THE THERMAL CONDUCTIVITY OF HYDROGEN DOPED HIGH PURITY VANADIUM

^S
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MASTER

M.S. Thesis Submitted to Iowa State University

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The thermal conductivity of hydrogen doped
high purity vanadium

by

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ABSTRACT

The electrical resistivity, thermal conductivity, and Seebeck coefficient of three hydrogen doped high purity vanadium rods have been measured during heating from 77 K to 300 K. Correlations are made of the anomalous effects observed in two of the samples with the temperature of transformation from a hydride in a solid solution matrix to a solid solution. An increase in electrical resistivity is observed after thermal cycling but no apparent change in transformation temperature was observed.

I. INTRODUCTION

Vanadium is a b.c.c. transition metal with important uses in ceramics, in catalysts, in steel production, and in structural material for nuclear applications.¹ Investigations of several physical properties have shown anomalous behavior in the temperature range 180 K to 320 K. Anomalies have been observed in the electrical resistivity,²⁻⁶ internal friction,^{2,7,8} thermal expansion,^{2,9} mechanical properties,^{2,10} and Seebeck coefficient.¹¹ Most of these investigations have not reported hydrogen concentration and the measurements were performed on vanadium containing large concentrations of other interstitials. Loomis and Carlson² have reported that hydrogen, by weight, is the most effective element (compared to carbon, nitrogen, and oxygen interstitials) in changing the temperature at which the anomalies occurred. The significance of O, N, and C acting as trapping sites was investigated by Chang and Wert.⁸ Chang and Wert's investigation involved correlated measurements of both electrical resistivity and internal friction studies on the same samples. They⁸ present a model for trapping in which the hydrogen solubility limit is increased by the presence of other interstitials.

The thermal conductivity of vanadium was measured by White and Woods.⁴ No anomaly was measured and no thermal conductivity maximum was observed as the sample was of intermediate purity with a RRR = 5.1.

Mackintosh and Sill¹¹ measured the Seebeck coefficient of vanadium and found a temperature hysteresis and an anomaly at 217 K as the sample

was heated. They discounted magnetic ordering and suggested an ordering of gaseous interstitials. Analysis was not reported for the sample measured but the residual resistivity ratio was reported at approximately 30. They suggested measurements be made on purer samples as they became available.

Measurements by Jung¹² on high purity vanadium of residual resistivity ratio = 1450 and concentration of O+N+C less than 15 wt ppm showed no anomalous behavior in the Seebeck coefficient, electrical resistivity, or thermal conductivity. Hydrogen concentration was less than 1 wt ppm.

While Jung has shown that high purity vanadium shows no anomalous behavior in electrical transport properties, his research did not show that anomalous behavior in the Seebeck coefficient was due to hydrogen. The present research attempts to show that hydrogen in high purity vanadium can cause anomalous behavior in the Seebeck coefficient and thermal conductivity as well as in the already observed electrical resistivity.^{6,8}

The low temperature phase equilibria of the vanadium-hydrogen system has been determined by resistometric methods,^{6,8} internal friction measurements,^{7,8} and electron and optical microscopy.^{10,13,14} The solvus curve of vanadium-hydrogen as determined from two different specimens containing different concentrations of interstitials is shown in Fig. 1 while the solubility limit is shown in Fig. 2. Above the solvus temperature the hydrogen is in an α solid solution in the b.c.c. vanadium. Below the solvus line a β hydride precipitates in the matrix. The solvus curve determined by Westlake⁶ is in agreement with deter-

minations of others¹⁰ and is typical of a sample with a concentration of 400 wt ppm O+N+C. The upper curve corresponds to a purer specimen such as found in this work. The solvus temperature was defined as the temperature at which anomalous behavior was initiated.

The theory for electrical resistivity, thermal conductivity, and Seebeck coefficient in metals, and particularly in transition metals have been reviewed by Wilson,¹⁵ Sondheimer,¹⁶ Bailyn,¹⁷ and Klemens.¹⁸ The theory is not accurate at intermediate temperatures of 77 K to 300 K, because vanadium has a Debye temperature of about 380 K. The situation is further complicated by the existence of a two phase material (the β hydride is scattered in the α matrix). As seen from the thermal conductivity and Seebeck coefficient plots (Figures 6 and 7), the temperature region investigated is in a region adjacent to the thermal conductivity maximum and the Seebeck phonon drag hump. This is a region where Umklapp processes are important and have to be included in the theory.¹⁸ No attempt was made in this research to fit the data to theory or to a polynomial expansion.

Figure 1. The displacement of the solvus line as the O+N+C interstitial concentration is varied. Top line is also the solvus for samples in this research. Bottom line corresponds to a 400 wt ppm O+N+C concentration.

Figure 2. Log of the solubility limit versus the reciprocal temperature.

II. EXPERIMENTAL PROCEDURE

A. Sample Preparation

The three vanadium specimens measured in this research were electro-transported rods¹⁹ prepared at the Ames Laboratory by Rick Schmidt. The initial interstitial impurities of the three specimens were estimated from the correlation of residual resistivity ratio (RRR) with the analyzed purity of similar specimens, and were found to be approximately 15 wt ppm O+N+C with less than 1 wt ppm hydrogen.

