

HYDROGEN SOLUBILITY IN VANADIUM ALLOYS AND LITHIUM ALLOYS. *

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OBJECTIVE

The objective of this program is to provide baseline solubility data for hydrogen in selected vanadium-base alloys and lithium alloys that will provide a basis for evaluating the hydrogen and tritium distribution in candidate fusion blanket systems.

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 a hydrogen solubility for V-4Cr-4Ti about 30% higher than that reported for unalloyed vanadium.

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 fusion applications. One of the key issues associated with this system relates to the development of an electrically insulating coating on the vanadium alloy channel walls to mitigate the magnetohydrodynamic (MHD) – induced pressure drop in the recirculating lithium coolant. Calcium oxide-based coatings are a leading candidate for this insulator application. Since tritium production in the lithium is essential for the fuel cycle, hydrogen transmutations will occur in the vanadium alloy structure, and hydrogen isotopes are highly mobile in most materials at elevated temperatures; tritium/hydrogen interactions are an important safety related issue and effects of hydrogen isotopes on the stability of the coating and integrity of the structure are important performance considerations for the V/Li system.

A procedure previously used at both ANL and REB Research 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 of obtaining accurate data caused by rapid redistribution of the hydrogen during cooling.

This task involves the accurate determination of hydrogen as a function of temperature and pressure in selected vanadium alloys, LiCa alloys and a SnLi alloy. Results for the vanadium alloys are important for evaluating the performance of these alloys in a fusion system, as baseline data for the distribution of hydrogen/tritium in the DHCE experiment to evaluate He effects in neutron irradiation tests, and to provide an accurate blank for the vanadium alloy capsules used for the hydrogen solubility tests for LiCa and SnLi. The effects of Ca in Li on the solubility of

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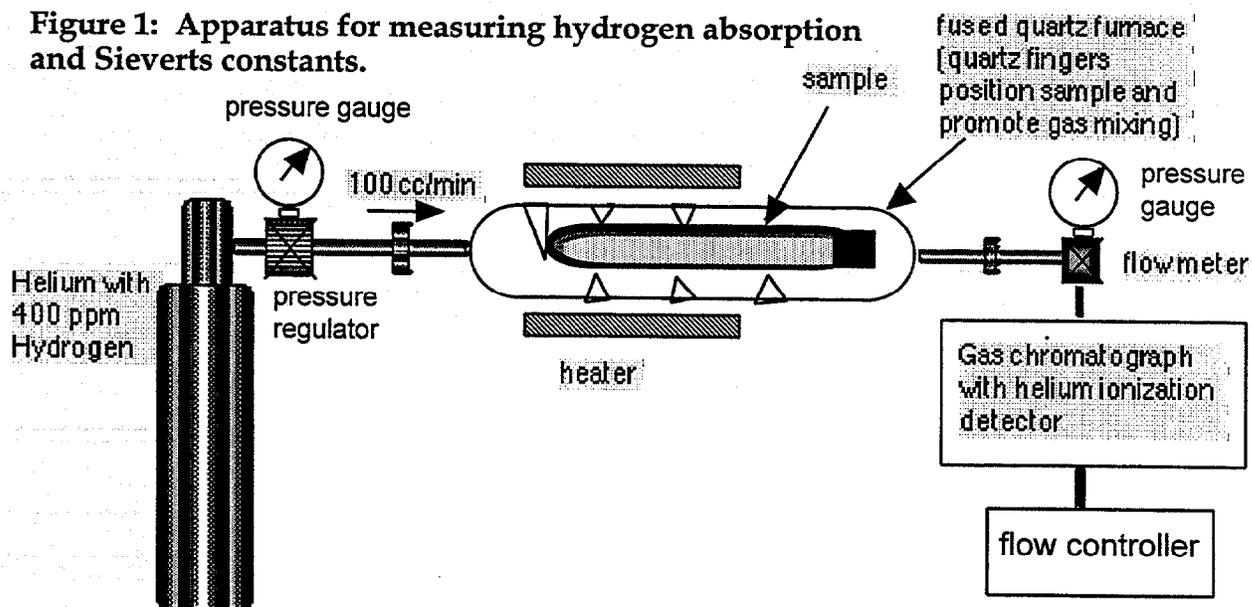
hydrogen/tritium are important to evaluate tritium inventory, tritium recovery, and the stability of the CaO coatings in lithium cooled systems. The measurements of hydrogen solubility in SnLi will provide baseline data for further evaluation of this alloy system for fusion applications.

