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AGING OF Pd UNDER TRITIUM: INFLUENCE OF ^3He GENERATION AND ASSOCIATED MECHANISMS

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† Michel Latroche participated to the redaction of the article until his death on 30th December 2021. This article is dedicated to his memory.

Abstract

An experimental and theoretical study has been conducted to improve the understanding of the Pd tritide aging process. Tritide aging due to tritium radioactive decay produces ^3He which create nanobubbles in the metal matrix. Pd samples are aged up to 20 years to cover the three steps of aging: bubble nucleation (\sim few days), bubble growth (\sim few years) and ^3He massive release (over 10 years, depending on the initial tritium loading). All the experimental measurements are used as input/output data for the theoretical aging mechanism modeling. The bubble nucleation/growth modeling is improved thanks to these additional data. A sample aged over 20 years has been fully characterized which allows proposing a mechanism and the corresponding modeling for the last step of the aging process: the ^3He release. The models **provide** a material behavior that agrees with microscopic and macroscopic observations.

1. Introduction

Using nuclear fusion to produce energy necessitates storing and manipulating tritium, the radioactive isotope of hydrogen. Solid-state storage is of great interest because of its compactness and safety. Pd and its alloys are commonly studied for the storage of hydrogen isotopes by using reversible metal hydrides at low equilibrium pressure. The storage of tritium is peculiar because its natural decay produces ^3He ($t_{1/2} \approx 12.3$ years) that is responsible for the gradual modification of most properties of the metal tritides.

^3He tends to remain trapped as nano-bubbles within the material, up to a critical content above which, ^3He is massively released in the gas phase. During this last stage, the ^3He pressure can increase

drastically in the storage container, which can compromise its design to ensure safety. It is therefore fundamental to understand and to be able to predict the aging process as a whole.

The aging process is divided in three major steps. The bubbles nucleation (several days of aging), the bubbles growth (few years of aging) and the ^3He massive release (over 10 years). For each aging step (nucleation, growth and release) a model is proposed to simulate the aging mechanism, requiring input and output data that, for most of them, can be experimentally acquired.

The bubble nucleation modeling involves a cellular automaton(1) describing the material at the atomic scale. The calculations involves tritium diffusion, tritium decay, ^3He diffusion, and ^3He self-trapping that lead to bubble nucleation. This calculation gives access to bubble spacing and bubble density in the storage material which can be studied by TEM(2,3) or electron tomography(4).

^3He bubble growth is modeled using a continuum mechanic calculation(5). The output parameters (bubble size, pressure, material swelling) can be experimentally measured by TEM(2,3), EELS(6), ^3He NMR, electron tomography(4) and pycnometry.

Last step, corresponding to the release of ^3He , has not been modeled yet and a new specific mechanism has to be proposed. Three mechanisms are commonly considered: material fracture (7,8), bubbles coalescence (9) and ^3He release (10–12).

The objectives of this work are to reinforce the modeling of nucleation and growth of the ^3He bubbles by new experimental results, and to complete it by developing the basis of the last phase of aging: the so-called “ ^3He massive release”. It implies to experimentally characterize the aging process and to adjust the corresponding mechanisms and calculations.

In previous works, experimental studies based on transmission electron microscopy (TEM) techniques have been performed on Pd tritide powders aged up to 8 years, corresponding to the bubble growth stage(2,3). These experiments allowed to estimate the density and the size distribution of ^3He bubbles by TEM, the inter-bubble distance distribution by electron tomography(4) and the ^3He pressure inside the bubbles by EELS(6). These data are necessary input or output of the different models.

In this work, we will present new complementary experimental data on Pd powders aged under tritium up to 20 years, to cover the three aging steps, using not only electron microscopy techniques but also NMR, pycnometry and tensile tests. NMR allow to estimate the average ^3He pressure inside the bubbles, pycnometry the swelling of the tritide and tensile test the mechanical properties. These results will then be used to improve the modeling of the aging process. This study presents a complete theoretical and experimental study of the three aging stage mechanisms for Pd tritide powders.

2. Experimental and Modeling Methods

Samples preparation

Pd powder samples are cleaned using deuterium absorption-desorption cycles before tritium loading. The samples are aged under tritium between 0 and over 20 years at room temperature, covering the three stages of aging. The decontamination process of tritide powders is achieved via an isotopic exchange with deuterium. During this stage, the tritide/deuteride is kept in β -phase (13). The $^3\text{He}/\text{Pd}$ molar ratio characterizes the material aging. It is determined by combining tritide stoichiometry and aging time ($\text{He}/\text{Pd}_{\text{theoretical}}$) which will be used as sample name in the following. The $\text{He}/\text{Pd}_{\text{real}}$ is the value measured by gas analysis that included the helium weeping during aging. Table 1 gathered main aging conditions

of the samples characterized in this microscopic study. Other similarly prepared samples are available for different types of measurements. All samples are aged at room temperature, most of them are replenished which means that they are kept in beta phase during aging.

Sample	Pd	PdHe _{0.02}	PdHe _{0.04}	PdHe _{0.17}	PdHe _{0.24}	PdHe _{0.30}	PdHe _{0.46}
Replenishment	-	yes	yes	no	yes	yes	no
He/Pd _{theoretical}	0.00	0.02	0.04	0.17	0.24	0.30	0.46
He/Pd _{real}	0.00	0.02	0.04	0.16	0.23	0.27	0.20
Aging temperature (K)	298	298	298	298	298	298	298
Aging step	-	nucleation	nucleation	growth	growth	growth	release
Aging period	-	Few months	Few months	Few years	Few years	Few years	> 20 years

Table 1 – Conditions of Pd aging under tritium and He/Pd ratio of samples characterized during microscopic study.

Analytical techniques

The TEM experimental techniques were already described for PdHe_{0.24} and PdHe_{0.30} in the following articles(2,3). Tomography measurements were conducted in HAADF mode (High Angle Annular Dark Field). The same techniques were applied to study the Pd, PdHe_{0.02}, PdHe_{0.17} and PdHe_{0.46} samples. For TEM, EELS and electron tomography measurements, the aged Pd powders were embedded in epoxy resins, which are then sliced by ultramicrotomy with a thickness close to 70 nm.

The measurements by EELS spectroscopy were conducted on PdHe_{0.24} and PdHe_{0.30} as detailed in reference(6) and then were applied to PdHe_{0.46}. The tomography first experiments were realized on samples PdHe_{0.17}, PdHe_{0.24} and PdHe_{0.30} as documented in article(4) and then applied to PdHe_{0.02} and PdHe_{0.46}.

³He NMR experiments were performed using Bruker Avance I 300WB (magnetic field 7.02 T) spectrometer operating at a Larmor frequency of 228 MHz. Low temperatures were achieved with a Spectrostat^{NMR} (Oxford Instrument) cryogenic system (operating with liquid helium or nitrogen) and a dedicated probe manufactured by NMR Service (<https://www.nmr-service.de>) were employed. Samples were packed in powder form and mixed with TiO₂ powder (50/50 in volume, aiming at reducing magnetic susceptibility effect) in sealed flame Pyrex tube (outer diameter 4 mm). The NMR signal was detected using a spin echo pulse sequence (90°-τ-180°-acq) with a typical RF pulse length of 5 μs for 90° and an echo delay (τ) of 100 μs. This delay was chosen in order to acquire the full echo which greatly minimized the baseline distortion. ³He spin-lattice relaxation time (*T*₁) was measured using an inversion-recovery pulse sequence with the above spin echo scheme for measuring the signal.

