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X-ray diffraction analysis of uranium tritide after aging for 420 days

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ABSTRACT

Uranium tritide aging leads to continuous creation of decayed product ^{3}He, vacancies, vacancy clusters, self interstitials, dislocations and helium bubbles. These defects result in the changes of material properties such as degradation of tritium storage, swelling, hardening and intergranular embrittlement. In our previous study, a simple hermetic sample holder that fits the Philip X'Pert Pro X-ray diffractometer has been developed for X-ray diffraction (XRD) analysis of uranium hydride. In order to help resolve unknowns regarding aging effects of uranium during long-term storage of tritium, XRD techniques with the hermetic method are applied to obtain the structural changes of aged uranium tritide. XRD analysis of uranium tritide aged for 420 days have shown that noticeable peak shifts appear in the diffraction patterns of uranium tritide, which indicate lattice distortion occurrence during the formation and growth of helium bubbles and other associated defects.

1. Introduction

Tritium is an isotope of considerable interest and has important technological applications, especially in the nuclear industry. However, the radioactive nature of tritium imposes many conditions on its handling and storage which are in addition to those required for the storage of its sister isotopes hydrogen and deuterium. It has been recognized for a long time that the best way to store hydrogen is in the form of a hydride, which has the advantage of safety, easy recovery, and also much larger quantities of hydrogen can be stored per unit volume than in its liquid form. Therefore, it is quite natural to propose the storage of tritium in the form of a tritide, and the metals such as palladium, titanium, zirconium, erbium, uranium, and the intermetallic alloys such as lanthanum–nickel and zirconium–cobalt, are commonly used for this purpose. Among these metals and alloys, uranium is regarded as the most promising material because of its noticeable characteristic of low decomposition pressure which is the most important one for safety. In fact, uranium is widely used in many tritium-handling systems [1–3].

However, like all other metal hydrides used for tritium processing, uranium tritide accumulates helium (^{3}He) produced by the β decay of tritium in the uranium tritide lattice. The decayed helium stays in the solid and does not release until a critical helium concentration has been reached. The presence of helium in the matrix induces structural changes which in turn considerably influence the tritium absorption–desorption characteristics of the metal tritides. Many researchers have investigated aging effects in uranium tritide, focusing on helium-release measurements [4–6]. However, the delicate handling of tritium in terms of safety has limited the number of experiments on the structural characterization of aged uranium tritide. Almost no literature is available on the structural changes of uranium tritide during long-time storage, mainly because its high toxicity and air sensitivity render appropriate experiments very difficult. Therefore, we have developed a hermetic sample holder that fits the Philip X'Pert Pro X-ray diffractometer and is designed to study the aging effects of uranium tritide during storage. XRD analysis of uranium hydride has demonstrated the security and accuracy of the sample holder for radioactive and air-sensitive materials [7].

In the present work, we focus our XRD analysis on aged uranium tritide. We present the first results of XRD patterns of uranium tritide after aging for 420 days. In addition, helium-release measurements are carried out and the relationship among the amount of decayed ^{3}He, aging time and lattice damage are also discussed.

2. Experimental

2.1. Helium-release measurements

As discussed above, many researchers have investigated aging effects in uranium tritide, focusing on helium-release measurements. ^{3}He release from stoichiometric uranium tritide (UT_3) consists of two stages as illustrated by Wilson [6]. The early release period consists of a small and constant release of ^{3}He; the second stage is accelerated release, characterized by a rapid evolution of ^{3}He after a critical age (or critical ^{3}He concentration) has been reached. The reported critical ages for uranium tritide vary from

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1 year to 3 years, which is mainly due to the definition of critical age. According to Wilson's report, critical age means the turning time that ^{3}He release rate at room temperatures increases drastically but does not reach the ^{3}He generation rate. However, other researchers [4,8,9] define critical age as the turning time that ^{3}He release rate equals to its generation rate. In fact, the ^{3}He release curves obtained by these authors are similar. In this paper, we adopt the Wilson's definition of ^{3}He release critical age.

