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Deuterium, tritium, and helium desorption from aged titanium tritides

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Abstract

Six samples of tritium-aged bulk titanium have been examined by thermal desorption and isotope exchange chemistry. The previously reported discovery of a lower temperature hydrogen desorption state in these materials has been confirmed in one new sample. The samples' helium release shows the more severe effects obtained from longer aging periods, i.e. higher initial He/M ratios. Several of the more aged samples were spontaneously releasing helium. The hydrogen isotope and helium desorption of the samples will be discussed.

Keywords: Thermal analysis; Gas–solid reactions; Hydrogen absorbing materials

1. Introduction

The Savannah River National Laboratory has been involved in studying the effects of tritium (T) decay in metal tritides for many years [1–3], and has reported a thermal desorption spectroscopy (TDS) study of a single sample of T-aged Ti previously [4], comparing it to prior He-release results on Ti thin films [5]. In that study, the hydrogen desorption peaks were suppressed by a Ti preabsorber bed located between the sample and the pressure sensor. This paper extends our prior work to six new samples, one of which was examined extensively and the others less so.

The primary impact of radioactive tritium decay, which produces one ^{3}He atom per ^{3}H (T) decay, is to load the bulk metal tritide with an increasing amount of ^{3}He. This He is highly insoluble and immediately starts to aggregate into bubbles inside the tritide material as has been described in detail [6]. The bubbles formed in this process retain the bulk of the ^{3}He produced, but a small fraction born close to a surface can diffuse to the surface and escape to the gas phase. Therefore, any metal tritide that has been in storage for a period of time must have the gas phase over it sampled and quantified to partition the gas between free ^{3}He and hydrogen isotopes. After a sufficient time, the He content of the tritide nears 'breakout', where the bubbles have grown large and possibly interlinked, and now crack through to the surface, releasing the retained He. At this point, the effective surface to volume ratio of the material is greatly increased and significant release of ^{3}He can occur, although some ^{3}He will still be retained if born far enough from an exposed surface to still be trapped in a closed internal bubble. At some point, the possibility of further retention becomes remote, and the He is all released to the gas phase, the so-called 'free release' stage. It is of technical interest to quantify the rate and extent of He release in aged metal tritides, as the sudden release of retained He can cause pressure vessel integrity problems. Furthermore, the aging process causes changes in the thermodynamic properties of metal tritides, and He removal by thermal desorption (or cycling) can partially reverse these changes. This process is also of quantitative interest.

In these studies, aged titanium tritides were initially sampled for gas phase composition, then thermally desorbed, which typically leaves a significant residual heel in these materials. They subsequently were reloaded with pure deuterium and desorbed in order to quantify tritium heel content and to study any additional He release during cycling.

Thermal desorption of hydrogen (H) or deuterium (D) from Ti in many forms has been studied extensively [7–20]. Hydrogen isotopes typically desorb in one high temperature peak. This peak does show the usual shifts due to heating rates, but additional discrepancies between studies have been noted. Shoulders, both at higher and lower temperatures were often noted, and in one case exposure to air collapsed a dual peak spectrum into a single peak [18].

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Table 1
Loading and initial thermal desorption conditions of Ti samples

Sample ID	Sample weight (g)	Load Q/M	%T	No release He/M	Q/M prior to TD	He/M
Ti-1	0.7523	1.9	100	0.78	1.12	0.41
Ti-2	1.6027	1.6	100	0.64	0.91	0.34
Ti-4	1.5830	1.8	50	0.36	1.45	0.35
Ti-5	1.5279	1.2	50	0.26	1.04	0.26
Ti-6	1.5911	1.5	50	0.30	1.22	0.29
Ti-7	1.6007	1.8	50	0.28	1.56	0.28
Ti-9	1.0185	1.9	100	0.81	1.50	0.43

Thermal desorption has also been used to study Ti-based alloys and/or composites. Wilson and Pontau [11] studied TiB_2 and TiC coatings. Ogawa et al. [17] also studied a Ti–Al alloy, as did Takasaski and Furuya [21,22]. Borchers et al. [23] examined Ti ballmilled with varying amounts of graphite. Taken together, these studies show TDS spectra that now have become more complex, showing multiple or ill-defined hydrogen desorption peaks, both leading and/or trailing the primary desorption peaks. One interesting study by Gruner et al. [24] using a Pd coating on bulk Ti showed a desorption maximized at ∼420 K, which agrees well with a TDS maximum of ∼430 K reported from Pd by Fernandez et al. [20].

