

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy.

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied: 1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or 2. representation that such use or results of such use would not infringe privately owned rights; or 3. endorsement or recommendation of any specifically identified commercial product, process, or service. Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

Deuterium, Tritium, and Helium Desorption from Aged Titanium Tritides. Part I.**Kirk L. Shanahan, Jeffrey S. Holder****Savannah River National Laboratory, Aiken, SC****Abstract**

Six new samples of tritium-aged bulk titanium have been examined by thermal desorption and isotope exchange chemistry. The discovery of a lower temperature hydrogen desorption state in these materials, previously reported, has been confirmed in one of the new samples. The helium release of the samples 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. Part I will discuss the new results on the new lower temperature hydrogen desorption state found in one more extensively studied sample. Part II will discuss the hydrogen/helium release behavior of the remaining samples.

Introduction

The Savannah River National Laboratory has been involved in studying the effects of tritium decay in metal tritides for many years [1,2,3], and has reported on a single sample of T-aged Ti previously [4] and compared it to prior Russian 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. In this paper, an examination of thermally induced hydrogen desorption from bulk Ti material by Thermal Desorption Spectroscopy (TDS) is presented for another sample that confirms the prior observation [4] of a new, lower temperature desorption state. (In a companion paper, initial tritium and tritium deuterium mixes and helium desorption from multiple samples is presented [6].)

Thermal desorption of hydrogen (or deuterium) from Ti in many forms has been studied extensively. Malinowski [7] followed the desorption of D₂ from thin films of TiD₂ prepared in vacuum. In that study, the Auger Electron Spectroscopy signal indicated a single desorption, peaking at approximately 570K. In 2005, Sandim, et al [8] used Thermogravimetric Analysis to study TiH₂ powder decomposition, and the integral form data would seem to indicate a more complex desorption with perhaps a major peak occurring at ~900K, but with both leading and trailing desorption as well. Aronsson, et al [9] studied a bulk form of Ti used in dental implants treated by glow discharge. Their results showed that such treatment induced significant broadening of the H₂ desorption, which was maximized at ~800K.

Additional studies of the desorption process using primarily TDS have added to the complexity of the situation. Schwarz, et al, [10] showed a coverage dependence in peak maximum for thin films, but only one broad peak in all cases. Wilson and Pontau [11]

noted one broad desorption from deuterium ion implanted Ti thin films centered at ~900K. Chatbi, et al [12] noted a sharp deuterium desorption at ~670K with a broader and weaker desorption centered near 570K. Takasaki, et al [13] electrochemically charged Ti and noted one reasonably sharp peak at ~800K, whose maximum shifted up as the heating rate increased as expected. Nowicka [14] and Nowicka and Dus [15] noted a major peak at ~550K from TiD₂ and TiH₂ (respectively) prepared from thin Ti films, with a lower temperature shoulder. But Reuss, et al, [16] noted a sharp D₂ desorption from TiD₂ films at 670K, with a higher temperature shoulder. Ogawa, et al [17], using chemical charging found a primary H₂ desorption at ~800K with a smaller desorption at ~600K in some cases. Malinowski [18] found peak shifts with changes in film thickness (peak maxima at ~570-600K) while Checchetto, et al [19] did not (shifts with heating rate were observed), nor did film deposition temperature matter. Fernandez, et al [20] showed clear shifts with heating rate (higher temperature peak at ~820K at lowest heating rate, maximum not measured at higher rates due to equipment limitations, lower temperature peak went from ~740K at 5 Ks⁻¹ to ~770K at 20 Ks⁻¹). (Note that air exposure in Malinowski's study [18] converted a doublet desorption to a singlet.)

Thermal desorption has also been used study Ti-based alloys and/or composites. Wilson, et al [11] studied TiB₂ and TiC coatings. Ogawa, et al, [17] also studied a Ti-Al alloy, as did Takasaki, et al [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 ~420K, 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. In the prior report[4], the computed capacity of the loaded sample exceeded the normal Ti Q/Ti = 2.0 (Q= H + D + T). In this work we were unable to confirm that excess capacity, but did observe the lower temperature desorption in agreement with the prior report.

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 mole % mixture of D₂/T₂. The sample loading Q/M ratios and the percent T and thermal desorption (TD) initial condition are shown in Table 1. The Q (=D+T)/M prior to TD is computed by accounting for radioactive decay of the tritium portion in the hydride. 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.

