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Retention of Very High Levels of Helium and Hydrogen Generated in Various Structural Alloys by 800 MeV Protons and Spallation Neutrons

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Abstract: A series of irradiations were conducted in the Los Alamos Neutron Science Center as part of the test program supporting the Accelerator Production of Tritium Program sponsored by US-DOE. In this irradiation campaign, a variety of candidate structural alloys were placed in various particle spectra, ranging from 800 MeV protons, to mixed energy distributions of both protons and spallation neutrons, and to primarily high energy neutrons. At proton energies on the order of hundreds of MeV, exceptionally high levels of gas atoms are generated in all elemental constituents of typical structural alloys, with helium typically at ~150 appm per dpa and hydrogen at approximately an order of magnitude greater. Since neither of these gases are considered to have a good effect on structural properties of interest, their retention after both recoil and diffusional losses is of strong interest.

Helium is essentially immobile at all temperatures of interest, but hydrogen has some limited temperature-dependent mobility. To assess the degree of retention, each gas was measured in a number of highly irradiated specimens of different alloy compositions and dpa levels. The results show that helium production is relatively insensitive to composition and its retention is nearly total. The retained hydrogen levels, however, are somewhat sensitive to composition, reflecting different levels of diffusional loss, but are still at very large concentrations. There is some speculation that co-generation of helium and hydrogen assists in the trapping of hydrogen, and results in relatively high levels of hydrogen retention even at higher irradiation temperatures.

The potential implications of these findings on the anticipated performance of structural alloys, especially at higher exposure levels, is discussed. The use of the measurements to provide benchmarks for determination of gas production cross sections is also examined.

Keywords: helium measurements, hydrogen measurements, Accelerator Production of Tritium (APT), hydrogen release, helium release, tungsten targets

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Introduction

The Accelerator Production of Tritium (APT) project *[1]* was proposed as a solution to the national need for tritium. In the APT concept, high-energy protons would impinge on a tungsten target producing high-energy spallation neutrons. These neutrons would in turn be multiplied using a lead blanket, then thermalized using water. Tritium production would occur through capture of the thermalized neutrons by ^{3}He gas. A main technical issue that was addressed during the APT design was radiation damage to materials in the mixed high-energy proton and neutron environment.

A series of irradiations were conducted in the Los Alamos Neutron Science Center as part of the test program supporting the APT Program *[2]*. In this irradiation campaign, a variety of candidate structural alloys were placed in various particle spectra, ranging from 800 MeV protons, to mixed energy distributions of both protons and spallation neutrons, and to primarily high energy neutrons. The irradiation temperatures of all specimens were 200°C or less, with most below 100°C.

At proton energies on the order of hundreds of MeV, exceptionally high levels of gas atoms are generated in all elemental constituents of typical structural alloys, with helium typically at ~150 appm per dpa and hydrogen at approximately an order of magnitude greater. Whereas the generation of these gases in typical fission neutron spectra are very sensitive to elemental composition, especially the nickel content, there is very little difference between the rates of gas generation of nickel, iron or chromium at high proton energies. The hydrogen is born in two roughly equal distributions with very different birth energies on the order of ~1 MeV and ~100 MeV. For typical specimen dimensions, the range of the latter results in near-total recoil loss from the irradiated volume, such that <50% of the hydrogen is retained while ~100% of the helium is retained.

Since neither of these gases are considered to have a good effect on structural properties of interest, their retention after both recoil and diffusional losses is of strong interest. Helium is essentially immobile at all temperatures of interest, but hydrogen has some limited temperature-dependent mobility. To assess the degree of retention, each gas was measured in a number of highly irradiated specimens of different alloy compositions and dpa levels. There is some speculation that co-generation of helium and hydrogen assists in the trapping of hydrogen, and results in relatively high levels of hydrogen retention even at higher irradiation temperatures.

The potential implications of these findings on the anticipated performance of structural alloys, especially at higher exposure levels, is discussed. The use of the measurements to provide benchmarks for determination of gas production cross sections is also examined.

Analysis Samples

A variety of structural alloys from the APT materials characterization program were analyzed for helium and hydrogen content, including Alloy 718, 300 series stainless steel (304L and 316L), and an iron based 9Cr-1Mo. A diagram of the experimental setup in the LANCE facility is shown in Figure 1. A typical sample holder for the TEM disks is shown in Figure 2. Details on the samples are given in Table 1. Calculated helium and hydrogen contents in each of the samples are given in the last two columns of the table.

Specimens for gas analysis were cut from each original sample using small diagonal wire cutters in a controlled environment. Before each use, the cutters were cleaned by wiping several times with a dry "Kimwipe". Each of the helium analysis samples was etched to remove a minimum of ~0.013 mm (~0.5 mil) of surface material prior to specimen preparation. This etching step was done to remove material that may have been affected by α-recoil either out of the sample or into the sample from adjacent materials during irradiation. After etching, two smaller specimens were cut from each sample for duplicate helium analysis. The hydrogen analysis specimens were cut in a similar manner from the un-etched original samples.

