

HELIUM ANALYSIS FROM THE DHCE-1 SIMULATION EXPERIMENT - D. L. Smith (Argonne National Laboratory)

Objective

The objective of this task is to provide an evaluation of the Proof-of-Principle Dynamic Helium Charging Experiment (DHCE-1). The current effort is focused on an analytical analysis of the helium generated in the vanadium alloys to compare with the measured helium concentrations.

Summary

A detailed calculation of the predicted helium generation rates in unalloyed vanadium and the reference V-4Cr-4Ti alloy irradiated in the DHCE-1 Proof-of-Principle experiment has been performed with the available data base on fundamental properties. Results of these detailed calculations indicate that the experimentally measured helium concentrations are in good agreement with the calculated values. Approximately 90% of the measured values are within a factor of 0.5 to 1.5 of the calculated values, which is quite good agreement. The validity of the experiment is further verified by a comparison of the experimental results from the other alloys included in the experiment with calculated correlation factors for each of the seven capsules. This paper presents a summary of the comparison of the results from the detailed calculations with experimental helium concentrations in the vanadium alloys in the DHCE-1 proof-of-principle experiment.

Introduction

A Dynamic Helium Charging Experiment (DHCE) was developed as a unique method for investigating the effects of fusion relevant helium generation rates on the properties of vanadium alloys irradiated in a fission reactor neutron spectrum [1]. The helium transmutation rate in candidate vanadium alloys at the first wall of deuterium-tritium fusion system from the high-energy neutrons is about 4 appm He/dpa (atomic parts per million helium for a neutron damage level of one atomic displacement per atom of the alloy). This value corresponds to a value of less than 0.02 appm He/dpa in a typical fast-fission reactor neutron spectrum. The effect of this high helium transmutation rate produced by high-energy fusion neutrons remains as the key issue regarding the performance limits of candidate structural materials for the fusion first-wall applications. Since we do not have a high flux 14 MeV neutron source for materials testing of the simultaneous effects of helium and neutron damage on the properties of materials for fusion applications, we must rely on simulation experiments, theory and modeling to evaluate these effects. The DHCE with vanadium alloys provides a unique method for providing insight and understanding of the effects of fusion-relevant helium generation on neutron irradiated materials. Features of the DHCE include:

- Close simulation to fusion neutron spectrum irradiation effects involving simultaneous helium production with neutron damage.
- Nearly constant He/dpa generation.
- He/dpa rates projected for a fusion environment can be obtained.
- Applicable to a range of He/dpa, fluence, temperature, and alloy composition variables.
- Applicable to existing heats of vanadium alloys; does not require preparation of special small heats.

A proof-of-principle (POP) experiment (DHCE-1) with a range of vanadium alloy compositions was conducted as part of the US/Japan (Monbusho) collaboration on fusion materials research. The DHCE-1 succeeded in demonstrating that the technique can achieve elevated He/dpa ratios in vanadium alloys for a range of conditions. Experimental measurements of the helium concentrations in the various alloys indicated that the helium generation rates from the DHCE ranged from ~10-1000 times the helium transmutation rates for pure alloys in the fission neutron spectrum. The ideal enhancement to reach the fusion-relevant value is a factor of ~200. For many of the specimens the enhancement factor was ~40, which was less than desired amount but a large enhancement compared to the helium transmutation rate in a fission neutron spectrum.

A detailed calculation of the predicted helium generation rates in unalloyed vanadium and the reference V-4Cr-4Ti alloy has been performed with the available database on fundamental properties. Results of these detailed calculations indicate that approximately 90% of the experimentally measured helium concentrations are within a factor of 0.5 to 1.5 of the calculated values, which is quite good agreement. The validity of the experiment is further verified by a comparison of the experimental results from the other alloys included in the experiment with calculated correlation factors for each capsule. This paper presents a summary of the comparison of the results from the detailed calculations with experimental helium concentrations in the vanadium alloys in the DHCE-1 proof-of-principle experiment.

