Hydrogen solubility in V–4Cr–4Ti alloy

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Abstract

A systematic investigation was conducted to provide an accurate determination of the hydrogen solubility in the V–4Cr–4Ti alloy at temperatures in the range 400–600 °C, which is of primary interest for fusion applications. Results have been obtained by the method of hydrogen absorption and desorption into flowing helium with controlled concentrations of hydrogen to provide accurate measurements of the Sieverts constants for the alloy. Results obtained in this investigation indicate that the temperature dependent Sieverts constant for the V–4Cr–4Ti alloy is very similar to that for unalloyed vanadium. The increase in hydrogen solubility produced by the titanium is essentially balanced by the decrease in hydrogen solubility produced by the chromium.
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1. Introduction

The self-cooled lithium system with a vanadium alloy structure offers a potential for a high performance, environmentally attractive first-wall/blanket system for magnetic fusion applications. The V–4Cr–4Ti alloy has been identified as a reference vanadium alloy for the fusion application [1]. Since the hydrogen isotopes deuterium and tritium are the fuel of choice for the plasma, tritium production in the lithium is essential for the fuel cycle, hydrogen transmutations will occur due to neutron interactions in the vanadium alloy structure, and hydrogen isotopes are highly mobile in most materials at elevated temperatures; hydrogen isotope interactions with the structural material are important considerations related to both safety and performance limits for a fusion first-wall/blanket system.

The solubility of hydrogen in vanadium has been determined by several investigators including Kofstad [2], Velekis [3], Eguchi [4], Lynch [5], Peterson [6] and Bleichert [7], with good agreement. Peterson and Eguchi, have shown that the hydrogen solubility in V–Ti binary alloys increases with titanium content as one would

predict from thermodynamic data; however, their results differ significantly. Peterson, Lynch and Eguchi have also shown that the solubility of hydrogen in V–Cr binary alloys decreases with chromium content, but with varying results. Limited results have been reported on the solubility of hydrogen in V–Cr–Ti ternary alloys by Park [8,9], DeVan [10] and Zaluzhnyi [11].

This paper presents results of an investigation of the hydrogen solubility in the reference V–4Cr–4Ti alloy. The procedure employed at Argonne National Laboratory and REB Research, Inc. to accurately determine the hydrogen solubility in metals and alloys involves quantitative absorption and desorption of specimens at various hydrogen partial pressures while maintaining the system at constant temperature. This procedure avoids the difficulties in obtaining accurate data at elevated temperatures caused by rapid redistribution of the hydrogen during cooling. Results are presented for the temperature range of 400–600 °C.

2. Experimental procedure

We have used the method of hydrogen absorption and desorption into flowing helium to provide accurate measurements of the Sieverts constant for V–4Cr–4Ti. A schematic diagram of the apparatus used for the hydrogen solubility measurements is shown in Fig. 1. It is a

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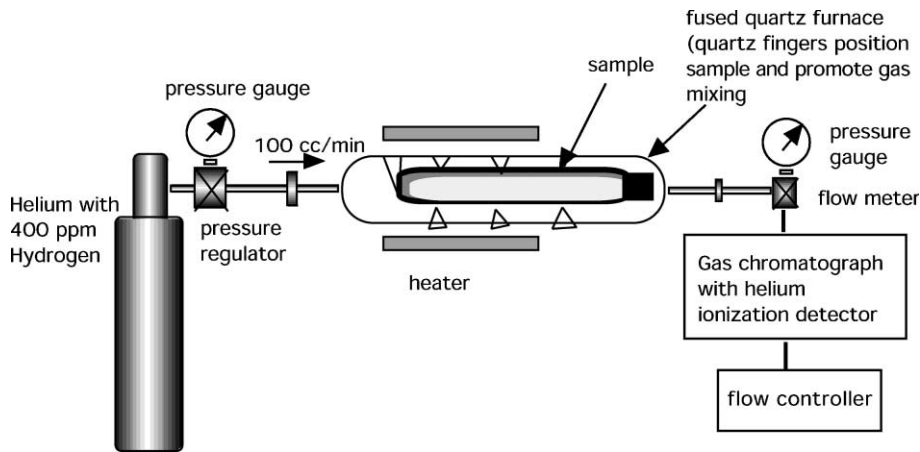*E-mail address:* dalesmith@anl.gov (D.L. Smith).

Fig. 1. Apparatus for measuring hydrogen absorption and Sieverts constants.

slightly modified version of the system used previously. The main changes have been to place the cut off valves closer to the furnace and to add a flow controller to more effectively control pressure drop instead of using the pressure regulator to determine the pressure and flow rate. This new control strategy makes the system less subject to atmospheric pressure variations. We also attached redundant thermocouple and pressure gauges to assure the reliability of the measured parameters.

