the first half of the aging period ($He/Pd < 0.15$, 5 first years); further aging causes a slower decrease in agreement with the literature [4]. This behaviour can be fitted by an exponential decay, as represented in Fig. 3. This figure also shows that the decrease is greater for absorption than for desorption leading to a decrease of hysteresis loop.

By contrast, the increase of plateau slopes is regular during aging and we did not observe any difference between the 'lower' and 'upper' parts of the plateau, in disagreement with previous studies in literature [2,3].

Displacements of α and β single phase solubilities are also quite regular during aging, as shown in Fig. 4. However, it can be noticed that the shift of the α single phase region is about twice as fast as the shift of the β single phase region, resulting in a slight decrease of the reversible storage capacity. The displacement of the α single phase solubility has already been observed in literature [3], but not the displacement of the β.

All these observations can be explained by structural and micro-structural evolutions due to the ^{3}He trapped in the lattice. The first effect of ^{3}He generation in the lattice is a swelling as ^{3}He radius is about twice that of tritium. Next, according to the self-trapping theory [7], the ^{3}He

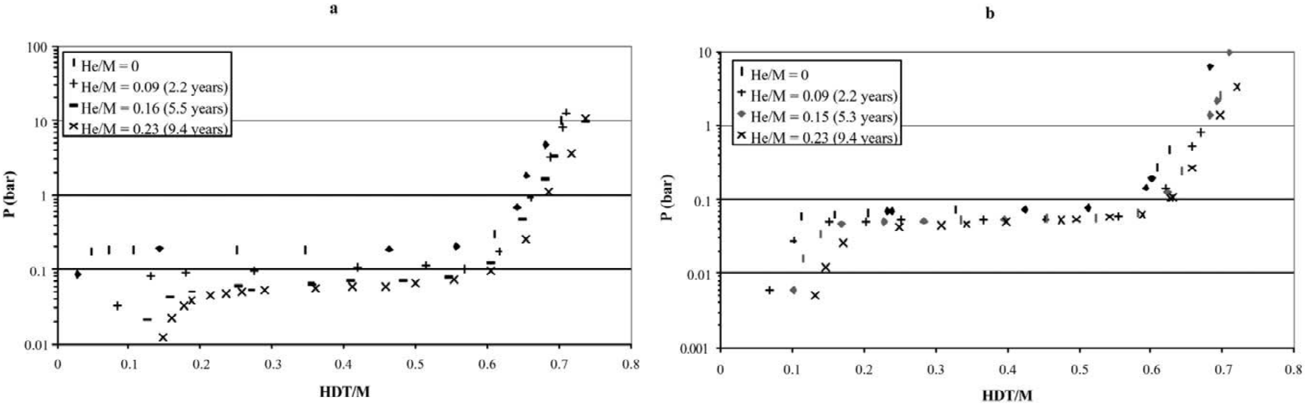

Fig. 1. *P–c* isotherms at 25 °C for the Pd–T_2 system at various ^{3}He contents. (a) absorption, (b) desorption.