Clearly, the details of the hydrogen or deuterium thermal desorption from Ti are potentially quite variable. It is likely that the cleanliness of the surface and perhaps the surface to volume ratio will impact the results. This study uses large ‘chunks’ of bulk Ti sponge that may have decrepitated during the experiments or during prior activation.

2. Experimental

The basic experimental protocols were reported previously [4]. For this study, some modifications were made. In the prior report, an isotopic heel exchange was typically ended by a multi-hour bakeout of the sample. It was suspected that this annealed the sample and accelerated the loss of the low temperature desorption state, so in the current study, this bakeout was not done. The samples were flashed to high temperature (873–973 K) and then immediately closed off and cooled for subsequent loading in another isotope exchange experiment. As well, computer data collection procedures were improved, but smoothed curves are still presented herein. All thermal desorption figures will present the dP/dt data on the ordinate. dP/dt was computed from the smoothed data by simple subtraction of the preceding P,t values from the current one and dividing.

The samples were originally either loaded with pure tritium or with a 50/50 mol% mixture of D_2/T_2. The sample loading Q/M ratios and the percent T and thermal desorption (TD) initial condition are shown in Table 1. The Q/M prior to TD is computed by accounting for radioactive decay of the tritium portion in the hydride. Grab samples of the gas over the sample always showed near 100% ^{3}He. Also shown are the computed no-release and pre-TD He/M ratios. The no-release He/M values are computed as if no release had occurred up to the point where the TD was run. The pre-TD number is computed by including any measured out-gassing of He into the sample cell gas phase, which was always quantified.

Sample weights varied somewhat and are shown in Table 1. System volumes are sometimes different in the various experiments which complicates direct pressure and pressure change comparisons, but the qualitative features of the TDS spectra remain unaffected.

Ti samples 1, 2, 5, 7, and 9 were from the same manufacturing lot. Samples 4 and 6 were from separate and different lots. Sample Ti-7 did not use a test cell with an internal thermocouple well [4]. The remaining samples however, used a test cell manufactured from two pipe end caps that had an internal thermocouple well added. Therefore, the temperature measurements made for this work most probably have achieved better sample temperature measurement.

3. Results and discussion

In the prior report [4], the first thermal desorption of sample Ti-7 was presented in Fig. 1 as a time plot of the change in system pressure and, separately, of the temperature. For comparative purposes, that same data is represented here in Fig. 1 as the change in pressure per unit time (dP/dt) versus the sample temperature. Fig. 1 also presents similar data obtained from sample Ti-5. As can be seen, significant differences are observed. Most notably a large peak has developed in the Ti-5 spectrum at low desorption temperatures (350–570 K) that was shown to be pure ^{3}He (99.96%) by mass spectroscopic analysis of a grab sample taken at the ∼510 K point. In the Ti-7 spectrum a very small and broad peak is observed from ∼420 to 620 K. In Ti-7, grab sample analysis indicated the ^{3}He appeared at the highest temperatures, with the leading edge of the major desorption peak (∼670–850 K) being produced by hydrogen isotope evolution.

In the prior report, the spectrum presented for the first thermal desorption shows two fairly well resolved peaks. Grab sampling was timed to probe the early desorption, the valley between the peaks, and the late desorption. Because of the good separation, the helium content analyses of the samples could be shown to be accurate. However, in the new batch of analyses, these resolution