Calculation of Helium in V-4Cr-4Ti and Vanadium

A detailed calculation of the predicted helium concentrations in unalloyed vanadium and the reference V-4Cr-4Ti alloys included in the DHCE-1 proof-of-principle experiment has been performed [1, 2]. The calculations include the helium generated during the irradiation cycle, helium generated during the reactor down time, and helium generated after termination of the irradiation but before the test specimens were retrieved and analyzed. The helium generation in the vanadium includes both generation from the tritium precharge as well as from tritium generated from ${}^6\text{Li}$ reactions during the irradiation. Helium loss due to burnout and reductions due to tritium leakage are also included in the calculation. Specific experimental parameters for each irradiation capsule are included in the calculation. Parameters for each capsule of the DHCE-1 are given in Table 1.

Helium in the vanadium is generated by the decay of tritium in the vanadium. The two sources of tritium are a precharge of tritium in a “mother alloy” contained in each capsule and from tritium generated from ${}^6\text{Li}$ during the irradiation. For the conditions of the DHCE-1, most of the tritium originates from the precharge. Varying amounts of tritium were precharged in the various capsules in an attempt to account for variations associated with the different experimental temperatures and to accommodate uncertainties in the database at the time. Variations in ${}^6\text{Li}$ were introduced as an experimental variable with higher enrichment at the higher temperatures to partially makeup for tritium losses by permeation through the capsule walls. A key feature of the experimental approach is not to inject tritium into the test specimens until the neutron damage is initiated. The tritium remains in the “mother alloy” until the capsule is heated upon insertion and startup of the reactor. The tritium rapidly redistributes upon heating such that tritium decay to helium is initiated at the same time as the neutron damage begins.

The redistribution of tritium to the vanadium alloy test specimens is dependent on the tritium precharge, the masses of lithium and vanadium in the capsules and the distribution coefficient of tritium between lithium and the vanadium alloys. The tritium distribution coefficient is dependent on the temperature and the alloy composition as will be discussed later. The tritium precharge and the masses of lithium and vanadium in each capsule are indicated in Table 1.

The distribution coefficient for tritium between lithium and vanadium is obtained from the hydrogen solubility expressed by the Sieverts' constants. The Sieverts' constants defined by Veleckis et al [3] for hydrogen in lithium, which differ slightly from the values used originally, are recommended as the most reliable. The Sieverts' constant for hydrogen in lithium as a function of temperature is given by

$$\ln K_{S(\text{Li})} = - 6.498 + \frac{6182}{T} \quad , \quad \text{atom fraction/atm}^{0.5} \quad (1)$$

The Sieverts' constants for vanadium obtained from a compilation of hydrogen solubility measurements is given by

$$\ln K_{S(\text{V})} = - 7.510 + \frac{3980}{T} \quad , \quad \text{atom fraction/atm}^{0.5} \quad (2)$$

Table 1. DHCE-1 Test parameters and ^3He analyses of vanadium and V-4Cr-4Ti alloy.

Capsule ID	4D1	4D2	5 E2	5D1	5 E1	5C1	5C2
Irradiation Temperature, C	430	430	430	500	500	600	600
Lithium Mass, g	0.765	0.765	0.67	0.938	0.952	0.808	0.955
Li(6) Fraction, %	5.0	4.5	1.0	6.5	1.0	8.0	8.0
Total Specimen Mass, g	5.86	5.38	5.38	5.77	5.82	5.82	5.95
Plenum Volume, ml	2.85	2.93	3.11	2.53	2.49	2.77	2.47
Distribution Coeff, Ka	56.9	56.9	56.9	40.3	40.3	27.1	27.1
Tritium Precharge, Ci	99	70	26	74	57	16	18
Precharge Tritium, appm in Li	30200	21350	9055	18400	13970	4620	4398
Calculated He-3 in V-4Cr-4Ti, appm							
Tritium leakage from TZM capsule	10.8	10.9	5.7	14.6	10.2	6.7	6.6
Tritium leakage from Mo capsule	10.8	10.9	5.7	14.6	10.2	4.1	4.0
Measured He-3 in V-4Cr-4Ti, appm							
	11.6	9.9	2.5	14.0	5.5	7.9	6.8
	9.9	20.9	2.5	14.1	5.6	8.0	74.0
Calculated He-3 in vanadium, appm							
Tritium leakage from TZM capsule	10.1	10.2	5.4	12.8	9.0	5.6	5.5
Tritium leakage from Mo capsule	10.1	10.2	5.4	12.8	9.0	3.4	3.3
Measured He-3 in vanadium, appm							
	8.8	15.2	2.5	31.6	12.3		10.4