Fig. 1 shows an overview of the experimental apparatus used to measure ^{3}He release from uranium tritide. The apparatus is a typical high-vacuum stainless-steel system for pressure–volume–temperature-composition (PVT-*c*) measurements. ^{3}He pressure and composition can be determined by combining residual-gas analyzer (RGA) and high-resolution pressure transducer. Uranium tritide samples are prepared by activated uranium powder reacting with pure tritium (prepared by hydrogen isotope separation and purification). The detailed information is given in our previous work [7].

After aging for 420 days, ^{3}He release from uranium tritide has reached the second stage, i.e. accelerated release period. The release fraction (the ratio of total ^{3}He released to total ^{3}He generated) of ^{3}He is about 8%. The results show that most of generated ^{3}He atoms still retain in the matrix.

2.2. XRD analysis of uranium tritide

Tritium belongs to the group of less toxic radionuclides. The main hazard of stored tritium is air leakage. The pulverization of uranium is caused to a large extent by reaction with tritium to form uranium tritide which is highly air-sensitive. When exposed to air, uranium tritide becomes pyrophoric mainly owing to the substantial reaction heat. In this event, tritium can be transformed into tritiated water by oxidation ($T_2 + 0.5O_2 \rightarrow T_2O$) and by isotope exchange ($HT + H_2O \rightarrow H_2 + HTO$). Both processes should be avoided from a radiation-protection standpoint, because tritiated water is much more dangerous than tritium gas. As measured by radioactive metrology, T_2O is 10000 times more hazardous than tritium gas and HTO is about 10000 times more toxic than HT [10]. This may be the primary reason that for almost no research has been reported on the structural characterization of aged uranium tritide. Uranium tritide sample handling and preparation are necessarily performed with gloves and tools that severely limit manual dexterity and the range of possible manipulations. For this reason, an effective sample holder is designed and successfully used to perform XRD analysis of uranium hydride. For XRD analysis of uranium tritide, we use the similar method. The only difference between XRD analysis of uranium hydride and uranium tritide is that the latter experiment requires much more strict radiation protection during the processes of sample preparation, transportation, XRD analysis and sample recovery.

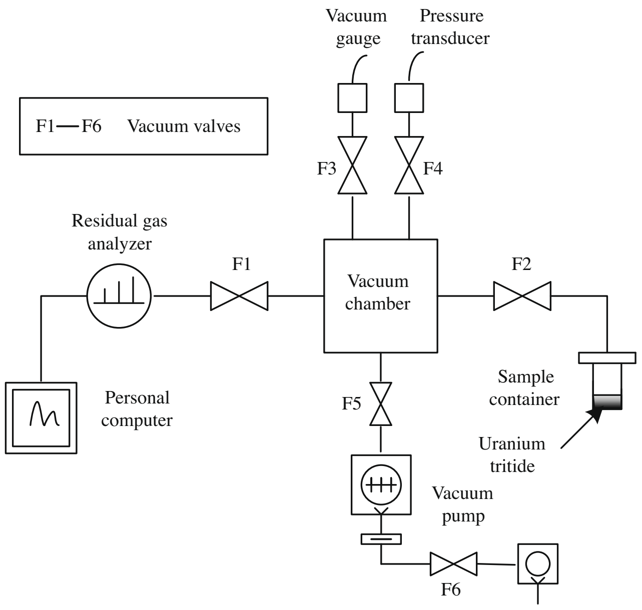

Fig. 1. Schematic of helium-release measurement apparatus.

For the newly synthesized uranium tritide that almost no helium has been produced in it, we suggest that the XRD patterns of uranium tritide are similar with those of uranium hydride except for the slight isotopic shifts mainly due to lattice constants. As shown in Fig. 2, the calculated patterns of UT_3 and UH_3 are nearly superposable. The slight peak shifts result from the slight differences in lattice constants of the two crystals. As for isotopic effects in solid, the lattice constants of the crystal containing lighter elements are usually larger than those containing heavier elements, which can be interpreted by lattice dynamics of solid [11]. Uranium hydride has two kinds of crystal cubic structures corresponding to the low-temperature (far below room temperature, α-UH_3) and the high-temperature (β-UH_3, space group *Pm3n*) phases. The lattice constants of β-UH_3 and β-UT_3 equal 6.6444 ± 0.0008 Å, and 6.625 ± 0.003 Å, respectively [12]. So, from the standpoint of radiation protection, the XRD analysis of fresh UT_3 is not necessary. We perform XRD analysis of uranium tritide after aging for 420 days. The typical working conditions of this XRD analysis include: CuK_α radiation (wavelength of $CuK_{\alpha1} = 1.54056$ Å), continuously scanning (0.05° every step), scan range 20°–60°, and room temperature.

