

^3He retention in LaNi_5 and Pd tritides: Dependence on stoichiometry, ^3He distribution and aging effects

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Abstract

This study compares the ^3He retention properties at room temperature of both LaNi_5 and Pd tritides after more than 18 and 13 years, respectively. The effects of stoichiometry have been investigated by following ^3He retention in sub-stoichiometric and stoichiometric samples for both tritides, and in replenished samples for Pd tritide. For both compounds, the change of thermodynamic and structural properties due to ^3He retention upon aging time has also been studied by PcT diagrams, X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS) measurements. Transmission electron microscopy (TEM) observations were also performed for Pd only.

Both LaNi_5 and Pd tritides retain more than 95% of ^3He for at least 9 years of aging. However, the influence of ^3He in the matrix has completely different effects since LaNi_5 tritide loses its thermodynamic and structural properties after 2.8 years of aging, whereas these properties are outstandingly well preserved in Pd tritide for at least 10 years. This difference has been attributed to a different distribution of ^3He atoms, leading to different kind of defects produced by ^3He retention in both materials.

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1. Introduction

Tritium is an essential element for future thermonuclear energy production. However, due to its high mobility and radioactivity, tritium handling and storage raise safety issues. The solution generally used is to store tritium as metal hydrides (then called 'tritides') with low equilibrium pressures. Moreover, some tritides have the ability to retain the ^3He generated in their matrix for several years [1], allowing the recovery of an almost ^3He -free gas. However, for all tritides when a critical ^3He concentration is reached in the material, the ^3He is released at a rate equal to, or higher than, the generation rate. This stage is known as the 'accelerated release' stage. During this stage, the ^3He pressure in a storage vessel increases dramatically, which can lead to a rupture of the vessel and tritium leak. Mastering

^3He retention and the accelerated release stage is thus of crucial importance.

Among the metals and compounds which absorb hydrogen reversibly, some are known to have very low critical ^3He concentrations. For instance, this is the case for Li, U and Ti which retain ^3He for only 2–3 years [2]. In this study, we have focused on two promising materials: LaNi_5 and Pd, which are known to have high critical ^3He concentrations [3–5]. ^3He retention has been studied at room temperature for more than 18 years in LaNi_5 tritide, and for 13 years in Pd tritide. For both tritides, effects of stoichiometry have been investigated by following ^3He retention in stoichiometric, sub-stoichiometric and replenished samples (Pd only). In the first part of this paper, ^3He retention measurements will be presented and LaNi_5 and Pd behaviours will be compared.

Owing to the fact that ^3He atoms are bigger than T atoms, ^3He retention in the matrix leads to the formation of a high density of defects. In turn, these defects produce evolutions in tritide properties, for instance, swelling or PcT curves alterations which are

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very important in tritium storage applications. All these evolutions are usually called ‘aging’ effects. Therefore, mastering ^3He behaviour and its distribution in tritides is fundamental to understand, and even predict, the following aging effects, as well as ^3He release. This is the reason why aging effects have been studied using PcT curves, X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS) measurements, as well as transmission electron microscopy (TEM) observations for Pd only. Results will be presented in the second part of this paper. The differences in the alteration of thermodynamic and (micro)structural properties between the two materials will equally be pointed out and discussed as a function of ^3He distribution.

2. Experimental

The experimental method used to study the ^3He retention is described in the following. For LaNi_5 , the starting powder ($<100\ \mu\text{m}$) was activated by absorption/desorption cycles with deuterium, so the particle size is supposed to be around $1\text{--}5\ \mu\text{m}$ after this treatment [6]. For Pd, the same activation process was used but there is no cracking for this metal during hydrogen uptake, so the particle size is supposed to be the same as for the starting material (between 10 and $25\ \mu\text{m}$). Each sample was made up of $10\text{--}20\ \text{g}$ of material. The powder was placed in a tight stainless steel sample holder, equipped with a transducer for pressure measurement (range between 0.1 and 0.6 MPa) and a valve. Void volumes for gas vary between 5 and $10\ \text{cm}^3$. Sample weight and void volume were measured accurately before tritium loading. Sample swelling during loading and further aging (which is not known accurately) was not taken into account. This represents an error of less than $0.5\ \text{cm}^3$.

All samples were loaded at room temperature with almost pure tritium (composition determined by high resolution mass spectrometry: $\text{T}_2 > 97.7\%$, $\text{D}_2 < 0.7\%$, $\text{H}_2 < 1\%$, $^3\text{He} < 0.8\%$, others: CO, N_2 , CO_2 , Ar, O_2 , CH_4 , ... $< 0.01\%$). Initial overpressures of tritium varied from 0.25 to 0.29 MPa for LaNi_5 and from 0.02 to 0.08 MPa for Pd. The total amount of tritium in each sample was determined by a calorimetric measurement. The stoichiometry of the tritide, expressed as the atomic ratio of tritium over metal T/M (M = La, Ni or Pd), was calculated by subtracting from this amount the tritium determined by the volumetric method, from the knowledge of void volumes and the measurement of temperatures and pressures, in the gas phase. Different stoichiometries have been reached, between 0.48 and 0.86 for LaNi_5 , and between 0.24 and 0.64 for Pd. Finally, aging was performed at room temperature. In this paper, aging will be characterized by two kinds of data: the aging time (usually in years), and the ^3He generated in the material expressed as the atomic ratio of ^3He born in the matrix over metallic atoms in this matrix.

The only data taken consistently over the years was the total pressure in the sample. Fig. 1 shows an example of the total pressure evolution in a sample holder. However, it is necessary to also know the composition of the gas phase

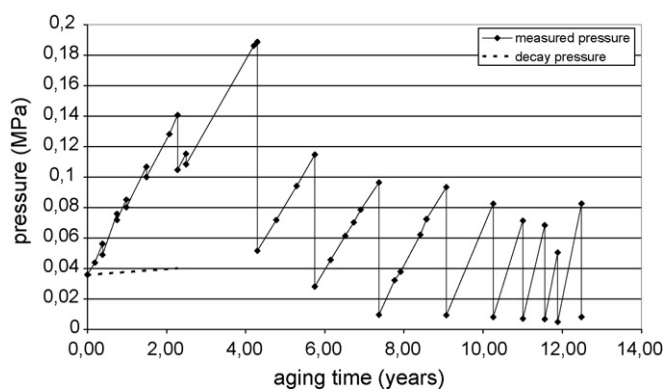


Fig. 1. Total pressure over Pd sample P7, during the first 13 years of storage.

to calculate accurately the quantity of ^3He released from the solid phase, so a small fraction of the gas phase was regularly removed from the sample to perform analyses by high resolution mass spectrometry. In Fig. 1, small drops of pressure are due to these gas samplings for analysis. Big drops are due to gas draining performed to keep the overpressure in the sample holder below the pressure transducer range. Of course, all gas removed from the sample holders is taken into account in further calculations. All gas quantities are determined by volumetry, as previously described for tritium.