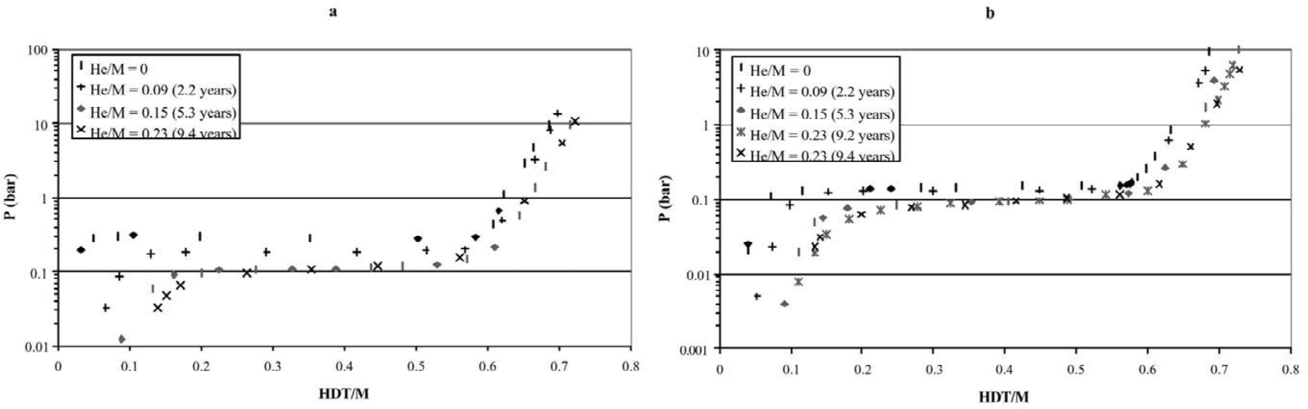

Fig. 2. P–c isotherms at 40 °C for the Pd–T_2 system at various ^{3}He contents. (a) absorption, (b) desorption.

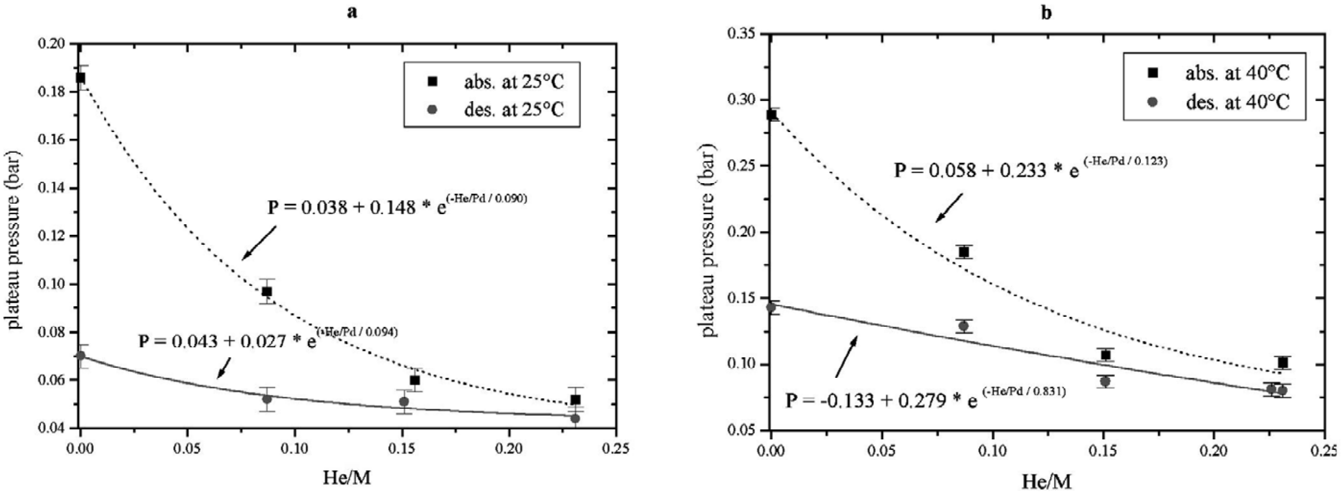

Fig. 3. Evolution of plateau pressures (a) at 25 °C, (b) at 40 °C vs. ^{3}He contents.

generated in interstitial sites has a strong tendency to precipitate into bubbles. At room temperature, bubble formation and growth implies the formation of structural defects such as self-interstitial atoms (SIA's), dislocation loops and dislocation networks. Experimental proof of these predicted phenomena has already been given in