Prior to analysis, each specimen was cleaned in acetone and air-dried. The mass of each specimen was then determined using a calibrated microbalance traceable to the National Institute of Standards and Technology (NIST). Mass uncertainty is estimated to be ±0.002 mg.

Helium Measurements

Helium Analysis System

Helium analyses were conducted by mass spectrometry at Pacific Northwest National Laboratory (PNNL). Details on the mass spectrometry system have been presented elsewhere *[3,4]*. Helium contents were determined by heating and/or vaporizing each sample in a resistance-heated crucible in one of the mass spectrometer system's high-temperature vacuum furnaces. Helium values were determined either by direct measurements of the mass spectrometer helium signal, or by an isotope-dilution technique where the released helium is compared with a known quantity of added ^{3}He "spike". The helium spikes were obtained by expanding and partitioning known quantities of gas through a succession of calibrated volumes*[3]*. The mass spectrometer was calibrated for mass sensitivity during each series of runs by analyzing known mixtures of ^{3}He and ^{4}He. Reproducibility of the analysis system for samples with known homogeneous helium content is ~0.5%. Absolute accuracy is generally better than 1%.

Helium Measurements

Helium analyses were conducted on a total of xx samples from the APT materials tests. Results of the analyses are shown in Table 2. Helium results are listed as total atoms of ^{3}He and ^{4}He, and total helium concentration in atomic parts per million (10^{-6} atom fraction). Some of the helium measurements on the Alloy 718 material included stepped-anneal analyses conducted to determine the extent of gas removal at temperatures up to ~1200°C. These analyses were followed by vaporization of the sample to completely remove the remaining helium. Because of alloying with the analysis crucibles, significant levels of helium were removed prior to 1200°C due to sample melting. The helium concentrations in the last two columns represent the sum of the stepped-anneal and vaporization analyses.

