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# On the correlation between mechanical and TEM studies of the aging of palladium during tritium storage

A. Fabre [a,*], B. Decamps [b], E. Finot [c], J.M. Penisson [d], J. Demoment [a], S. Thiebaut [a], S. Contreras [a], A. Percheron-Guegan [b]

[a] *Commissariat à l'Energie Atomique de Valduc, F-21120, Is-sur-Tille, France*
[b] *Laboratoire de Chimie Métallurgique des Terres Rares, UPR CNRS 209, F-94320-Thiais, France*
[c] *Laboratoire de Physique, UMR CNRS 5027, Université de Bourgogne, F-21011 Dijon, France*
[d] *Département de Recherche Fondamentale sur la Matière Condensée CEA-Grenoble F-38041, Grenoble cedex, France*

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## Abstract

Tritium has considerable technological applications in nuclear industry. Since it is a radioactive element, its storage is often considered in the form of tritides which ensure the required safety. However, the decay of tritium into $^3$He alters the tritide properties during aging. With the aim of understanding the aging mechanisms of palladium tritide, a macroscale approach coupled with a microscopic study was performed on palladium aged up to eight months after tritium loading. The macroscale investigation based on the vibration of microcantilevers allowed the mechanical response of the material to be followed during its aging. The microscopic study was performed by Transmission Electron Microscope (TEM) and led to the observation of $^3$He nanometric bubbles within the material at different ages. The Young's modulus was found to grow mainly during the first weeks of aging. The bubble density was found to remain almost constant after the first month while their diameter grew very slightly after further aging. As a result, both methods showed the importance of the phenomena occurring during the first month of aging in the case of palladium tritide.

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## 1. Introduction

Palladium is a reference material for tritium storage in tritium facilities because of its ability to easily absorb as well as release tritium and to retain the $^3$He produced by radioactive decay [1–6]. Understanding the aging process of palladium tritide is of practical interest for future thermonuclear energy production. Tritium has a high mobility in many metals and its natural radioactive decay produces $^3$He atoms which migrate and form nanometric clusters within the tritide matrix. A population of 1 nm diameter $^3$He bubbles uniformly distributed within palladium was investigated by Transmission Electron Microscopy (TEM) from 1 to 3 months of aging [7,8], thereby suggesting rather low pressure within the bubbles (less than 1 GPa) and raising the issue of the proportion of $^3$He atoms inside the bubbles. From another source, the internal $^3$He density was extrapolated

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[*] Corresponding author. Tel.: +33 3 80 23 4970; fax: +33 3 80 23 5220.
*E-mail address:* arnaud.fabre@antigone.cea.fr (A. Fabre).

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from Nuclear Magnetic Resonance performed on bulk samples and was found to decrease within the bubbles from 0.21 ($t = 6$ months) to 0.15 mol cm$^{-3}$ ($t = 96$ months) [9,10], thereby suggesting internal pressures much higher than 1 GPa. Electron Energy Loss Spectroscopy (EELS) has shown its ability to determine the density and the state of $^3$He bubbles implanted in aluminum film [11,12]. The local $^3$He density within a single bubble naturally grown in a palladium-platinum alloy was recently measured, thereby deducing an internal pressure within the range of several hundreds of MPa [13] that suggests an agreement with previous results [7,8].

However, the delicate handling of tritium in terms of security has limited the number of experiments related to the physical parameters of the He bubbles. The growth kinetics of cluster is not yet determined due to the lack of in situ measurements. The lattice parameter $a$ of the palladium tritide was determined as a function of the [$^3$He]/[Pd] ratio by X-rays. Thermomechanical models have been proposed to describe the bubble growth [14–16] based on the mechanical properties of the palladium tritide matrix, the tritium radioactive decay and the He diffusion.

The purpose of this article is to follow the evolution of the $^3$He bubbles in palladium tritide during the first 8 months of aging. The main feature was to combine two different approaches, respectively, based on macroscale and microscale observations. In situ measurements are highly recommended to satisfy the equilibrium between the solid metal phase and the fluid tritium phase. Millimeter-scale samples enable us to minimize the hydriding time. The mechanical response of the sample was measured over time using a new approach recently developed [17]. This technique based on the detection of vibrational modes of microcantilevers has already provided results on Young's modulus of polycrystalline palladium microcantilevers under vacuum (128 ± 3 GPa), hydrogen (111 ± 5 GPa), deuterium (117 ± 5 GPa) [18] and tritium (119 ± 5 GPa) [19]. Monitoring the chamber pressure (of known volume) over time permits the sample composition to be determined.