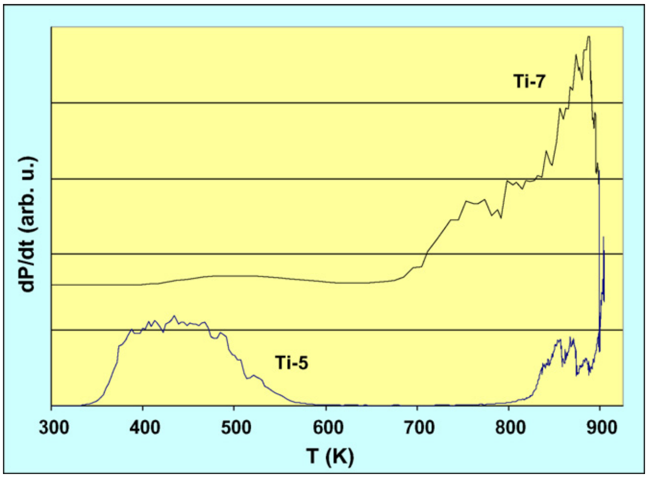

Fig. 1. dP/dt vs. T for the initial desorption from Ti-5 and -7. The curve for Ti-7 has been offset and reduced by 50% for clarity.

conditions were not met, which can be understood by comparing to Rhodin and Surenyants' thin film data [5].

In favorable comparison [5], the more aged samples are showing low temperature He release. In Ref. [5], this peak was not completely shown, but was indicated by the immediate baseline increase for the film with the highest He content. That data also showed a second, higher temperature He desorption peak. In our studies typically we did not go high enough in temperature to observe this peak for low He content cases. But in the case of the most aged thin film sample, this peak appears to have moved down to the same region where we observe hydrogen desorption, which causes He and Q_2 release overlap in our spectra.

Unfortunately, in our new work, there were some direct indications of inadequate mixing, i.e. helium analyses disagreed with the apparent composition derived crudely from the spectra. Thus all but the very first grab sample analyses had to be discounted in the attempt to understand the first thermal desorption spectra. Sampling of the later thermal desorption spectra arising from the isotope exchange experiments may have given more reliable numbers, but again, lack of peak separation hampered confirming this. As well, the standard deviations obtained from duplicate analyses were quite large in several cases in these studies. The primary impact of these problems was to make it impossible to accurately calculate the heel composition and amount derived from the first thermal desorption, which impacted the similar numbers from the later runs as well. Therefore, this paper will not present detailed results on hydrogen- and helium-to-metal ratios for other than the initial state after aging (Table 1).

In the prior report [4], the computed capacity of the loaded sample exceeded the normal Ti Q/Ti = 2.0 (Q = H + D + T) when showing the new lower temperature desorption state. TDS results for one sample (Ti-5) confirm the prior observation of a new, lower temperature desorption state. As a side note, the Q/M ratios computed previously for Ti-7 were found to need some corrections. The corrected values are: initial Q/Ti for third desorption (Fig. 2, [4]) = 1.65, initial He/Ti for third desorption = 0.06; heel Q/Ti after third desorption = 0.72; initial Q/Ti for fourth desorption (Fig. 3, [4]) = 2.62 (still anomalously high); heel Q/Ti after fourth desorption = 0.79; heel Q/Ti after fifth desorption = 0.83; initial Q/Ti for sixth desorption (Fig. 4 [4]) = 1.02; heel Q/Ti after sixth desorption = 0.61. In this report, the anomalously high absorption obtained in the fifth desorption cannot be confirmed. However, the development of the unusually low temperature desorption TDS peak was confirmed (see below).

The high temperature desorption peaks also show some significant differences. In Ti-7, the first peak, beginning at ~670 K (Fig. 1), was shown by grab sample analysis to be primarily Q_2. As shown in Fig. 1, in Ti-5 the desorption begins at ~820 K instead. The desorption peak structure is also somewhat complicated in Ti-5, with several maxima being observed. In contrast the Ti-7 desorption does not seem to show this. As will be discussed below, the remaining Ti samples also showed variant and complex desorption profiles in this region. This does not seem to be associated with heating curve problems or any other known experimental artifact, and remains an unexplained feature of the results. It also seems that some He release was occurring in the high temperature desorptions as well, but this could not be resolved as easily as in the prior report.