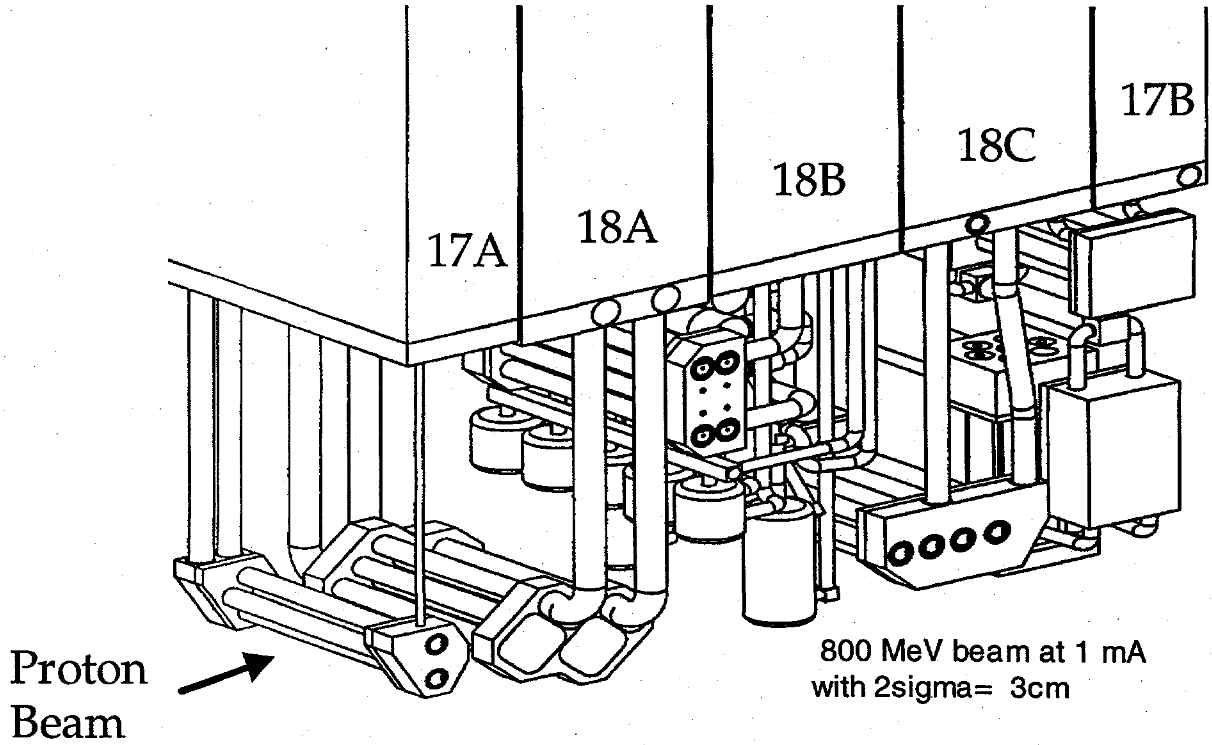

Figure 1 – *APT Mockup in the LANCE Irradiation Facility*

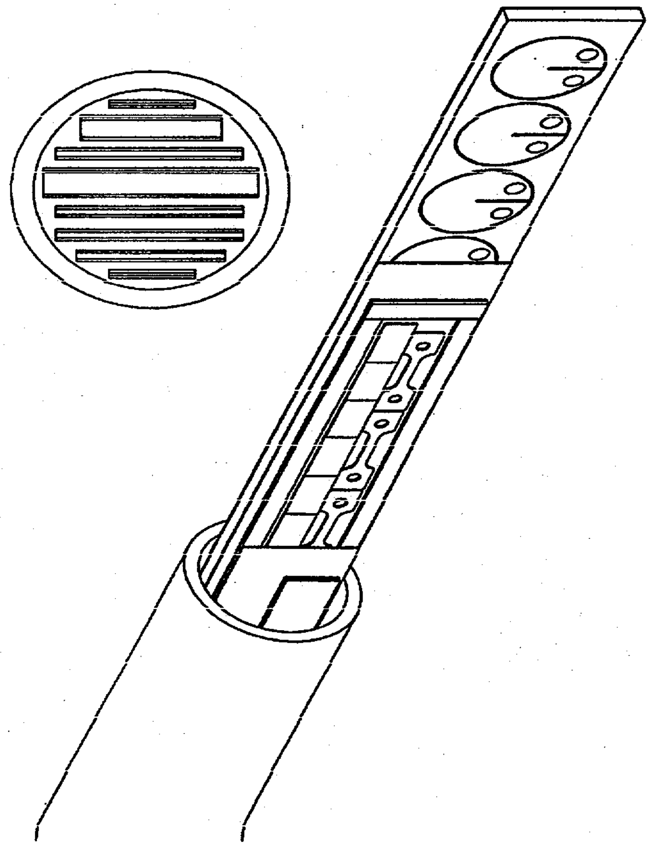

Figure 2 – *TEM Sample Holder in APT Mockup*

Table 1 – *APT Sample Summary*

Sample	Material	Tube + No.[a]	Location[b] (mm)	Dose (dpa)	Calculated Gas Content (appm)	
					Helium	Hydrogen
IN43	Alloy 718	1-1-10	0	13.77	1097	9544
IN53		21-2-31	8.0	4.15	272.3	2446
INE4		21-2-11	10.0	3.87	252.1	2270
INO1		1-1-7	-12	9.92	757.4	6603
IN66		21-2-1	-31.2	1.45	87.2	787.9
IN25		21-2-22	-31.2	1.45	87.2	787.9
4121	304L	22-2-12	8.0	3.82	243.3	2151
4077		4-2-11	0.0	9.77	695.1	5967
6138	316L	24-2-22	-31.2	1.34	74.4	657.8
6053		24-2-10	8.0	3.92	237.7	2101
6040		24-2-29	4.1	4.07	249.0	2207
6100		4-2-33	2.0	10.3	730.7	6246
MDC1	9Cr-1Mo	4-2-41	40.0	1.1	55.8	475.8
MD67		4-2-13	3.8	9.55	698.9	5905

[a]Tube-envelope-ID#.
[b]Location from beam centerline.

Table 2 – *Measured Helium in APT Alloys*

Sample	Material	Anal. Type[a]	Specimen Mass[b] (mg)	Measured Helium (10^{13} atoms) ^{3}He	^{4}He	Helium Concentration (appm)[c] ^{3}He	^{4}He	Total	Mean[d]
IN43	Alloy 718	V	1.407	32.4	265.0	223	1829	2052	2060
		V	0.900	21.2	170.4	229	1838	2067	±11
IN53		A	1.714	10.53	90.36				
		V		-	0.62	59.6	512	572	532
		V	1.074	5.731	48.62	51.8	440	492	±56
INE4		A	1.890	11.03	95.65				
		V		-	0.28	56.7	492	549	548
		A	1.356	8.11	68.38	58.0	490	548	±0
IN66		V	0.738	1.76	11.17	17.1	147	164	172
		V	1.027	2.59	17.19	18.8	162	181	±12
IN25		A	3.164	5.99	51.40				
		V		-	0.25	18.4	159	177	
4121	304L	V	1.320	90.9	704.8	63.8	494.4	558	
4077		V	1.095	263	1868	220	1565	1785	1813
		V	1.632	404	2869	227	1613	1840	±39
6138	316L	V	0.539	11.3	79.12	19.4	135.9	155	163
		V	0.710	16.4	114.1	21.4	148.8	170	±11
6053		V	0.271	14.4	110.9	49.2	378.9	428	420
		V	0.801	40.9	315.3	47.3	364.5	412	±12
6040		V	0.866	55.0	428.5	58.8	458.2	517	
6100		V	1.451	385	2746	246	1752	1998	1979
		V	1.287	329	2395	237	1723	1960	±27
MDC1	9Cr-1Mo	V	1.682	30.1	213.4	16.6	117.5	134	134
		V	1.551	27.6	195.7	16.5	116.8	133	±1
MD67		V	0.874	206	1462	218	1549	1767	1737
		V	1.181	266	1911	209	1498	1707	±42