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 slightly modified version of the system described previously [1]. 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 that we were getting the right values for these parameters.

Figure 1: Apparatus for measuring hydrogen absorption and Sieverts constants.



The test sample of V-4Cr-4Ti for this test was fabricated from alloy heat #832665 and was annealed at 1050°C for 2 hours. In the current series of tests cylindrical specimens (~4.75 mm dia x 100 mm long) are used. The weight of the V-4Cr-4Ti specimen was 10.0251 g, which corresponds to 0.1971 mols 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 microns thick. The sample was then placed in the apparatus shown and exposed to flowing helium and to a helium-hydrogen mixture at a flow rate of 53.1 standard cc's per minute. This flow rate was maintained constant within $\pm 1\%$. 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 0.000494 atmospheres or 50.01 Pascals.

A series of runs were used to calibrate the gas chromatograph 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 at a constant level. A low sweep gas flow 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 minutes ± 0.1 minute. 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 $\pm 1\%$.

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 (x) represents one reading of the gas chromatograph, which occurred every 22 minutes. The sample absorbed virtually every molecule of hydrogen for the first 4 hours. The specimen then rapidly approaches saturation, and after 10 to 15 hours the sample appears to be saturated with the hydrogen in helium mixture at 1.253 atmospheres.

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.

$$\text{H}_2 \text{ absorption rate} = \frac{(\text{peak area})(\text{original H}_2 \text{ conc.})(\text{gas flow rate})}{(\text{original peak area})}$$

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 mols H₂. Given the sample mass, this corresponds to a Sieverts' constant of 0.2186 atom ratio/atm⁵ at 400°C.

For the second experiment, we raised the sample temperature 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 4 times that shown previously, which corresponds to a hydrogen partial pressure of 0.00132 atm. This corresponds to a Sieverts' constant at 500 °C of 0.1098 atom ratio/atm⁵, 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 0.000494 atm. The integral of the desorption data in Figs. 2 and 3 are combined to give 0.0002484 mols of hydrogen at this pressure, or a Sieverts' constant of 0.1134 atom ratio/atm⁵, which is in good agreement with the value obtained above. Figure 3 also shows that the peak area after saturation at 500°C is that 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 serve as a check on the other sorption experiments.

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. [2] for V-4Cr-4Ti, a revised correlation of Park's data, a correlation from Zaluzhnyi et al. [3] and the 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, approximately 10%, than that in unalloyed vanadium.

REFERENCES

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2. J. H. Park, G. D. Ragel, R.A. Erck, D.L. Smith, and R. E. Buxbaum, US/DOE Report DOE/ER-0313/19 ,p. 59 (April 1995)
3. A. G. Zaluzhnyi et al., Fusion Engr. & Design 41 (1998) 181-185.

Table 1: Values of the Sieverts' constant of V4%Cr4%Ti measured in these experiments. Sample size = 10.0251 gms.