The observed XRD patterns of UH_3 and UT_3 aged for 420 days are shown in Fig. 3. In order to understand structural changes in UT_3, we presume XRD patterns of UH_3 as XRD patterns of fresh UT_3. Compared with the theoretical XRD patterns of UH_3 and UT_3, considerable line broadenings are observed in the measured XRD patterns, which are mainly due to pulverization of the crystals after hydriding–dehydriding cycles. The peak shifts of observed XRD patterns of UH_3 are negligible. However, noticeable peak shifts appear in the XRD patterns of aged UT_3 when compared with theoretical and observed XRD patterns of UH_3. This may be the common phenomena for the XRD patterns of metal tritides after a period of storage [13,14]. The peak shifts generally attribute to helium bubble strains and crystal defects during the continuous

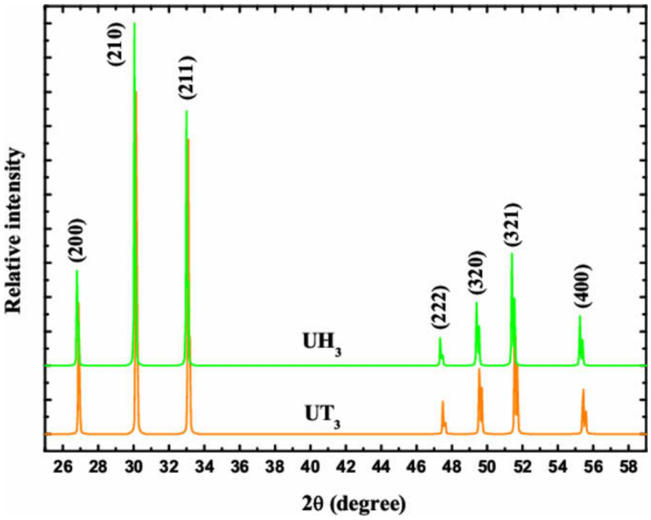

Fig. 2. Calculated XRD patterns of UT_3 and UH_3.

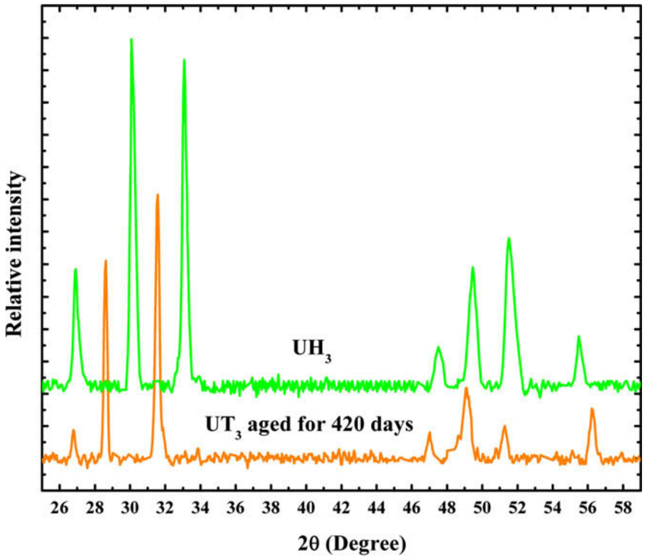

Fig. 3. Observed XRD patterns of UH_3 and aged UT_3.

Table 1
The estimated lattice constants from different planes of XRD patterns of UT_3 aged for 420 days. a_0 is the lattice constant of fresh UT_3 and a is the lattice constant of aged UT_3. $\Delta a = a - a_0$.