As tritium decays in the gas phase, one T_2 molecule gives birth to two ^3He atoms, and a pressure increase is expected without exchange between the solid and the gas phases, as represented by the dotted line in Fig. 1. However, the total pressure measured experimentally is usually above the one expected from tritium decay in the gas phase: this difference is attributed to the ^3He released from the solid phase. Thanks to the small void volumes of the sample holders, even a weak helium release produces a measurable pressure increase as can be seen in Fig. 1. As already said, ^3He release can be calculated accurately only after a gas analysis. The calculation is done assuming that there is no tritium exchange between the solid and the gas phases between two consecutive analyses. The ^3He expected in the gas phase is then equal to the ^3He left after the previous analysis plus the ^3He due to tritium decay in the gas phase. The excess of ^3He measured in the gas phase is thus attributed to ^3He released from the solid phase. ^3He release is expressed here as the ratio of ^3He released from the solid phase over ^3He born in this phase. All data shown in this paper is cumulative data, which means that, at a given storage age, we have plotted the total ^3He released relative to the total ^3He born in the solid phase.

Different techniques have been used to characterize the aging effects. Thermodynamic properties have been studied by PcT curve measurements, while structural properties have been followed by XRD (long-range order) and EXAFS (local order) experiments. Micro structural properties have also been studied, for Pd only, by TEM observations (that is precluded for LaNi_5 due to the strong deformations in the compounds). The details about sample preparations, and characterization techniques used, will not be given here as they can be easily found in the references [7–11].

3. Section I: ^3He retention

3.1. LaNi_5 compound

3.1.1. Stoichiometric sample

Only one LaNi_5 sample was initially loaded which was fully stoichiometric: sample L1 (T/M = 0.86). For this sample, we have been able to calculate the ^3He release during the first 2 years only. The values obtained vary between 0.4 and 0.7% only, as shown in Fig. 2. Moreover, the pressure increase over this sample was very limited during at least the first 7 years of storage ($\text{He}/\text{M} < 0.28$), which means that the ^3He release was weak during this period. To finish, a sharp increase of pressure

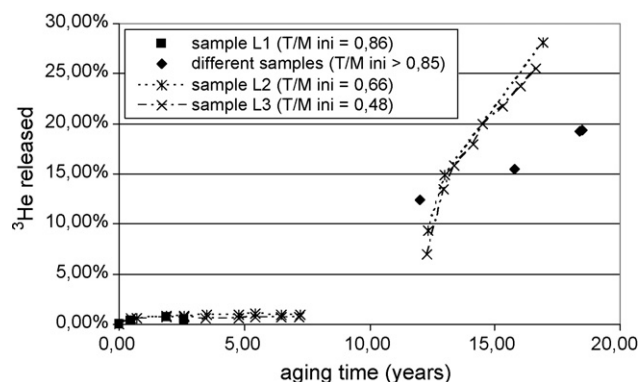


Fig. 2. Percentage of ^3He out gassed as a function of time for different LaNi_5 samples.

Table 1
 ^3He release from different LaNi_5 samples

Sample	Age (years)	Initial T/M	He/M created	^3He released (%)
L11	12	0.92	0.45	12.4
L12	15.8	0.93	0.55	15.5
L13	18.4	0.85	0.55	19.2
L14	18.5	0.86	0.55	19.4

was observed before 13 years ($\text{He}/\text{M}=0.44$), which could correspond to accelerated release, but this cannot be undoubtedly established as a precise ^3He release calculation is not possible during this period.

To try to get better information about ^3He release in fully stoichiometric LaNi_5 samples, we have performed pressure measurements and gas analyses on different samples that were aging without pressure monitoring. Results are summarized in Table 1. From this data, it seems that ^3He release has become significant before 12 years ($\text{He}/\text{M}=0.45$), because of the great cumulative release of 12.4% calculated at that moment. For longer aging times, ^3He release continues to increase, from 15.5% at 15.8 years ($\text{He}/\text{M}=0.55$) to about 19% at 18.5 years ($\text{He}/\text{M}=0.55$). However, this raise seems to be surprisingly moderate. It should correspond to an ‘instantaneous’ release of about 50% during this period which is not exactly the definition of accelerated release.

3.1.2. Sub stoichiometric samples

Two LaNi_5 samples were initially loaded which were sub stoichiometric: samples L2 ($\text{T}/\text{M}=0.66$) and L3 ($\text{T}/\text{M}=0.48$). Fig. 3 shows the evolution of the total pressure during storage for sample L3, which is approximately the same as for sample L2. In these cases, ^3He release has been calculated during the whole aging time and results are shown in Fig. 2. The first noticeable thing is that the two samples behave exactly the same way, which could mean that the initial stoichiometry has no effect on ^3He release. The second thing is that ^3He release is very low during the first 7 years of aging ($\text{He}/\text{M}=0.21$ and 0.15 for samples L2 and L3, respectively). It varies between 0.5 and 1% for the two samples, which also corresponds with observations made on the stoichiometric sample. This confirms that the initial sto-

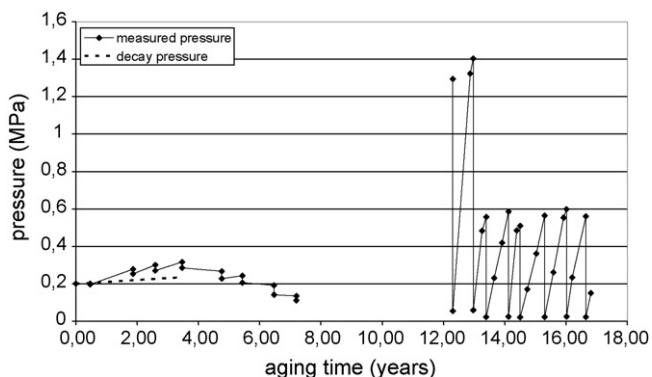


Fig. 3. Total pressure over the sub-stoichiometric LaNi_5 sample L3, during the first 17 years of storage.

ichiometry of the sample seems to have no influence on ^3He release.

It is noteworthy that gas analyses were not performed for these samples between 7 and 12 years of aging. However, during this period, accelerated release has obviously begun, as suggested by both the evolution of pressure (Fig. 3) and the calculation of ^3He release (Fig. 2). Of course, the beginning of ^3He release cannot be precisely determined from this data. Nevertheless, we can try to estimate it from the shape of the different curves, assuming that there is no transition between the first stage (when ^3He is retained at more than 99%) and the accelerated release stage. This gives values between 9.5 years ($\text{He}/\text{M}=0.27$ and 0.20 for samples L2 and L3, respectively) and 12 years ($\text{He}/\text{M}=0.32$ and 0.23 for samples L2 and L3, respectively) of aging. Once again, these results are in agreement with those obtained on the stoichiometric sample (beginning of accelerated release before 13 years) and confirm the fact that the initial stoichiometry of the sample has no influence on ^3He release.

