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

Deuterium, Tritium, and Helium Desorption from Aged Titanium Tritides. Part II.

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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 discussed 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 results on Ti thin films [5]. This paper extends that work to six new samples, one of which was examined extensively and the others less so. The primary techniques used in these studies are thermal desorption and isotopic heel exchange. For more discussion of these methods see Part I [6].

The primary impact of radioactive tritium decay, which produces one 3He atom per 3H (T) decay, is to load the bulk metal tritide with an increasing amount of 3He. This He is highly insoluble and immediately starts to aggregate into bubbles inside the tritide material. This process has been described in detail by Lasser [7]. The bubbles formed in this process retain the bulk of the 3He 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 3He and 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 ration of the material is greatly increased and significant release of 3He can occur, although some 3He 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'. 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, and subsequently reloaded with pure deuterium and desorbed in order to quantify tritium heel content and to study any additional He release in subsequent cycling.

Experimental

The basic experimental protocols were reported previously [4,5]. The samples were originally either loaded with pure tritium or with a 50/50 mole % mixture of D2/T2. The sample loading Q(=H+D+T)//M ratios and the percent T and thermal desorption (TD) initial condition are shown in Table 1 (see description in [5]).

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 thermal desorption and mass spectroscopic data obtained from all the listed samples. Sample weights varied somewhat. Listed in the order of Table 1, they are: 0.7523, 1.6027, 1.5830, 1.5279, 1.5911, 1.6007, and 1.0185 grams. 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.

Results and Discussion

Each sample processed in these studies had a slightly different processing history. All thermal desorptions recorded are shown in Figures 1 – 12, excepting those already presented in Part I [6] and ref [4]. The initial thermal desorption for Ti-4 was lost due to a valving error and is not shown. The initial thermal desorption for samples Ti-2 and Ti-6 begin at higher than room temperature due to problems with data acquisition. Figures 1-4 show the initial thermal desorption for sample Ti-1, Ti-2, Ti-6, and Ti-9. (Those spectra for sample Ti-5 and Ti-7 are shown in Figures 1 and 2 of Part I.) Figures 5-9 show the thermal desorptions arising from the first deuterium loading (heel exchange) experiment on samples Ti-1, Ti-2, Ti-4, Ti-6, and Ti-9. (Equivalent spectra are shown as Figure 3 in part I for Ti-5, and in Figure 2 of [4] for Ti-7.) No further heel exchanges were conducted on sample Ti-1, Ti-2, and Ti-9. Only one additional heel exchange (3^{rd})

was conducted on samples Ti-4 and -6, shown in Figures 10 and 11, respectively. Ti-5 had two more heel exchanges conducted on it, and the spectra are shown in Part I. Ti-7 had a total of six heel exchange experiments conducted on it. Shown here in Figure 12 is the 2nd heel exchange spectrum. This TD spectrum begins at 350C because the sample was heated to foster absorbtion, and the TD initiated from the heated condition. Spectra for the 3^{rd} and 4^{th} exchange were shown in ref. [4]. The spectra arising from the 5^{th} and 6^{th} runs on Ti-7 were not significantly different from that shown for the 4^{th} heel exchange experiment, and are not shown here.

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 250-300C. Grab sampling during these runs indicted these peaks are composed of 100% 3He. This behavior is consistent with the most fully aged Ti thin film results [5] that also showed a low temperature He desorbtion. That study also showed higher temperature He desorbtions, unaffected by coincident hydrogen desorbtions, as the hydrogen species were gettered away by a separate Ti bed. In these studies gettering was not done, and the higher temperature desorbtions show coincident He and hydrogen production. Unfortunately, insufficient mixing in the lines of the Sieverts' apparatus caused the mass spectral analysis of the latter grab samples taken during the initial thermal desorbtions to disagree with the actual pressure and dP/dt spectra. Therefore we are unable to accurately compute final He/M and Q/M ratios.

The low temperature He desorbtion (labeled thusly because grab samples taken at or past the trailing edge of the peak all showed 100% 3He content) are broad, spanning a 150-250 degree range, and relatively featureless. The high temperature desorbtion however, presumably composed of both hydrogen and helium desorbtions, often display complex structure. The behavior of Ti-7 is notably different. Ti-7 had been initially loaded to an 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 processing was done on it. 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. Presumably the transition from nearly full retention to significant partial release has caused the downwards shift of the He desorbtion noted in these studies. Structural studies of the samples would seem to be an interesting avenue of research to clarify the cause of the differences.

With the exception of Ti-5 and Ti-7 (discussed in Part I), none of the remaining samples were processed enough to obtain the unusual low temperature hydrogen desorbtion described in refs [4] and [6]. 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 desorbtion occurring at higher temperature (550-600C) with a very small lower temperature desorption in the 300-375C range. This small desorption is most likely another He desorbtion, 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 hydrogen desorptions described in refs [4] and [6] 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. Figure 13 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.

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 TDS
Ti-1	2343	.40	.43	.072	3459
Ti-2	2308	.33	.36	.053	3437
Ti-6	2182	.22	.26	.001	3287
Ti-9	2170	.37	.41	.088	3293

The annotations “t=0”, “last point”, and “in gas” refer to Figure 13. “Days aged to TDS” represents the total aging time the samples experienced up to the day the first TDS was conducted. The sample Ti-6 was essentially not releasing He at any appreciable rate. Its curve is multiplied by 100 and replotted on Fig. 13 to illustrate that the evolution rate was non-linear.

Initial points on Figure 13 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 Ti-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 Figure 13 and the point where the first thermal desorbtion was conducted (~1100 days) had been released, i.e. the rate was nearly 100% vs. the 70% observed over the span shown in Figure 13. The slight curvature observed in the Ti-1 and Ti-9 curves suggests a smooth transition from the 70% to 100% release rate.

Conclusions

Eight 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 1/3 to ½ of the total normal hydrogen capacity of the materials. All samples have been passivated at this time and are awaiting removal from test cells for subsequent physical/chemical analyses.

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.

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Figure 1.