Table 1. Loading and Initial Thermal Desorption Conditions of Ti Samples

Sample ID	Load Q/M	%T	No release He/M	Q/M prior to TD	He/M
Ti-1	1.9	100	.78	1.12	.41
Ti-2	1.6	100	.64	0.91	.34
Ti-4	1.8	50	.36	1.45	.35
Ti-5	1.2	50	.26	1.04	.26
Ti-6	1.5	50	.30	1.22	.29
Ti-7	1.8	50	.28	1.56	.28
Ti-9	1.9	100	.81	1.50	.43

This paper will focus on comparing the data obtained from sample Ti-5 with that of the prior report [4], which focused on data from Ti-7. The results from the other samples will be reported elsewhere [6]. Ti-5 contained 1.57 grams of Ti and Ti-7 contained 1.60 grams, however 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.

The experimental section from the prior report is applicable, with the exception of material batches and test cell configurations. Ti samples number 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.

Results and Discussion

In the prior report [4], the first thermal desorption of sample Ti-7 was presented in Figure 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 Figure 1 as the change in pressure per unit time (dP/dt) versus the sample temperature. Figure 2 then presents the 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 (80-300 C) that was shown to be pure ^3He (99.96%, within experimental error of 100%) by mass spectroscopic analysis of a grab sample taken at the ~240 C point. In the Ti-7 spectrum a very small and broad peak is observed from ~150 – 350 C. In Ti-7, grab sample analysis indicated the ^3He appeared at the highest temperatures, with the leading edge of the major desorption peak (~400-575 C) being produced by hydrogen isotope evolution.

Initial loading levels and the decayed load conditions at the start of the first thermal desorptions are reported in Table 1. 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 absorption. 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 conditions were not met, which can be understood by comparing to the Russian thin film data [5].

In favorable comparison to the Russian data [5], the more aged samples are showing He release at low temperature. In the Russian report, this peak was not completely shown, but was indicated by the immediate baseline increase for the film with the highest He content. The Russian 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 Q2 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 heel 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 (shown in Table 1).

As a side note, the Q/M ratios computed previously for Ti-7 [4] were found to need some corrections. The corrected values are: initial Q/Ti for 3rd desorption (Fig. 2 [4]) = 1.65, initial He/Ti for 3rd desorption = 0.06; heel Q/Ti after 3rd desorption = 0.72; initial Q/Ti for 4th desorption (Fig. 3 [4]) = 2.62 (still anomalously high); heel Q/Ti after 4th desorption = 0.79; heel Q/Ti after 5th desorption = 0.83; initial Q/Ti for 6th desorption (Fig. 4 [4]) = 1.02; heel Q/Ti after 6th desorption = 0.61. In this report, the anomalously high absorption obtained in the 5th desorption cannot be confirmed. However, the development of the unusually low temperature desorption TDS peak was confirmed.

The high temperature desorption peaks also show some significant differences. In Ti-7, the first peak, beginning at ~400 C (Fig. 1), was shown by grab sample analysis to be primarily Q2. As shown in Figure 2, in Ti-5 the desorption begins at ~550 C 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 (although part of the reason may be the difference in spectral resolution). As will be discussed elsewhere [6], 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.

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 D2 loading produced a desorption profile with a weak and diffuse peak centered at ~400C (see Figure 2 of [4]). This was an apparent upwards shift in temperature for the broad desorption centered at ~250C shown in Figure 1. The main desorption peak was centered at ~590C. 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 thusly for ~6 hours.) Therefore in studying Ti-5, these extended anneals were avoided, which allowed probing of more intermediate stages in the development of the new state. In [4] the discovery of the new state was 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 clearly not the relevant variables. It should also be noted that the correct loaded Q/Ti value for the 6th desorption from Ti-7 does not allow one to conclude the new state had been annealed away. Furthermore, comparison of Figures 3 and 4 of [4] suggest that the anomalously high loading computed for Figure 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%. (Recall that a second thermal desorption was conducted on Ti-7 without reloading, which had reduced He content.) 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 increases. This is qualitatively seen in the desorption spectra.