A TEM study was conducted in parallel to measure the cluster size for 3, 5 and 8 months aged samples. Comparisons between the mechanical and microscopic information are discussed in order to get a better understanding of the helium behavior in the palladium.

## 2. Experimental procedure

### 2.1. Elastic properties

The experimental setup is based on the periodic excitation of the fixed end of a cylindrical cantilever and the detection of its natural resonance frequency $f_0$. The Young's modulus $E$ is obtained by measuring $f_0$ and knowing the sample geometry and density as follows:

$$E = \frac{4}{3}\left(\frac{\pi L^2 f_0}{r}\right)^2 \rho, \tag{1}$$

where $L$ is the length, $r$ is the radius and $\rho$ is the mass density of the cantilever. Three millimeter length microcantilevers were taken from 500 μm diameter palladium wire supplied by Goodfellow.

The experimental setup previously developed for non radioactive experiments has been adapted in this study to fulfill requirements of tritium handling, as described in Fig. 1. The measurement cell and the detection system were placed within a glove box atmosphere while electronic devices remained in the room area. The electric signals were conveyed through airtight connections inserted in the walls of the glove box.

Palladium samples have been activated under a secondary vacuum to outgas and clean the palladium surface and heated thereafter to facilitate the tritium absorption. During the aging the tritium pressure was fixed to 0.92 bar in order to maintain the sample in the β-phase.

### 2.2. TEM observations

Three millimeter diameter discs were punched out from 0.13 mm thick palladium foils supplied by Goodfellow. They were annealed during 24 h at 1000 °C and then put into stainless steel containers suitable for handling a 5 bars tritium pressure to form palladium tritide. Tritium absorption and aging up to 3, 5 and 8 months were achieved at room temperature. The $^3$He amount was deduced from both the initial tritium content and the aging time, assuming that all the $^3$He generated in the solid is retained. Tritium was removed by isotopic exchange with deuterium at room temperature. The final gas desorption was performed at room temperature to avoid a $^3$He rearrangement usually induced by high temperature treatments.

Discs were thinned down by jet-electropolishing using a 70% acetic acid and 30% perchloric acid electrolyte kept at room temperature under 30 V to be observed by TEM. Images were obtained from a JEOL 4000EX TEM and a HITACHI Topcon 200 kV TEM. The imaging conditions and specimen orientations were chosen so that no important Bragg reflection is excited. Bubble contrast was highlighted through a large positive defocus where they appear as darks dots surrounded by a white fringe and through a large negative defocus where they appear as white dots surrounded by a dark fringe. The mean size of the bubbles has been estimated by measuring the size of the dots in the through-focus series. In the previous work [8], these measurements have been confirmed using high resolution and a cavity model