The test sample of V–4Cr–4Ti for this test was fabricated from alloy heat #832665 and was annealed at 1050 °C for 2 h. In the current series of tests cylindrical specimens ($\simeq$4.75 mm dia × 100 mm long) are used. The weight of the V–4Cr–4Ti specimen was 10.0251 g, which corresponds to 0.1971 moles of metal atoms. The V-alloy rod was then coated with palladium to increase the hydrogen absorption/desorption rates and to prevent any oxidation of the vanadium from impurities in the helium gas. The weight of the specimen after coating was 10.0962 g. Assuming a uniform palladium distribution over the entire surface area, this weight gain corresponds to a coating thickness of 5.22 μm thick. The sample was then placed in the apparatus shown and exposed to flowing helium or to a helium-hydrogen mixture at a flow rate of 53.1 standard cm³ per minute. This flow rate was maintained constant within ±1%. The pressure was measured at the cylinder and again at the gas chromatograph (GC). For hydrogen–helium mixture, the measured pressure corresponded to an average pressure of 1.253 atm. The concentration of hydrogen in the gas mixture was determined by the gas supplier (BOC) to be 394 parts per million. The input hydrogen partial pressure is thus 5.001×10^{-4} bar or 50.01 Pa.

A series of runs were used to calibrate the GC to determine the peak area corresponding to a given concentration and pressure. We maintained a constant total pressure to minimize any error that might have been created during sample insertion, and also used the time of peak maximum to check that the sweep gas flow rate was constant. A low sweep gas flow rate would increase the peak area for a given hydrogen concentration and could cause errors if not detected and corrected for any difference. A decrease in the GC sweep gas rate also shows up as an increase in the peak arrival time. During these experiments, the hydrogen peak arrived at (4.5 ± 0.1) min. This variation was included in the data analysis. At normal flow conditions this concentration produced an average peak area 1 267 091 counts on the GC ± 1%.

3. Results

Before beginning the experiments, the sample was heated to 400 °C under flowing helium to degas any hydrogen it contained. A significant amount of hydrogen degassed from the sample. The helium gas was then switched off and replaced by the hydrogen–helium mixture. The peak areas were measured and plotted as shown in Fig. 2. Each data point represents one reading of the GC, which occurred every 22 min. The sample absorbed virtually every molecule of hydrogen for the first 4 h. The specimen then rapidly approaches saturation, and after 10–15 h the sample appears to be saturated with the hydrogen in helium mixture at 1.268 bar.

The rapidity of the ascent suggests that the long thin sample produced some chromatographic saturation. This behavior is exploited in later degassing experiments to get two values for the Sieverts constant from each run.

The rate of hydrogen absorption is calculated from the flow rate and the difference between the GC count area with absorption and without. This relation is shown below.
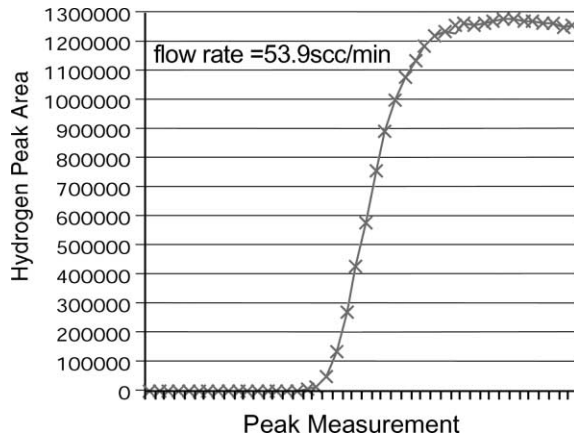
Fig. 2. Hydrogen sorption by V–4Cr–4Ti at 400 °C from He gas with 394 ppm H_2 at 1.268 bar.

H_2 absorption rate

$$= \frac{(\Delta \text{ peak area})(\text{original } H_2 \text{ conc.})(\text{gas flow rate})}{(\text{original peak area})}.$$

The total absorption is the integral of the absorption rates from the beginning of the experiment until saturation. In this way we determined that the sample absorbed 0.0004788 moles of H_2. Given the sample mass, this corresponds to a Sieverts constant of 0.2186 atom fraction/atm$^{0.5}$ at 400 °C. For the second experiment, the sample temperature was raised to 500 °C while keeping the same hydrogen and helium mixture flowing at the same pressure and flow rate. This produced the hydrogen peak areas shown in Fig. 3. The hydrogen concentration measured increased approximately four times that shown previously, which corresponds to a hydrogen partial pressure of 0.00134 bar. This corresponds to a Sieverts constant at 500 °C of 0.1098 atom fraction/atm$^{0.5}$, or approximately half that at 400 °C.