When decreasing the temperature, *T*₁ evolution shows a discontinuity that signs the ³He solid-fluid transition giving access to bubble pressures in aged Pd tritide (14–18). PdHe_{0.04}, PdHe_{0.24} and PdHe_{0.46} were studied between 30 K and 320 K.

The macroscopic density of Pd powders aged under tritium were studied by pycnometry (Quantachrom Micro Ultrapyc 1200E) to determine the tritide swelling. Pycnometry measurements were performed on 1 to 2 g of powder.

Tensile tests under hydrogen/deuterium atmosphere (5 bar) give access to mechanical properties. The H_2/D_2 pressure enables to keep the tritide in the β phase(16)¹². The palladium tritide is maintained in β phase all along, from synthesis to rupture.

Modeling methods

All the codes used for modeling were written in Fortran language. There is one model per aging step (bubble nucleation, bubble growth and 3He release). The bubble nucleation mechanism is a self-trapping one. It is modeled using a cellular automaton that was published in the following article(1). The bubble growth is modeled using a mechanical model described in the following article (5). The release step is modeled using a tritide saturation law.

3. Results and discussion

The first part summarizes the main experimental results obtained during this study. The experimental results are further detailed in the Supplementary Materials. In the following parts these results are used to adjust/develop the modeling of the aging phenomenon

3.1 Experimental results

The TEM characterizations of $PdHe_{0.02}$, $PdHe_{0.24}$ and $PdHe_{0.46}$ (aged over 20 years) are presented in the Supplementary Materials. 3He bubbles can be observed as white and black spots in over-focused (+1 μm) and under-focused (-1 μm) TEM images (see SM 1).

Bubble spatial repartition obtained by electron tomography after segmentation and reconstruction for $PdHe_{0.46}$ sample is **illustrated** on Figure 1 (left) and for other samples in Supplementary Materials (see SM 2). The distances between bubbles extracted from tomography acquisitions for all Pd samples aged under tritium is presented on Figure 1 (right).

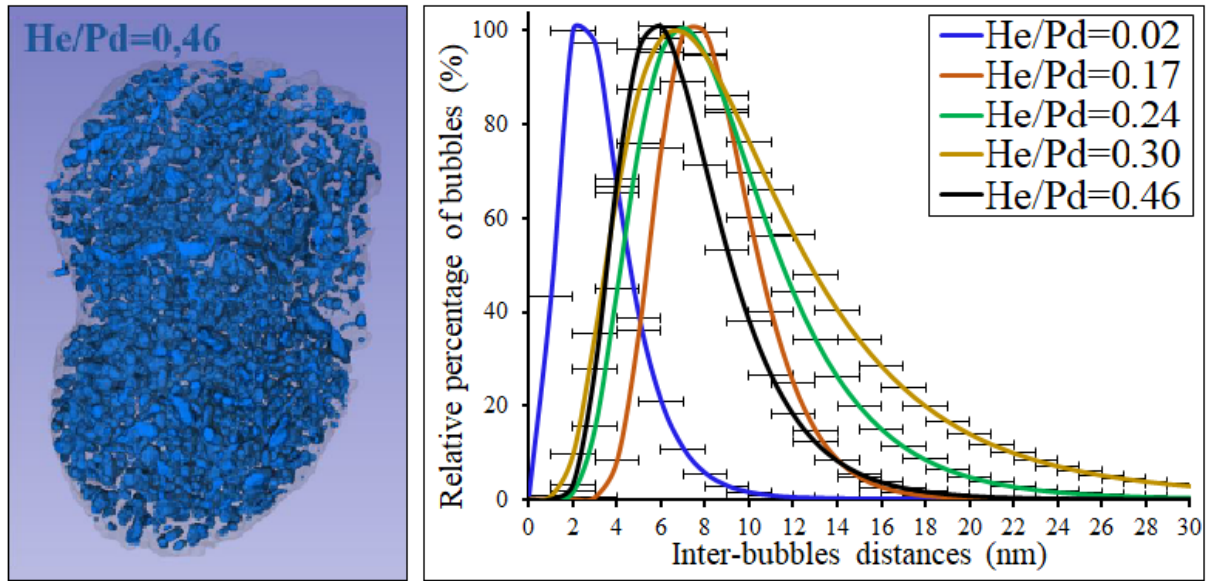


Figure 1 – 3D model of PdHe_{0.46} sample obtained by electron tomography (left) and log-normal fitting of distances between ³He bubbles for five Pd powders aged under tritium from few days to over 20 years measured by electron tomography (right).

Figure 1 reveals that after several years of aging the distances between bubbles rose by 5 nm, shifting from 3 nm after few months of aging to 7-8 nm after years of aging. However, it seems that bubbles distances do not evolve much after nucleation step. These values are in agreement with those from reference (19).

This result is consistent with the bubbles densities values measured by TEM and electron tomography during the same aging period (see SM 3). TEM allows to measure “surface” bubble density (bubble/m²) which is then converted to “volume” density (bubble/m³) using the sample thickness measured by EELS spectroscopy.

³He bubble diameters in Pd samples aged under tritium obtained by TEM and electron tomography are displayed in Figure 2. Table 2 summarizes the number of bubbles that were measured for each technique.

Sample	PdHe _{0.02}	PdHe _{0.17}	PdHe _{0.24}	PdHe _{0.30}	PdHe _{0.46}
TEM	3009	2009	3023	2450	6292
HAADF tomography	3257	2580	1906	2100	2002

Table 2 – Number of bubble measured during this study for each microscopy technique.

Alongside the ³He density in bubbles measured by solid-state NMR in three aged Pd samples is presented in Figure 2.

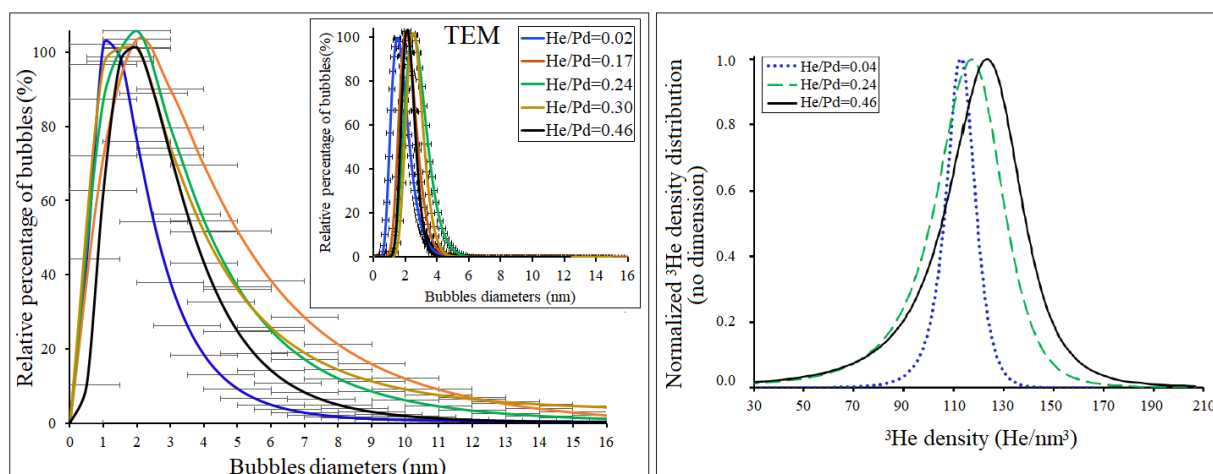


Figure 2 – Log-normal fitting of ^3He bubbles diameters measured by TEM and by electron tomography (left) and ^3He density distribution in nanobubbles measured by solid-state NMR (right) for Pd powders aged under tritium from few days to over 20 years (left).