Plane	a (Å)	$\Delta a/a_0$ (%)
(200)	6.673	0.73
(210)	6.881	3.86
(211)	6.857	3.49
(320)	6.672	0.72
(400)	6.537	−1.33

decayed process of tritium in the tritides. As shown in Fig. 3, most of the peaks (especially for the lower indices planes) shift to the lower diffraction angles corresponding to larger lattice constants, and only the peak with the highest indices plane shifts to higher diffraction angle corresponding to smaller lattice constants. As a whole, the lattice constants increase and UT_3 expands after aging for 420 days. The results clearly show the lattice distortion exhibit anisotropic characteristics and it is difficult to accurately calculate the lattice constants of aged UT_3 from its XRD patterns. The estimated lattice constants from different diffraction planes are shown in Table 1. He to U atomic ratio reaches about 0.16 after aging for 420 days. As is well known, the atom radius of He is much larger than that of tritium atom, so the total volume of the lattice must increase. Many researchers have reported the lattice expansion of aged metal tritides. As a result of high helium content, high-pressure helium bubble (at GPa level) should be formed and result in complex dislocation evolutions and plastic deformation. Obviously, helium bubbles randomly distribute in UT_3 powder, so uniform lattice distortion and plastic deformation occur. In addition, the particle sizes of aged uranium tritide are estimated to be between 1000 Å and 2000 Å by using Sherrer's equations from the widths of different diffraction lines.

3. Discussion

Helium (^{3}He or ^{4}He) is a closed-shell inert gas and is extremely insoluble in metals. Helium atoms can be introduced into solid materials by ion implantation, or (n, α) nuclear reaction especially for fusion reactors, or radioactive decay of tritium in metal tritides. Due to their very low solubility helium atoms in metals or alloys agglomerate into bubbles which have detrimental effects on mechanical and tritium-storage properties. In the tritide case, ^{3}He atoms are generated in the materials itself. The key difference between helium ion implantation (or nuclear reaction) and ^{3}He generated by decay is that the latter case is not associated with initial lattice damage (the average ^{3}He energy of about 1 eV is too low for displacements of metal atoms) [15]. By contrast, helium atoms implanted into materials, produce initial displacement damage in the form of Frenkel (vacancy and self interstitial atom) defects or, at higher energies, displacement cascades. Obviously, the vacancies or vacancy clusters in the implantation case will influence helium atoms diffusion and may serve as suitable nucleation sites for helium bubble nucleation and growth. In the tritide case, no such instantaneous nucleation site is formed. Here, agglomeration of several ^{3}He interstitial atoms results in 'self-trapping' by the spontaneous formation of a Frenkel defect once more than 5–7 ^{3}He atoms cluster together [16,17]. This Frenkel pair/^{3}He atom cluster is the nucleation site for a bubble. When trapping further ^{3}He atom it continuously ejects metal atoms either in form of single atoms, or else, interstitial loop (dislocation-loop punching). In addition, tritium in metal tritide transmutes into ^{3}He, so metal tritide is a time-dependent ternary system in which the increase in the helium concentration corresponds to the decrease in the tritium concentration and ^{3}He will release from tritide at room temperature when ^{3}He concentration reaches a certain value [18]. For the implanted helium atoms, helium-release measurements are usually performed at elevated temperatures (for example, thermal desorption spectroscopy experiments) because of relatively low helium concentration in the materials.

Compared with other metal tritides, ^{3}He in uranium tritide has a higher ^{3}He release rate and quickly reaches critical concentration [18,19]. ^{3}He release in metal tritides results from helium bubble formation, migration and coalescence. As reported by Bowman and Attalla [8], ^{3}He bubbles are quickly formed in uranium tritide after aging for only two months. By using pulse nuclear-magnetic-resonance (NMR) techniques, they have investigated the ^{3}He distribution in uranium tritide and found that the radii of ^{3}He bubbles are less than 100 Å. In the initial storage period, most of the decayed ^{3}He atoms are trapped in the bubbles which are expected to expand as the ^{3}He concentration increases and the bubbles continue to grow by trapping newly decayed ^{3}He atoms. In this period, only a small quantities of ^{3}He gas near the surface and interface release from the tritides. ^{3}He bubbles in metals cannot always grow because of crystal stress. When ^{3}He bubble reach its critical size or critical pressure, the particles containing those ^{3}He bubbles begin to fracture from the internal stress (^{3}He bubble pressure at GPa level), which leads to the accelerated ^{3}He release. Thus, the specific surface area increases and the probability of ^{3}He escaping correspondingly increase. The physical mechanism is pictorialized in Fig. 4. In the metal–helium system, grain boundaries are usually