Recent results on the Sieverts' constant for the V-4Cr-4Ti alloy [4] are given by

$$\ln K_{S(V44)} = -6.725 + \frac{3500}{T}, \text{ atom fraction/atm}^{0.5} \quad (3)$$

Based on these equations the distribution coefficients for hydrogen between lithium and vanadium and V-4Cr-4Ti expressed in atom fraction of hydrogen are given by

$$\ln K_A(H_{Li}/H_V) = 1.002 + \frac{2202}{T}, \text{ atom fraction} \quad (4)$$

$$\ln K_A(H_{Li}/H_{V44}) = 0.227 + \frac{2682}{T}, \text{ atom fraction} \quad (5)$$

The distribution coefficients for hydrogen in the Li/V and Li/V-4Cr-4Ti systems are plotted as a function of temperature in Figure 1.

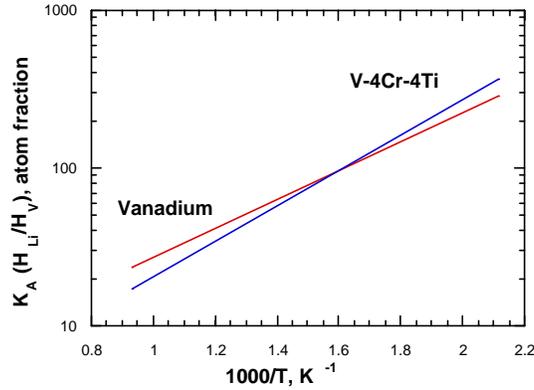


Figure 1. Distribution coefficient for hydrogen for the lithium Vanadium and Lithium V-4Cr-4T systems.

These hydrogen distribution coefficients are valid for hydrogen concentrations up to the saturation value for LiH formation in equilibrium with hydrogen in solution in lithium. The saturation value of hydrogen in lithium for LiH formation is given as a function of temperature by

$$\ln N_{LiH} = 3.769 + \frac{5472}{T}, \text{ mole-fraction} \quad (6)$$

The helium generated in the V-4Cr-4Ti and unalloyed vanadium is calculated for each capsule in the DHCE-1 based on the experimental parameters given in Tables 1 and 2.

Table 2. Experimental parameters of DHCE-1.

Irradiation Time	203 days at Irradiation Temperature
Off cycle Time	92 days at 365°C
Time after reactor shutdown	300 days at 200°C
Time until specimens analyzed	90-180 days at RT

This detailed calculation for helium generation in the V-4Cr 4Ti alloy and vanadium specimens in DHCE -1 includes the following:

- He generated from tritium precharge during irradiation at temperature
- He generated from tritium produced from ${}^6\text{Li}$ during irradiation
- He loss due to burn-out during irradiation
- He generated during the off-cycle of the reactor
- He generated after reactor shutdown before removal of subassembly from reactor
- Reduction in He generation as a result of tritium loss due to permeation through the capsule wall.
-