In Figure 2 (left), the maximum of bubble diameter repartition is around 1 nm for the younger sample. It then increases towards 2 nm with aging in agreement with previous studies (3,20). Bubble sizes seem to stabilize around 2 nm even after 20 years of aging despite reaching the ^3He release step.

In Figure 2 (left), both 2D-TEM and 3D-HAADF tomography measurements reveal **little** evolution of bubble diameters between few years and over 20 years of aging. However, the swelling pycnometry and tomography data in Figure SM 4 show an increase of swelling with aging (reaching 20% after few years). It could seem inconsistent, but it only reveals the importance of 3D measurements. Indeed, if a 2 nm bubble swells by 20% the resulting diameter is 2.1 nm. Not impossible, but hardly detectable by TEM. The redundancy of the information of the 3D model allows to highlight a swelling that was not obviously emphasized by 2D-conventionnal means.

In Figure 2 (right), the ^3He density distributions inside nanobubbles measured by NMR reveal maxima between 100 He/nm^3 (few months aging) and 130 He/nm^3 (several years aging). These values correspond to pressures of several GPa. The broadening of the peaks indicates a larger internal pressure distribution which is probably related to the wider diameter distribution with aging.

The ^3He densities inside bubbles were measured by STEM-EELS was developed in a previous study (6) and applied to the sample that reached the release step. The measurements are gathered in Supplementary Materials (see SM 5). For all samples the average density is close to 100 He/nm^3 . The fact that the ^3He bubble density seems to be unaffected by ^3He release favors a mechanism that does not involve the release of ^3He atoms **from** inside the bubbles.

A comparison of the ^3He density distribution measured by EELS and by NMR is provided on Supplementary Materials (see SM 6). As STEM-EELS measurements are limited to over 4 nm bubbles, the ^3He density distribution is maximum at lower density than the corresponding NMR measurement. This is consistent with the fact that density (or pressure) rises with decreasing size.

Swelling of Pd tritide is observed upon aging time. A small part of swelling can be attributed to Pd lattice expansion due to local defects (around 1 % (21,22)). This conservation of the metal lattice is explained by the fact that ^3He bubbles are formed outside the crystal lattice. Subsequently, swelling refers here as bubble-caused swelling.

Pd tritide swelling measurements obtained by electron tomography and pycnometry are compared in Supplementary Materials SM 4. In tomography the swelling is the volume ratio between the nanobubbles and the palladium. For pycnometry it is a mass/volume ratio. Swelling increases continuously with ^3He content. It starts at 2% for $\text{PdH}_{0.02}$ and reaches 20% for samples aged several years. For $\text{PdHe}_{0.46}$ swelling is close to 30%. Both techniques provide very consistent results despite relying on different physical principles and scale.

To conclude, several Pd powders aged under tritium have been studied covering all steps of aging. Redundant techniques were used at different scale and provide consistent results. It allowed to widely characterize ^3He and Pd tritide behavior. For the first time, a sample witnessing ^3He release step has been studied. It tends to favor a mechanism that does not involve important structural changes since all characterizations reveal that nanobubbles microstructure, pressures and material swelling are well preserved. Among the three hypothesis (fracture, coalescence, diffusion), helium diffusion seems the most appropriated. ^3He gas release measurements are presented and discussed in Section 3.4

3.2 Modeling Nucleation (first year)

The cellular automaton is a serie of cells that represent the FCC crystalline structure of Pd tritide. The cells states evolve in time with the diffusion, generation and self-trapping laws of tritium and ^3He . At the initial state the system contains neither bubble nor $^3\text{He}(1)$. At each calculation step (1 s) the cell state is evaluated. Its change depends on the neighboring cells and on the evolution rules. A cell is a 0.14 nm side cube and the automaton is 150 cells wide. Table 3 presents the main inputs and outputs of the calculations.

Input Data		Output Data	
Parameter	Status	Parameter	Status
Tritium decay ($t_{1/2} \approx 12.3$ years)	Known	Bubble spacing	Measured (tomography)
Tritium diffusion coefficient	Known	Bubble density	Measured (TEM, tomography)
^3He diffusion coefficient	Unknown (scale)		

Table 3 – Input and output data for the cellular automaton calculation that models ^3He bubble nucleation (bold \equiv new data).

To adjust the automaton, the calculations after 10 days of aging are compared with experimental data acquired on the youngest available sample $\text{PdHe}_{0.02}$. The experimental and calculated distribution of inter-bubbles distances are reported in Figure 3.

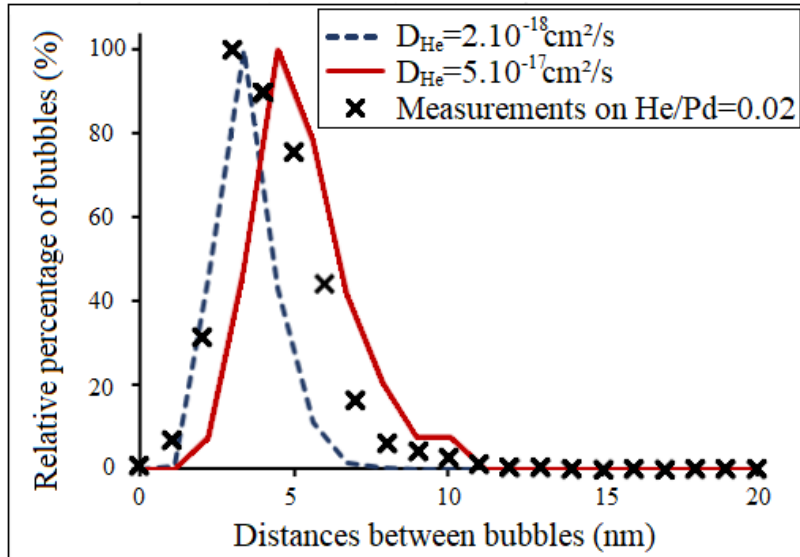


Figure 3 – Inter-bubble distances calculated by the cellular automaton after 10 days of aging for two ^3He diffusion coefficients $D_{\text{He}}=2.10^{-18} \text{ cm}^2/\text{s}$ (dot blue line) and $D_{\text{He}}=5.10^{-17} \text{ cm}^2/\text{s}$ (red line). Comparison with the inter-bubble distances measured by electron tomography on $\text{PdHe}_{0.02}$.