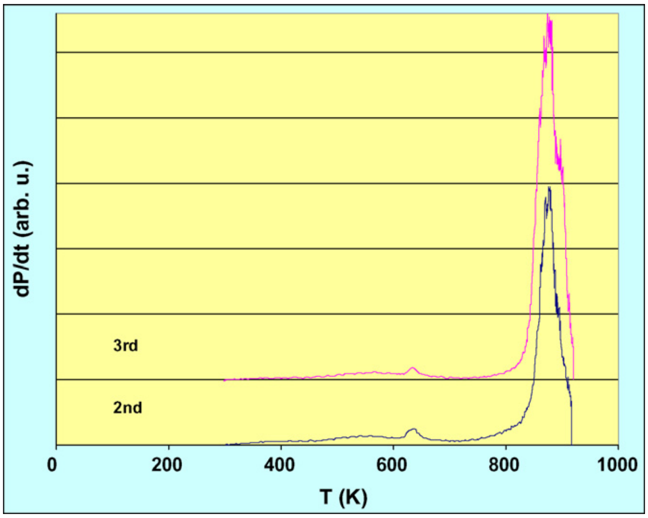

Fig. 2. d*P*/d*t* vs. *T* for the first and second deuterium heel exchange desorption (second and third thermal desorptions) from Ti-5 (third desorption offset for clarity).

As was done with Ti-7, Ti-5 was reloaded using pure deuterium in order to attempt to determine the tritium content of the remaining heel, and to determine if the changes observed in Ti-7 with repeated desorption–anneal–absorption cycles were also to be observed in Ti-5. As noted above, the prior study suggested some procedural improvements to the experimental protocol which were implemented in the current study. In the prior work, a second thermal desorption was run on Ti-7 which produced minimal gas evolution, but did reduce the He content to nearly zero. Then the desorption after the first D_2 loading produced a desorption profile with a weak and diffuse peak centered

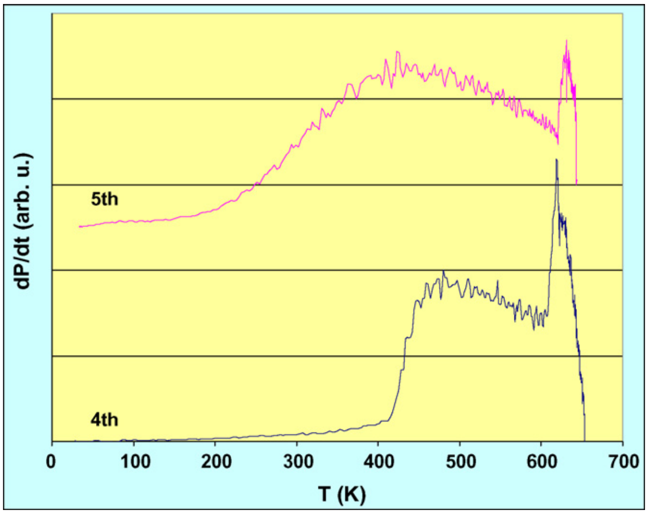

Fig. 3. d*P*/d*t* vs. *T* for the third and fourth deuterium heel exchange desorptions (fourth and fifth thermal desorptions) from Ti-5 (fifth desorption offset for clarity).

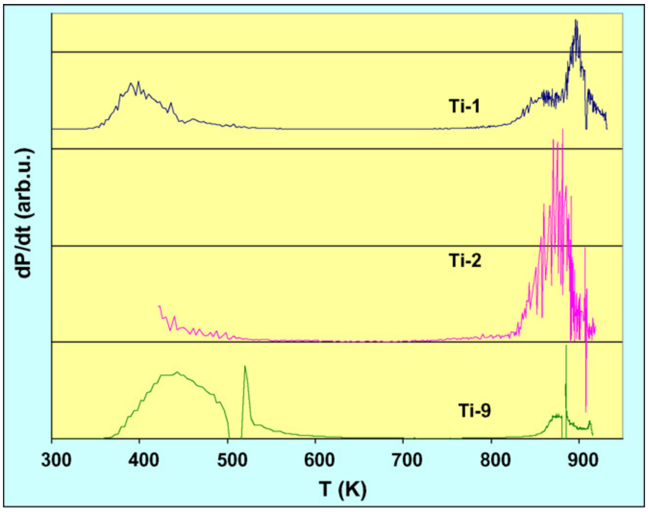

Fig. 4. First thermal desorptions (d*P*/d*t* vs. *T*) from samples Ti-1, -2, and -9. Displaced for clarity. Ti-9 grab sampling induced transients near 520 and 880 K removed for clarity.