Figures 3 – 6 present the thermal desorption profiles from the first through fourth deuterium loadings on sample Ti-5. Clearly observed is the development and evolution of the new low temperature peak at lower desorption temperatures in the third and fourth desorptions (Figs. 5 and 6). Figure 6 in particular is highly reminiscent of the Ti-7 spectrum shown in Figure 3 of [4]. However, Figure 5 shows a spectrum where the new peak is apparently in development, with the leading edge of the desorption being relatively sharp as opposed to the smoother profile shown in Figure 6 (and Figure 3 of [4]). In addition, Figures 3 and 4 show some weak peaks in the 200-400 C that seemingly disappear as the number of cycles increases. (Most of the other Ti samples also showed these structures as well, see [6].) The loading data presented above suggest that one or more additional cycles should have been attempted on Ti-5 if time had allowed.

With Ti-7, most of the He was removed rapidly, and by the time the first deuterium load was attempted, the He content was ~ 0.06 He/M. However, the He/M content of Ti-5 at the first D₂ 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.

Conclusions

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 mixing under plug flow conditions and high variance mass spectral analysis 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 desorption state which initiates at ~ 200 C. This discovery is fundamentally interesting and bears further experimental study to clarify the numerous questions raised regarding its origin and development, especially in relation to the current bulk He content. However, a redesigned experimental apparatus, probably equipped with an on-line mass spectrometer, should be employed in further studies.

Acknowledgement

This work was supported by Westinghouse Savannah River Company under U.S. Department of Energy Contract Number DE-AC09-96SR185000. Dr. J. R. Wermer, currently of Los Alamos National Laboratory is thanked for his preliminary work on preparing and loading the samples.

References

1. Kirk L. Shanahan, Jeffrey S. Holder, David R. Bell, Joe R. Wermer, *J. Alloys and Compounds* 356-357C, (2003), 382, and references therein
2. Kirk L. Shanahan and Jeffrey S. Holder, *J. Alloys and Compounds*, 348 (2003) 72-75, and references therein
3. Kirk L. Shanahan, J. S. Holder, J. R. Wermer, *J. Alloys and Compounds*, 293-295 (1999) 62-66, and references therein
4. Kirk L. Shanahan, Jeffrey S. Holder, *J. Alloys and Compounds*, 404-406 (2005) 365
5. A. M. Rhodin, V. S. Surenyants, *Russ. J. Phys. Chem.* 45(5) (1971) 612
6. Kirk L. Shanahan, Jeffrey S. Holder, "Deuterium, Tritium, and Helium Desorption from Aged Titanium Tritides. Part II., in preparation
7. M. E. Malinowski, *J. Vac. Sci. Tech.* 16 (1979), 962
8. Sandim, H. R. Z., Morante, B. V., Suzuki, P. A., *Mat. Res.* 8 (2005) 293
9. Aronsson, B.-O., Hjorvarsson, B., Frauchiger, L., Taborelli, M., Vallotton, P.-H., Descouts, P., *J. Biomed. Mat. Res.*, 54 (2001), 20
10. Schwarz, J. A., Polizzotti, R. S., Burton, J. J., *Surf. Sci.* 67 (1977) 10
11. Wilson, K. L., Pontau, A. E., *J. Nuc. Mat.* 93&94 (1980) 569
12. Chatbi, H., Vergnat, M., Marchal, G., *Appl. Phys. Lett.* 64 (1994) 1210
13. Takasaki, A., Furuya, Y., Ojima, K., Taneda, Y., *J. Al. Comp.* 224 (1995) 269
14. E. Nowicka, *Vacuum* 47, (1996), 193
15. Nowicka, E., Dus, R., *Lang.* 12 (1996) 1520
16. Reuss, R. H., Chalamala, B. R., *J. Vac. Sci. Tech. B*, 20 (2002) 1132
17. Ogawa, T., Yokoyama, K., Asaoka, K., Sakai, J., *J. Al. Comp.* 396 (2005) 269
18. M. E. Malinowski, *J. Less Com. Met.* 89 (1983) 27
19. Checchetto, R., Gratton, L. M., Miotello, A., Tomasi, A., Scardi, P., *Phys. Rev. B* 58, (1998), 4130

20. Fernandez, J. F., Cuevas, F., Sanchez, C., J. Al. Comp. 298 (2000) 244
21. Takasaki, A., Furuya, Y., J. Al. omp. 243 (1996) 167
22. Takasaki, A., Furuya, Y., J. Al. Comp. 292 (1999) 287
23. Borchers, C., Khomenko, T. I., Morozova, O. S., Galakhov, A. V., Kurmaev, E. Z., McNaughton, J., Yabloskikh, M. V., Moewes, A., J. Phys. Chem. B 110 (2006) 196
24. Gruner, R., Streb, B., Brauer, E., in Titanium Science and Tech., Proc. Of the 5th Int'l Conf. on Ti, vol. 4, ed. Lutjering, G., Zwicker, U., Bunk, W., (1984), 2571