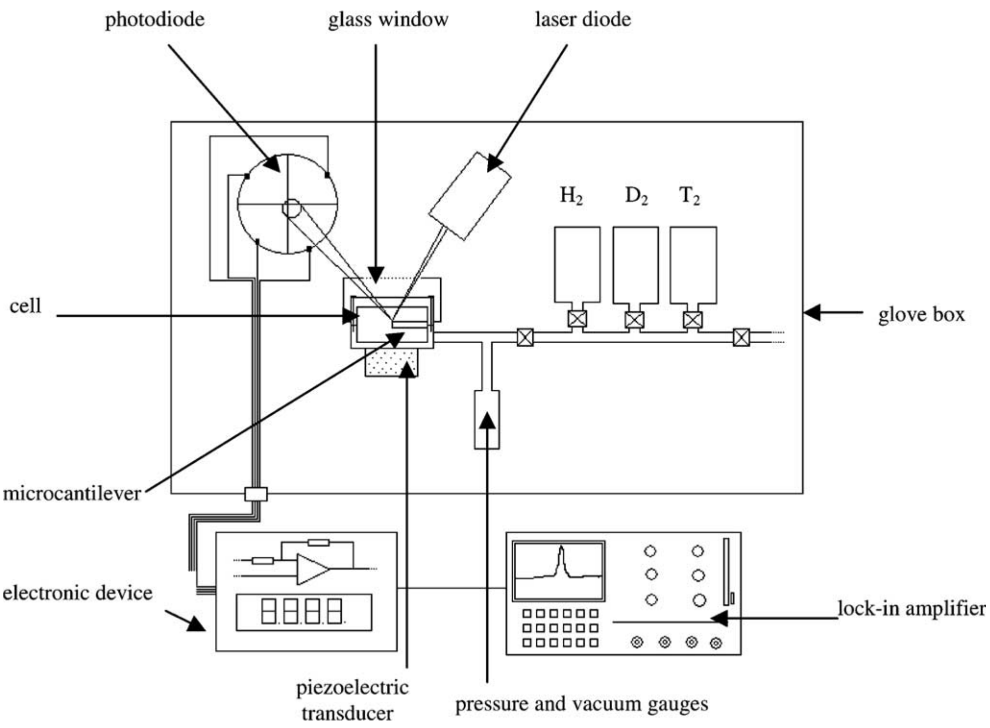

Fig. 1. Experimental setup.

showing that the size of the dot is similar to that of the cavity in these conditions. Bubble density was estimated using an automated procedure, which includes an image filtering (annular mask removing low and high spatial frequencies) and a detection of local intensity minima for overfocused images and maxima for underfocused images [20]. It has been verified that the two types of measurements (on white and dark dots) give equivalent results. The density calculation requires the determination of the specimen thickness which is performed using two beam bright-field images displaying thickness fringes. The density results are confirmed by purely manual measurements.

## 3. Experimental results

### 3.1. Mechanical approach

Fig. 2 shows typical frequency response of the palladium cantilever placed first under vacuum during 1 h and then in hydrogen, deuterium or tritium gas. The frequency shift was used to calculate the Young's modulus $E$ given the sample swelling. $E$ for the polycrystalline palladium used in that study is 128 GPa under vacuum. $E$ decreases to 119 GPa 1 h after immersion in 1 tritium bar.

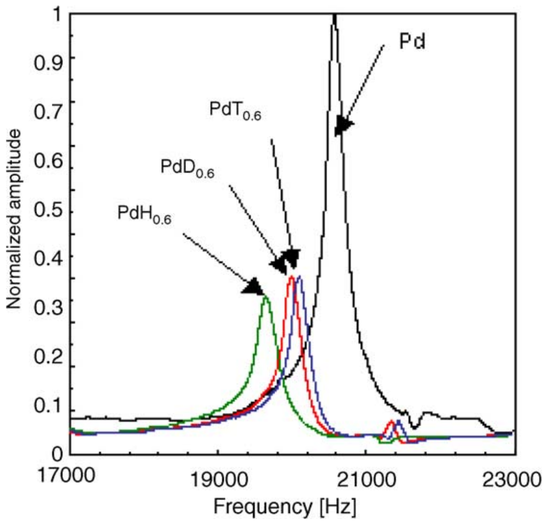

Fig. 2. Resonance frequency peaks of palladium cantilever under vacuum, hydrogen, deuterium and tritium.

The resonance frequency $f_0$ was then monitored over time as shown in Fig. 3. According to the excellent sensitivity of the technique [17], $f_0$ grew significantly in the first days and slowed down after 10 days followed by a much slower growth after about 20 days. These

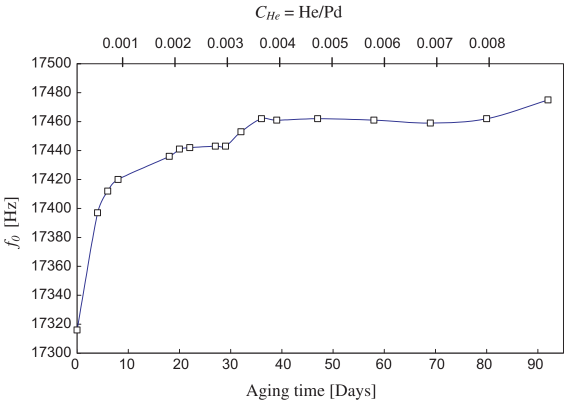

Fig. 3. Resonance frequency $f_0$ as a function of aging time.