[a]Stepped-anneal (A) or vaporization (V) analysis.
[b]Mass uncertainty is ±0.002 mg.
[c]Helium concentration in atomic parts per million (10^{-6} atom fraction) with respect to the total number of atoms in the specimen. Values for samples that were both stepped-anneal and vaporized is the total of the two analyses.
[d]Mean and standard deviation (1σ) of duplicate analyses

Hydrogen Measurements

Hydrogen Analysis System

Hydrogen analyses were conducted using a newly developed analysis system at PNNL. Details of the system have been presented elsewhere *[5]*. The system is based on a low-volume extraction furnace in combination with a quadrupole mass spectrometer, and has a detection limit of ~1 appm for steel. Samples for analysis are loaded into the sample holder carousel located above the extraction furnace. Sample analyses are conducted by dropping the individual specimens into the heated crucible sequentially. Hydrogen release, in terms of current output from the electron multiplier, is measured as a function of time. Total hydrogen released is determined from the integral of the hydrogen release curve and the measured system sensitivity.

Measurements of hydrogen release with temperature were also made on a few samples of Alloy 718 material. These measurements were made by ramping the crucible temperature in an approximately linear profile from about 250°C to 1200°C over a 400 second time period. The temperature profile was determined following the measurements using a thin-walled K-type thermocouple inserted from the upper sample loading area.

Calibration of the system is accomplished using a hydrogen leak source attached to the vacuum line between the extraction furnace and the detector volume. This calibrated leak has a very small trapped volume, resulting in virtually no lowering of the leak rate with time. Calibration measurements are conducted before and after each sample analysis, and typically show an overall reproducibility of ~2 to 3%. The system has been determined to be linear up to a total hydrogen release of at least 10^{17} atoms, which for a 0.5 mg steel sample, represents a hydrogen concentration of ~20,000 appm.

Measurements are also routinely conducted on specimens of a standard, hydrogen-containing steel maintained in the laboratory. The stated content of the steel is 5.2 ± 0.3 wppm. The average hydrogen content measured in more than 90 specimens ranging in mass from ~2 to ~8 mg is 5.3 wppm with a reproducibility of ~30% (1σ). It is speculated that the variability observed in the standard samples is associated with actual heterogeneity in the hydrogen content at this small mass level.

Retained Hydrogen in APT Alloys

Hydrogen measurements were made on a total of samples from the APT materials characterization tests, and on unirradiated control samples of the same materials. The results of the control analyses are given in Table 3. The retained hydrogen measured in the irradiated materials are shown in Table 4. Mean and standard deviation of the replicate measurements are given in the last two columns of the table. The data in the last two columns of the table represent the "net" hydrogen retained in the samples after subtraction of the measured hydrogen in the unirradiated materials in Table 3. Absolute uncertainty (1σ) in the hydrogen analyses is estimated at ~20%, and is due partly to the uncertainty in the calibrated hydrogen leak source discussed above. Additional uncertainty may also be present from possible hydrogen release from remaining water layers or hydrated metal oxides on the surface of the sample that are subsequently dissociated by the hot crucible.

Table 3 – *Hydrogen in Unirradiated Alloy Material*

Sample	Material	Mass (mg)[a]	Measured Hydrogen (10^{15} at.)	Hydrogen Concentration (appm)[b]	Hydrogen Concentration Mean[c]
In-blk	Alloy 718	1.931	3.45	174	190
		2.014	4.14	200	±20
304L-blk	304L	3.824	13.3	319	320
		4.940	17.2	320	±0
316L-blk	316L	3.014	11.7	360	448
		3.844	22.2	535	±124
9Cr-1Mo-blk	9Cr-1Mo	2.821	1.94	64	58
		4.089	2.30	52	±8

[a]Mass of specimen for analysis. Mass uncertainty is ±0.002 mg.
[b]Helium concentration in atomic parts per million (10^{-6} atom fraction) with respect to the total number of atoms in the specimen.
[c]Mean and standard deviation (1σ) of duplicate analyses.