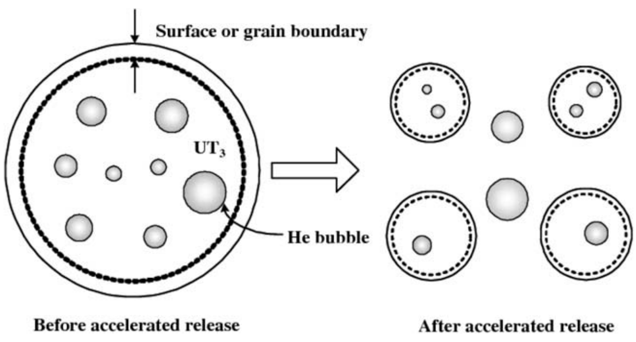

Fig. 4. Schematic illustration of helium releasing from UT_3.

viewed as the typical paths of helium release. The size and content of grain boundaries can be increased by dislocation rearrangement and high-pressure helium bubbles. We consider that the size and content of grain boundaries are increasing during the aging process of UT_3 until helium content reaches its critical value.

Although, there is no initial lattice damage in metal tritide, various crystal defects such as isolated vacancy and self interstitial atom (SIA) are continuously created during the process of tritium decay. The point defects cluster together to form more steady defects clusters, such as vacancy clusters, SIA clusters and ^{3}He-vacancy clusters. Moreover, these defects may transform into other extended defects such as void, dislocation loop and grain boundary [13,19,20]. It is widely recognized that high pressure ^{3}He bubbles in tritide may solely contribute to peak broadening of XRD patterns, without contributing significantly to peak shift. This is no longer true for the aged uranium tritide. Interestingly, there is no noticeable peak broadening in the XRD patterns of uranium tritide aged for 420 days, but significant peak shift occurs. Here, we must point out that uranium hydride is unique in that it does not fall in the class of volatile hydrides, salt-like hydrides or interstitial solution hydrides [21]. It is a metal-like hydride of perfectly definite composition, and with a structure completely unrelated to any of the three forms of uranium metals. In particular, metal–metal bonds are practically non-existent in this hydride. Provided that every decayed ^{3}He occupies the lattice site of tritium atom, lattice constants will definitely increase because the radius of ^{3}He atom is several times greater than that of tritium atom. In addition, one can expect that distortion or expansion of the lattice is isotropic. In fact, it is not completely true for aged uranium tritide as shown in Fig. 3. ^{3}He atoms are unsteady in uranium tritide. Although, newly decayed ^{3}He atoms randomly distribute in the tritide, it will diffuse to more steady site, because ^{3}He atoms cannot bind with metal uranium atoms or tritium atoms. The relatively steady sites for ^{3}He atoms are those with lower electronic density such as vacancy-like defects because of its closed electronic structure. Because, the vacancy concentration in uranium tritide is lower than in fusion reactor or helium ion implanted materials, ^{3}He bubbles in uranium tritide may be formed by 'self-trapping' mechanism as discussed above. However, for this mechanism the number of ^{3}He atoms at one defect-free nucleation site must exceed a certain value. This kind of nucleation site is always with relatively large free space. As is well known, the lower indices planes are attributed to the larger plane distances. So we conclude that initial ^{3}He atoms prefer to occupy the interstitial sites with lower indices where ^{3}He bubbles form and grow. Crystal stretching stresses resulted from ^{3}He atoms cluster and ^{3}He bubbles formation lead to lattice expansion, while on the contrary, the pressing stresses forcing on higher indices planes lead to lattice contraction.

4. Conclusion

^{3}He release measurements for aged uranium tritide are performed. XRD techniques with our own developed hermetic method are applied to obtain the structural changes of uranium tritide aged for 420 days. ^{3}He release reaches the accelerated stage in which ^{3}He bubbles at GPa level pressure lead to the fracture of crystals. XRD analysis of aged uranium tritide shows that noticeable peak shifts appear in the diffraction patterns of uranium tritide, which indicate lattice distortion occurrence during the formation and growth of ^{3}He bubbles and other defects. The anisotropic distortion results from ^{3}He atoms diffusion into lower indices planes. However, these results cannot be applied to fully understand the time-dependent helium effects during long-time storage of uranium tritide. Works are under way to obtain XRD patterns of uranium tritide aged more than two years.

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