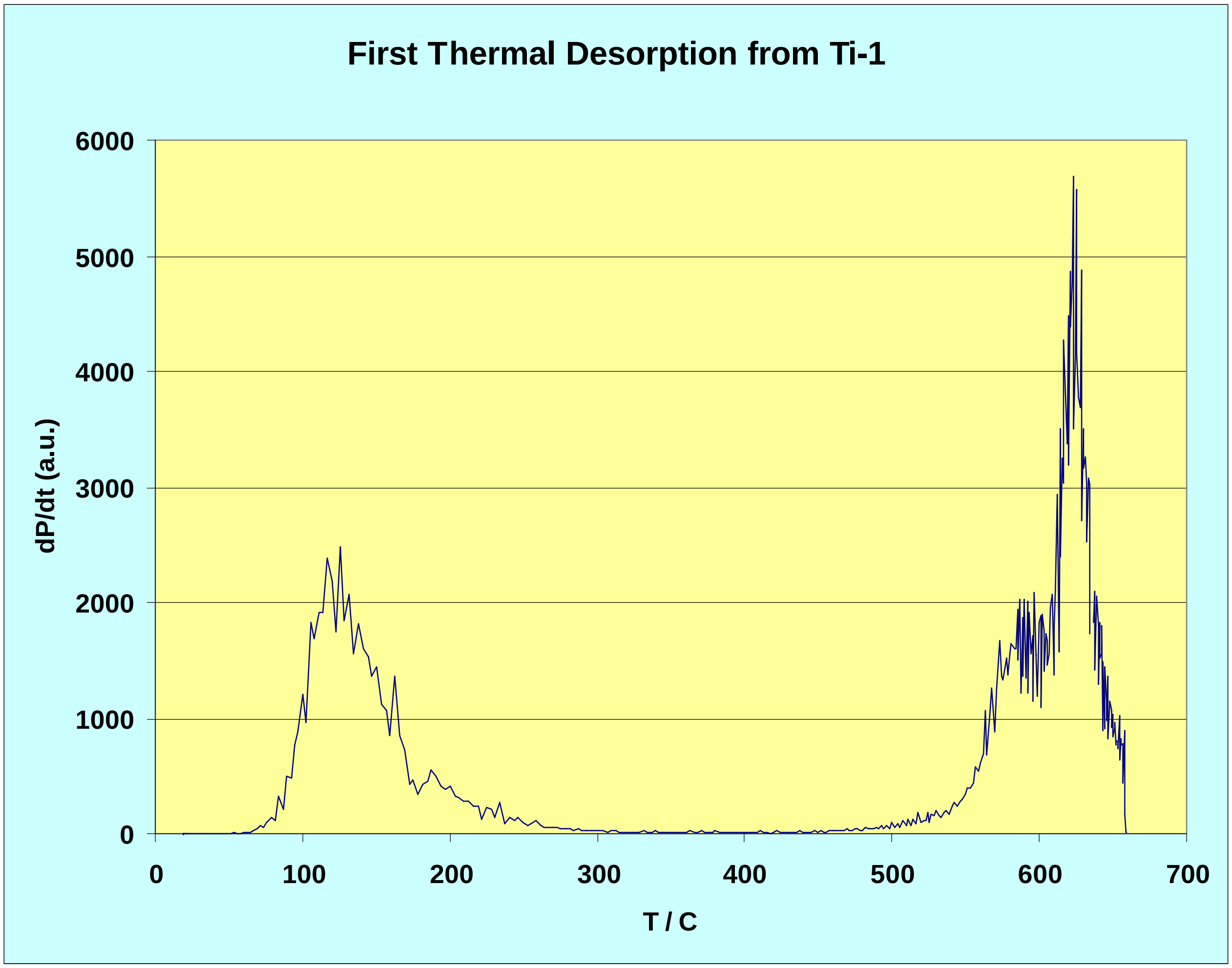

First Thermal Desorption from Ti-1
dP/dt (a.u.)
0
1000
2000
3000
4000
5000
6000
T / C
0
100
200
300
400
500
600
700

Figure 2.

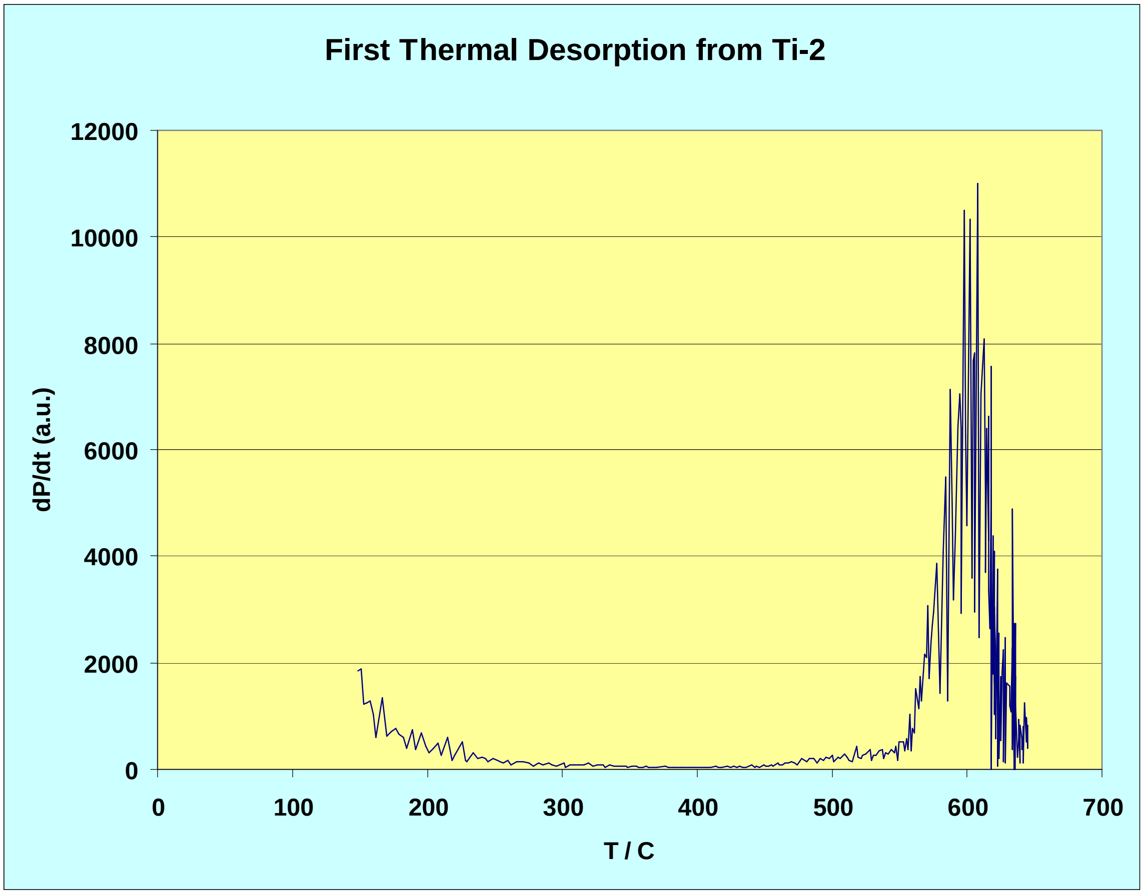

First Thermal Desorption from Ti-2
12000
10000
8000
6000
4000
2000
0
dP/dt (a.u.)
0
100
200
300
400
500
600
700
T / C

Figure 3.