Finally, between 12 and 17 years, the accelerated release stage is confirmed by the calculation of the ‘instantaneous’ release for the two samples: it varies from 70 to 170%. Here, there is a discrepancy with the results obtained on the stoichiometric samples. This can be due to a real difference between stoichiometric and sub stoichiometric samples, or to the fact that for the formers we have used different samples with different aging times, which were not loaded exactly with the same initial stoichiometries.

3.2. Palladium

3.2.1. Stoichiometric samples

One example of total pressure evolution above a stoichiometric Pd tritide sample has already been shown in Fig. 1. This data, together with gas analyses, have allowed the calculation of ^3He release from this sample. Results are given in Fig. 4 for the cumulative data, with instantaneous data in the insert. In this case, the first thing that stands out is that three different stages can be identified. The first one, during approximately the first 1.5 years of storage ($\text{He}/\text{Pd}<0.05$), is characterized by a relatively high ^3He desorption which tends to decrease. This phenomenon is usually called ‘early’ release. Next, from 1.5 to 9 years ($\text{He}/\text{Pd}=0.23$), the ^3He release rate is stable, around 4%. Lastly, after 9 years of aging ($\text{He}/\text{Pd}>0.23$), ^3He release begins to increase but this raise is relatively slow. During this stage, both instantaneous and cumulative release rates increase but accelerated release is not reached. For instance, for the last measurement (12.5 years, $\text{He}/\text{Pd}=0.29$), the ‘instantaneous’ release rate is equal to 17% only, and the cumulative release is less than 6%.

Seven samples (P1 to P7), with initial stoichiometries bigger than 0.6, have been followed by pressure monitoring. They have all given similar results, as can be seen in Fig. 4.

3.2.2. Sub stoichiometric samples

Three samples have been initially loaded with stoichiometries lower than 0.6: sample P8 ($\text{T}/\text{Pd}=0.43$), sample P9 ($\text{T}/\text{Pd}=0.36$) and sample P10 ($\text{T}/\text{Pd}=0.24$). ^3He retention is globally the

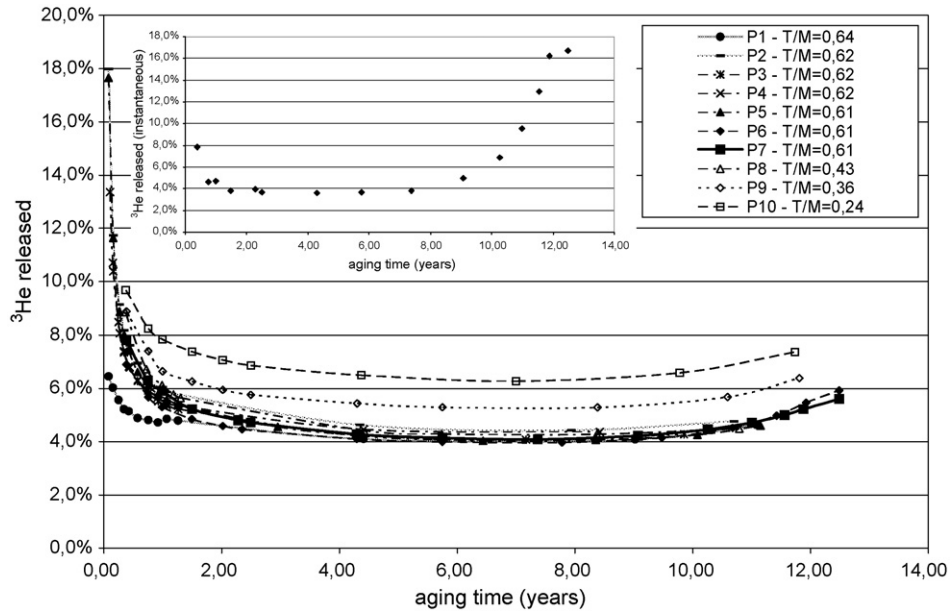


Fig. 4. Percentage of ^3He out gassed as a function of time for all Pd samples. In the insert, ‘instantaneous’ release for Pd sample P7 (bold curve) is shown.

same as for the stoichiometric samples, with the three different stages happening at the same aging times, as can be seen from Fig. 4. However, the amount of ^3He released is, expressed in relative terms, greater when the initial stoichiometry is smaller. For instance, the ^3He release rate during the stabilized stage is around 5% for sample P9 and 6% for sample P10 (no measurable difference has been observed for sample P8 which has the greatest initial stoichiometry).

The main difference between stoichiometric and sub stoichiometric samples, is that, in the latter, the α phase exists at the beginning of aging, whereas it appears progressively in time in the former. As a consequence, one possible explanation for the greater ^3He release in sub stoichiometric samples would be a different behaviour between α and β phases towards ^3He retention.

For each sub stoichiometric sample, we have calculated α and β phases proportions considering that $\alpha_{\text{max}} = 0.05$ and $\beta_{\text{min}} = 0.59$ (data deduced from PcT curves measured at 25 °C for the same Pd powder, see Fig. 8). At a given age, for instance 6 years, it is possible to calculate approximately ^3He concentration in α and β phases assuming that tritium concentration is constant in the two phases: 0.02 and 0.20, respectively. Lastly, assuming that the β phase behaviour is the same in all the samples (^3He released $\approx 4\%$), it is possible to estimate the ^3He released from the α phase only between 50 and 90%. These values are realistic (release $<100\%$), even though high and dispersed between the two samples.

3.2.3. Replenished samples

Several samples have been connected to a reservoir of 50 cm³ initially loaded with 2 MPa of tritium, during their entire storage period. This reservoir allows the replacement of the tritium atoms, which have disappeared by radioactive decay in the solid phase, leaving the stoichiometry of the sample almost constant

in time. An example of total pressure evolution in this case is shown in Fig. 5.