A better measure of the Sieverts constant is found from the complete data at 500 °C, particularly from the total amount of hydrogen at the end of the degassing run and the hydrogen partial pressure at this point, which is 0.00050 bar. The integral of the desorption data in Figs. 2 and 3 are combined to give 0.0002484 moles of hydrogen at this pressure, or a Sieverts constant of 0.1134 atom fraction/atm$^{0.5}$, which is in good agreement with the value obtained above. Fig. 3 also shows that the peak area after saturation at 500 °C is the same as that after saturation at 400 °C at the end of the previous experiment. This demonstrates that no baseline creep occurred, which provides increased confidence in the data. A similar procedure was followed to obtain the Sieverts constant at 600 °C (see Fig. 4). The hydrogen desorption experiment shown in Fig. 4 also serves as a check on the other sorption experiments.
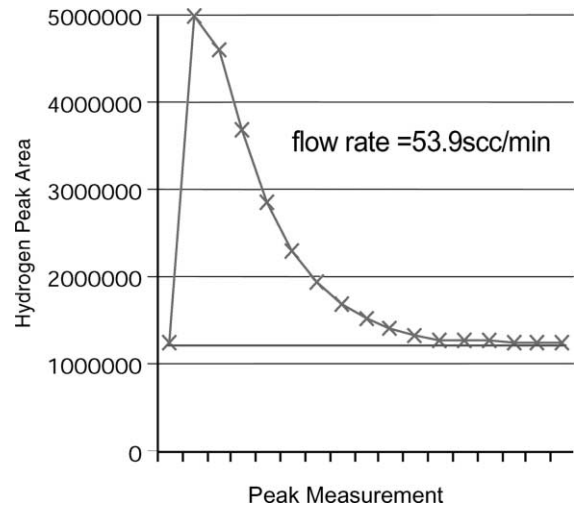

Fig. 3. Hydrogen desorption by V–4Cr–4Ti at 500 °C into He gas with 394 ppm H_2 at 1.268 bar.

The results from all these experiments are summarized in Table 1 and the Sieverts values from these experiments are plotted in Fig. 5 and given by the following equation:

$$K_s = 0.00120 \exp(3500/T)(\text{ atom fraction/atm}^{0.5}).$$

Also plotted in Fig. 5 are earlier correlations from Park et al. [9] for V–4Cr–4Ti, a revised correlation of Park's data, a correlation from Zaluzhnyi et al. [11] and an average solubility curve for unalloyed vanadium. The results from this series of experiments indicate that the solubility of hydrogen in the V–4Cr–4Ti alloy is only slightly higher, $\approx$10%, than that in unalloyed vanadium.
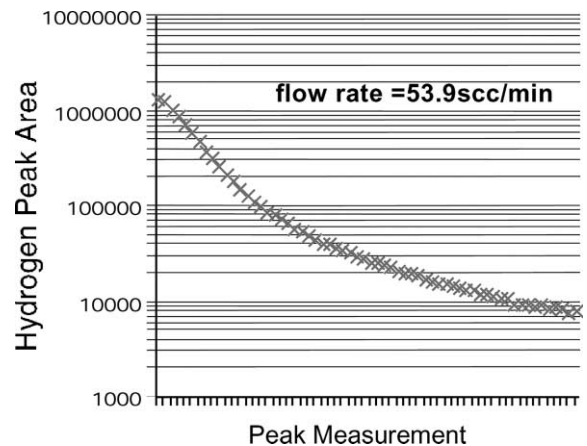

Fig. 4. Hydrogen desorption by V–4Cr–4Ti at 600 °C into He gas at 1.268 bar.

Table 1
Values of the Sieverts constant of V–4Cr–4Ti measured in these experiments (sample size = 10.0251 g)

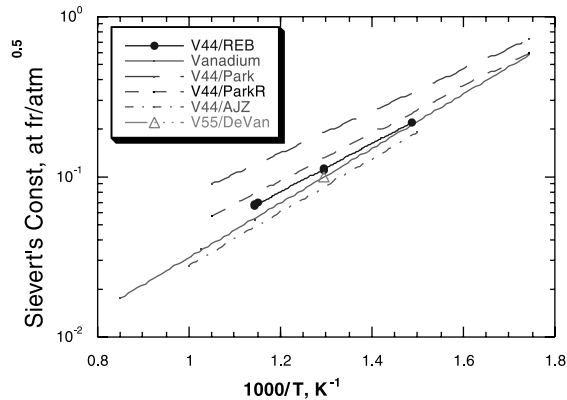| Temperature (°C)	Experiment type	H_2 in sample (mmol)	H_2 partial pressure (mbar)	Sieverts constant (atom fraction/atm$^{0.5}$)
400	Hydrogen sorption	0.479	0.494	0.219
500	Temperature spike	0.479	1.959	0.110
500	Hydrogen sorption	0.248	0.494	0.113
595	Temperature spike	0.248	1.320	0.069
600	Hydrogen sorption	0.148	0.497	0.067
600	Degassing into He	0.144	0.497	0.065

Fig. 5. Sieverts constant for V–4Cr–4Ti, atom ratio/atm$^{0.5}$.

4. Summary

A systematic investigation was conducted to provide an accurate determination of the hydrogen solubility in the V–4Cr–4Ti alloy at temperatures in the range 400–600 °C, which is of primary interest for fusion applications. Results have been obtained by the method of hydrogen absorption and desorption into flowing helium with controlled concentrations of hydrogen to provide accurate measurements of the Sieverts constants for the alloy. In the procedure used, the alloy specimen was maintained at constant temperature for each test to avoid the rapid redistribution of hydrogen that occurs during cooling down of the specimens. The results indicate that a hydrogen solubility for V–4Cr–4Ti is only slightly higher, less than 10% for temperatures of 400–600 °C, compared to the reported hydrogen solubility data for unalloyed vanadium.

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