Figure Captions

Figure 1. dP/dt vs T for the initial desorption from Ti-7

Figure 2. dP/dt vs T for the initial desorption from Ti-5

Figure 3. dP/dt vs T for the first deuterium heel exchange desorption from Ti-5

Figure 4. dP/dt vs T for the second deuterium heel exchange desorption from Ti-5

Figure 5. dP/dt vs T for the third deuterium heel exchange desorption from Ti-5

Figure 6. dP/dt vs T for the fourth deuterium heel exchange desorption from Ti-5

Figure 1.

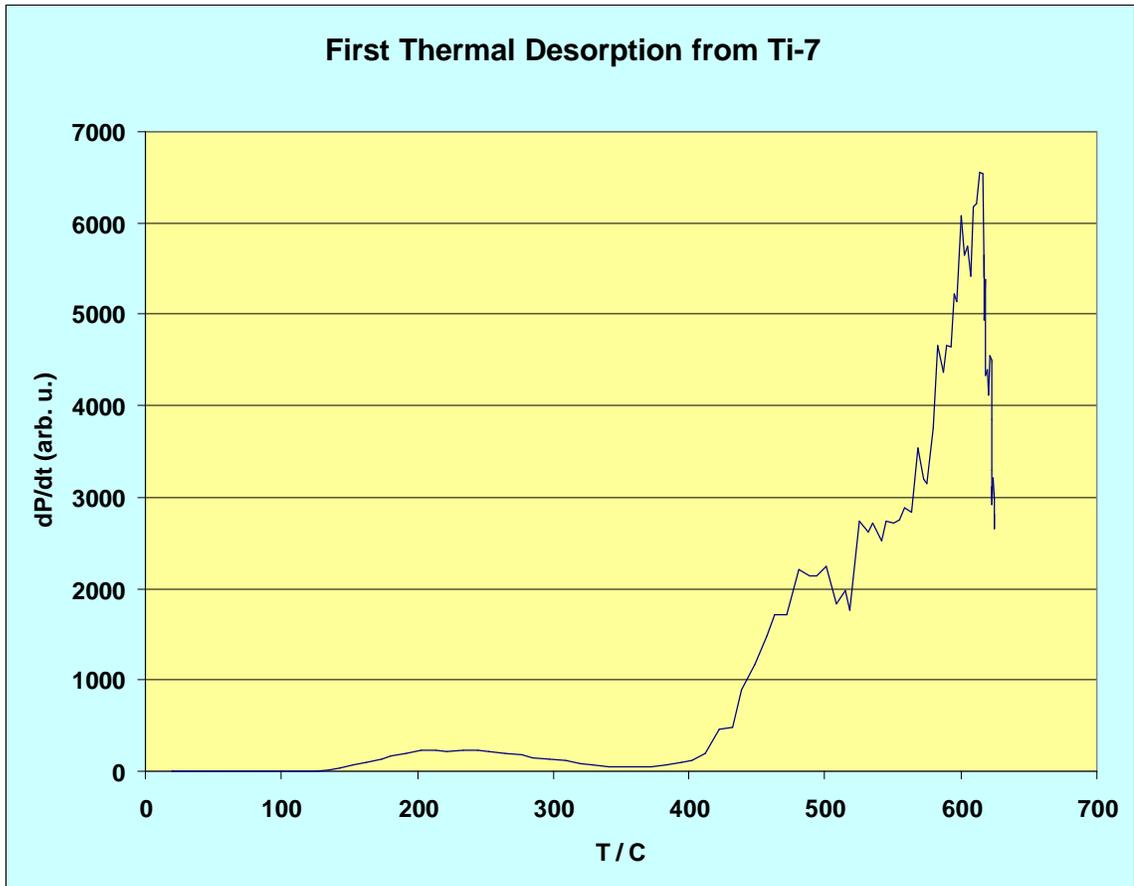


Figure 2.