Based on previous experience with hydrogen, the tritium redistributes rapidly between the vanadium alloy specimens and lithium after a change in temperature. Results of the calculated ${}^3\text{He}$ concentrations in vanadium and V-4Cr-4Ti are given for each capsule in Table 1. These results are plotted in Figs. 2 and 3 for the V-4Cr-4Ti alloy and vanadium, respectively. With few exceptions, the results of the experimentally determined ${}^3\text{He}$ concentrations are in quite good agreement with the calculated values that account for the parameter variations in the experiment. In all cases (capsules), most of the ${}^3\text{He}$ in the vanadium specimens is generated from tritium from the precharge. Most of the ${}^3\text{He}$ (~ 86%) is generated in the specimens during the irradiation. Only about 13% is generated during the off-cycle time since the tritium tends to redistribute to the lithium at the lower temperature (365°C). Only about 1% of the ${}^3\text{He}$ is generated after the reactor shutdown and before the specimens were analyzed even through this was a relatively long time (several months). This again is due to the tritium distribution at low temperatures. Since the ${}^6\text{Li}$ content was varied for each capsule, the ${}^3\text{He}$ generated from tritium produced from ${}^6\text{Li}$ varied considerably. Higher ${}^6\text{Li}$ concentrations were used in the 600°C capsules in an attempt to partially balance the higher tritium leakage. Indeed, the ${}^3\text{He}$ generated from the ${}^6\text{Li}$ produced tritium varied from ~2 to 20% of the total. The ${}^3\text{He}$ burn-out varies as the concentration of ${}^3\text{He}$ increases but is a relatively small fraction (<10%). The tritium leakage is negligible for the two lower temperatures 430 and 500°C, but could result in a maximum reduction of about 30% at 600°C. The worse case scenario is based on calculated permeation rates for molybdenum. Recent results by Altunoglu and Braithwaite [5] indicate that the diffusivity of hydrogen in TZM alloy (used for the DHCE-1 capsules) is considerably less than that for molybdenum. They also indicate significant reductions in the diffusivity of hydrogen in TZM with lower hydrogen pressures. The actual permeation rates for the TZM capsules may also be reduced by a thin oxide film which is characteristic of the capsule surfaces. The tritium loss by permeation remains as the largest uncertainty at temperatures of 600°C and above. However, the calculated ${}^3\text{He}$ concentrations tend to support the possibility that tritium permeation rates based on molybdenum data may over predict the tritium losses. All experimental values are within a factor of two of the calculated values except for one analysis (74 appm ${}^3\text{He}$) of V-4Cr-4Ti in capsule 5C2 at 600°C. This is good agreement for a proof-of-principle experiment of this complexity. It certainly appears that the one alloy specimen from 5C2 must have gotten mixed up during one of the many handling procedures. As discussed later, the ${}^3\text{He}$ concentrations in several other alloy specimens analyzed at the same time had ${}^3\text{He}$ concentrations as high or higher than the specimen in question.

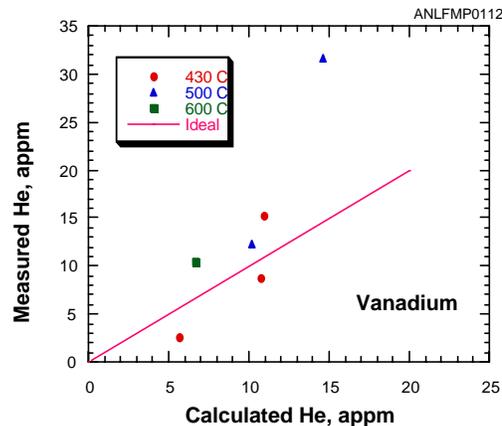


Figure 2. Measured vs. calculated ${}^3\text{He}$ concentrations in vanadium irradiated in the DHCE-1.

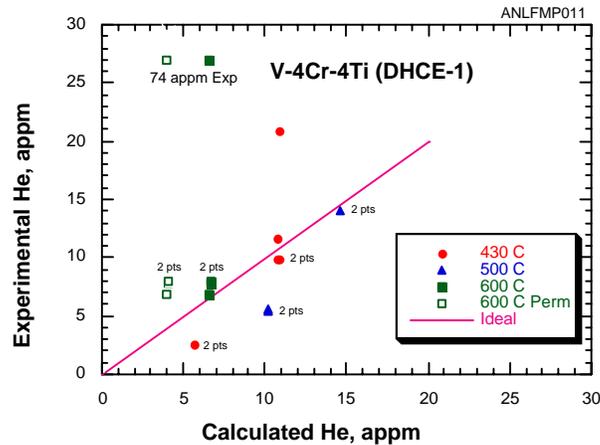


Figure 3. Measured vs. calculated ^3He concentrations in vanadium irradiated in the DHCE-1.