at $\sim$670 K (see Fig. 2 of Ref. [4]). This was an apparent upwards shift in temperature for the broad desorption centered at $\sim$520 K shown in Fig. 1. The main desorption peak was centered at $\sim$860 K. The protocols in use at that time included annealing at high temperature potentially for several hours to reduce the heel content to a minimum (Ti-7 was annealed for $\sim$6 h). Therefore in studying Ti-5, these extended anneals were avoided, which was thought to allow probing of more intermediate stages in the development of the new state. In Ref. [4], the discovery of the new state was possibly attributed to a higher loading pressure used in the last two absorptions. However, in the studies on Ti-5, the same high loading pressure was used in all loads, so this is not the relevant variable. It should also be noted that the correct loaded Q/Ti value for the sixth desorption from Ti-7 does not allows one to conclude the new state had been annealed away. Furthermore, comparison of Figs. 3 and 4 of Ref. [4] suggest that the anomalously high loading computed for Fig. 3 is incorrect, but we are unable to ascertain why that might be at this time. A likely candidate is load gas leakage through a valve into another part of the manifold, but we cannot confirm that actually happened.

It is of interest to compare the loading and helium release behavior of the two samples (under the assumption that the He analyses are valid for Ti-5). Three successive absorption–desorption cycles on Ti-7 produced the following results (change in Q/M (negative), %He in offgas): 0.68, 9.4%; 1.02, 2.0%; 1.84, 0.2%. Four successive absorption–desorption cycles on Ti-7 produced the following results: 0.35, 23.9%; 0.44, 10.4%; 0.89, 3.3%; 1.03, 1.2%. As can be observed, as He content in the offgas decreases, the amount of hydrogen isotope absorption and desorption increases. This is qualitatively seen in the desorption spectra.

Figs. 2 and 3 present the Ti-5 thermal desorption profiles from the first through fourth deuterium loadings. Clearly observed is the development of the new low temperature peak at lower desorption temperatures in the fourth and fifth desorptions (Fig. 3). The fifth desorption in particular is highly reminiscent of the Ti-7 spectrum shown in Fig. 3 of [4]. However, Fig. 3 also shows a spectrum where the new peak is apparently in development, with the leading edge of the desorption being relatively sharp (fourth) as opposed to the subsequent smoother profile (fifth). In addition, Fig. 2 shows some weak peaks near 470–670 K that seemingly disappear as the number of cycles increases. Most of the other Ti samples also showed these structures as well.

With Ti-7, most of the He was removed rapidly, and by the time the first deuterium load was attempted, the He content was $\sim$0.06 He/M. However, the He/M content of Ti-5 at the first D_2 loading was probably higher since a high temperature anneal was not used and a second desorption without reloading was not implemented. This lower extent of He removal from the bulk is most likely the reason why more intermediate states are observed in the development of the new low temperature state with Ti-5.

Each sample processed in these studies had a slightly different processing history. Select thermal desorptions for the remaining samples are shown in Figs. 4 and 5. Initial thermal desorption for samples Ti-1, -2, and -9 are shown in Fig. 4, while that for Ti-6 is shown in Fig. 5 (compare to Figs. 1 and 2). The initial thermal desorption for samples Ti-2 and -6 begin at higher than room temperature due to problems with data acquisition.

Fig. 5 also shows the thermal desorption arising from the first deuterium loading (heel exchange) experiment on sample Ti-6 (equivalent spectra are shown as Fig. 3 for Ti-5, and in Fig. 2 of Ref. [4] for Ti-7). Similar results were obtained for samples Ti-1, -2, -4, and -9 and are not shown here. No further heel exchanges were conducted on samples Ti-1, -2, and -9. Only one additional heel exchange (third) was conducted on samples Ti-4 (not shown) and Ti-6 (Fig. 5). Ti-5 had two more heel exchanges conducted on it (Fig. 3). Ti-7 had a total of six heel exchange experiments conducted on it, but those spectra not shown here did not illustrate any significant differences.