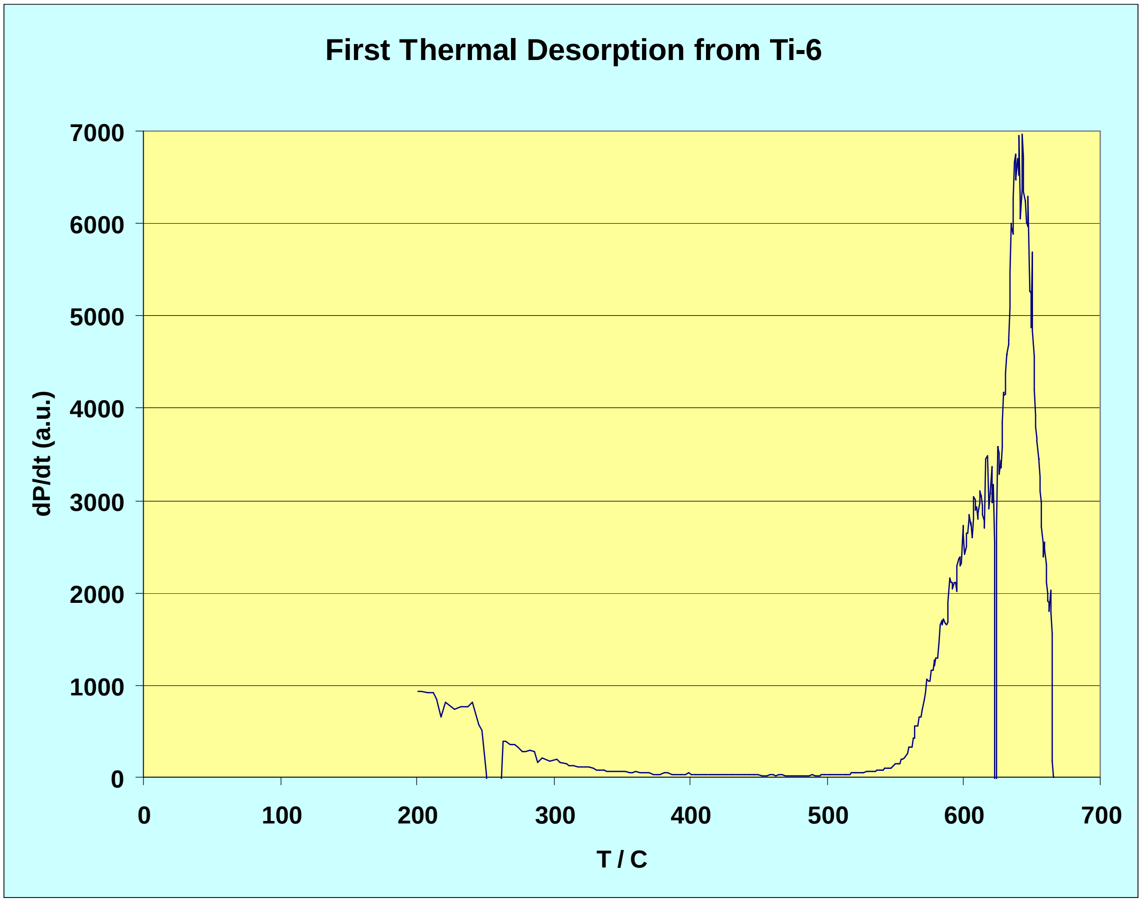

First Thermal Desorption from Ti-6
dP/dt (a.u.)
7000
6000
5000
4000
3000
2000
1000
0
0
100
200
300
400
500
600
700
T / C

Figure 4.