In Figure 3, the calculated bubble spacing distribution is close to the one measured on $\text{PdHe}_{0.02}$ aged sample. The maxima are between 3 and 5 nm, depending on the ^3He diffusion coefficient. These values are in agreement with those measured on similar Pd compounds (19). As seen in Table 4, the calculated bubble densities remain in the same order of magnitude than experimental data.

TEM	Electron tomography	Cellular automaton
$4.10^{23} \text{ bubble}/\text{m}^3$	$2.8.10^{24} \text{ bubble}/\text{m}^3$	$2.0.10^{24} - 1.1.10^{25} \text{ bubble}/\text{m}^3$ ($5.10^{-17} > D_{\text{He}} > 2.10^{-18}$)

Table 4 – Bubble density measured for $\text{PdHe}_{0.02}$ compared with calculations after 10 days of aging.

The spatial repartitions of ^3He bubbles obtained with the cellular automaton are close to the ones measured by TEM or tomography. This model explains the material behavior during the first days of aging. The nucleation step, governed by a self-trapping mechanism, implies that the bubbles microstructure is set up during the early stage of aging.

Table 4 reveals a small bubble density gap between TEM and tomography measurement, which does not appear for other samples (see Supplementary Materials SM 3). The youngest sample will be further investigated with a better resolved TEM to conclude on this difference.

3.3 Modeling Growth (from 2 to 10 years)

The second aging step is the bubble growth. It lasts about 10 years during which the tritide retains ^3He atoms. This step is modeled using Continuum Mechanics (CM) described in references(5,16). CM allows studying solid deformation.

The main hypothesis for CM calculation consists in considering a system large enough compared to matter scale (atomic, molecular) for its properties to be continuous which enables using continuous (or even derivable) mathematical tools. The modeling returns the geometrical and mechanical evolution of a Representative Elementary Volume (REV) of the system. In this study the REV is a ^3He bubble surrounded by a spherical layer of Pd tritide.

Two mechanical calculations were constructed to model bubble growth. The first model assumed an elastic-viscoplastic mechanical behavior of the metal matrix (5). Tensile tests on Pd hydride and deuteride revealed a low sensitivity to strain rate (16,23). Consequently, a second model based on a plastic law was created. For both models the metal matrix behavior is assumed isotropic, the bubble repartition uniform and the bubbles spherical.

The input and output data are identical for both models (see Table 5) only mechanical laws differ. Bubble growth rises thanks to ^3He diffusion from the Pd tritide matrix to the bubble.

Input Data		Output Data	
Parameter	Status	Parameter	Status
Mechanical	Unknown (scale)	Bubble diameter	Measured (TEM, tomography)
Bubble density (radius of REV)	Measured (TEM, tomography)	Swelling	Measured (tomography , pycnometry)
^3He diffusion coefficient	Unknown (scale)	Bubble pressure	Measured (EELS, NMR)

Table 5 – Input and output data for the mechanical calculation that models ^3He bubble growth (bold = new data).

After several sensitivity tests on input data, Figure 4 presents the calculations that best agree with experimental measurements. These calculations are obtained taking as input parameters a yield stress $\sigma_0=170$ MPa (see (16)), a tensile stress $\sigma_m=1200$ MPa, an initial bubble radius $a_0=0.1$ nm, an initial radius of REV $R_0=6.7$ nm (equivalent to $5.0 \cdot 10^{23}$ bubble/ m^3 , see (3,23)). These values result from either direct measurements (σ_0, R_0) or return outputs that fit experimental data (σ_m, a_0).

Using a tensile stress at $\sigma_m=1200$ MPa could seem large compared to the value measured on Pd hydride/deuteride ($\sigma_m < 300$ MPa(16,23)). However, it was demonstrated that ^3He bubbles embrittle significantly the matrix and consequently increase tensile stress value(24).

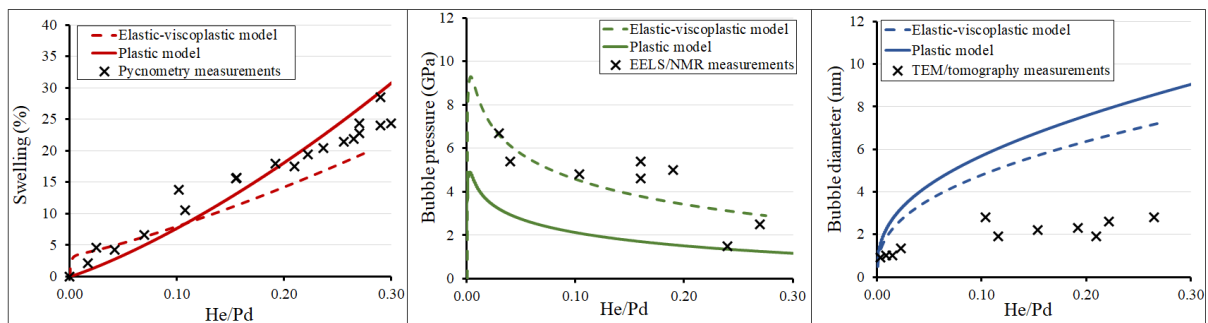


Figure 4 – Pd tritide swelling, ^3He bubble pressure and diameter after 10 years of aging under tritium, calculated for the optimized mechanical model and comparison with the target experimental data obtained by TEM/EELS/NMR/pycnometry/tomography.

As shown in Figure 4, both models succeed in replicating the Pd tritide swelling measured by pycnometry and tomography. The material swelling yields 25% after 10 years of aging under tritium. Bubble pressures are close to the values measured by EELS and NMR (1-8 GPa) but does not reach values over 5 GPa for the plastic model. For both models, bubble size is overestimated, this might result from the applicability's limit of CM to nanometric bubbles.

We attempt measuring tritide mechanical properties. Tensile tests were conducted under 5 bar of deuterium, but ^3He bubbles put such a great strain on Pd tritide that those were not conclusive (metal

breaks before the application of mechanical stress). This needs to be further investigated to bypass those issues to be able to conclude on the accuracy of taking $\sigma_m=1200$ MPa as an input.

Mechanical models accurately reproduce bubble growth stage. The modeling returns perfectly the material swelling and the bubble size/pressure remains in the expected order of magnitude. Perspective on the calculation is to introduce an EOS (Equation Of State) that suits nano-object to lower pressure (increase bubble size) at the beginning of the calculation, which could allow reproducing better bubble size characteristics.

3.4 Modeling ^3He release (after 10 years)

^3He slightly weeps from Pd tritide all along the aging process (~3% of generated ^3He atoms). The so-called ^3He release step begins when ^3He is massively released in the gas phase (21,25–27). The objective for this last part is to initiate a model that could explain ^3He release phenomenon.

Questioning around this mechanism is not new (28). However, to date, no experimental data were available on old-enough Pd tritide that could have turn the search toward one mechanism. In this work, we had the opportunity to study such a sample (over 20 years under tritium). The experimental results favor the helium-diffusion based mechanism since it involves few structural changes compared to material fracture or bubble coalescence.