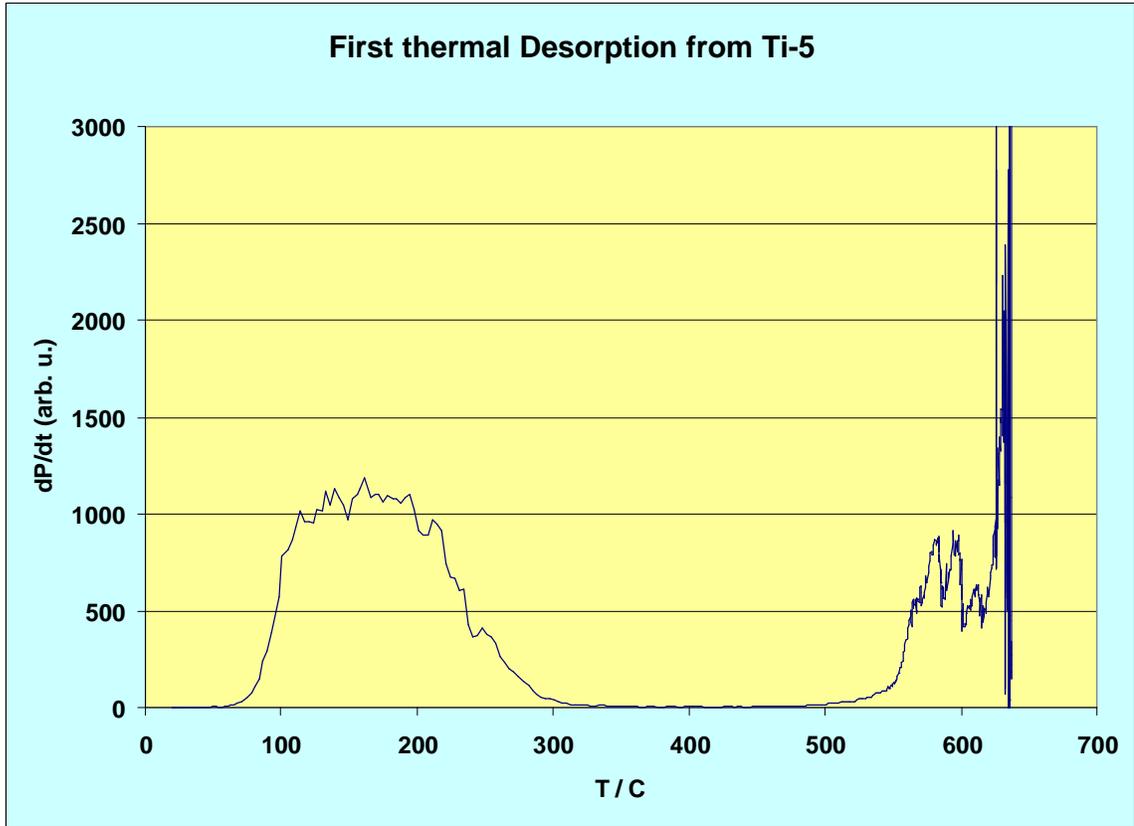


Figure 3.