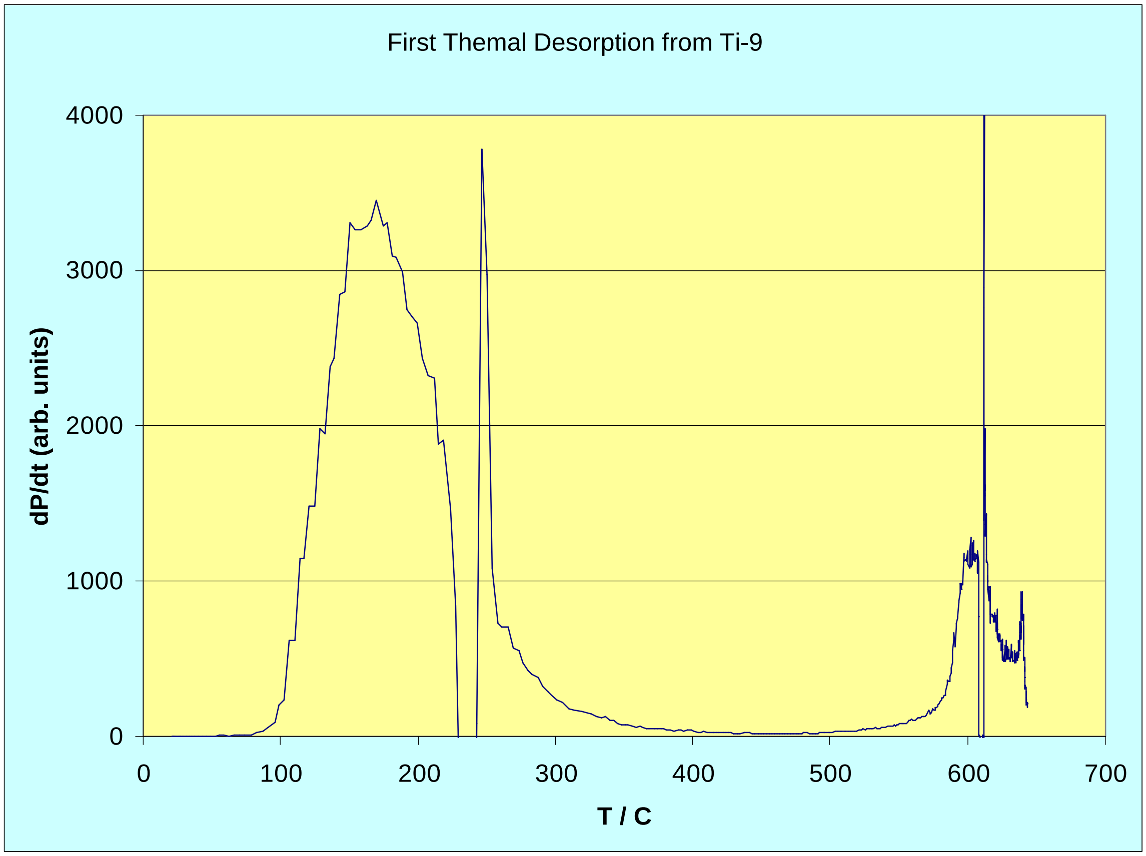

First Themal Desorption from Ti-9
4000
3000
2000
1000
0
dP/dt (arb. units)
0
100
200
300
400
500
600
700
T / C

Figure 5.

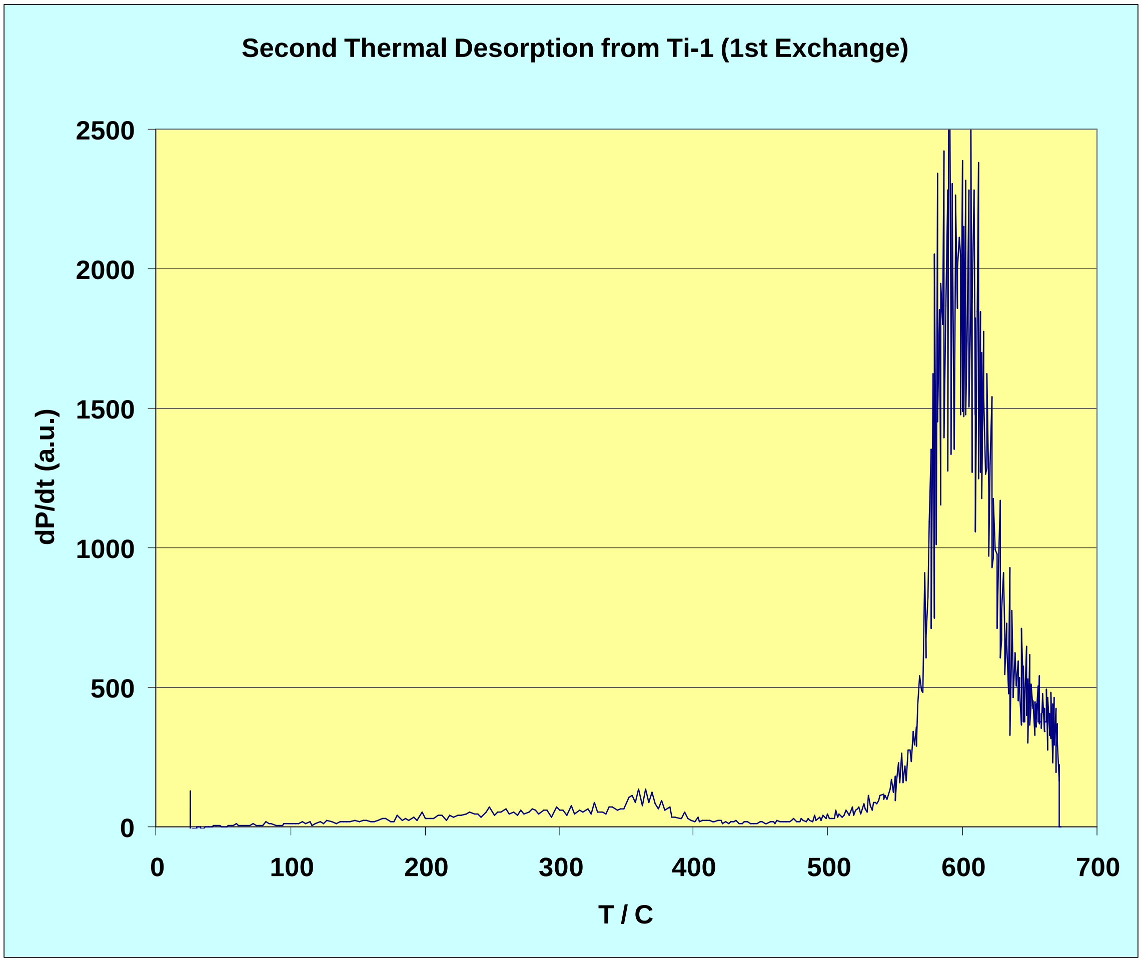

Second Thermal Desorption from Ti-1 (1st Exchange)
dP/dt (a.u.)
2500
2000
1500
1000
500
0
0
100
200
300
400
500
600
700
T / C

Figure 6.