Temperature	Exp't type	mols H2 in sample	partial pres. H2 atmospheres	sieverts value atom ratio/atm.5
400°C	hydrogen sorption	4.788e-4	4.937e-4	2.186e-1
500°C	temperature spike	4.788e-4	1.959e-3	1.098e-1
500°C	hydrogen sorption	2.484e-4	4.937e-4	1.134e-1
595°C	temperature spike	2.484e-4	1.320e-3	6.936e-2
600°C	hydrogen sorption	1.478e-4	4.972e-4	6.723e-2
600°C	degassing into He	1.435e-4	4.972e-4	6.530e-2

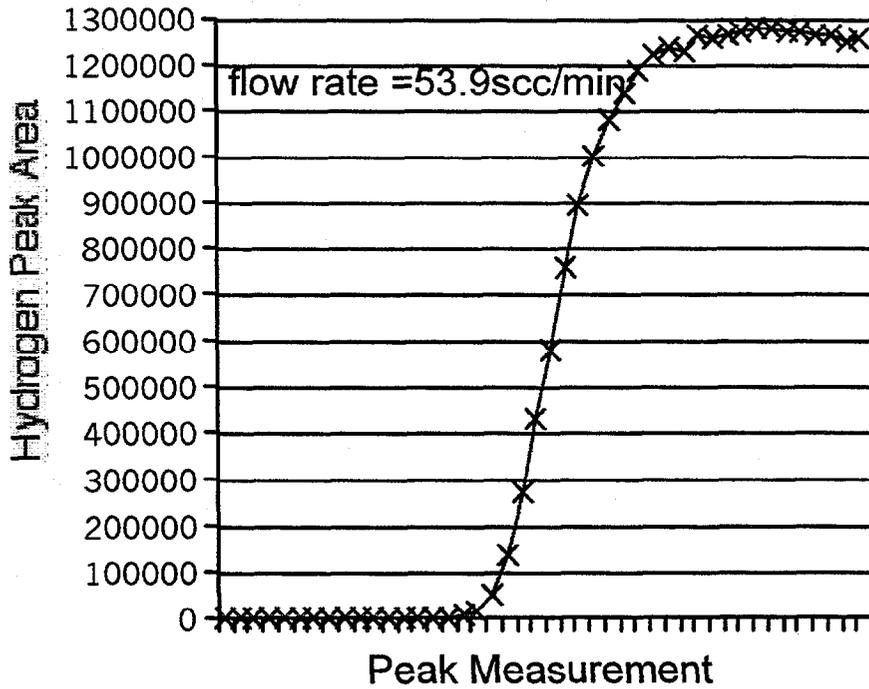


Figure 2: Hydrogen sorption by V4%Cr4%Ti at 400°C from a He, 394 ppm H2 mix at 1.253 atm.

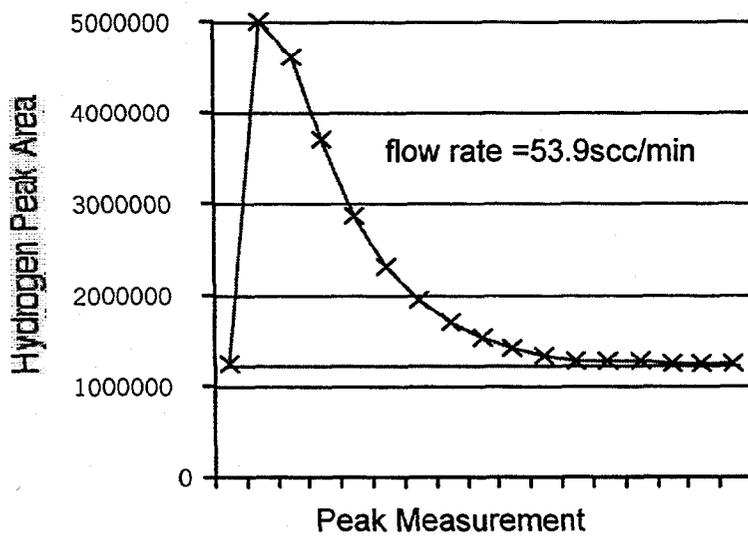


Figure 3: Hydrogen desorption by V4%Cr4%Ti at 500°C into a He, 394 ppm H2 mix at 1.253 atm.