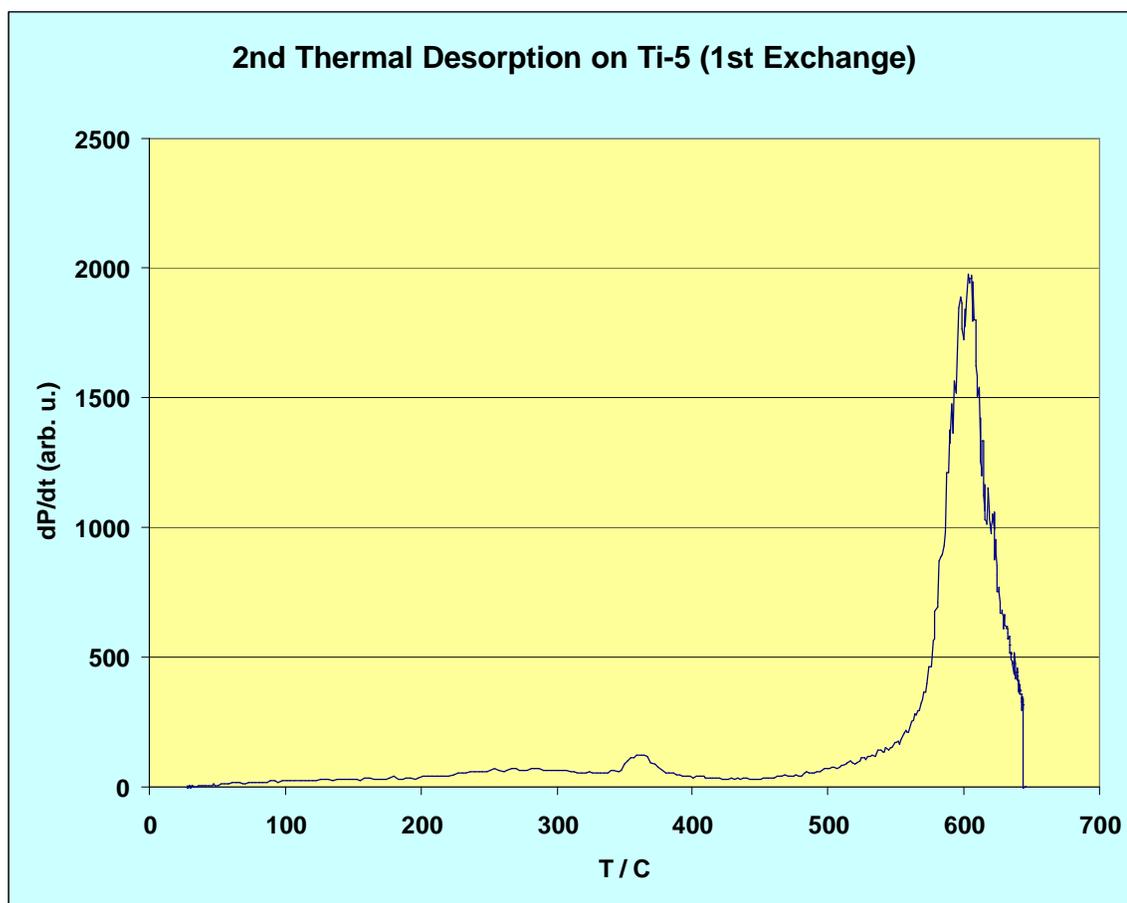


Figure 4.