Correlation of Experimental Results

In addition to the vanadium and the V-4Cr-4Ti alloy discussed above, the ^3He content was measured for nine other vanadium alloys irradiated in the same seven capsules. These alloys consisted primarily of binary alloys of vanadium with ~5% alloying additions of interest for fundamental studies. Results of the experimental analyses are summarized in Table 3. It is apparent from these results that three of the alloys, viz., V-1Si, V-5Fe, and V-5Cr-5Ti (Si, Al, Y), exhibited much higher ^3He contents than the other alloys. These differences are attributed primarily to differences in the hydrogen distribution coefficients between lithium and these alloys. Since we do not have well defined Sieverts' constants for hydrogen in these alloys, we cannot calculate the ^3He concentrations accurately. However, a correlation of the results from these alloys with the results from the vanadium and V-4Cr-4Ti alloy are given at the bottom of Table 5. The ratios of the measured ^3He concentrations for the other alloys to these normalized concentrations of helium in vanadium and V-4Cr-4Ti alloy for each capsule were calculated (see Table 3). The ratios for each alloy are averaged to provide a measure of the hydrogen distribution for each alloy compared to the normalized distribution for the vanadium and V-4Cr-4Ti alloy. For example, the average ^3He concentration of the V-1Si alloy is 8.9 times the reference value (average of vanadium and V-4Cr-4Ti), that of the V-5Fe is a factor of 9.6 higher, and that of V-5Nb is lower by a factor of 0.87. For the total 48 analyses presented in Table 3, only 5 analyses (including the 74 appm ^3He for V-4Cr-4Ti in capsule 5C2) vary outside the range 0.5 – 1.5 of the average for each alloy composition. Figure 4 is a plot of the normalized concentrations for each alloy (measured ^3He concentration divided by the normalized ^3He concentration for the vanadium and V-4Cr-4Ti alloy) as a function of the calculated ^3He concentration for the V-4Cr-4Ti alloy in each capsule. The line represents an ideal correlation.

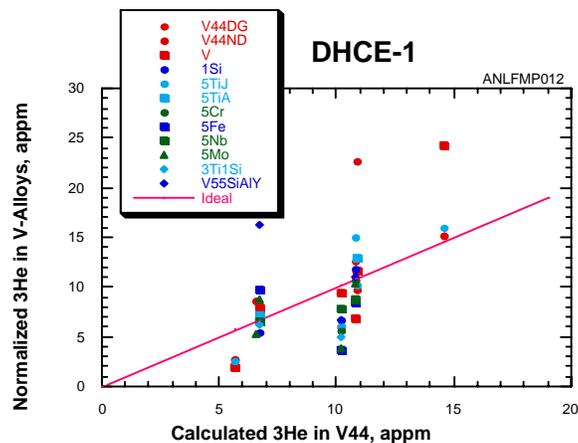


Figure 4. Normalized ^3He concentrations in Twelve Vanadium alloys at a function of the calculated ^3He .

This figure indicates that results from all alloys provide a reasonably good correlation with the calculated values for V-4Cr-4Ti. Further, these results show some consistent patterns. For example, all alloys in capsule 5E2 indicated measured ^3He concentrations lower than predicted. This would indicate that the tritium in this capsule was slightly lower than expected. The results from all alloys in capsule 5E1 indicate similar behavior. The results from the other five capsules are in good agreement with the ideal correlation. As indicated earlier, only five analyses show substantial deviations from the ideal correlations and three of these analyses differ only by about a factor of two.

Conclusions

Results of a detailed calculation for the ^3He generation in vanadium and V-4Cr-4Ti alloy irradiated in the DHCE-1 experiment show good agreement with the measured ^3He concentrations except for one analysis, which is most likely, the result of a mix-up in specimens during handling. The detailed analysis includes variations in temperature, tritium precharge, ^6Li enrichment, masses of V-alloys and lithium, variations in reactor operating cycle, post irradiation effects, ^3He burn-out, and tritium leakage from the capsules. Correlations of measured ^3He concentrations from all alloys analyzed indicate consistent results for all but five of the 48 specimens analyzed. These correlations indicated that the tritium in two of the seven capsules was slightly lower than expected. Tritium leakage through the TZM capsule remains as the largest uncertainty at the higher temperatures (600°C and above), but the leakage rate may be lower than originally assumed.

The results of these analyses and the consistency of the experimental results support the position that the DHCE-1 successfully demonstrated that this method can be used to investigate effects of fusion relevant helium generation rates with fission reactor irradiations of vanadium alloys. The average ^3He generated in the vanadium alloy specimens was about 40 times the He transmutation rate in vanadium alloys exposed to a typical fast fission neutron spectrum.