Table 4 – *Retained Hydrogen in APT Tungsten*

Sample	Material	Mass (mg)[1]	Measured Hydrogen (10^{15} at.)	Hydrogen Concentration (ppm)[b]		
				Measured	Corrected[c]	Mean[d]
IN25	Alloy 718	0.587	10.6	1760	1570	1810
		0.509	9.41	1790	1600	±380
		0.683	17.2	2440	2250	
INE4		1.059	29.7	2720	2530	2600
		0.732	21.6	2860	2670	±100
IN43		2.386	117	4750	4560	4710
		1.912	103	5250	5060	±300
		1.328	64.3	4700	4510	
IN01		0.342	19.7	5590	5400	5200
		0.693	37.9	5310	5120	±180
		0.539	29.2	5260	5070	
IN66		1.639	30.7	1820	1630	1870
		2.366	56.0	2300	2110	±340
4121	304L	1.215	17.3	1300	980	1050
		2.336	37.0	1450	1130	±110
4077		1.806	78.0	3960	3640	3560
		0.955	39.7	3810	3490	±110
6138	316L	1.126	10.7	882	434	459
		1.305	13.1	932	484	±35
6053		1.283	21.6	1560	1110	1460
		1.741	42.4	2260	1810	±490
6040		2.407	40.4	1550	1100	1100
		3.497	58.8	1560	1110	±10
6100		1.391	61.0	4060	3610	3460
		1.030	41.8	3760	3310	±210
MDC1	9Cr-1Mo	1.071	85.0	735	677	687
		1.580	12.9	754	696	±13
MD67		1.910	89.5	4340	4280	4260
		2.050	95.2	4300	4240	±30

[a]Mass of specimen for analysis. Mass uncertainty is ±0.002 mg.
[b]Helium concentration in atomic parts per million (10^{-6} atom fraction) with respect to the total number of atoms in the specimen.
[c]Mean and standard deviation (1σ) of duplicate analyses.