This calculation is not based on bubbles coalescence since no bubble coalescence was observed by TEM or HAADF imaging on the over 20 years-old sample (see(23) and Supplementary Materials SM 1). Since that no evolution of bubble density (or spacing) occurs after the first few of aging, it seems unlikely that coalescence is the predominant mechanism for helium release.

Very few fractures were observed by TEM or HAADF imaging on the over 20 years-old sample even after over 100 focus TEM series. Moreover, helium release rate is quite continuous (seems incompatible with sudden fracture). Consequently, the modeling proposition does not involve sample fracture.

The bubble-by-bubble STEM-EELS analysis of the over 20 years aging sample revealed that the nanobubbles are still filled with helium-3 (see Supplementary Materials SM 5). Moreover, NMR results show that the global helium-3 density in bubbles does not evolve much between a sample aged few years and the one that reached release step (Figure 2). EELS/NMR measurements suggest that helium-3 density remains unchanged, consequently ^3He release does not come from bubbles (23), it can only come from isolated ^3He atoms. The model is based on a slow, continuous release by single ^3He atoms diffusion. Since each ^3He atom quickly integrates a bubble in previous steps, this means that the Pd tritide (or the bubbles) intrinsically face some storage limit, or saturation. Maximum molar ratio He/Pd defines the storage limit.

The calculation researches the duration that is needed to reach ^3He release step (^3He saturation of the tritide). Before saturation, tritide matrix retains all of the ^3He (excepted for the 3% weeping). When the material reaches this limit, all newly created atoms are released in the gas phase. In this hypothesis, ^3He release rate from the tritide follows the ^3He production rate from radioactive decay.

Before reaching the limit, the helium quantity that is stored in Pd tritide follows Equation (1):

$$\frac{He}{Pd}(t) = (1 - W) \times \frac{v_{He} \times t}{\rho_{Pd}} \quad (1)$$

where v_{He} is the ^3He generation rate (in He/nm³/month), t is time (in month) and W is the slight weeping of ^3He during aging.

The storage limit (molar ratio He/Pd) is fixed by maximum swelling and ^3He density (measurable parameters). These are the inputs of the calculation, as expressed in Equation (2):

$$\frac{He}{Pd_{limit}} = \frac{\rho_{He} \times S}{\rho_{Pd}} \quad (2)$$

where ρ_{He} is the ^3He density in bubbles (in He/nm^3), S is the material swelling (in %) and ρ_{Pd} is the tritide density (in Pd/nm^3).

If the calculated aging time needed to reach ^3He release matches the one that is observed experimentally the values of the parameters defining the storage limit are fixed.

When ^3He release step begins, Equations (3) and (4) govern material evolution:

$$\frac{He}{Pd}(t) = \frac{He}{Pd_{limit}} \quad (3)$$

$$He_{desorbed}(t) = \left(1 - \frac{\frac{He}{Pd_{limit}}}{\frac{v_{He} \times t}{\rho_{Pd}}} \right) \quad (4)$$

Table 6 gathers the input and output data of the model.

Input Data		Output Data	
Parameter	Status	Parameter	Status
Swelling	Measured (tomography , pycnometry)	He/Pd	Measured (gas)
^3He density	Measured (EELS, NMR)	^3He release	Measured (gas)

Table 6 – Input and output data for the ^3He release model (bold = new data). “Gas” refers to measurements oh He content in the gas phase.

After several tests on input data (Figures SM 9 and SM 10 in Supplementary Materials), the best agreement between calculation and experimental result (on output data: helium release/storage) is obtained for $S=20\%$ and $\rho_{He}=100 \text{ He}/\text{nm}^3$ or $S=25\%$ and $\rho_{He}=80 \text{ He}/\text{nm}^3$. These swelling (S) and ^3He density (ρ_{He}) values are very close from experimental measurements by tomography/pycnometry (swelling) (16,23) and EELS/NMR (^3He density) (4,6). The result of one calculation is reported in Figure 5. The output data (^3He release and He/Pd ratio) are compared to the direct gas weeping measurement.

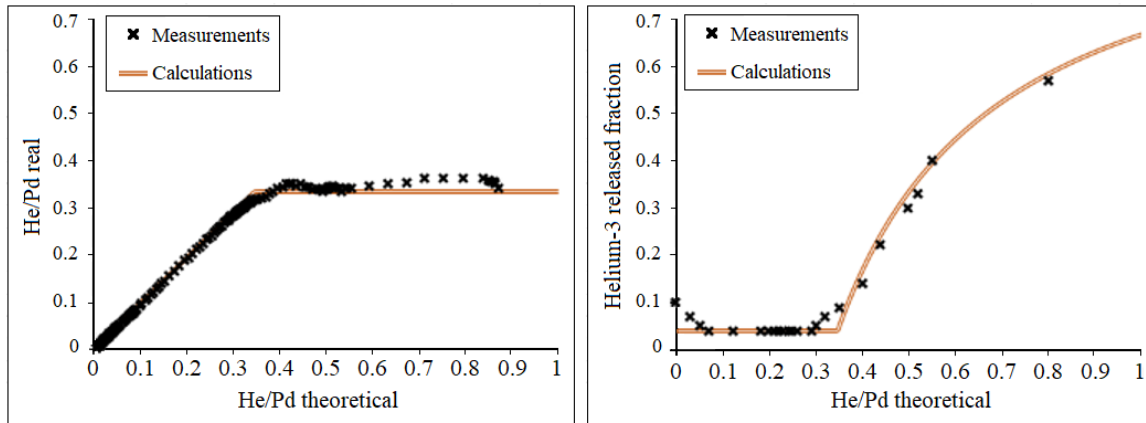


Figure 5 – Calculated ratio of real He/Pd (left) and ^3He fraction (right) desorbing depending on the He/Pd theoretical ratio. Tritide swelling is set at 20% and ^3He density at $100 \text{ He}/\text{nm}^3$.

Results in Figure 5 confirm the good agreement between the He/Pd ratio calculated by the ^3He release model and the experimental values. The calculation sets the beginning of massive release at He/Pd=0.33 which is close to the measured value. Using a discontinuous calculation allows returning accurately the ^3He quantities that are stored in the tritide and released in the gas phase.

Thanks to experimental results on the PdHe_{0.46} sample and modeling, ^3He release phenomenon in aged Pd is better understood. Experimental study of old-Pd sample demonstrates that the ^3He bubbles microstructure is well preserved even after reaching massive release phase. It highlights the fact that the release mechanism must not involve large structural changes but rather a threshold in ^3He bubbles storage in tritide. The developed model based on these observations suits perfectly the experimental measurements on ^3He retention and ^3He release. Despite the contribution of this model on tritide ^3He release phenomenon comprehension, it must be underlined that it is phenomenological and not explanatory. Further study is needed to explain the limit of He content that can be stored inside bubbles. Nevertheless, it reinforces the consistency of all the acquired experimental data.

Conclusion

All experimental results in the present study yield a significant progress in aging understanding and bring a new insight in the ^3He role. The new experimental data obtained on Pd powders aged over 20 years provide valuable input and recalibration data for the theoretical modeling of Pd tritide aging processes. NMR measurements will be further detailed in a dedicated article.