Of course, the calculation of ^3He desorption is slightly different here and requires some hypotheses on tritium distribution between gas and solid phases. As a first approximation, we have assumed that the stoichiometry of the sample is constant. Then, tritium content in the gas can be deduced directly from the radioactive decay law. With a constant stoichiometry, it is also easy to calculate the ^3He content born in the solid: $\text{He}/\text{Pd} = \text{T}/\text{Pd} \times \ln 2 \times t/\tau$, where t is the aging time and τ the radioactive period of tritium. ^3He content in the gas phase can then be directly deduced from the total ^3He quantity produced by radioactive decay. These simple rules allowed us to calculate a theoretical pressure in the system if no ^3He is released from the solid phase (dotted curve in Fig. 5). In this case, it can be noticed that the total pressure decreases all the time, because of tritium absorption by the Pd sample, despite the fact that one tritium molecule gives birth to two ^3He atoms. As for the non-replenished samples, when the measured pressure is above the

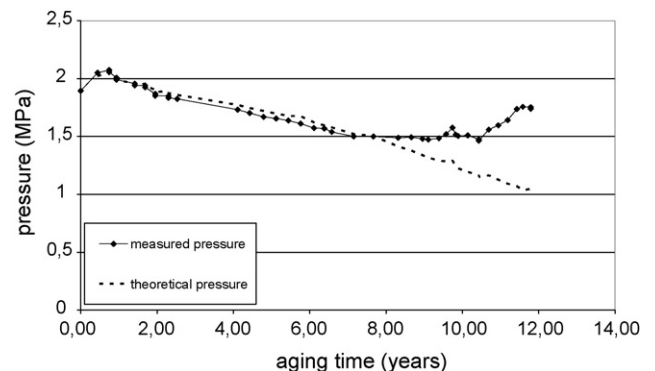


Fig. 5. Total pressure over the replenished Pd sample PR4, over the first 12 years of storage.

theoretical one, it is attributed to ^3He release and, due to gas analyses, it is possible to calculate accurately the amount of ^3He out gassed from the solid phase.

First of all, we have to underline that the measured pressure is under the theoretical one during some periods. This can be attributed to an increase of the stoichiometry of Pd samples, which leads to a deficit of tritium in the gas phase. Indeed, a displacement of the β branch of Pd towards greater stoichiometries has been observed by PcT curve measurements, as will be shown in the second part of this article (Fig. 8). This hypothesis is confirmed by gas analyses as the amount of ^3He released calculated is always found to be positive as shown in Fig. 6. Another difficulty here is that no gas analysis was performed between 2 and 10 years of aging, whereas a large ^3He release obviously occurred during this period, as can be deduced from the cumulative release greater than 10% after 10 years of aging. Nevertheless, we can say that the ^3He release behaviour is globally the same as for non-replenished samples with an early release, which is slightly less marked, during the first 2 years (He/Pd < 0.08) of storage and, at the end, an accelerated release. After the early release and before the accelerated one, we suppose a stabilization period from 2 years (He/Pd = 0.08) to 9 years (He/Pd = 0.33) as indicated by the very small difference between theoretical and measured pressures during this period. The stabilized release rate should be around 4%, as suggested by the last results obtained after about 2 years of aging. The main point here is to try to estimate the beginning of accelerated release. As we have already said, if no significant ^3He release occurs, the total pressure will decrease continuously with time. This is the reason why we have assumed that accelerated release began when the total pressure had stopped decreasing. We also believe that this criterion is more adequate than the difference between measured and theoretical pressures, since tritium content in the solid is not sufficiently mastered, as already underlined. Using this hypothesis, the accelerated release could have begun after 9 years of storage (He/Pd \approx 0.33). At that time, the fact that the accelerated release stage is reached, is confirmed by the calcula-

tion of the ‘instantaneous’ release rate between 10 and 12 years which is around 110%.

Five different samples have been aged with the same replenishment. They all give similar results, as can be seen in Fig. 6. For all of them, there is an early release during the first 2 years of aging (He/Pd < 0.08) and the beginning of accelerated release can be estimated after 8.5–9 years of storage (He/Pd \approx 0.33). During the intermediate period, a stabilization of ^3He release rate can be assumed from the total pressure evolution, with values varying from 2 to 4%. After 9 years of storage, the accelerated release is confirmed by the calculation of the ‘instantaneous’ release rate which varies between 80 and 110% for the different samples.

4. Section II: Aging effects

In this section, we will present a summary of the different studies made in the past on the changes in LaNi_5 and Pd tritide properties.

4.1. LaNi_5 compound

4.1.1. Thermodynamic properties

The tritium desorption isotherms have been measured at 313 K for several LaNi_5 samples after different aging times, from 0 to 2.8 years [7]. For aging times under 8 months (He/M \leq 0.03), a decrease of the plateau pressure and a shift of the α and β branches towards larger stoichiometries are observed. At this stage, the loss of stoichiometry is almost equal to the ^3He content (He/M). Then, the slope of the isotherms increases progressively and after 1.8 years of storage (He/M \geq 0.09), the plateau has disappeared. The amount of deep trapped tritium which cannot be desorbed from the solid phase, increases with aging time, reaching about T/M = 0.33 after 1.8 years. This leads to a decrease of capacity greater than the ^3He content (He/M). To summarize, we can say that the storage properties are therefore, almost lost for longer aging times.

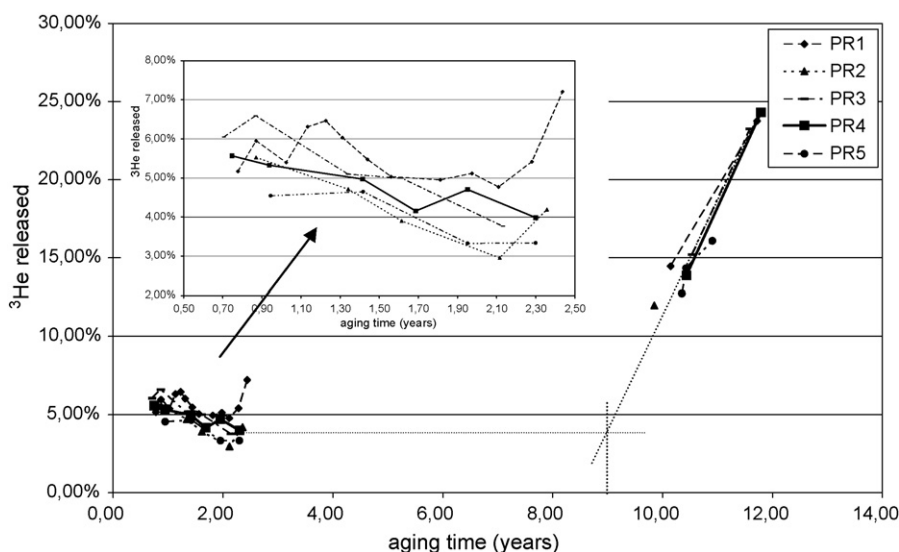


Fig. 6. Percent of ^3He out gassed as a function of time for all replenished Pd samples. In the insert, magnification of the ‘early release’ data.