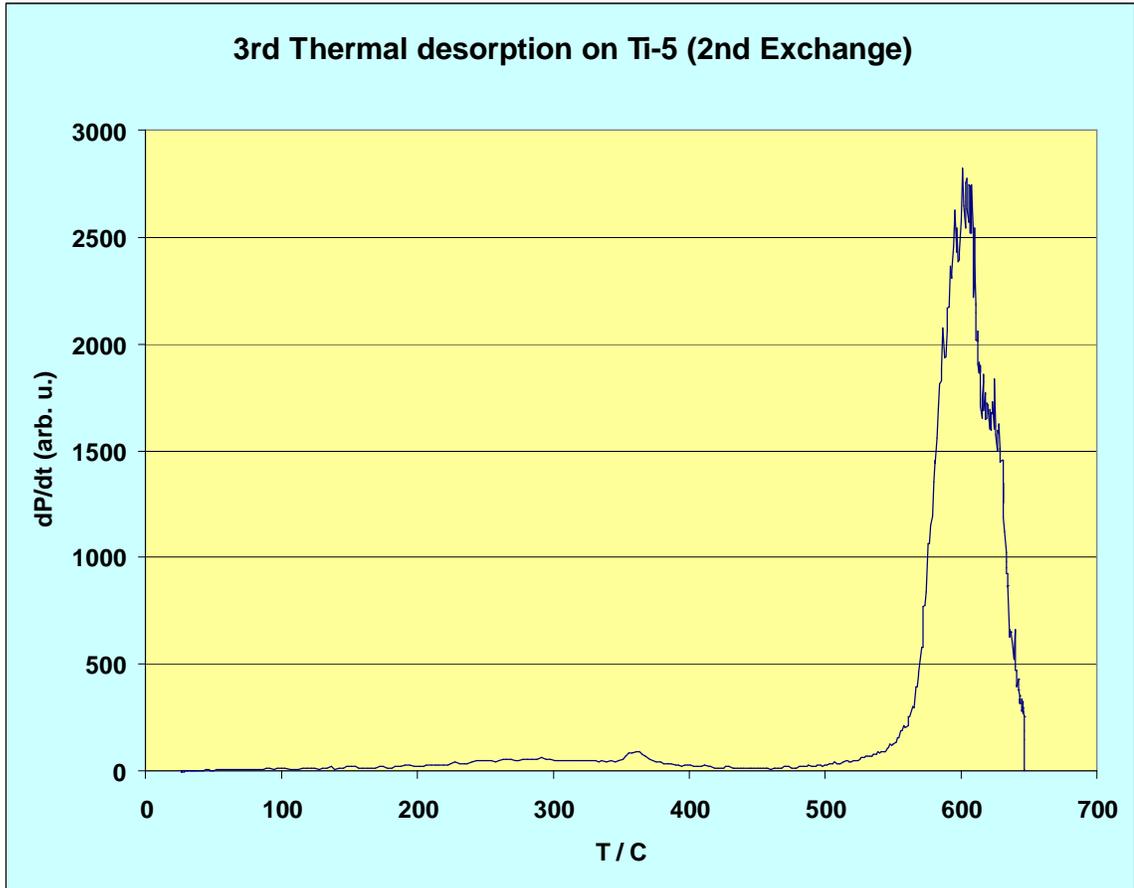


Figure 5.

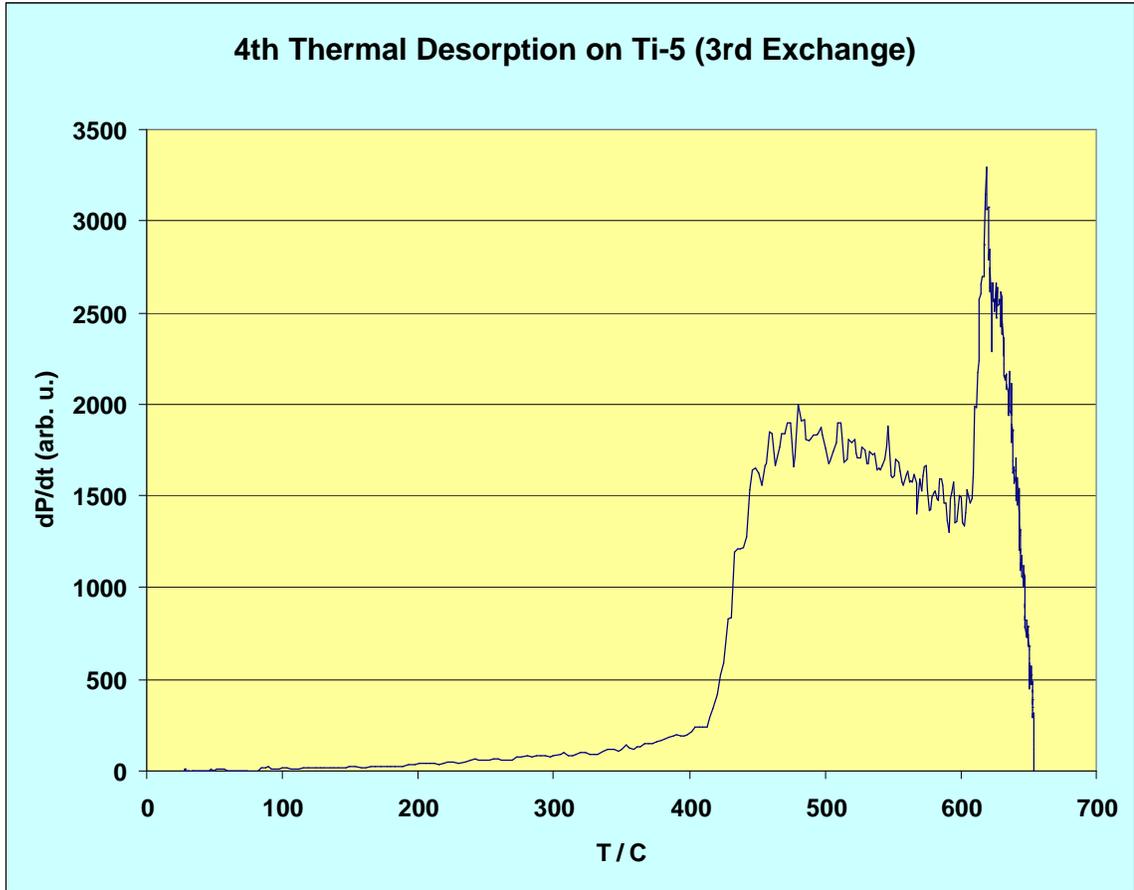


Figure 6.