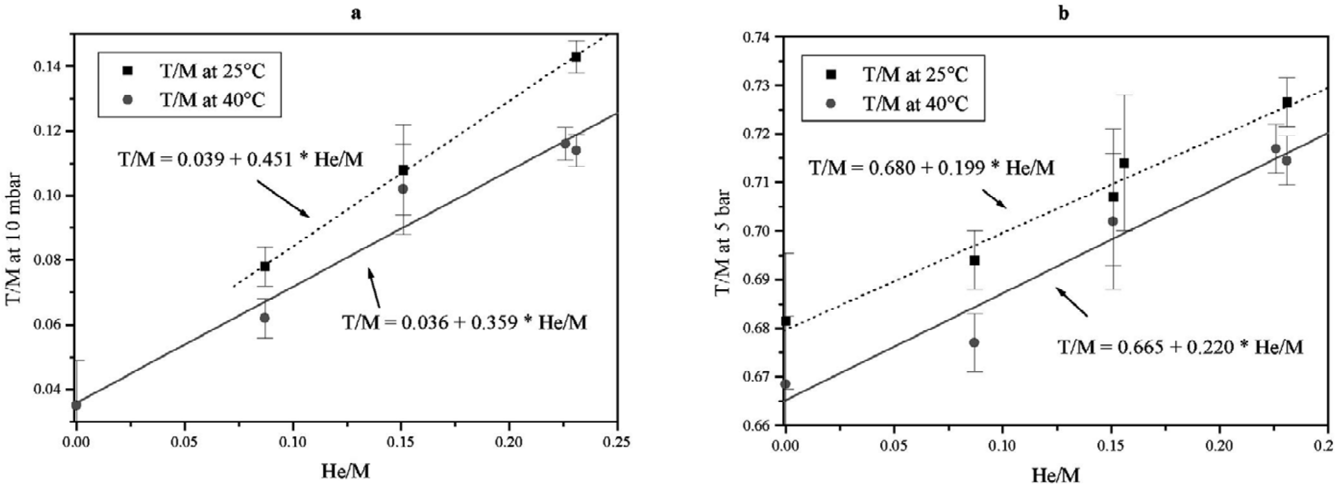

Fig. 4. Shift of α (a) and β (b) single phase solubilities versus ^{3}He contents.

previous studies by X-ray and neutron diffraction, X-ray absorption [5] and TEM [6] at the beginning of aging (He/Pd≤0.16, 5 years).

Thus, conservation of storage properties can be linked to the conservation of short range order (demonstrated by extended X-ray absorption fine structure (EXAFS) measurements [5]) as tritium, when forming the tritide, is especially sensitive to the interstitial site characteristics. Bubble formation (evidenced by TEM [6]) is here predominant by concentrating ^{3}He atoms and induced defects (lattice deformation, SIA, . . .), leaving the rest of the lattice almost intact and those interstitial sites free for tritium occupancy.

The decrease of plateau pressures can be correlated to the lattice swelling, in agreement with the geometric model [9] which predicts a linear evolution of the desorption pressure logarithm vs. the host lattice cell (i.e. the metallic cell) volume. In situ X-ray diffraction experiments [5] have shown that the main evolution of the tritide lattice parameter is observed at the beginning of aging and that further aging only leads to a slower increase of lattice parameter, similarly as the plateau pressure behavior (see Fig. 5a). This confirms the strong correlation between lattice parameter and tritide stability. By analogy with the geometric model, we have represented in Fig. 5b the evolution of $\log(P_{\mathrm{des}})$ vs. the tritide lattice cell volume; the $\log(P_{\mathrm{des}})$ values used here have been calculated from extrapolation of data (see Fig. 3). This evolution is not linear (even if the tendency is correct according to the model), but this may be due to the fact that we have considered the tritide lattice parameter, instead of the host (metal) lattice parameter, which is dependent on the applied pressure via the tritium content (in the samples studied here, which are sealed, the tritium pressure is continuously decreasing by radioactive decay, so the tritide stoichiometry is not constant and tritide lattice cell variations can be slightly different from metallic cell ones).

The increase of plateau slopes can be attributed to the dispersion of interstitial sites volume (which was clearly established from Debye-Scherrer lines broadening in neutron diffraction experiments [5]), according again to the geometric model.

The decrease of the hysteresis loop may be linked to the strain and the great density of dislocations appearing even at small ^{3}He content, as demonstrated by the broadening of the Debye-Scherrer lines observed in neutron diffraction experiments [5]. In this case, the exact relationship between dislocations density and hysteresis is not clear since the origin of hysteresis itself is not well established. But, it is commonly admitted that plastic deformation and dislocations generation during hydride formation/decomposition are responsible for hysteresis [10,11] and, if the starting material is already strained and almost saturated with dislocations, absorption or desorption will cause less deformation and may even release a part of the strain during the phase transition.