The bubble nucleation modeling by self-trapping mechanism in a cellular automaton successfully describes the bubble spatial repartition during the first days of aging. The calculated bubbles density and bubble spacing values agree with those measured experimentally. One small uncertainty remains on bubble density at the very early stage that will be investigated using better-resolved TEM.

The mechanical bubble growth model revealed that using high tensile stress and other data from experimental measurements allow calculating most of the ^3He bubble properties (size, swelling, pressure). However, the modeling tends to overestimate bubble size (*i.e.* underestimated bubble pressure). Perspective of this work is to introduce a nano-compatible EOS at the beginning of the calculations (which should rebalance both tendency). Mechanical characterization of aged materials should also be pursued.

The exhaustive characterization of PdHe_{0.46} sample furnished very valuable information on the last step of aging. It allowed us to establish a first hypothesis on ³He release mechanism based on the existence of a storage limit. This mechanism, depending on swelling and ³He density, was embedded in a model. The calculations obtained with the model successfully describe the material behavior, particularly ³He quantities (storage/release). Further work on ³He release will consist in characterizing other old samples to confirm all properties. Next step will be to propose a full mechanism that not only describes the material behavior but also explains the origins of the storage limit.

This study focuses on Pd tritide. However, it seems that many metal tritides behave similarly (25,27,29). In conclusion, those theoretical models could be tested on other materials.

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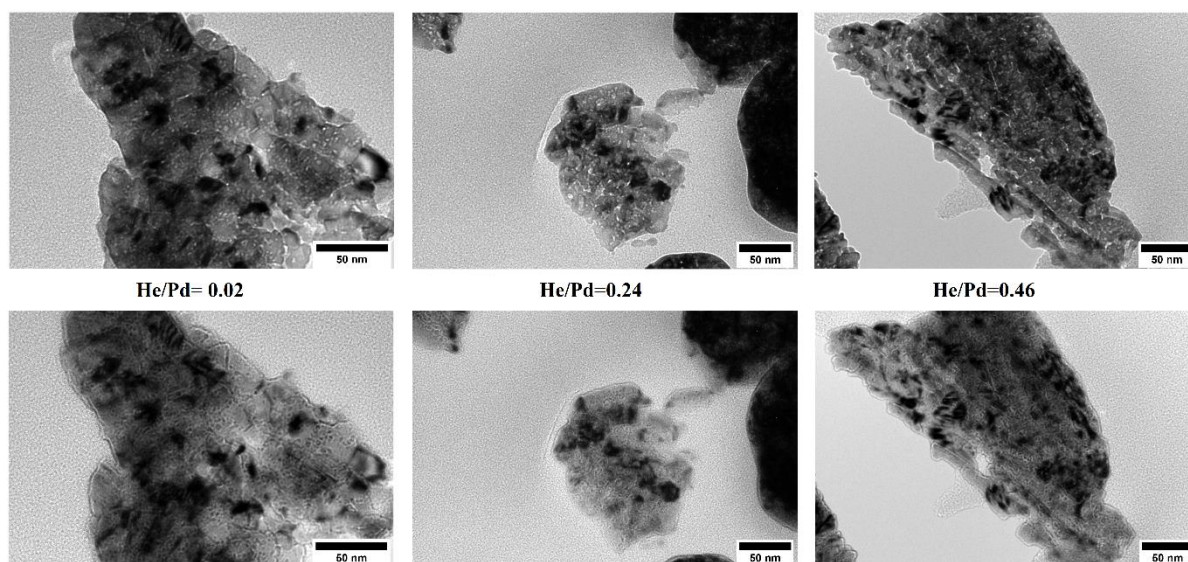
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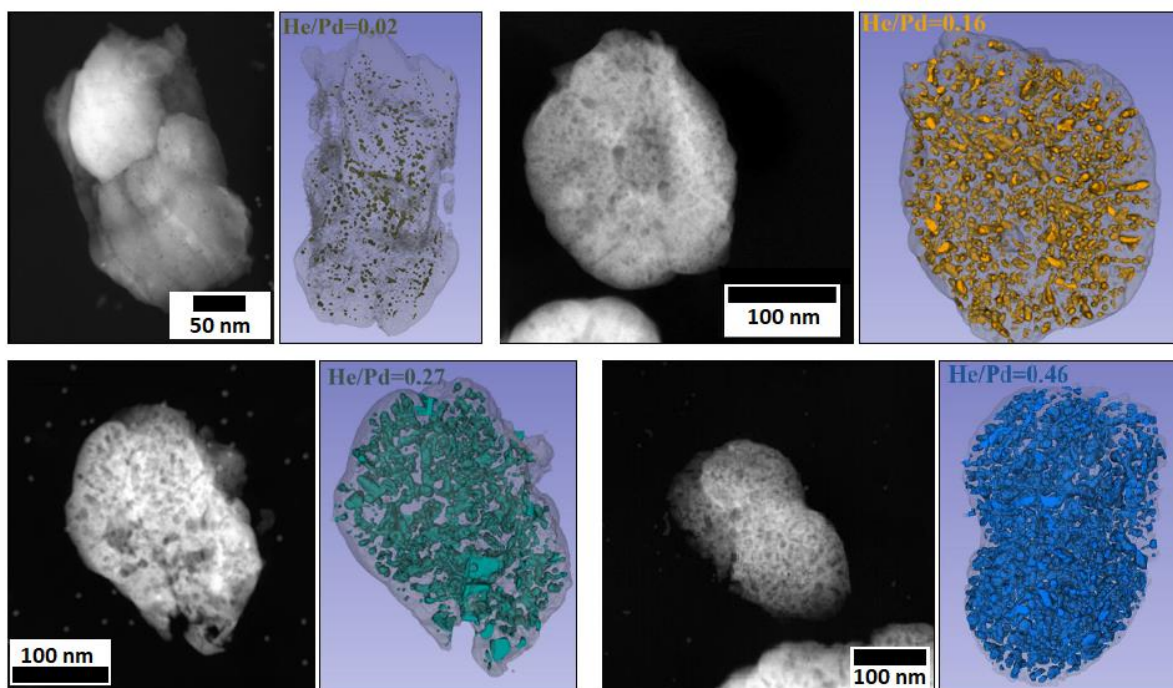
SUPPLEMENTARY MATERIAL