measurements have been reproduced with different samples. Surface degradation of the cantilever after 4 months of aging makes the measurement very difficult due to the diffusion of the reflected laser spot. To deduce $E$ from the evolution of $f_0$, the sample swelling should be estimated. The palladium tritide is known to swell as the concentration $C_{\mathrm{He}} = {}^3\mathrm{He/Pd}$ increases with the radioactive decay of tritium atoms. A linear increase in volume ranging from 1.34% to 1.7% per year has been estimated from macroscopic measurements [10,21,22]. Fig. 4 shows the evolution of the lattice parameter $a$ of the palladium tritide as a function of the $^3$He content as studied by X-ray diffraction [23]. For $C_{\mathrm{He}} < 0.01$ corresponding to the 3 first months of natural aging, the lattice deformation increases linearly with increasing $^3$He amount such as: $(\frac{\Delta a}{a})_{\mathrm{He}} = 0.02 \times C_{\mathrm{He}}$. For $C_{\mathrm{He}} \geqslant 0.02$, namely after 6 months of natural aging, the lattice swelling is reduced by two orders of magnitude $(\frac{\Delta a}{a})_{\mathrm{He}} = 3.10^{-4} \times C_{\mathrm{He}}$.

The macroscopic expansion of a polycrystalline material is assumed to vary as the lattice swelling as a first approximation. The palladium tritide density varies as follows:

$$\rho_{C_{\mathrm{He}}} = \frac{\rho_0}{1 + 3 \times \left(\frac{\Delta a}{a}\right)_{\mathrm{He}}}. \tag{2}$$

The Young's modulus $E_{\mathrm{PdT}_x}$ of the palladium tritide can be therefore calculated as a function of $C_{\mathrm{He}}$

$$E_{\mathrm{PdT}_x} = \frac{4\pi^2}{3}\left(\frac{\left(1 + \left(\frac{\Delta a}{a}\right)_{\mathrm{He}} \times C_{\mathrm{He}}\right)\left(1 + \left(\frac{\Delta a}{a}\right)_T \times x\right)L_0^2 f_0}{r_0}\right)^2 \rho_{C_{\mathrm{He}}}. \tag{3}$$

The initial stoichiometry of the studied tritide was estimated to 0.63 ± 0.05 by measuring the variation in tritium pressure within the measurement cell. Fig. 5 shows the relative deviation $\Delta E_{\mathrm{He}}$ from the initial value of $E_{\mathrm{PdT}_x} = 119$ GPa. Note that the experimental method used here is especially accurate in terms of relative values of Young's modulus because all measurements were performed in situ on the same sample, changing only the surrounding atmosphere [17].

$\Delta E_{\mathrm{He}}$ increases exponentially with increasing the He to Pd ratio. The 1.5% increase in $E$ is quite complex to interpret.

### 3.2. TEM results

The question of the distribution of helium atoms within the palladium tritide matrix must be addressed. The following microscopic study, performed by TEM, provided additional information to interpret the macroscopic results.

TEM observations have been performed on palladium samples aged during 3, 5 and 8 months. The detailed conditions of aging of each sample are reported in Table 1. The presence of He bubbles has previously been revealed using through-focus experiments on 1–3 months old palladium samples [8]. The same investigation method has been applied to our own samples in order to confirm the previous results on 3-month old

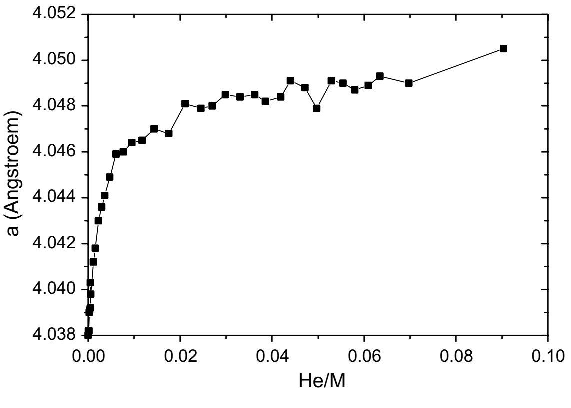

Fig. 4. Lattice parameter $a$ of palladium tritide as a function of helium concentration He/M.