The shift of the α single phase region towards greater stoichiometries, which corresponds to deeply trapped tritium, can be correlated to the presence of defects like ^{3}He bubbles, dislocation loops and dislocations (observed by TEM [6]), which are efficient tritium traps because tritium has a great affinity to metallic atom « voids » like bubble surfaces and dislocation core. Here again, an exact quantification is not possible but both shift of the α phase solubility and defects (dislocations and bubbles) densities increase continuously during aging.

At last, the shift of the β single phase region towards greater stoichiometries, at a rate about half of that for the α, may be the most difficult to explain. If the β solubility did not shift, it would mean that all the deeply trapped tritium occupies sites which are no longer available for reversible tritium occupancy. We have already seen that this is clearly not the case. On the contrary, if the β solubility was shifting at the same rate as the α, this would

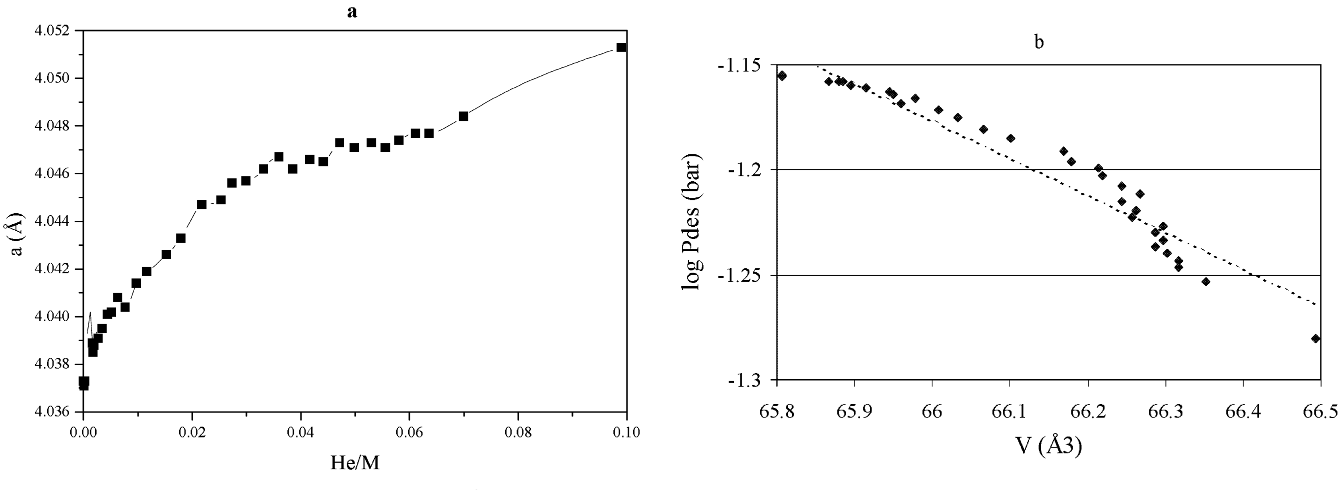

Fig. 5. Evolution of the Pd tritide lattice parameter vs. ^{3}He content (a) and correlation between logarithm of the desorption plateau pressure at 25 °C vs. Pd tritide lattice volume (b). The straight line is only a guideline to evidence the non linear behaviour.

mean that the host lattice is perfectly preserved during aging. This is not totally correct, either. As the reversible capacity is only decreasing slowly during aging, this may be correlated to the small decrease of short range order, observed by EXAFS [5]: the generation of great densities of defects (bubbles, dislocations) may finally induce this small decrease of short range order in the metal matrix, leading to the disappearence of some interstitial sites.

4. Conclusions

We have measured $P-c$ isotherms for the Pd–T_2 system at 25 and 40 °C until He/Pd$=$0.23 (9 years). The small modifications observed have been explained by structural and micro-structural evolutions expected according to the self trapping theory. This theory was validated in previous studies at the begining of aging (He/Pd$\leq$0.16, 5 years) and the evolution of $P-c$ isotherms is continuous during the whole period studied here, so the self trapping theory seems to apply for at least 9 years of aging. Nevertheless, future work will try to get structural and microstructural information on materials with ^{3}He contents similar to materials studied by $P-c$ measurements. Those experiments will also be pursued on older Pd samples.

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