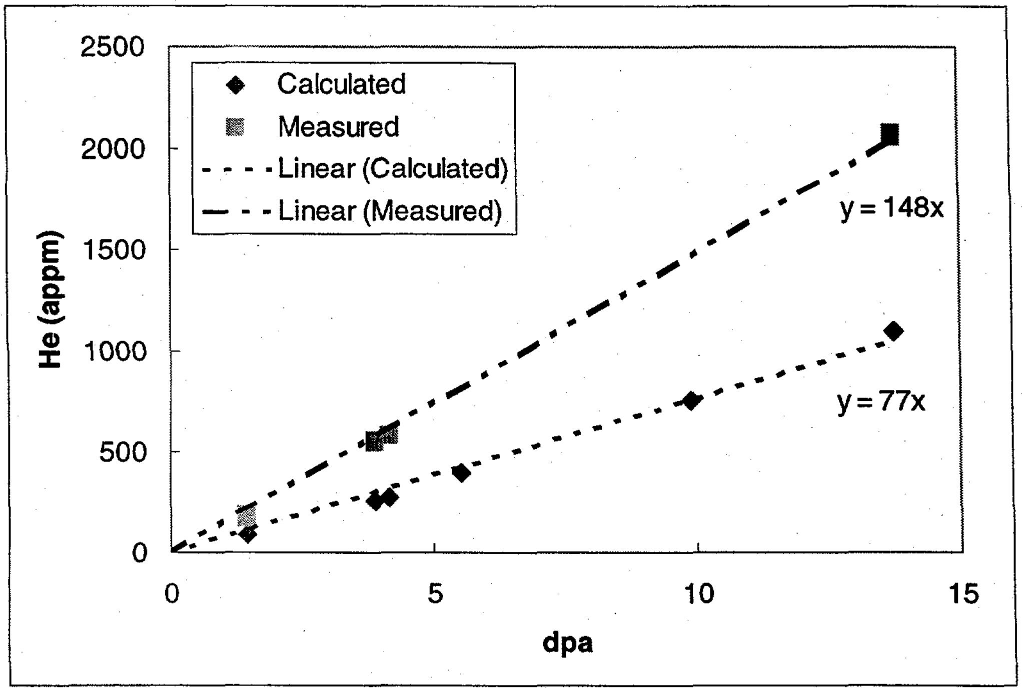

Figure 3 – *Measured Helium in Alloy 718 vs. dpa*

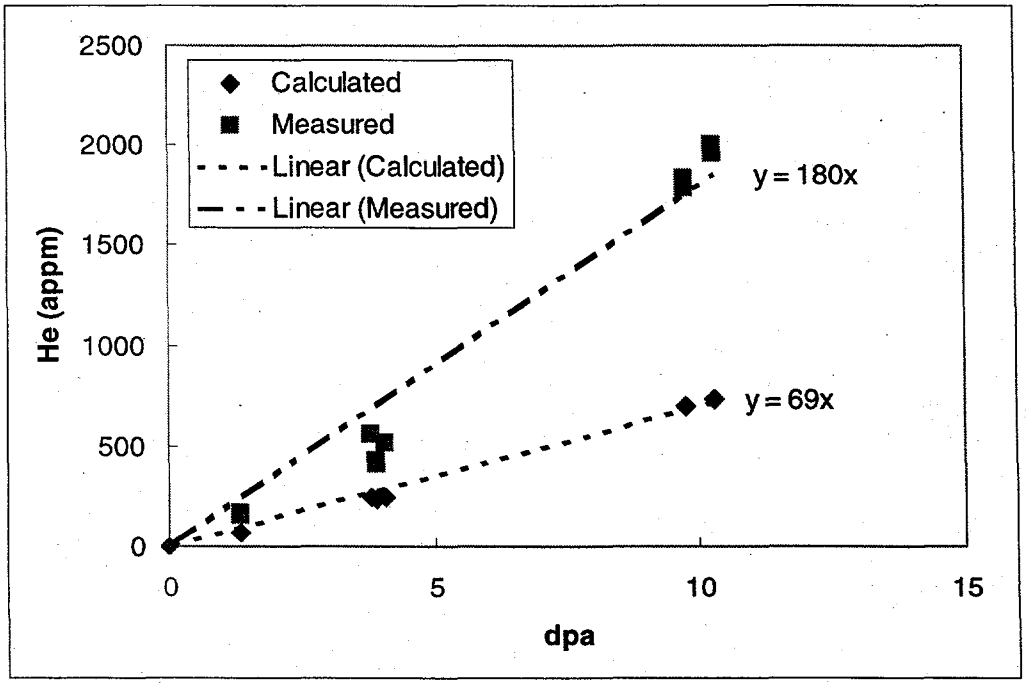

Figure 4 - *Measured Helium in 300 Stainless Steel vs. dpa*

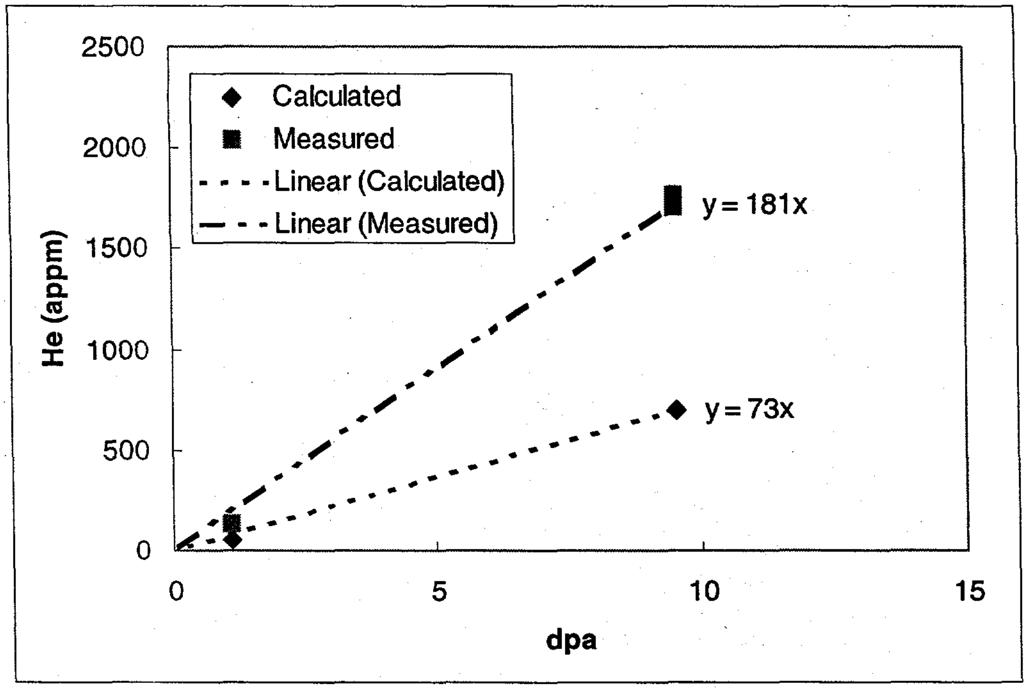

Figure 5 – *Measured Helium in 9Cr-1Mo vs. dpa*

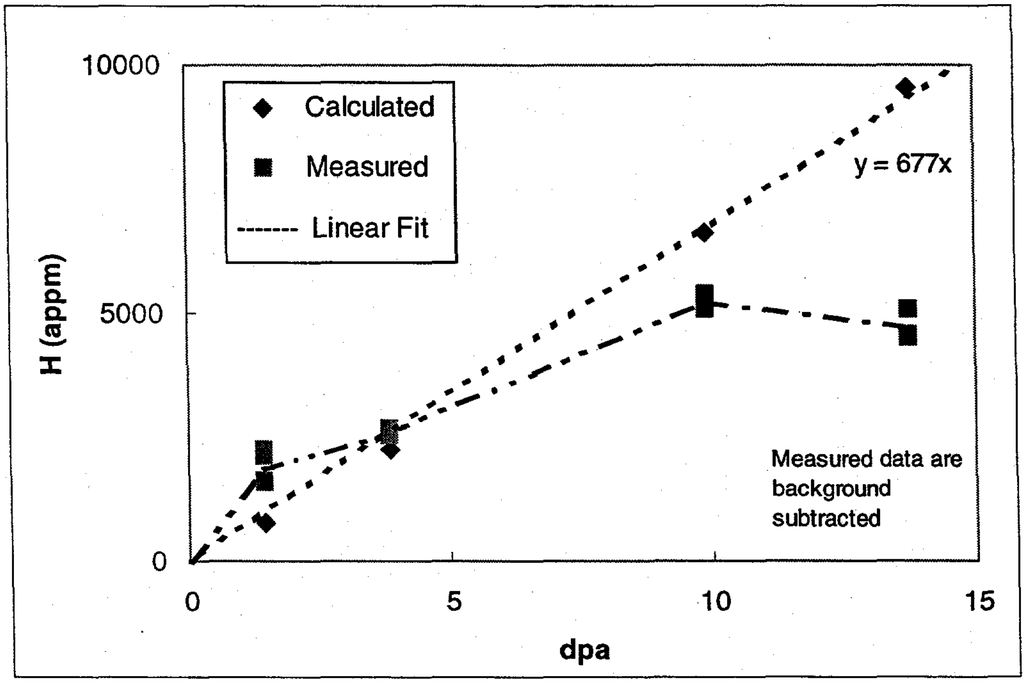

Figure 6 – *Retained Hydrogen in Alloy 718 vs. dpa*

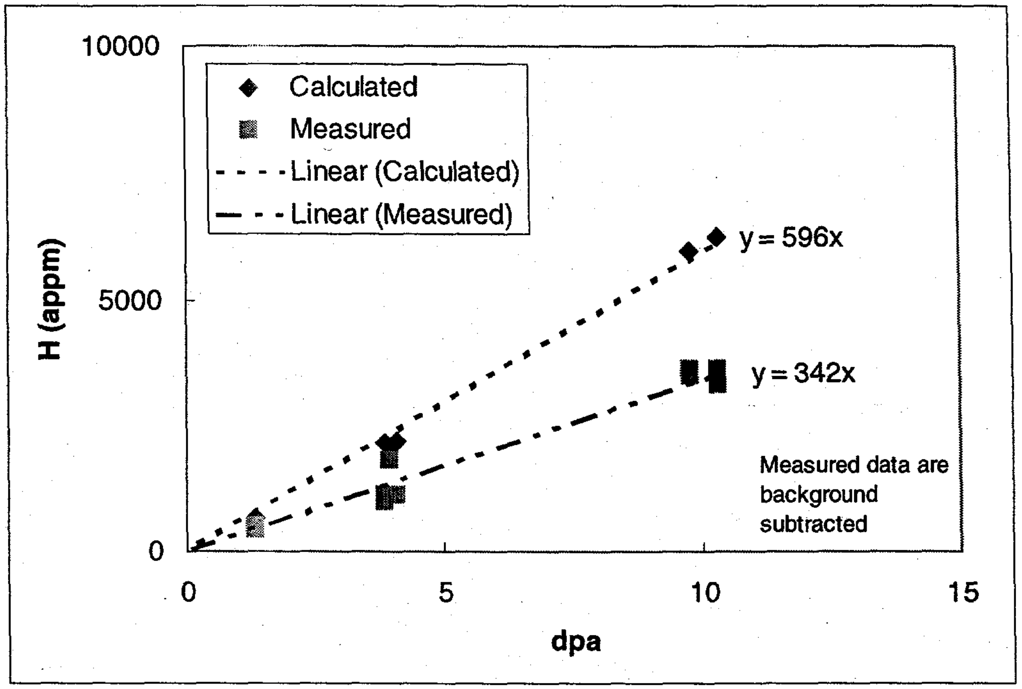

Figure 7 – *Retained Hydrogen in 300 Stainless Steel vs. dpa*

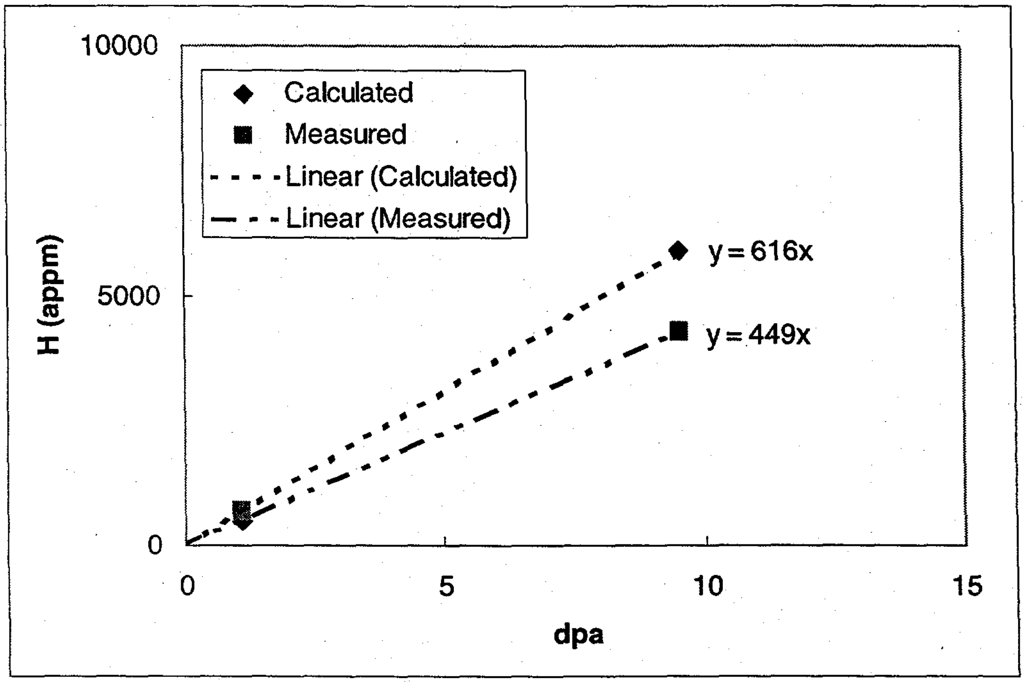

Figure 8 – *Retained Hydrogen in 9Cr-1Mo vs. dpa*

Discussion and Conclusions

Helium levels measured in the APT alloys ranged from 134 appm to 2060 appm, and followed an approximately linear trend with dpa. Plots of measured helium versus dpa are given in Figures 3 - 5. Helium generation relative to dpa was the highest for the iron based alloys (300 series SS, and 9Cr-1Mo) at ~180 appm/dpa. Helium generation for the Alloy 718 was slightly lower at ~150 appm/dpa, however, the general trend was that helium generation was relatively insensitive to composition for these mid-Z materials. Because of the changing contribution of neutron and protons to the helium generation at different beam locations, the trend of helium concentration with dpa is expected to be somewhat nonlinear, and this trend was observed here.

Calculated helium generation versus dpa values are also shown in the Figures. As is evident, in all cases, the measured helium levels are considerably higher than calculated. Calculated cross sections for He and H were generated using the LAHET code system *[6]*, version 2.83. The Bertini intranuclear cascade model was used with pre-equilibrium turned on. The