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Helium analysis from the DHCE-1 simulation experiment

Dale L. Smith [a,*], H. Matsui [b]

[a] *Fusion Power Programme, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA*
[b] *Institute of Materials Research, Tohoku University, Sendai 980-77, Japan*

Abstract

The combined effects of high helium transmutation rates with the displacement damage produced by high energy fusion neutrons remains the key issues in the evaluation of the performance and lifetime limits of candidate vanadium alloys for fusion first-wall structure applications. A dynamic helium charging experiment (DHCE) has been 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. In this simulation, decay of tritium in the vanadium alloy to helium during fission reactor irradiation is used to provide constant He/displacement damage ratios characteristic of a fusion neutron environment. A proof-of-principle experiment (DHCE-1) was conducted in the FFTF reactor. Detailed calculations of the predicted helium concentrations in unalloyed vanadium and the reference V–4Cr–4Ti alloy included in the DHCE-1 indicate quite good agreement with experimental results and demonstrate the validity of the DHCE technique.
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1. Introduction

Vanadium-base alloys have been identified as a leading candidate material for fusion first-wall/blanket structure applications [1–4]. The V–Cr–Ti alloys exhibit good fabricability, a potential for high performance and long operating lifetime in a fusion environment, and favorable safety and environmental features. The current focus is on the V–Cr–Ti alloy system with (3–9 wt%) Cr and (3–10 wt%) Ti with a V–4Cr–4Ti alloy as the reference composition. The combined effects of high helium transmutation rates with the displacement damage produced by high energy fusion neutrons remain the key issues in the evaluation of the performance and lifetime limits of candidate structural materials for fusion first-wall applications. 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 [5,6]. The helium transmutation rates 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 <0.02 appm He/dpa for V–4Cr–4Ti in a typical fast-fission reactor neutron spectrum. 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 with significant advantages compared to other simulation techniques for providing insight and understanding of the effects of fusion-relevant helium generation rates 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 can be obtained.
- He/dpa rates projected for a fusion environment can be obtained.

* Corresponding author. Tel.: +1-630 252 4837; fax: +1-630 252 5287.
E-mail address: dalesmith@anl.gov (D.L. Smith).

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- 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.
- Applicable to large-size mechanical test specimens.

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 V–Cr–Ti alloys 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 updated database on fundamental properties to further validate the experiment. 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 alloy. 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 POP experiment and recommendations for the conduct of an effective DHCE.

2. DHCE-1 experiment

Vanadium alloy specimens in the DHCE-1 were irradiated in the fast flux test facility (FFTF), a sodium-cooled fast reactor, at 430, 500 and 600 °C. The test specimens were contained in molybdenum alloy (TZM) capsules with lithium bonding. A description of the DHCE is given in Ref. [5]. Experimental parameters for the DHCE-1, which contained seven capsules, are given in Tables 1 and 2.

3. 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 POP experiment has been performed. 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 pre-charge as well as from

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

Table 1
DHCE-1 test parameters and ^{3}He analyses of vanadium and V–4Cr–4Ti alloy

Capsule ID	4D1	4D2	5E2	5D1	5E1	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 coefficient, Ka	56.9	56.9	56.9	40.3	40.3	27.1	27.1
Tritium pre-charge, Ci	99	70	26	74	57	16	18
Pre-charge tritium, appm in Li	30 200	21 350	9055	18 400	13 970	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	9.0	2.5	14.0	5.5	8.0	6.8
	9.9	20.9	2.5	14.1	5.6	7.9	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

tritium generated from ^{6}Li reactions during the irradiation. Helium loss due to neutron reactions and losses due to tritium leakage are also included in the calculation. Specific experimental parameters for each of the seven irradiation capsules 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 pre-charge of tritium in a 'mother alloy' contained in each capsule and from tritium generated from n-^{6}Li reactions during the irradiation. For the conditions of the DHCE-1, most of the tritium originates from the pre-charge. Varying amounts of tritium were pre-charged 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}Li were introduced as an experimental variable with higher enrichment at the higher temperatures to partially make-up for tritium losses by permeation through the capsule walls. A key feature of the experimental approach is to prevent tritium from transferring 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 then 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 pre-charge, 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 varies with alloy composition as will be discussed later. The tritium pre-charge 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. [7] 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

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

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

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

Recent results on the Sieverts' constant for the V–4Cr–4Ti alloy [8] 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 Fig. 1. 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.