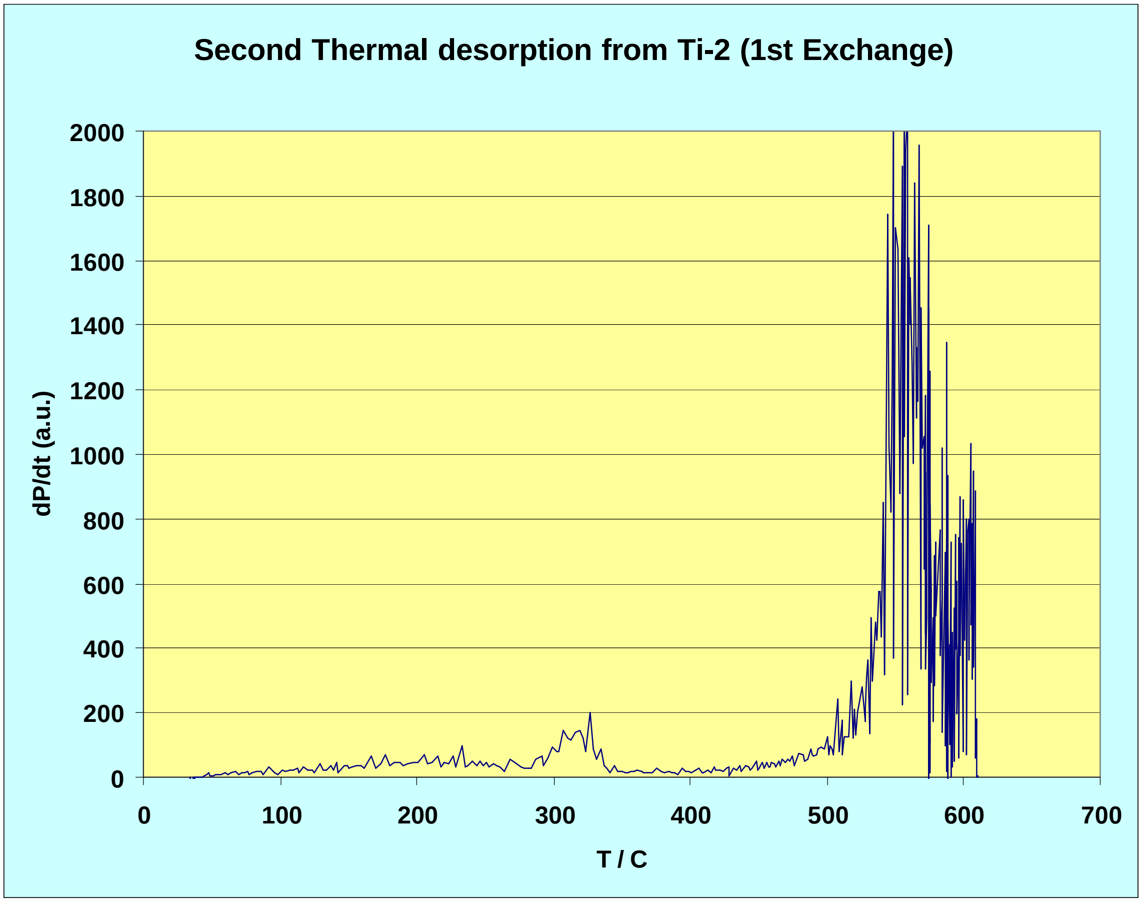

Second Thermal desorption from Ti-2 (1st Exchange)
dP/dt (a.u.)
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0
100
200
300
400
500
600
700
T / C

Figure 7.

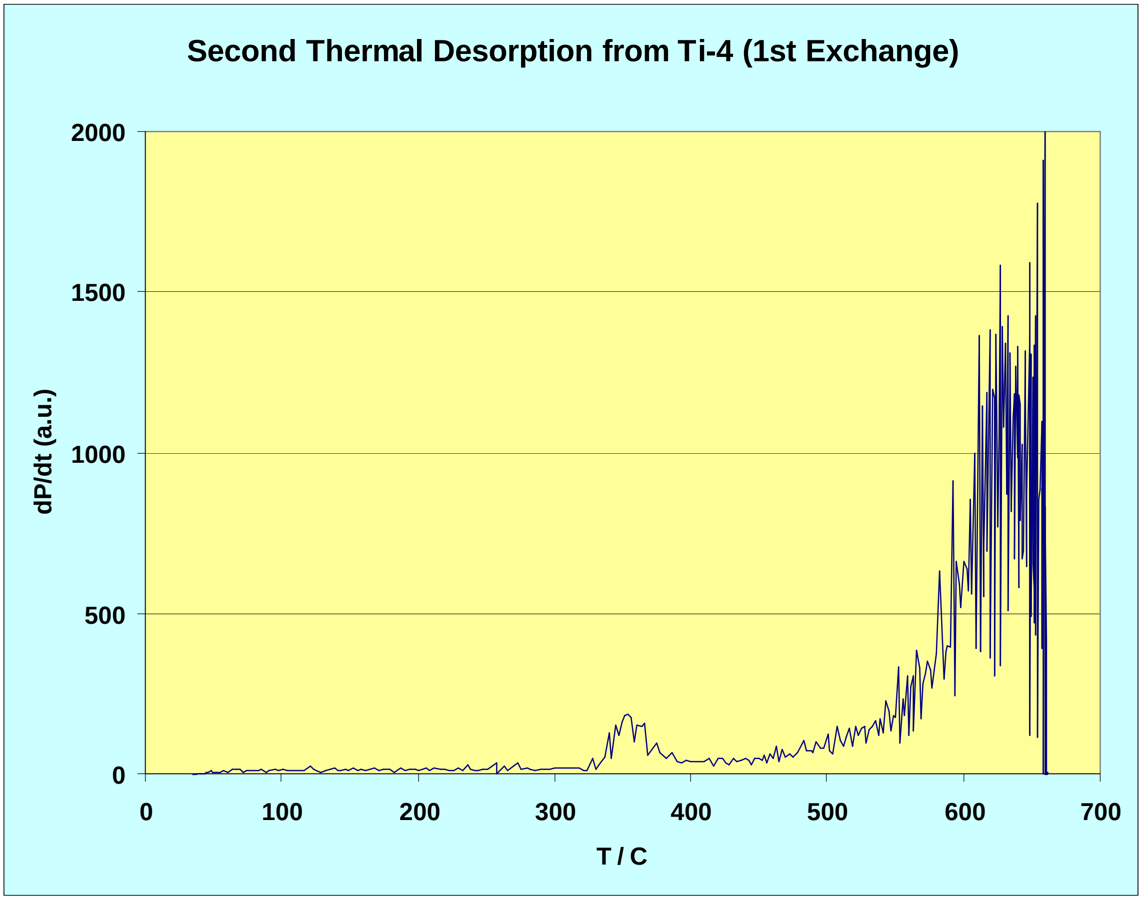

Second Thermal Desorption from Ti-4 (1st Exchange)
dP/dt (a.u.)
2000
1500
1000
500
0
0
100
200
300
400
500
600
700
T / C

Figure 8.