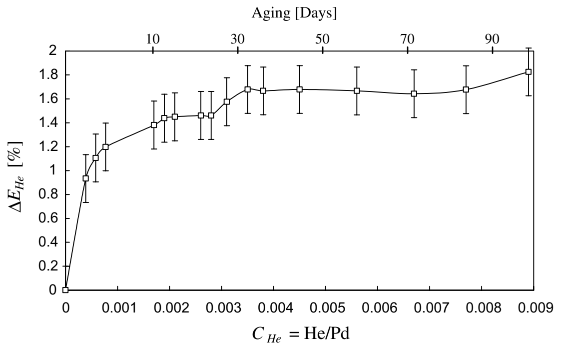

Fig. 5. Young's modulus $E_{\mathrm{He}}$ of palladium tritide as a function of time and He/M.

Table 1
Aging conditions of palladium samples observed by TEM

| Palladium sample number | Aging [day] | Load pressure [bar] | Stoichiometry T/Pd at $t = 0$ | % of T transformed into $^3$He | Content ratio $^3$He/Pd |
|---|---|---|---|---|---|
| 1 (3 months) | 96 | 5.0 | 0.68 | 1.47 | 0.010 |
| 2 (5 months) | 154 | 5.0 | 0.68 | 2.34 | 0.016 |
| 3 (8 months) | 236 | 5.0 | 0.68 | 3.57 | 0.024 |

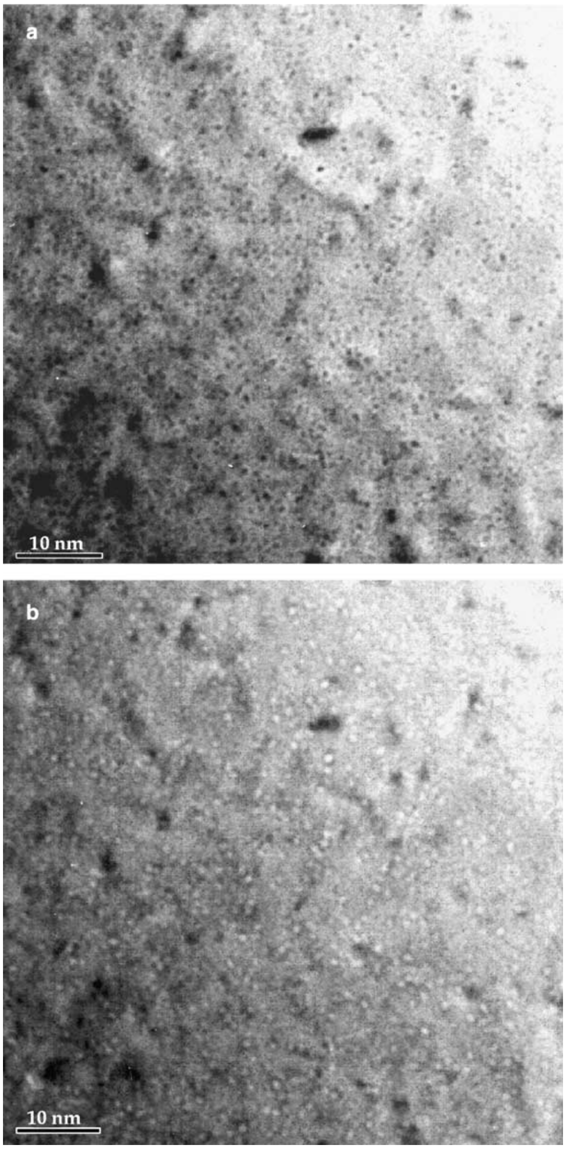

Fig. 6. (a) TEM image of a three-month old palladium sample, negative defocus and (b) TEM image of a 3-month old palladium sample, positive defocus.