AGING Pd UNDER TRITIUM: INFLUENCE OF ^3He GENERATION AND ASSOCIATED MECHANISMS

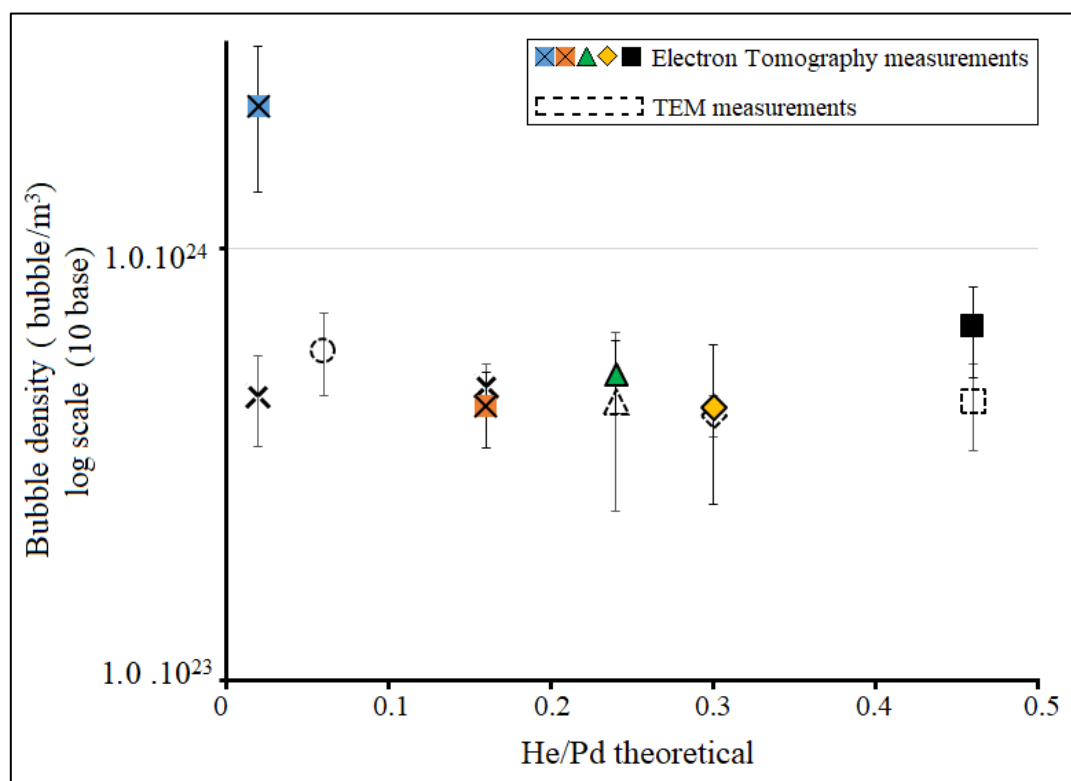
Characterization of palladium samples aged under tritium.



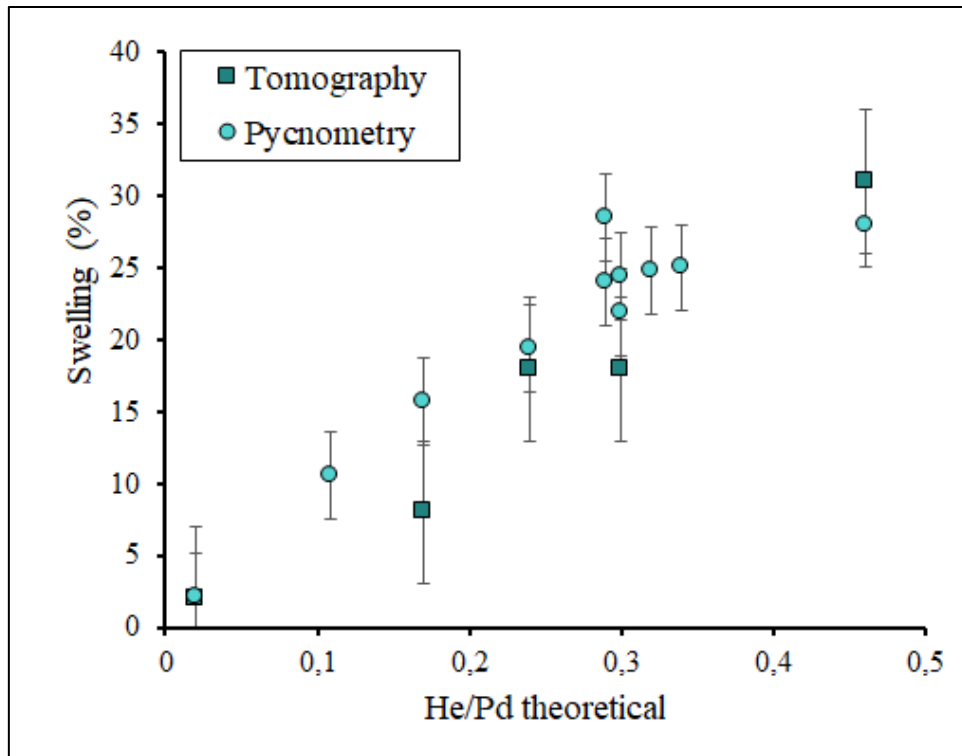
SM 1 – TEM images of palladium aged under tritium (from few months to tens of years). Top-images are over-focused (+1 μm) and the bottom ones under-focused (-1 μm).



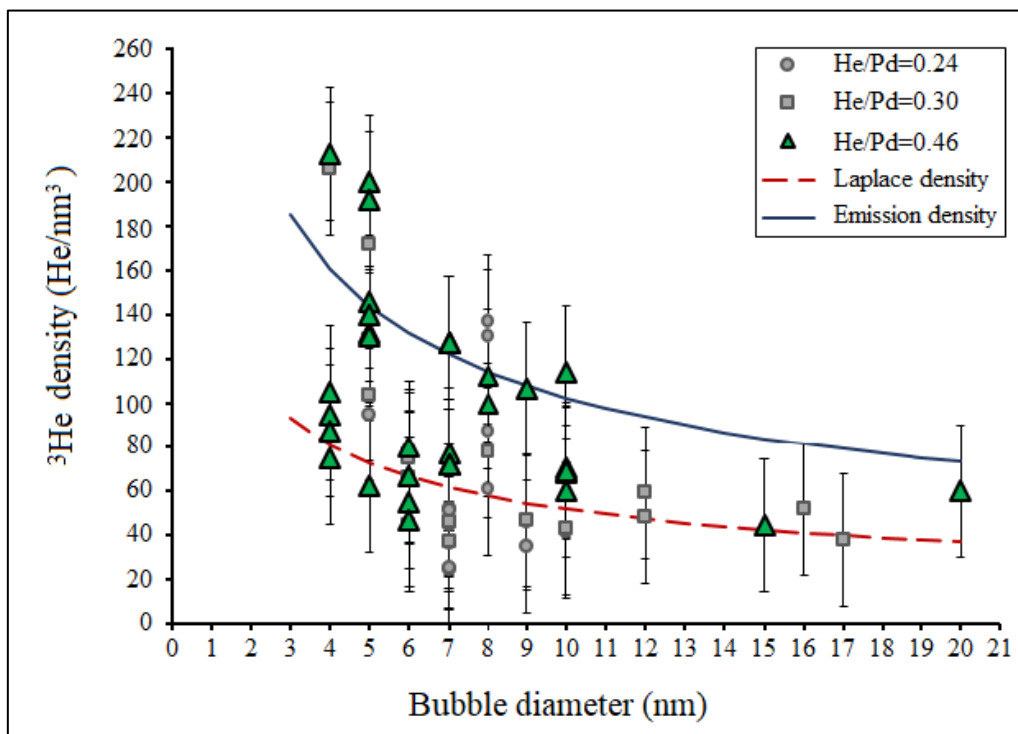
SM 2 – HAADF images at 0° tilt (left) and bubble spatial repartition 3D model (right) obtained by electron tomography after segmentation and reconstruction for palladium samples aged between few months to over 20 years.