References

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2. H. M. Chung, B. A. Loomis and D. L. Smith, J. Nuclear Materials 233-237 (1996) 466.
3. E. Veleckis, R. M. Yonco, and V. A. Maroni, "The Current Status of Fusion Reactor Blanket Thermodynamics", IAEA Report IAEA-SM-236/56 (1986) p. 3.
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Table 3. Measured and calculated $^3\text{He}^{33}$ concentrations in vanadium alloys irradiated in

Capsule		4 D 1	4 D 2	5 E 2	5 D 1	5 E 1	5 C 2	5 C 1	Avg Factor	
V	Measured He-3, appm	8.83	15.2	2.54	31.6	12.3	10.4			
	Normalization Factor	0.87	1.01	1.01	1.59	1.58	1.81		1.3	
	Normalized He-3, appm	6.79	11.69	1.95	24.31	9.46	8.00			
V-1Si	Measured He-3, appm	1.05				59.9	48.8			
	Normalization Factor	10.39	0.00	0.00	0.00	7.68	8.51		8.9	
	Normalized He-3, appm	11.80	0.00	0.00	0.00	6.73	5.48			
V-5Ti	Measured He-3, appm	18.0	12.2	3.05	19.2	7.19	8.10			
	Normalized Factor	1.78	0.81	1.21	0.97	0.92	1.41		1.2	
	Normalized He-3, appm	15.00	10.17	2.54	16.00	5.99	6.75			
V-5Ti(BL-47)	Measured He-3, appm		15.5				8.59			
	Normalized Factor	0.00	1.03	0.00	0.00	0.00	1.50		1.2	
	Normalized He-3, appm	0.00	12.92	0.00	0.00	0.00	7.16			
V-5Cr	Measured He-3, appm	6.45				3.35	26.3			
	Normalized Factor	0.64	0.00	0.00	0.00	0.43	4.59		0.6	
	Normalized He-3, appm	10.75	0.00	0.00	0.00	5.58	43.83			
V-5Fe	Measured He-3, appm	80.6				34.9	93.4			
	Normalized Factor	7.97	0.00	0.00	0.00	4.47	16.29		9.6	
	Normalized He-3, appm	8.40	0.00	0.00	0.00	3.64	9.73			
V-5Nb	Measured He-3, appm	7.65				6.78	5.70			
	Normalized Factor	0.76	0.00	0.00	0.00	0.87	0.99		0.87	
	Normalized He-3, appm	8.79	0.00	0.00	0.00	7.79	6.55			
V-5Mo	Measured He-3, appm	9.81				3.56	8.22			
	Normalized Factor	0.97	0.00	0.00	0.00	0.46	1.43		0.94	
	Normalized He-3, appm	10.44	0.00	0.00	0.00	3.79	8.74			
V-5Mo	Measured He-3, appm						5.02			
	Normalized Factor	0.00	0.00	0.00	0.00	0.00	0.88		0.94	
	Normalized He-3, appm	0.00	0.00	0.00	0.00	0.00	5.34			
V-3Ti-1Si	Measured He-3, appm	34.7				5.02	6.25			
	Normalized Factor	3.43	0.00	0.00	0.00	0.64	1.09		1.0	
	Normalized He-3, appm	34.70	0.00	0.00	0.00	5.02	6.25			
V5Cr5Ti5AlY	Measured He-3, appm	1.77				1.08	2.60			
	Normalized Factor	17.51	0.00	0.00	0.00	13.85	45.35		1.6	
	Normalized He-3, appm	11.06	0.00	0.00	0.00	6.75	16.25			
V4Cr4Ti	Measured He-3, appm	11.6	9.0	2.5	14.0	5.5	6.8	8.0		
	Normalized Factor	1.15	0.60	0.99	0.70	0.71	1.19		0.92	0
	Normalized He-3, appm	12.61	9.78	2.72	15.22	5.98	7.39	8.7		
V4Cr4Ti	Measured He-3, appm	9.9	20.9	2.5	14	5.6	7.4	7.9		
	Normalized Factor	0.98	1.39	0.99	0.70	0.72	1.291		0.92	-1.1734
	Normalized He-3, appm	10.76	22.72	2.72	15.22	6.09	80.43	8.6		
Avg V/V44	Measured He-3, appm	10.11	15.03	2.51	19.87	7.80	5.73			
Calc He in V44	appm He-3	10.8	10.9	5.7	14.6	10.2	6.7	6.6		