samples and to extend them to 5- and 8-month old samples. Through-focus series reveal the presence of He bubbles for the three aging times (3, 5 and 8 months). As expected, one nanometer diameter bubbles are present in the sample aged 3 months (typical pictures are given in Fig. 6), that is to say as white dots surrounded by a dark fringe for negative defocus (see Fig. 6(a)) and as black dots surrounded by white fringe for positive defocus (see Fig. 6(b)). Bubbles are evenly distributed within the studied areas. A similar average bubble size is also found for the sample aged 5 months (figures not presented in this paper). For 8 months of aging, the observations reveal a slight increase of the bubble diameter to 1.2–1.5 nm (see Fig. 7(a) and (b)). The bubble density is estimated as mentioned above (see Section 2.2) and is found to range from $0.5 \times 10^{25}$ to $2.0 \times 10^{25}$ bubbles per m$^3$ for all aging times, this large uncertainty arising from the difficulty to accurately access the exact thickness of the thin area investigated by TEM. Comparing the three aging times, it appears that although the bubble density seems to increase with the aging time (3 and 5 months), the measured increment is within the uncertainty range. This effect is not so clear for 8 months of aging where the observations reveal a slight increase of the bubble size. Bubble contrast given by the conventional overfocus/underfocus images and the absence of detectable elastic field around the bubbles are consistent with previous observations suggesting that they are not over pressurized, as mentioned in the previous study [8].

## 4. Discussion

Classical mechanical models estimate that the Young's modulus of a material containing inclusions decreases in linear proportion with the volume fraction of the inclusions [24]. This is not in agreement with what we observed for the first months of aging of palladium tritides containing $^3$He bubbles. However, these macroscopic assumptions cannot be further supported when inclusions are nanometric clusters containing just a few tens of helium atoms, especially at the beginning of the aging. For instance, according to values taken from the literature, an atomic volume of $^3$He atoms within the clusters can be estimated between 8 Å$^3$ (estimated from NMR experiments [9,10]) and 20 Å$^3$ (recent results estimated from TEM observations [8,25]). In these conditions, the number of $^3$He atoms within a one

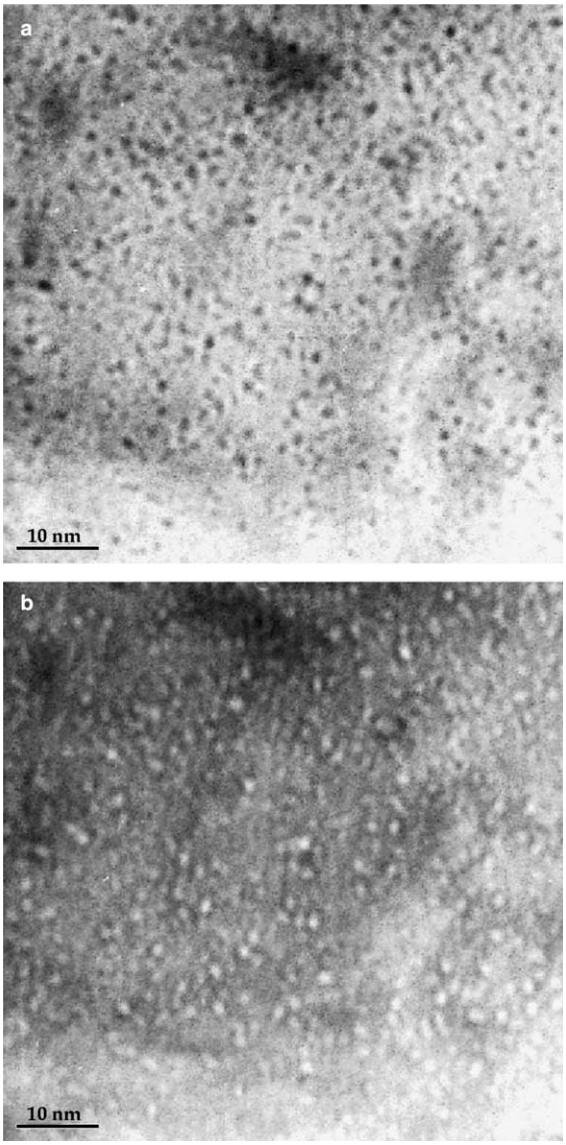

Fig. 7. (a) TEM image of an 8-month old palladium sample, negative defocus and (b) TEM image of an 8-months old palladium sample, positive defocus.

nanometer bubble would not exceed 70. Models used in the composite field are certainly not reliable at the early stage of the aging [26].

The swelling of the palladium tritide is also expected to lead to a slight decrease of its Young's modulus. As a result, the increase in *E* should correspond to a hardening and/or an embrittlement of the material due to the presence of helium atoms in the matrix. A decrease in the ductility of the palladium tritide due to helium production has already been experimentally observed [27] and theoretically suggested according to electronic structure calculations [28]. Anyway, the behavior of the Young's modulus, especially during the first month of aging, raises the problems of interstitial helium atoms, their distribution and their effect on the elastic properties of the whole material.