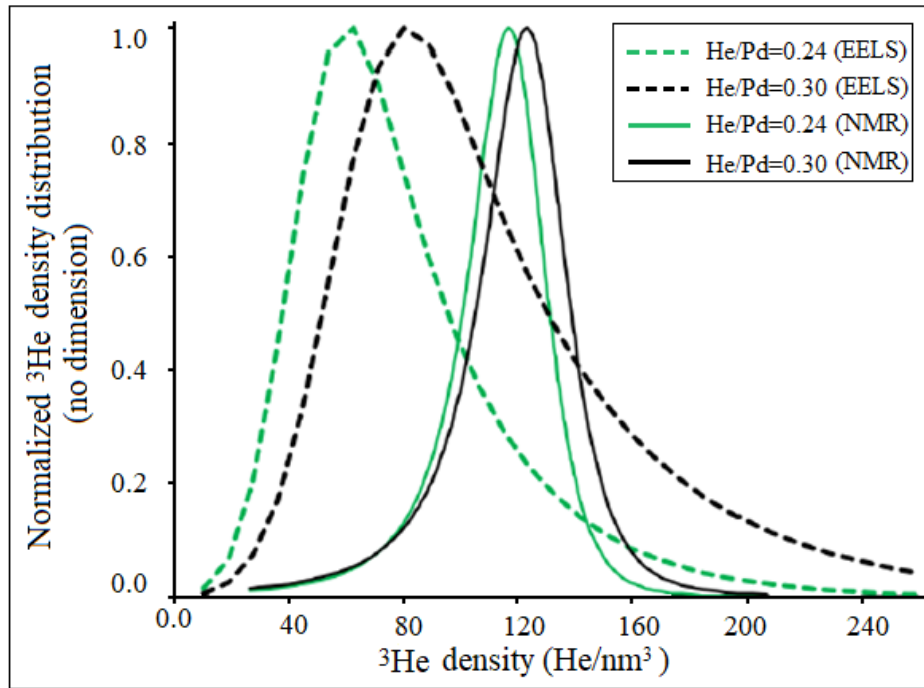
SM 3 – Bubble densities in palladium samples ages under tritium between few months to over 20 years.



SM 4 – Palladium tritide swelling measurements by pycnometry and tomography for samples aged between few months to over 20 years.

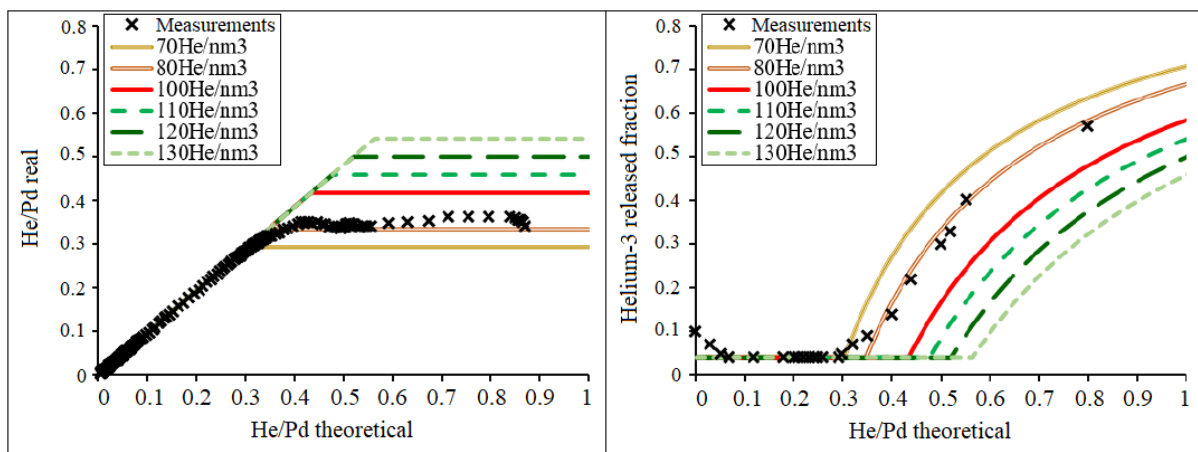


SM 5 – Helium-3 densities as a function of bubble diameter measured by EELS for palladium samples aged under tritium between several years to over 20 years. Laplace density is the theoretical density calculated by $P=2\gamma/r$ (where γ is the surface tension and r the bubbles radius). Emission density is the maximum pressure before emitting a dislocation loop calculated by $P=2\gamma+\mu b/r$ (where μ is the shear modulus and b the Burger vector).

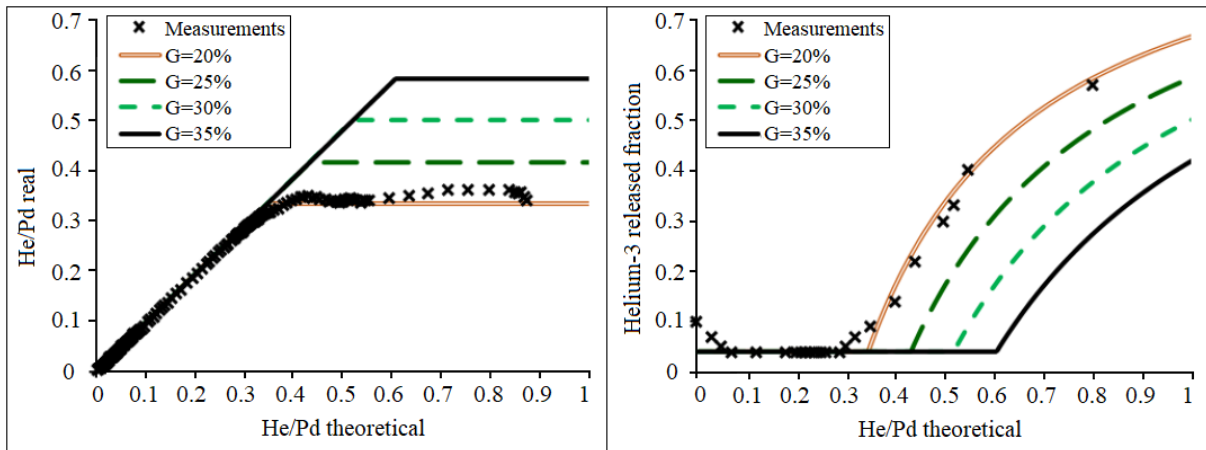


SM 6 – Comparison of ^3He density distribution measured by EELS and by NMR on palladium samples aged few years.

Adjusting the input parameter on helium-3 release modeling.



SM 7 – Calculated ratio $\text{He/Pd}_{\text{measured}}$ (left) and helium-3 fraction (right) desorbing depending on the $\text{He/Pd}_{\text{theoretical}}$. Tritide swelling is set at 20% and helium-3 density between 70 and 130 He/nm^3 .



SM 8 – Calculated ratio He/Pd_{measured} (left) and helium-3 fraction (right) desorbing depending on the He/Pd_{theoretical}. Helium-3 density is set at 35 He/nm³ and tritide swelling is between 20 and 35%.