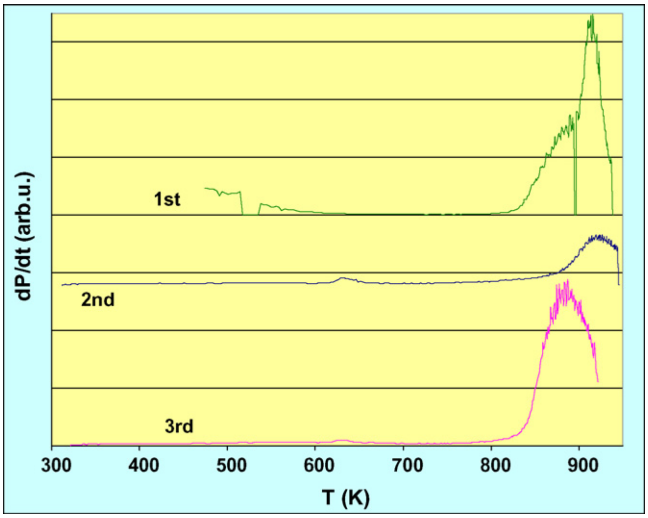

Fig. 5. First, second and third thermal desorptions (d*P*/d*t* vs. *T*) from sample Ti-6, displaced for clarity. Grab sampling induced transients in first TD near 520 and 880 K removed for clarity.

The recorded spectra arising from the initial thermal desorptions of all samples except Ti-7 clearly show evidence of an initial desorption peak beginning just above room temperature and extending up to about 520–570 K. Grab sampling during these runs indicted these peaks are composed of 100% ^{3}He. This behavior is consistent with the most fully aged Ti thin film results [5] that also showed a low temperature He desorption.

The low temperature He desorptions are broad, spanning a 150–250 °C range, and are relatively featureless. The high temperature desorption however, presumably composed of both hydrogen and helium desorptions, often displayed complex structure. The behavior of Ti-7 is notably different. Ti-7 had been initially loaded to a T/M ratio of 0.9 (also loaded with D/M = 0.9), and was aged for approximately 6 years (producing a theoretical He/M = 0.28) before experimentation. The remaining samples were all loaded at roughly the same time to different T/M levels, but aged for ~10 years instead. Several of the samples had started releasing significant fractions of the He that had been born inside them, as can be seen by comparing theoretical (‘no-release’) and actual initial He/M ratios shown in Table 1, but Ti-7 had not reached that state prior to the experimental work.

With the exception of Ti-5 and -7, none of the remaining samples were processed enough to obtain the unusual low temperature hydrogen desorption described above. Consistent behavior was seen across all the samples except for Ti-7 for the first deuterium heel exchange experiment. The spectra all show a large desorption occurring at higher temperature (820–870 K) with a very small lower temperature desorption in the 570–650 K range. This small desorption is most likely another He desorption, as in the next set of heel exchanges (conducted on Ti-4, -5, and -6), this peak was almost totally absent. While the absolute values of He content of the grab samples was untrustworthy, the trend to lower offgas He content as samples progressed through the processing was clear. The unusual low temperature hydrogen desorptions seemed only to occur once all He had been evolved.

Several samples (Ti-1, -2, -6, and -9) had been placed in test cells that were equipped with a pressure transducer, and periodic readings were taken from these transducers. Fig. 6 presents that data (converted to He/M ratio units in the cell gas space) as a function of relative time. Table 2 lists the starting and ending He/M ratio for each sample for the time period shown.

Initial points on Fig. 6 arise from leftover residual gas from grab sampling/pressure reduction activities on the samples. Ignoring these first points the rate of pressure increase is roughly linear, but not at the 100% of generated rate. Instead, the three releasing samples are all releasing ~70% of the generated He, leading to a slowly increasing He/M ratio in the solid. However, the last few points on the curves for Ti-9 and -1 can be seen to positively deviate from the linear rate of rise observed in the earlier data points for those samples. The “last point” numbers in Table 2 should be compared to the pre-TDS actual He/M numbers in Table 1. Approximate agreement within experimental error (~0.05 He/M) is obtained, but the fact that these values are obtained at ~500 elapsed days indicates that almost all remaining generated He produced between the end state shown in Fig. 6 and the point where the first thermal desorption was conducted (~1100 days) had been released, i.e. the rate was nearly 100% versus the 70% observed over the span shown in Fig. 6. The slight curvature observed in the Ti-1 and -9 curves suggests a smooth transition from the 70 to 100% release rate.