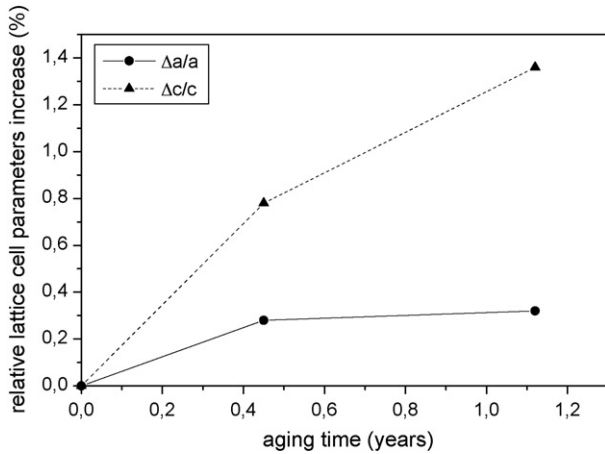


Fig. 7. Evolution of the relative cell parameter increase ($\Delta a/a$ and $\Delta c/c$) of LaNi_5 samples at different aging times.

4.1.2. Structural properties

4.1.2.1. Long-range order. XRD measurements have been performed on four LaNi_5 samples aged for zero, 0.5 year ($\text{He}/M=0.02$), 1.1 year ($\text{He}/M=0.06$) and 2.8 years ($\text{He}/M=0.13$) [7]. During the first year of aging ($\text{He}/M \leq 0.06$), a swelling of the lattice cell is observed (Fig. 7). The hexagonal cell extends mainly along the c axis: the swelling is about 1.35% for the c axis, whereas it is only 0.32% for the a axis after 1 year of storage. This corresponds to a total swelling of 2.04% of the lattice cell volume.

For longer aging times, the line widths progressively increase and the signal on noise ratio decreases. For the sample aged 2.8 years ($\text{He}/M=0.13$), all the lines beyond 45° in 2θ have disappeared and the calculation of the cell parameters is thus, impossible. At that stage, the long-range order is lost.

4.1.2.2. Local order. In addition to XRD, EXAFS experiments have been performed on three LaNi_5 samples aged for zero, 0.4 year ($\text{He}/M=0.02$) and 2 years ($\text{He}/M=0.11$), at the Ni K-edge

and the La L_{III} -edge. The Fourier Transforms are available in the reference [7]. As the aging time increases, the peak intensities decrease progressively with a more pronounced effect around La atoms, but without significant shift of their positions. These results are compatible with the XRD ones, as EXAFS is less sensitive to distance variations than XRD. The changes of intensities are observed after only 0.4 year ($\text{He}/M=0.02$). According to the structure of LaNi_5 , the first peak at the Ni edge corresponds to 7.2 Ni atoms at 2.48 \AA around a Ni atom, and the first peak at the La edge corresponds to 6 Ni atoms at 2.88 \AA and 12 Ni atoms at 3.20 \AA around a La atom. The analysis of the back-Fourier Transforms of these peaks indicates that the Ni–Ni and La–Ni distances do not change whereas the Debye–Waller factors increase with aging time, especially around La atoms.

These results indicate that the chemical order is not modified and that there is mainly a static disorder, that is, an increase of the distance distribution, especially around La atoms.

4.2. Pd

4.2.1. Thermodynamic properties

The desorption isotherms of Pd samples with various ^3He contents, from zero to 0.33 (13.1 years), have been measured at 313 K [8]. Results are shown in Fig. 8. During aging, there is a small decrease of the plateau pressure, and a shift of the α branch towards larger stoichiometries leading to a small amount of deeply trapped tritium ($T/\text{Pd}_{\text{max}} \approx 0.12$). The main changes occur at the beginning of aging, that is to say, for ^3He contents smaller than about 0.15 (aging time ≤ 5 years). For greater ^3He contents, the two parameters tend to stabilize. The behaviour of the β branch is slightly different. For $\text{He}/\text{Pd} \leq 0.22$ (aging time ≤ 7 years), the β branch also shifts towards larger stoichiometries, whereas for higher ^3He contents the β branch shifts back towards smaller stoichiometries. This generates a small decrease of the reversible capacity.

All these variations are very slight, and the most noticeable thing here is that the storage properties of Pd are outstandingly

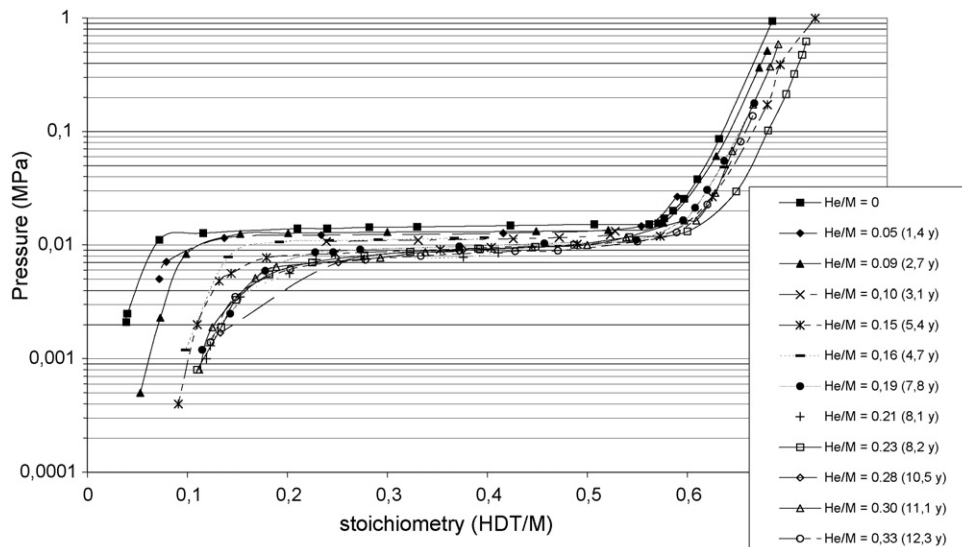


Fig. 8. Tritium desorption PcT curves at 313 K for Pd samples with different ^3He contents (various aging times).

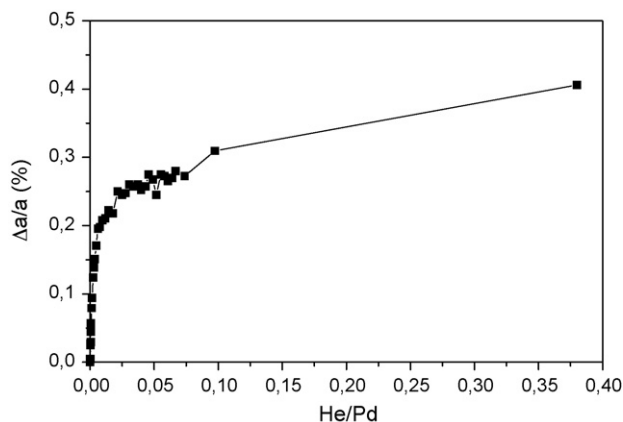


Fig. 9. Evolution of the relative cell parameter increase of a Pd sample (*in situ* measurements).

well preserved during aging, even for ^3He contents up to 0.33 (13.1 years of aging).