TEM observations strongly suggest that most of the bubbles are formed within the first month of aging [8]. Their diameter is shown to grow very slightly during the following 8 months. It is noticeable that this behavior can easily be correlated to the similar results obtained on $\delta$-$ZrT_{1.6}$ by Schöber et al. concerning the same aging times [29]. This behavior is in agreement with the evolution in *E* to indicate that the first month is of fundamental importance in the aging of palladium tritides. Most of the clusters are generated very early during the first weeks. If we compare these results with the literature, it is noticeable that Thomas et al. observed helium bubbles of 2 nm after almost 2 months of aging. They also determined a density ranging from 5 to $10 \times 10^{23}$ bubbles per $m^3$, that is to say 10 to 20 times smaller than estimated in this paper. This comparison suggests that the number of bubbles may be strongly influenced by the defect density within the initial material. Defects such as atomic vacancies, dislocations, grain boundaries or impurity atoms, are known to be good trapping sites for $^3He$ interstitial atoms. Such a hypothesis is strengthened by our previous TEM observations which demonstrate that a very large population of dislocations is produced during the first month of aging [8]. As the number of bubbles seems to grow very slightly, the size of the bubbles is likely to accommodate more or less quickly the $^3He$ atoms produced by radioactive decay.

As the radioactive decay law permits us to know the $^3He$ atoms ratio in the tritide (see Table 1) and assuming that all the helium produced remained in the matrix [20], one may estimate the ratio He/M existing within the material for any aging time. Thus, it is possible to calculate the fraction of He localized in bubbles of given size and density, once the volume occupied by one He atom is known. Data such as bubble size and density are directly obtained from TEM measurements for different aging times. Furthermore, the upper limit pressure within the bubble may be estimated as the TEM images of bubbles show that there is no detectable elastic field around the bubbles [8]. Though the imaging conditions are not the most favourable here to evidence such elastic fields, this could indicate that the internal pressure should be lower than 0.75 GPa according to numerical simulations [30,31]. Such an assertion has just been strengthened by preliminary results using EELS in a palladium–platinum alloy after 8 months of aging [13]. From this upper value of the pressure, the smaller volume occupancy of a helium atom within the bubble can be estimated to be 20 $Å^3$ from the formula established by Le Toullec et al. [25]. Then, estimating volumes for palladium (based on the lattice parameter data) and for helium (20 $Å^3$ [8–10]) and using bubble diameters and densities measured from samples aged up to 8 months, simple evaluations suggest that all $^3$He atoms are not necessarily within the observed bubbles. A quantity up to several tenths of percents of the $^3$He atoms may remain in interstitial sites or in smaller bubbles that we did not observed by TEM. Densities from NMR experiments [9,10] or atomistic calculations [32] suggest that all the $^3$He atoms are within the bubbles but this involves internal pressures of at least 8 GPa. However, as experimental uncertainties appear to be too large to clearly solve this problem when the aging time increases, complementary techniques like EELS should be of great interest to determine $^3$He atoms densities within the bubbles and to complete these results.

## 5. Conclusion

The agreement between both mechanical and microscopic studies tends to highlight the importance of the early stages of aging in the case of palladium tritides. The Young's modulus of the palladium tritide was found to grow during the first two weeks of aging before to slightly increase afterward. The $^3$He bubbles were studied by TEM and a homogeneous distribution of bubbles was observed. The bubble diameter appeared to grow very slightly during the first 8 months of aging ranging from 0.8–1.0 nm to 1.2–1.5 nm. These results tend to indicate an internal pressure smaller than 0.75 GPa, thereby suggesting that all $^3$He atoms are not within the bubbles at least after the first months of aging [8]. However, the bubbles observed by MET were larger than 0.8 nm and this does not exclude the existence of smaller bubbles whose contribution was taken into account by techniques like NMR for instance. So, the increase of the Young modulus during the first month of aging could be related to the formation of dislocations and/or to the presence of interstitial helium atoms as shown by the TEM observations.

The fundamental phenomena occurring from the earliest stages of the aging remain to be elucidated. Further work will need to focus on the first weeks of aging with an investigation by TEM of the earliest aging time corresponding to clearly visible bubbles. Theoretical work such as atomistic simulations of the growth of helium bubbles in metal is required to understand the effect of interstitial $^3$He atoms.