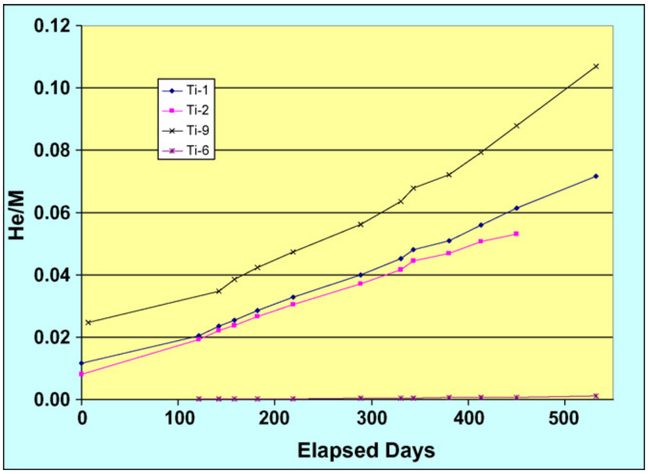

Fig. 6. Helium content of sample gas phase (expressed as He/M units) for samples Ti-1, -2, -6, and -9 for a selected time period computed from on-board pressure sensor readings (the last point on the Ti-2 curve is approaching maximum sensor value, and may be artificially low). Ti-6 had just begun releasing He.

It is of interest to note the difference in the initial He desorption behavior between sample Ti-7, which had been aged for ~6 years and had not started releasing significant He, and the remaining samples that had been aged for ~10 years. All the more aged samples showed the lower temperature desorption, even when those samples had not begun significant He release, such as Ti-6. Apparently, the actual time held in storage was having an effect above and beyond the impact of the varying He/Ti

Table 2
He/Ti ratios for evolved He

Sample	Days aged to $t = 0$	He/M ($t = 0$)	He/M (last point)	He/M (in gas)	Days aged to TD
Ti-1	2343	0.40	0.43	0.072	3459
Ti-2	2308	0.33	0.36	0.053	3437
Ti-6	2182	0.22	0.26	0.001	3287
Ti-9	2170	0.37	0.41	0.088	3293

The annotations “$t = 0$”, “last point”, and “in gas” refer to Fig. 6. “Days aged to TD” represents the total aging time the samples experienced up to the day the first TD was conducted. Ti-6 was just beginning to release He at an noticeable rate.

ratios obtained due to differences in initial T content (Table 1). As can be seen from Table 1, the He/Ti ratio in Ti-7 was quite similar to those of samples Ti-4, -5, and -6. Structural studies would be an interesting avenue of research to possibly clarify the cause(s).

4. Conclusions

Seven Ti samples have been subjected to tritium aging for ∼10 years and then studied by thermal desorption and isotope exchange techniques. The most highly aged samples, as indicted by He/M ratios, were all evolving He at significant rates, perhaps at nearly the 'free-release' condition in the latest stages. Hydrogen heels were significant, and the hydrogen desorption profiles changed as the bulk He content changed. Unfortunately, because of poor mixing in the apparatus, accurate mass spectral data was unavailable, making it impossible to exactly quantify the heels, but it was obvious that they represented nearly one-third to one-half of the total normal hydrogen capacity.

Repeated thermal desorption–reloading cycles have now been shown to develop a new lower temperature desorption state in two samples of tritium-aged bulk titanium. The prior report of a higher than normal capacity in such an altered sample has not been confirmed however. Differences in He release behavior and processing conditions may or may not account for these differences. Unfortunately inadequate mass spectral results make it difficult to know exactly what the He/Ti ratios were. It is also possible that some unknown error has affected the anomalously high Q/Ti computation in the prior report [4]. What is certain however is the appearance of the lower temperature hydrogen isotopes desorption state which initiates at ∼470 K. What is equally interesting is the movement of the He desorption to near room temperature that does not seem to be correlated to He/M ratio, but seems to be more a simple aging time effect. These discoveries are fundamentally interesting and bear further experimental study to clarify the numerous questions raised regarding their origin and development.

Acknowledgements

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