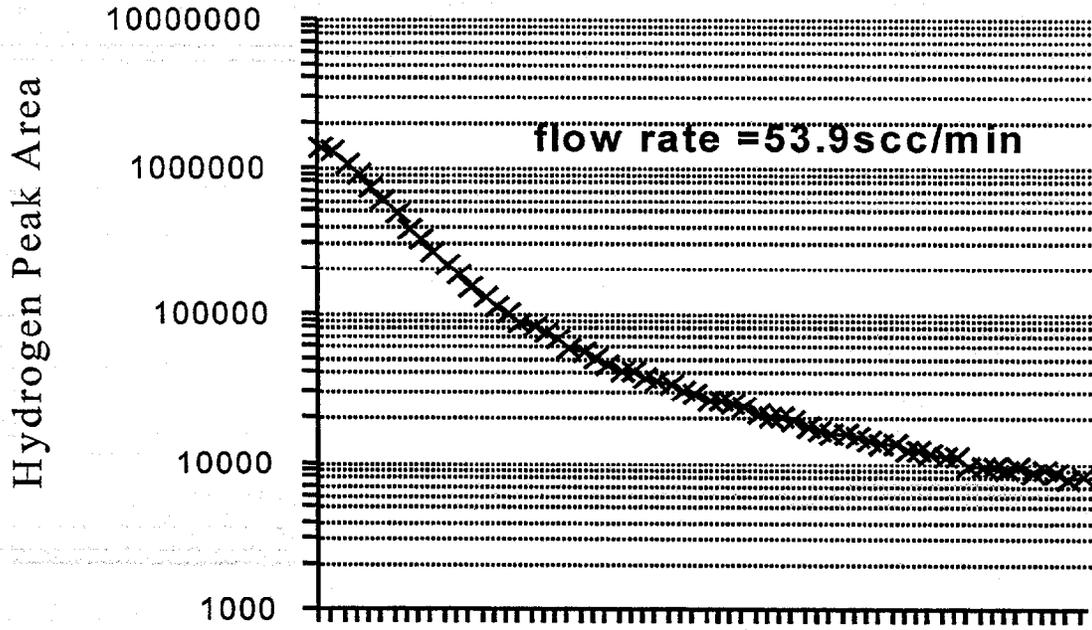


Figure 4: Hydrogen removal from V4%Cr4Ti sample at 600°C into He gas at 1.374 atm.

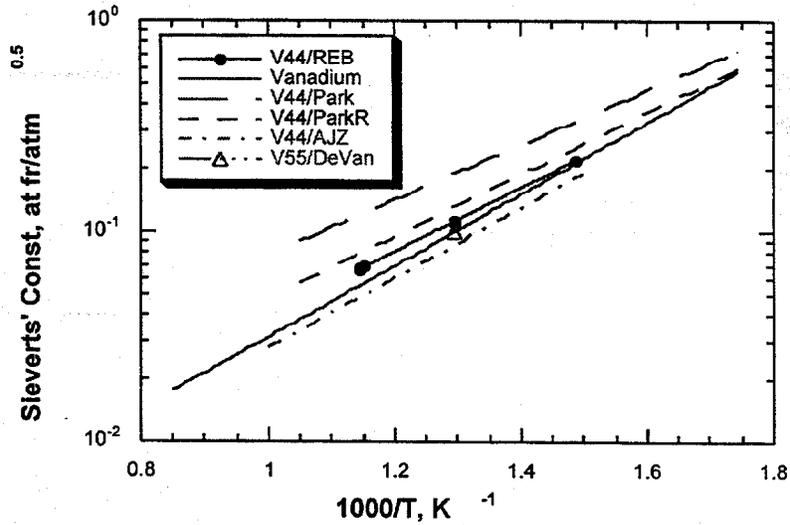


Figure 5: Sievert's Constant for V4%Cr4Ti, atom ratio/atm^{0.5}