level density model used was that of Gilbert-Cameron-Cook-Ignatyuk (GCCI) *[7,8]*. The LCS is the neutronic tool used for the design of APT and the estimation of radiation damage parameters, such as DPA and gas production. The physics options employed in LAHET as the standard APT settings were chosen primarily to provide the proper n/p ratios for high-Z targets such as tungsten. Accuracy in He production for mid-Z (Fe, Ni, Cu) elements in known to be poor *[9]* using these assumptions, however. Using these assumptions, the calculated He cross sections are generally low by about factor of 2 for mid-Z elements, in agreement with that seen here, and in earlier high-energy proton irradiations in LAMPF *[10]*.

As expected, significant levels of ^3He were also measured in the alloys. $^4He/^3He$ ratios varied from 7.0 to 8.6, and showed little variation with dpa. The helium 4/3 ratio was the highest for Alloy 718, and appear to scale with the level of high-Z components in the material, rather than with the major component Fe or Ni. Measurements in LAMPF showed helium 4/3 ratios from 8.16 for Ni to 13.7 for W *[10]*.

Retained hydrogen in the APT alloys ranged from 459 appm to 5200 appm. Plots of retained hydrogen versus dpa are shown in Figures 6 – 8. The data in the plots are the net retained hydrogen after subtraction of the measured residual hydrogen in the unirradiated materials. As with the helium, the retained hydrogen in the 300 series SS and in the 9Cr-1Mo scaled approximately linearly with dpa at ~600 appm/dpa. The Alloy 718, however, showed a marked non-linearity in the retained hydrogen, with three decreasing trend lines, one from 0 up to ~1.5 dpa, a second from ~1.5 to ~10 dpa, and a third above ~10 dpa. The complex hydrogen behavior observed in Alloy 718, can perhaps be attributed to a rather complex microstructural evolution in the material compared to that of the other alloys.

Calculated hydrogen generation values with dpa are also shown in the figures. Opposite to that observed with the helium, the calculated values generally over predict the hydrogen content. The possible exception is the initial slope observed in the Alloy 718 up to ~1.5 dpa. The calculations do not account for hydrogen diffusion during or post-irradiation, possibly accounting for some of the discrepancies. For the alloys studied here, calculated hydrogen generation is generally insensitive to alloy composition.

In summary, within the respective uncertainties of the gas measurements and calculations, several observations can be made:

- As anticipated, total helium production per dpa is not very sensitive to alloy composition for the alloys in this study.
- Gas generation is slightly nonlinear with dpa due to changing balance of neutron and proton fluxes.
- Essentially all helium generated in the specimens should be retained, but the amount measured is roughly twice that calculated, indicating that calculated helium values for Fe, Cr, Ni require an upward adjustment.
- Retained hydrogen is generally less than predicted.
- While the calculated hydrogen production is also relatively insensitive to alloy composition, the retained hydrogen is somewhat sensitive. The most complex hydrogen behavior is observed in Alloy 718, which undergoes a rather complex microstructural evolution compared to that of the other alloys.

Acknowledgements

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