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 pre-charge during irradiation at temperature.
- He generated from tritium produced from ^{6}Li during irradiation.

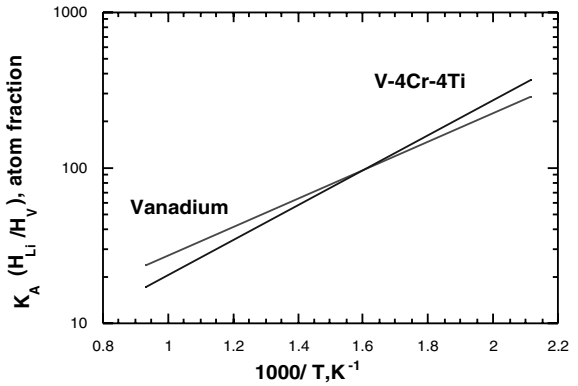

Fig. 1. Distribuiton coefficient for hydrogen in the lithium/vanadium and lithium/V–4Cr–4Ti system.

- He loss due to n-^{3}He reactions during irradiation.
- Reduction in He generation as a result of tritium loss due to permeation through the capsule wall.
- He generated during the off-cycle of the reactor.
- He generated after reactor shutdown.

Results of the calculated ^{3}He concentrations in vanadium and V–4Cr–4Ti are given for each capsule in Table 1. The measured ^{3}He concentrations are plotted as a function of the calculated concentrations in Figs. 2 and 3 for the Vanadium and V–4Cr–4Ti alloy and vanadium, respectively. With few exceptions, the results of the experimentally determined ^{3}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}He in the vanadium specimens is generated from tritium from the pre-charge.

Most of the ^{3}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}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}Li content was varied for each capsule, the ^{3}He generated from tritium produced from ^{6}Li varied considerably. Higher ^{6}Li concentrations were used in the 600 °C capsules in an attempt to partially balance the higher tritium leakage. Indeed, the ^{3}He generated from the ^{6}Li produced tritium varied from 2% to 20% of the total. The ^{3}He burn-out varies as the concentration of ^{3}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

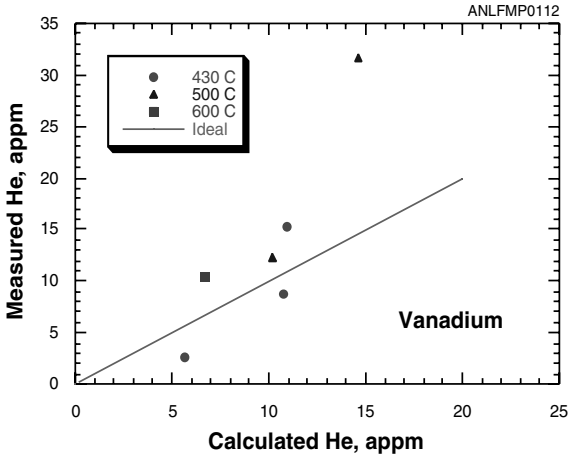

Fig. 2. Measured vs. calculated ^{3}He concentrations in vanadium irradiated in the DHCE-1.

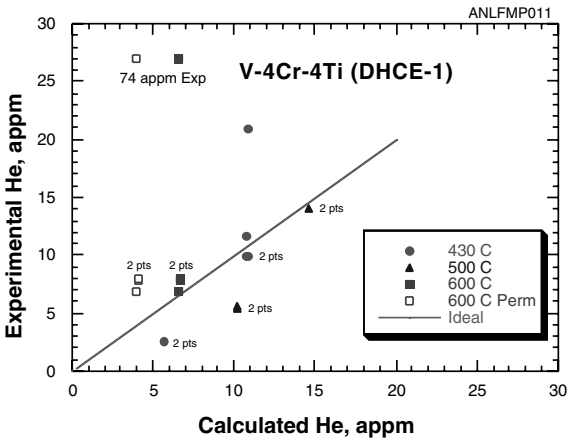

Fig. 3. Measured vs. calculated ^{3}He concentrations in V–4Cr–4Ti irradiated in the DHCE-1.

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 [9] 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}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}He) of V–4Cr–4Ti in capsule 5C2 at 600 °C. This is good agreement for a POP experiment of this complexity. It certainly appears that the one alloy specimen from 5C2 must have been mislabeled or mixed up during one of the many handling procedures. As discussed later, the ^{3}He concentrations in several other alloy specimens analyzed at the same time had ^{3}He concentrations as high or higher than the specimen in question.