4.2.2. Structural properties

4.2.2.1. Long-range order. XRD measurements have been performed *in situ* (in special sample holders with a beryllium window and a reservoir of tritium) on different Pd samples for more than 10 years [9]. During aging, a swelling of the cubic cell is observed, as can be seen in Fig. 9. The major part of this swelling happens for ^3He contents smaller than 0.01 (aging time ≤ 3 months). During this stage, the lattice cell parameter increases by about 0.2%. For larger ^3He contents, the lattice cell parameter continues to rise at a smaller rate. For He/Pd = 0.38 (10.5 years), the total increase of the lattice cell parameter is 0.4%, which corresponds to a swelling of 1.2% in volume. This value is extremely low, compared to the ^3He content. Moreover, it is noticeable here that the long-range order is kept even for ^3He contents up to 0.38 (10.5 years).

4.2.2.2. Local order. EXAFS measurements have been performed on several Pd samples with ^3He contents ranging from zero to 0.265 (9.8 years) [9]. The first experiments were carried out at LURE (Orsay, France), the second ones at ANKA (Karlsruhe, Germany) on the INE beamline which allows the handling of radioactive samples. The evolution of the Fourier Transform at the Pd K-edge is reported in Fig. 10a and b for these two experiments. The main peak of the Fourier Transform, corresponding to Pd–Pd distances, is not shifted and a significant decrease of its intensity is only observed for He/Pd ≥ 0.16 (5.4 years). Further aging, up to He/Pd = 0.265 (9.8 years), does not generate any measurable evolution. The analysis of the back-Fourier Transform of the main peak indicates that the Pd–Pd interatomic distances are not modified within the precision of the technique (0.01 Å). These results are therefore, compatible to XRD ones. The intensity decrease of the first peak corresponds to a small increase of the Debye–Waller factor from 0.08 to 0.09 between He/Pd ≤ 0.03 (0.8 year of aging) and He/Pd ≥ 0.16 (5.4 years of aging). The Debye–Waller factor increase could be explained by a larger distance distribution around Pd atoms, that is, to a small local disorder.

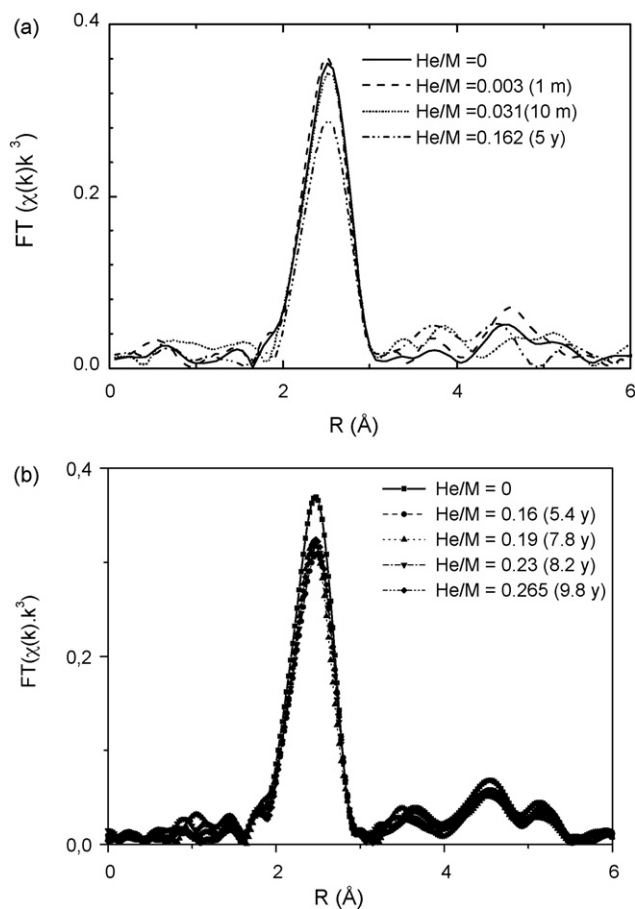


Fig. 10. Fourier transforms of Pd oscillations at the Pd K-edge for different aging times: (a) first experiment in LURE, (b) second experiment in ANKA.

4.2.3. Micro structural properties

Finally, the evolution of the micro structural properties of Pd after aging has been studied by TEM observations. Different ^3He contents have been studied: 0, 0.003 (1 month), 0.007 (2 months), 0.010 (3 months), 0.016 (5 months) and 0.024 (8 months) [10,11]. A very large density of dislocations and of small interstitial type defects is observed, even for the smaller ^3He content. To reveal ^3He bubbles, we have used special imaging conditions [12]. ^3He bubbles have been observed for every aged Pd sample. Examples are shown on Fig. 11 for Pd samples with He/Pd varying from 0.010 (3 months) to 0.024 (8 months). In these cases, the bubble diameter is around 1 nm, and the bubble density is in the range $0.5\text{--}2 \times 10^{25}$ bubbles/m 3 . The great uncertainty concerning bubble density is due to the difficulty to estimate the sample thickness by TEM.

^3He bubbles are therefore, formed very quickly in the Pd tritide, before the first month of aging. From He/Pd = 0.003 (1 month) to He/Pd = 0.024 (8 months), the increase of ^3He content does not generate any significant evolution. It seems that bubble diameter slightly increases (from 0.8 nm at He/Pd = 0.003 to 1.5 nm at He/Pd = 0.024). The bubble density stays within the uncertainty range (from, $0.3\text{--}1 \times 10^{25}$ bubbles/m 3 at He/Pd = 0.003, to $0.5\text{--}2 \times 10^{25}$ bubbles/m 3 at He/Pd = 0.024). Attempts to observe older Pd samples have failed because of the rupture of Pd samples during aging.