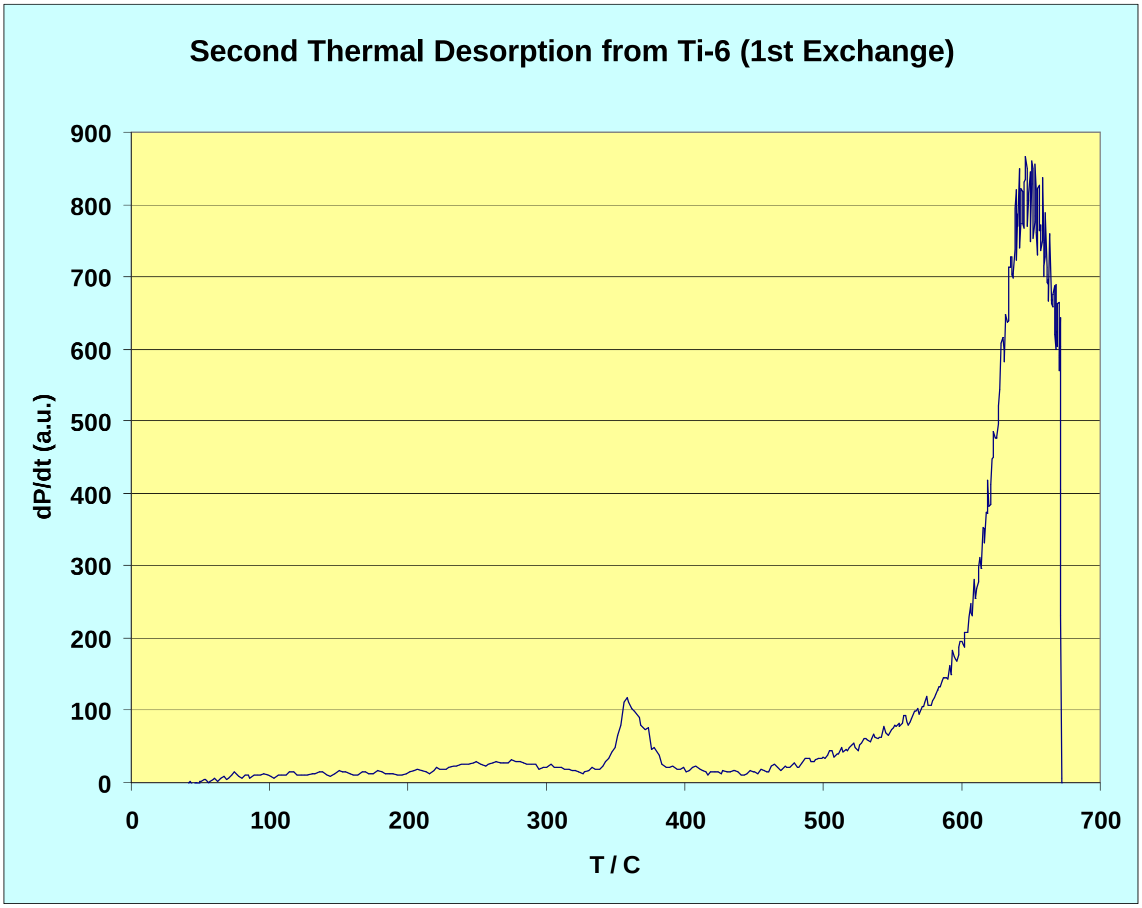

Second Thermal Desorption from Ti-6 (1st Exchange)
dP/dt (a.u.)
900
800
700
600
500
400
300
200
100
0
0
100
200
300
400
500
600
700
T / C

Figure 9.

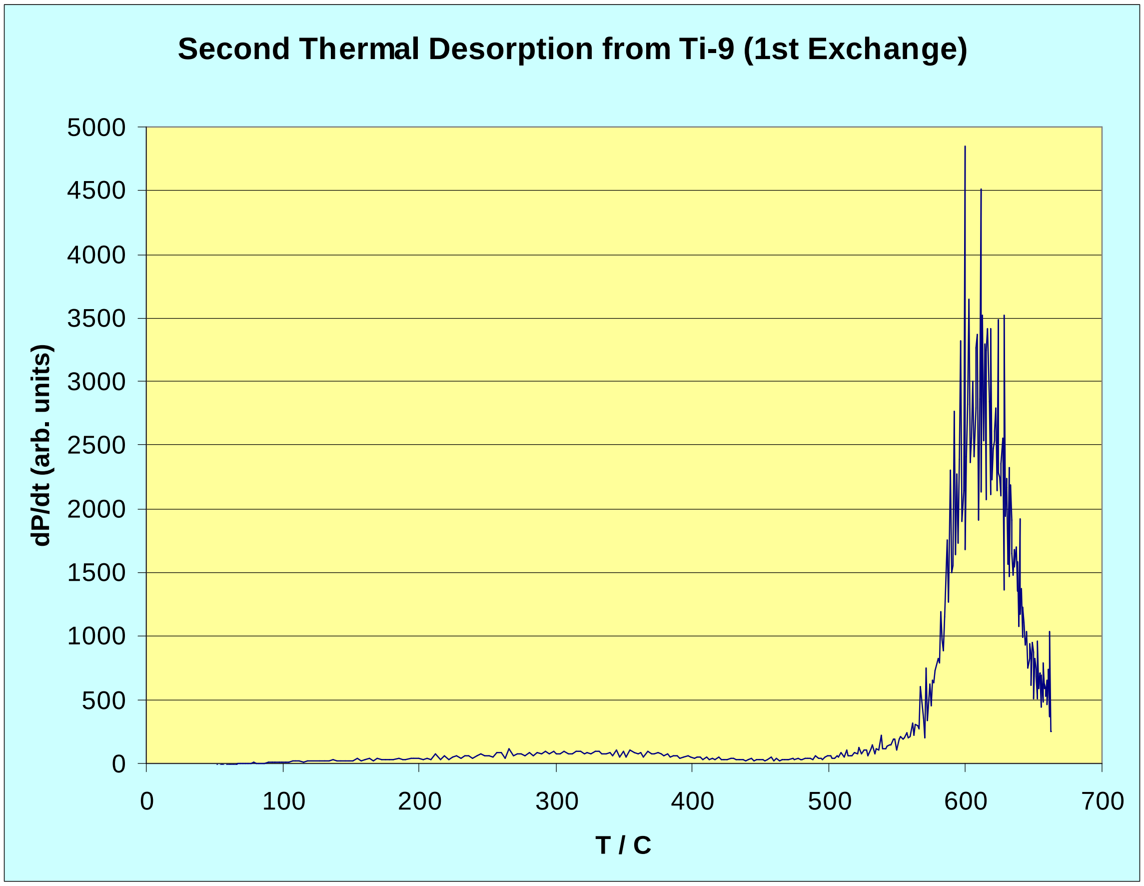

Second Thermal Desorption from Ti-9 (1st Exchange)
dP/dt (arb. units)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
100
200
300
400
500
600
700
T / C

Figure 10.