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## References

[1] F.A. Lewis, The Hydrogen Palladium System, Academic Press, London, 1967.
[2] W.M. Meuller, J.P. Blackledge, G.G. Libowitz, Metal Hydrides, Academic Press, New York, 1968.
[3] E. Wicke, H. Brodowsky, H. Zuchner, in: G. Alefeld, J. Völkl (Eds.), Hydrogen in Metals, Springer, Berlin, 1978.
[4] Y. Fukai, The Metal Hydrogen System, Springer, Berlin, Heidelberg, 1992.
[5] A.A. Lucas, Physica 127B (1984) 225.
[6] R. Lässer, Tritium and Helium-3 in Metals, Springer, Berlin, 1989.
[7] G.J. Thomas, J.M. Mintz, J. Nucl. Mat. 116 (1983) 336.
[8] S. Thiébaut, B. Décamps, J.M. Pénisson, B. Limacher, A. Percheron-Guégan, J. Nucl. Mater. 277 (2000) 217.
[9] G.C. Abell, A. Attalla, Phys. Rev. Lett. 59 (9) (1987) 995.
[10] G.C. Abell, A. Attalla, Fus. Technol. 14 (Sep.) (1988).
[11] K. Ohtaka, A.A. Lucas, Phys. Rev. 18 (9) (1978) 4643.
[12] C.A. Walsh, J. Yuan, L.M. Brown, Philos. Mag. A 80 (7) (2000) 1507.
[13] D. Taverna, M. Kociak, A. Fabre, O. Stephan, L. Henrard, E. Finot, B. Décamps, A. Percheron-Guégan, C. Colliex, Phys. Rev. Lett. (in press).
[14] H. Trinkaus, Rad. Effects 78 (1983) 189.
[15] W.G. Wolfer, J. Nucl. Mater. 93&94 (1980) 713.
[16] G.W. Greenwood, A.J.E. Foreman, D.E. Rimmer, J. Nucl. Mater. 1 (1959) 305.
[17] A. Fabre, E. Finot, J. Demoment, S. Contreras, J.P. Goudonnet, Rev. Sci. Instrum. 72 (10) (2001) 3914.
[18] A. Fabre, E. Finot, J. Demoment, S. Contreras, Ultramicroscopy 97 (2003) 372.
[19] A. Fabre, E. Finot, J. Demoment, S. Contreras, J. Alloy Compd. 356–357 (2003) 372.
[20] B. Décamps, J.-M. Pénisson, S. Thiébaut, A. Percheron-Guégan, in: Proceedings of the 14th International Congress on Electron Microscopy, Cancun, vol. 3, ICEM 14, Symposium GG, 1998.
[21] G.T. McConville, D.A. Menke, D. West, C.M. Woods, in: S.P. Arthur (Ed.), MLM-3799, Technical Publications, 1994.
[22] J.A. Emig, R.G. Garza, L.D. Christensen, P.R. Coronado, P.C. Souers, J. Nucl. Mater. 187 (1992) 209.
[23] S. Thiébaut, V. Paul-Boncour, A. Percheron-Guégan, B. Limacher, O. Blaschko, C. Maier, C. Tailland, D. Leroy, Phys. Rev. B 57 (1998) 10379.
[24] J.D. Eshelby, Proc. Roy. Soc., London A241 (1957) 376.
[25] R. Le Toullec, P. Loubeyre, J.P. Pinceaux, Phys. Rev. B 40 (4) (1989) 2368.
[26] A. Reuss, Z. Angew. Math. Mech. 9 (1929) 49.
[27] G.J. Thomas, Radiat. Eff. 78 (1983) 37.
[28] R.P. Gupta, M. Gupta, Phys. Rev. B 66 (2002) 014105.
[29] T. Schöber, Fus. Technol. 14 (1988) 637.
[30] B. Cochrane, P.J. Goodhew, Phys. Stat. Sol. A 77 (1983) 269.
[31] K.J. Stevens, P.B. Johnson, J. Nucl. Mater. 245 (1997) 17.
[32] S.M. Foiles, J.J. Hoyt, Sandia National Laboratories Report, Sand2001-0661, Unlimited Release, 2001.