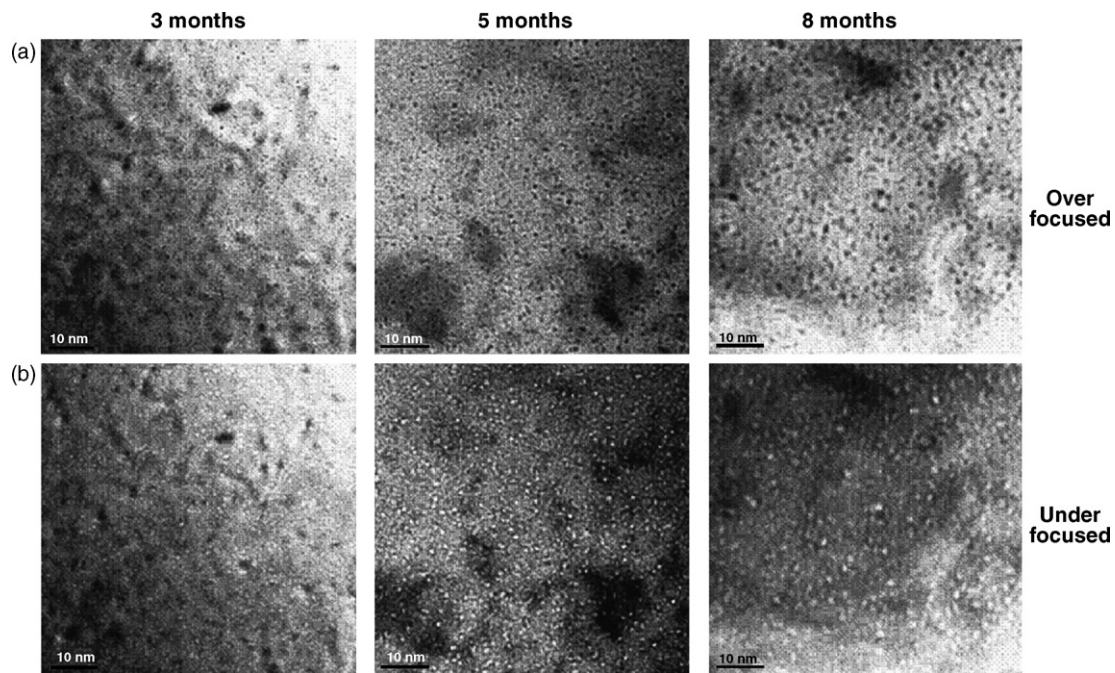


Fig. 11. Bright through-focal series of He bubbles in Pd at He/Pd=0.010 (3 months) [10], 0.016 (5 months) and 0.024 (8 months) [11] (a) under focus, (b) over focus. For negative defocus (under focus of the objective lens), bubbles appear as white dots surrounded by a dark fringe while for positive defocus (over focus), the dots are black and the fringe is white.

The tendency of ^3He atoms to form bubbles in the Pd tritide is therefore, clearly demonstrated by these TEM observations, even for very low ^3He contents.

5. Discussion

^3He retention studies have shown that in LaNi_5 tritide, ^3He is retained in the matrix at more than 99% for at least 7 years, and probably more. This is in line with the literature where no measurable ^3He release has been observed during the first 2400 days (6.6 years) of storage [3]. Moreover, it seems that there is no effect of the initial stoichiometry of the sample on ^3He retention, at least during the first 12 years of aging (that is to say, before the accelerated release stage is reached). In other words, this means that the α and β phases have the same behaviour towards ^3He retention before the accelerated release stage is reached. Later, during the accelerated release stage, it seems logical that the ^3He out gassed comes from the β phase which has the highest concentration in ^3He . It is thus, possible to calculate a ‘critical’ ^3He concentration for the β phase only. This gives value of critical ^3He content between He/M=0.50 (9.5 years) and He/M=0.63 (12 years) in the β phase. Nevertheless, the aging time is the significant parameter to describe aging in LaNi_5 tritide, and not the total ^3He content which depends on the initial stoichiometry.

In the case of Pd tritide, ^3He is globally well retained in the matrix during at least 9 years. Nevertheless, the initial stoichiometry of the sample and the presence or not, of a replenishment, have a great influence on ^3He retention.

For the not replenished samples, ^3He is retained in stoichiometric samples at more than 95% from 2 to 12 years. These

results are significantly different from the ones given in the literature. Indeed, in the main article published on this subject [5], the ^3He release rate was found to vary between 0 and 2% from 5 years (He/Pd=0.15) to 17 years (He/Pd=0.37) of storage, with a subsequent increase to about 10% after 19 years (He/Pd=0.39) of aging. Thus, the difference lies both in the percentage of ^3He released during the stabilized period, and the beginning of the increase in ^3He release rate. One possible explanation of such differences could lie in the starting material. For instance, the powder used in the literature had a significantly larger particle size (44–100 μm) compared to the one used in this study (10–25 μm).

Moreover, for sub stoichiometric samples, we have observed a great difference between α and β phases behaviour. For all these samples, the accelerated release stage has not been reached after 12.5 years of aging (He/Pd \leq 0.29) and the slight increase of ^3He release could be due to the $\beta \rightarrow \alpha$ phase transition. Indeed, this transformation leads to a decrease of about 10% of the lattice cell volume, and could create new strains in the lattice and therefore, could induce the desorption of a small fraction of the ^3He trapped in the lattice.

For the replenished samples, ^3He is also retained at more than 95% during the first 9 years of aging. After, the accelerated release stage is reached, which corresponds to a saturation value of ^3He content equal to He/M=0.33. Again, these results are significantly different from the ones available in the literature. In one article [4], the ^3He release rate was established to be about 5% during 5000 days (14 years), with a saturation value of ^3He content in Pd of He/Pd=0.5. In another article [5], the ^3He release rate was estimated to be under 3% during 6000–6200 days (17 years) with a saturation value of

He/Pd = 0.51 to He/Pd = 0.54. Thus, if the ^3He release rate is about the same during the stabilized period in the different studies, there is a huge difference on the beginning of accelerated release (9, 14 and 17 years) and/or saturation value of ^3He (0.33, 0.5 or 0.54), even between the two references. As previously mentioned, this could be due to a difference in the starting material, and the particle size in particular.

As a consequence of these stoichiometry effects, it seems that the best parameter to characterize the aging of Pd tritide is the helium content and not the aging time.

To summarize this ^3He retention study, we can say that LaNi_5 and Pd tritides globally have similar ^3He retention properties: ^3He is retained at more than 95% during at least the first 9 years of aging. However, we have seen that the effects of the presence of ^3He in the matrix (i.e. the ‘aging’ effects), are completely different between the two tritides. For LaNi_5 , the thermodynamic and structural properties are lost after only 1.8 year (He/M = 0.09) and 2.8 years (He/M = 0.13) of aging, respectively. On the contrary, for Pd thermodynamic and structural properties they are outstandingly well preserved, even after 10 years of aging (He/Pd = 0.27). This contrasts with the behaviour of LaNi_5 tritide. The same observation was made by Nobile et al. between Pd and $\text{LaNi}_{4.25}\text{Al}_{0.75}$ tritides [13]. This difference could be due to a different localization of ^3He atoms.

In the case of LaNi_5 tritide, all aging effects could be explained by the trapping of a part of ^3He atoms at least in the largest interstitial sites of the LaNi_5 structure, that is, the tetrahedral sites La_2Ni_2 6m. At first, this could explain the loss of storage properties, as interstitial sites are no longer available for tritium occupancy, and equally the large disorder at both long-range and local scales. Indeed, the ^3He atoms are approximately two times bigger than the T atoms and their presence in the interstitial sites generates large lattice distortions. The disorder in the lattice also contributes to the loss of storage properties. Furthermore, this could also explain the asymmetric swelling of the lattice cell as the two La atoms of the 6m site are located along the *c* axis, and this could lead to the greatest dilatation along this axis. Finally, this site is also the richest one in La atoms, so its occupation could create the large disorder observed mainly around La atoms by EXAFS measurements.