4. Correlation of experimental results

In addition to the vanadium and the V–4Cr–4Ti alloy discussed above, the ^{3}He content was measured for nine other vanadium alloys irradiated in the same seven capsules. These alloys consisted primarily of binary alloys of vanadium with about 5% alloying additions of interest for fundamental studies [10,11]. 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 ^{3}He contents than the other alloys. These differences are attributed primarily to differences in the tritium solubility of these alloys due to compositional effects or possibly trace impurity effects. A correlation of the results for all alloys tested has been developed by averaging the ratios of the ^{3}He concentrations for each alloy with the corresponding ^{3}He concentration of the vanadium and the V–4Cr–4Ti alloy. 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 ^{3}He 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 obtained, only 5 analyses (including the 74 appm ^{3}He for V–4Cr–4Ti in capsule 5C2) vary outside the range 0.5–1.5 of the average for each alloy composition. Fig. 4 is a plot of the normalized concentrations for each alloy (measured ^{3}He concentration divided by the normalized ^{3}He concentration for the vanadium and V–4Cr–4Ti alloy) as a function of the calculated ^{3}He concentration for the V–4Cr–4Ti alloy in each capsule. The line represents an ideal correlation. 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 capsules 5E2 and 5E1 indicate measured ^{3}He concentrations lower than predicted. This would indicate that the tritium in this capsule was slightly lower than expected. It was noted that some tritium was lost from these two capsules during final welding. 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 correlation and three of these analyses differ only by about a factor of two.

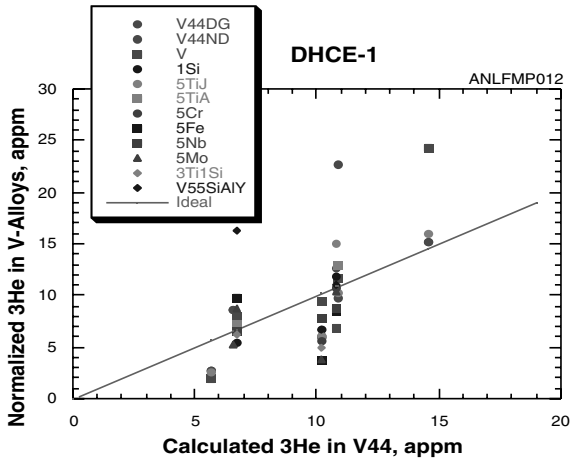

Fig. 4. Normalized ^{3}He concentrations in twelve vanadium alloys as a function of the calculated ^{3}He in V–4Cr–4Ti specimens in the same capsule.

5. Conclusions

Results of a detailed calculation for the ^{3}He generation in vanadium and V–4Cr–4Ti alloy irradiated in the DHCE-1 experiment show good agreement with the measured ^{3}He 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 pre-charge, ^{6}Li enrichment, masses of V-alloys and lithium, variations in reactor operating cycle, post irradiation effects, ^{3}He burn-out, and tritium leakage from the capsules. A correlation of measured ^{3}He concentrations from all alloys analyzed indicate consistent results for all but five of the 48 specimens analyzed. The correlation indicated that the tritium in two of the seven capsules was slightly lower than expected. It was noted that some tritium was lost from these two capsules during the welding operation. 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. For experiments at 600 °C or above, a double containment approach is proposed to reduce the tritium leakage to negligible levels. At temperatures below 500 °C the He generation rate is limited to $<$40 appm/yr in V–4Cr–4Ti alloy because of the LiH saturation in Li. Higher helium generation rates are achievable at higher temperatures and for vanadium alloy compositions with hydrogen distribution coefficients higher than those for the V–4Cr–4Ti alloy. In all cases the thermal neutron flux must be limited to low levels to avoid excessive burnout of the He by neutron reactions. This is not a problem in a fast reactor spectrum.

The results obtained from the DHCE-1 POP experiment and the analyses presented here demonstrate that the DHCE concept provides a unique approach for investigating the effects of fusion-relevant helium generation rates in vanadium alloys during fission reactor irradiations for a wide range of experimental parameters. He generation rates of $>$100 appm/yr are achievable in V–4Cr–4Ti at temperatures above 600 °C.

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