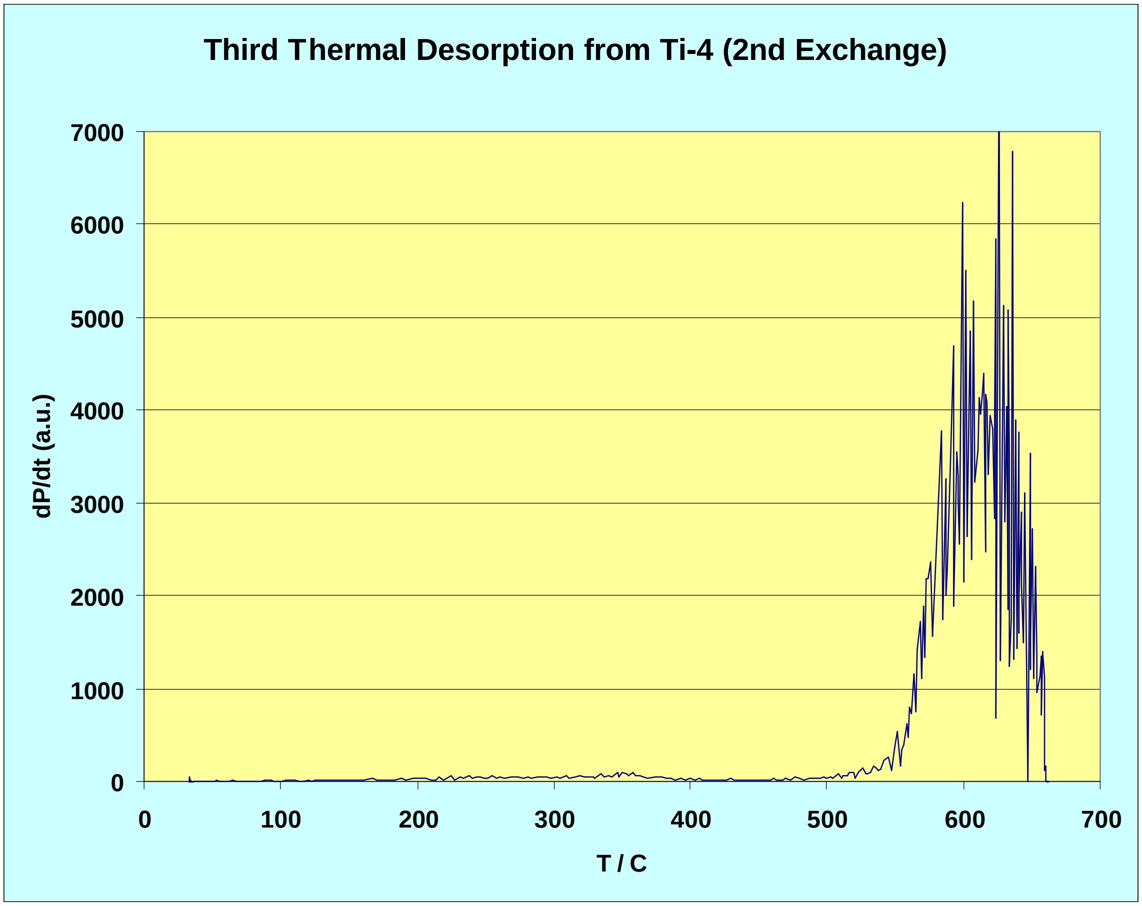

Third Thermal Desorption from Ti-4 (2nd Exchange)
dP/dt (a.u.)
7000
6000
5000
4000
3000
2000
1000
0
0
100
200
300
400
500
600
700
T / C

Figure 11.

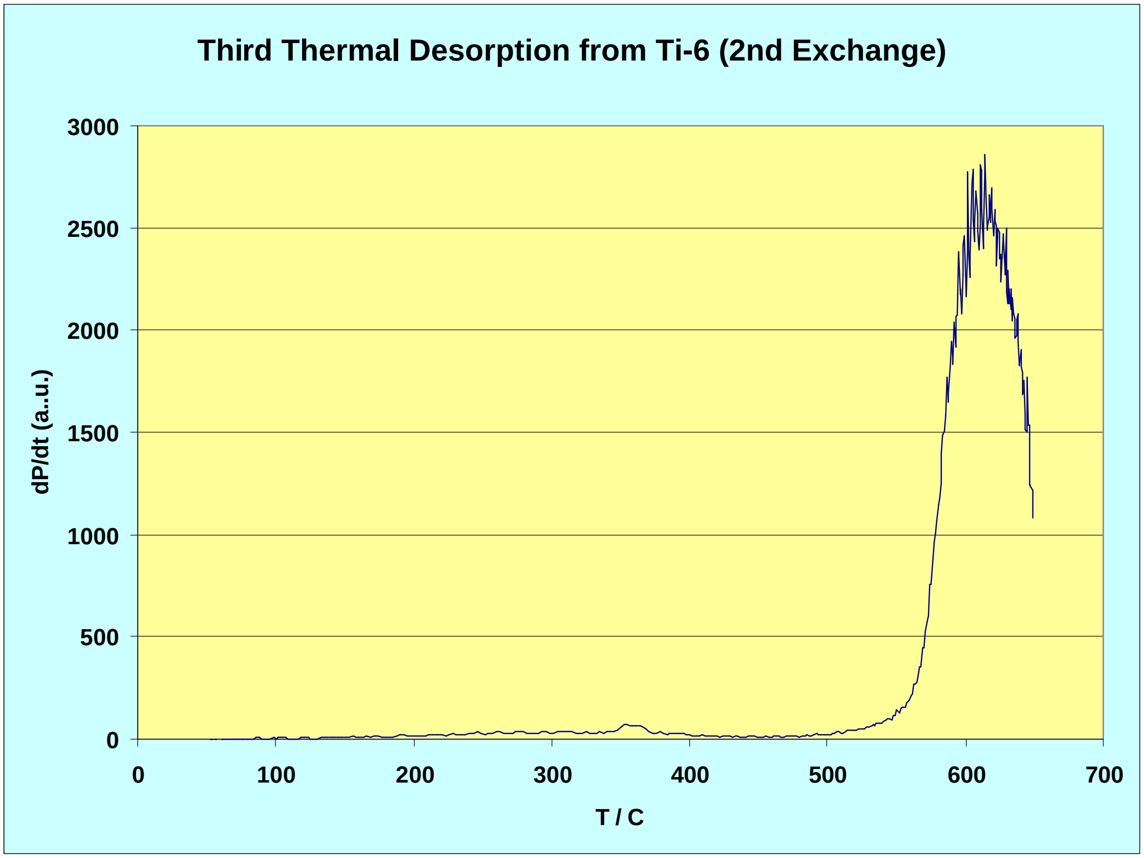

Third Thermal Desorption from Ti-6 (2nd Exchange)
dP/dt (a..u.)
3000
2500
2000
1500
1000
500
0
0
100
200
300
400
500
600
700
T / C

Figure 12.