On the contrary, in the case of Pd, it has been demonstrated that ^3He atoms tend to rapidly precipitate into bubbles. ^3He atoms thus, do not stay in interstitial sites, leaving these sites available for tritium occupancy. Moreover, bubbles can be considered as ‘local’ defects (i.e. defects of finite volume) and this kind of defects has only a weak influence on the lattice cell, inducing a small swelling of the cell as observed experimentally by XRD measurements even for high ^3He contents, up to He/Pd = 0.265 (9.8 years of aging). Self interstitial Pd atoms, produced by bubble growth, will also participate to the cell parameter increase versus ^3He content, whereas the extended dislocations, formed by arrangement of self interstitial atoms and dislocation loop transformation, are responsible for the line width broadening [9,14]. This corresponds exactly to our measurements. In addition, the formation of ^3He bubbles has, of course, no influence on local order around Pd atoms, except the ones on the bubbles surface, explaining thereafter the very small

evolution observed experimentally by EXAFS measurements even for high ^3He contents (He/Pd \leq 0.265). This preservation of the lattice structure, together with the vacancy of interstitial sites, explains the conservation of storage properties. Finally, the lattice swelling can explain the decrease of plateau pressures, according to the geometrical model [15], whereas the formation of defects such as bubbles and dislocations can explain the irreversible trapping of tritium, because of the well known affinity of tritium atoms for ‘voids’ in the material (bubbles surface, dislocations, . . .).

The formation of ^3He bubbles in metallic tritides, according to the self-trapping theory, has already been described in the literature [16]. Moreover, in the case of Pd tritide, prior work complements well the present observations and conclusions. The main results in this field were obtained by NMR studies for ^3He nuclei [17–20]. They have clearly demonstrated the formation of ^3He nanobubbles in Pd samples aged from 6 months to 8 years. These previous studies have also established that ^3He bubbles grow with time, leading to a distribution of bubble sizes and internal ^3He densities.

In the case of LaNi_5 tritide, the fact that ^3He atoms are trapped in interstitial sites also explains the ^3He retention particularities in this material. Indeed, this quite simple trapping mechanism explains the relative simplicity of ^3He retention properties. For instance, the trapping of ^3He atoms in interstitial sites explains that there is no effect of the initial stoichiometry and that α and β phases have the same behaviour before the accelerated stage is reached, as the characteristics of interstitial sites are similar between the two phases. It could also explain that no effect of the initial material properties (particle size, purity, . . .) was observed, in agreement with literature [3]. Lastly, the accelerated release could be due to the saturation of interstitial sites with ^3He atoms, or to a saturation of lattice distortion, in the β phase. Whatever, the total occupancy of 6m sites would correspond to an ^3He content of He/M = 0.32, but we have seen that higher ^3He contents can be reached, for instance in sample L1. This shows that some ^3He atoms must be trapped in other places than the 6 m sites. They could be stored in other distorted interstitial sites and in dislocations. In addition, the formation of ^3He bubbles cannot be completely excluded, but could not be observed due to the difficulty to perform TEM experiments in such material. It is therefore, difficult to determine which mechanism is responsible for the accelerated release.

In the case of Pd tritide, we have seen that bubbles are supposed to be generated by self-trapping of ^3He atoms [16]. In other words, ^3He atoms diffuse in the matrix where they can be trapped by a defect (vacancy, impurity, . . .); or meet another ^3He atom; or diffuse to the surface to be released. The trapping on pre-existing defects such as impurities and vacancies (first case) explains the influence of the starting material characteristics on ^3He release. The last case is responsible for the fact that ^3He is never retained at 100% in the solid phase, and also for the influence of particle size as the bulk/surface ratio is very important in the probability for an ^3He atom to reach the surface without being trapped on a defect. In the second case, when two ^3He atoms meet, they form a very stable pair as ^3He atoms have more affinity for other ^3He atoms than for metallic atoms. This pair

will thus, have a very low probability of dissociating. This less mobile pair will not diffuse in the matrix. It will constitute the first step of the formation of an ^3He cluster, as new ^3He atoms diffusing to this pair will remain trapped because of ^3He atom affinities. Step by step, this cluster will grow and transform into a visible bubble (1 nm).

Theoretical calculations, made for Pd tritide, indicate that only 2 days are necessary to form 90% of the bubbles [21]. According to this author, the progressive formation of bubbles is responsible for the early ^3He release. Indeed, at the beginning of aging, when all the defects are not yet formed and/or when ^3He clusters are very small, the probability for an ^3He atom to reach the surface without being trapped is great. This leads to a significant release rate. When the aging time increases, defect density and also size increase. They become more efficient traps for ^3He atoms and the release rate decreases, until the accelerated release stage is reached. The same mechanism could apply to the α phase. In this phase, the tritium concentration is weak, as is the ^3He concentration. The formation of ^3He pairs, clusters, and finally bubbles by ^3He self-trapping is thus, significantly less efficient than for the β phase. As a consequence, we can suppose that the density of defects remains small in the α phase, whatever the aging time. The case of the α phase could thus, be similar to the one of the β phase at the beginning of aging, with a great ^3He release rate (equivalent to the ‘early’ release). Lastly, this model could explain that the major changes (on PcT curves, lattice structure, . . .) are observed at the beginning of aging. This stage could correspond to the formation of clusters and bubbles, further growth of these bubbles only leading to small effects on the tritide properties.

Ultimately, two mechanisms are possible for accelerated release. The first one is the fracture of the matrix as a result of the stress caused by the high pressure in bubbles. The second one is the impossibility for freshly created ^3He atoms to insert bubbles because of a pressure that is too high, leading to a diffusion of these atoms towards the surface. Unfortunately, this study has not allowed us to establish which mechanism is responsible for accelerated release. TEM observations of samples, which have reached the accelerated release stage and/or measurements of the internal pressure of ^3He bubbles may permit the determination of the proper mechanism. Future experiments will try to answer this question.

6. Conclusion

LaNi_5 and Pd are both interesting materials for tritium storage. Their main advantage is their ability to retain the ^3He generated in their matrix for at least 9 years. However, for tritium processing applications, aging effects are an important consideration. For LaNi_5 tritide, structural and thermodynamic

properties are dramatically altered after about only 2 years of storage. LaNi_5 can thus, be used as a buffer, for very short periods of storage or, on the contrary, for long term storage if the tritium has not to be stored and removed regularly. Indeed, tritium can still be removed definitely by heating the material whatever its aging time. Another possibility to use LaNi_5 beds for all applications is to replace the beds regularly, as the material is relatively inexpensive. However, in this case the ultimate treatment of the beds as waste has to be considered, which explains why it can be more interesting to use Pd. In fact, we have seen that all properties of Pd tritide are outstandingly well preserved even after 10 years of aging. This allows the use of Pd beds for all applications. The only disadvantage is then the cost of the starting material.

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