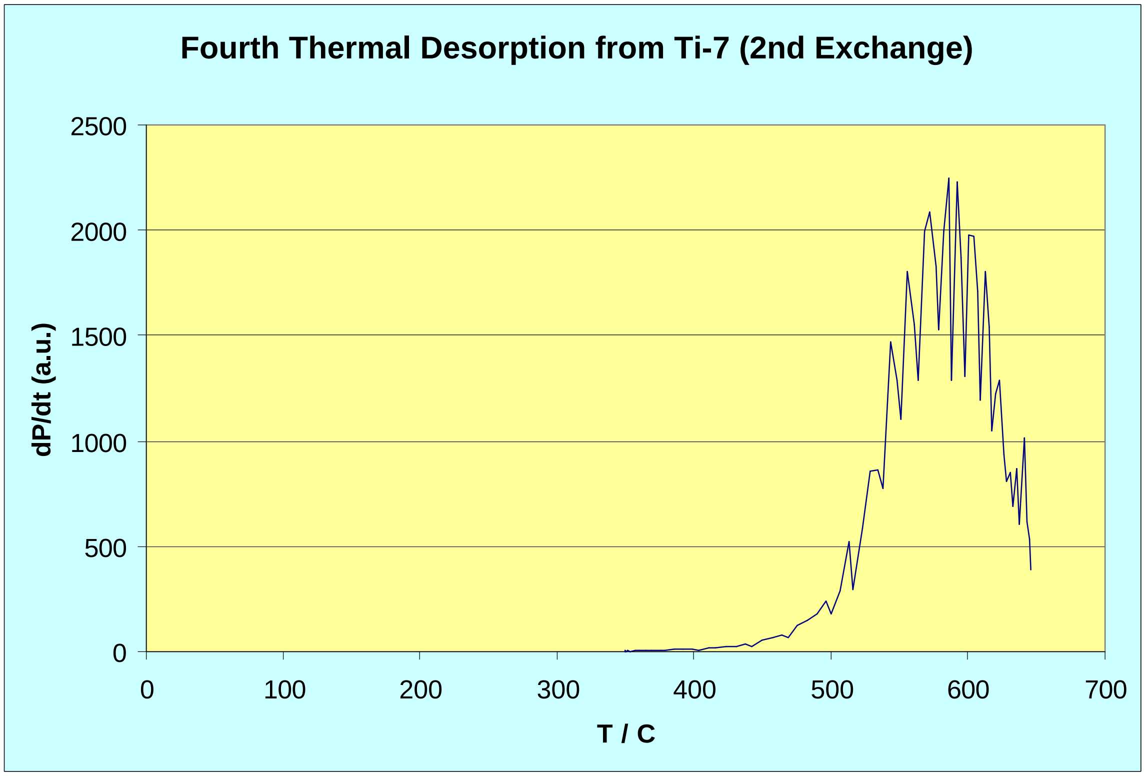
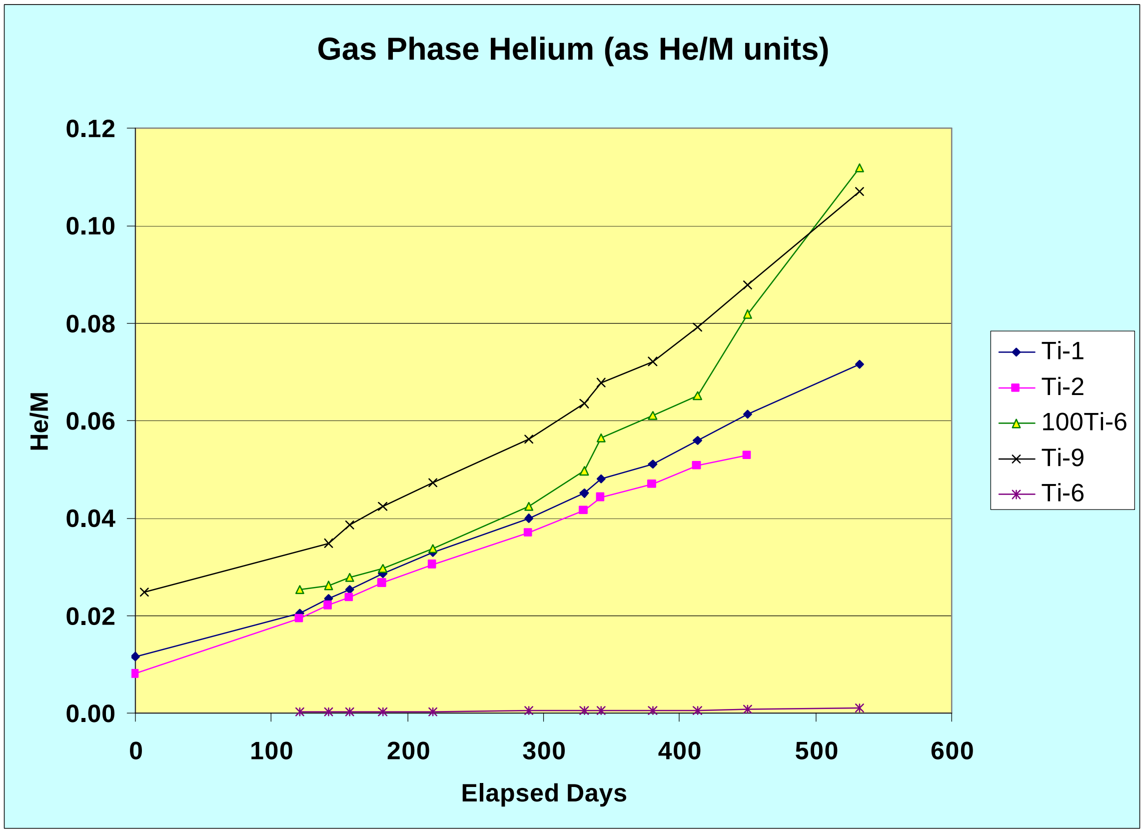

Fourth Thermal Desorption from Ti-7 (2nd Exchange)
dP/dt (a.u.)
2500
2000
1500
1000
500
0
0
100
200
300
400
500
600
700
T / C

Figure 13.


Gas Phase Helium (as He/M units)
He/M
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
100
200
300
400
500
600
Elapsed Days
Ti-1
Ti-2
100Ti-6
Ti-9
Ti-6