Prior to charging with hydrogen, the vanadium samples were electro-polished in a 94%-6% methanol-perchloric acid solution for one-half minute to remove surface contamination, in particular, an oxide layer that would inhibit entrance of hydrogen into the sample. After electropolishing, the vanadium was placed in a 304 stainless boat inside a 304 stainless vacuum furnace. The furnace was evacuated by a mechanical pump until the operational pressure of a carbon vane molecular pump was reached. The chamber was pumped on overnight by the molecular pump to a pressure of 10^{-7} Torr. The furnace was then turned on and heated to 1000°C in approximately one and one-fourth hours. The furnace was then cooled to 800°C and a measured pressure of purified hydrogen gas was admitted to the fixed volume of the sample chamber. The source of hydrogen was from thermal decomposition of UH_3 . The system and technique has been used before to load hydrogen in vanadium.¹⁰

The time that the sample was hot and vulnerable to interstitial pickup and diffusion was approximately two hours. Estimated interstitial

pickup for the time and temperature at which the sample was loaded was calculated from sticking coefficient data.²⁰ Less than 10 wt ppm was predicted. A long, high temperature anneal was not used as this would increase the impurity concentration.

The effects of preparation techniques on vanadium have been investigated by Westlake²¹ and Lang and Bressers²² who suggest that exposure of the samples to air after purification will result in surface contamination diffusing into the sample at high temperatures. In this research, equipment was not available to load hydrogen without exposing the samples to room pressure before loading. Sample characteristics and interstitial concentrations are shown in Table 1. Analysis for O, N, and H were performed by vacuum fusion. Carbon analysis was accomplished by a combustion technique.

Table 1. Sample characteristics

Sample	Length (cm)	Diameter (cm)	Impurity Concentrations (wt ppm)				
			H	O	N	C	O+N+C
VH330	4.3	0.230	330	140	10	15	165
VH260	3.92	0.244	260	60	3	18	81
VH54	2.9	0.242	54	27	1	11	39
VH1	3.65	0.205	<1	-	-	-	15

Sample VH1 was measured by Jung.¹² Although his specimen contains less O, N, and C than those measured in this research, a specimen containing 157 wt ppm O+N+C was measured by Jung that did not differ from VH1 above 130 K.

B. Measurement Techniques

The electrical conductivity, thermal conductivity, and Seebeck coefficient were measured in the same apparatus with identical probe separation for both thermal and voltage measurements. The electrical and thermal conductivity were measured by a four probe method with both measurements in the longitudinal direction. Since simultaneous measurements of the electrical conductivity and thermal conductivity are not compatible, separate runs were made. A #26 copper wire was added between the gradient heater and stainless steel shield during electrical resistivity measurements to serve as one current lead. No thermal gradient was allowed for electrical resistivity measurements and no net current flow was permitted for thermal measurements. The Seebeck coefficient and thermal conductivity were measured during the same run.

The Seebeck coefficient was measured by measuring the Seebeck voltage of the vanadium relative to the Seebeck probe leads. The Seebeck coefficient of the copper probe leads had been determined previously by calibration against a lead sample using the data of Christian *et al.*²³ Measurement of the Seebeck voltage of the thermal gradient thermocouple and the Seebeck voltage of the sample included thermal

offsets due to the connecting leads. Since the ends of the leads were thermally anchored to copper blocks at room temperature and at the refrigerant bath temperature, the offsets should not have changed when a thermal gradient was established in or removed from the sample. The observed sample voltage with no gradient was subtracted from the observed sample voltage with a gradient established. The effects of thermal emfs when making resistance measurements were reduced by measuring emfs with the current in the forward and reversed direction.

The electrical resistivity, thermal conductivity, and Seebeck coefficient were calculated in the following manner, where I is the electrical current, Q the heat current, and V the observed voltage between probes. The temperature of the upper thermocouple clamp is T while the temperature of the bottom clamp is $T+\Delta T$. The probes are a distance L apart.

The electrical resistivity when $\Delta T=0$ is

$$\rho(T) = \frac{A}{L} \cdot \frac{V}{I} \quad (1)$$

If the thermal conductivity $\lambda(T)$ is approximated to first order for a small region about T by

$$\lambda(T) = B+CT \quad ,$$

then

$$Q = \frac{A}{L} \int_T^{T+\Delta T} \lambda(T') dT' \quad (3a)$$

$$= \frac{A}{L} \left[BT' + \frac{C(T')^2}{2} \right]_T^{T+\Delta T} \quad (3b)$$

$$= \frac{A}{L} \left[B + C\left(\frac{\Delta T}{2} + T\right) \right] \Delta T \quad (3c)$$

$$= \frac{A}{L} \left[\lambda\left(T + \frac{\Delta T}{2}\right) \right] \Delta T . \quad (3d)$$

So that for small ΔT and no net electric current, neglecting electric fields,

$$\lambda\left(T + \frac{\Delta T}{2}\right) = \frac{L}{A} \frac{Q}{\Delta T} . \quad (4)$$

A similar expression for the sample Seebeck coefficient $S(T)$ can be obtained to reduce the following expression for the measured voltage V , where $S_c(T)$ is the Seebeck coefficient of the copper probe leads. The measured Seebeck voltage V is then

$$V = \int_T^{T+\Delta T} S_c(T') dT' - \int_T^{T+\Delta T} S(T') dT' \quad (5a)$$

$$= \int_T^{T+\Delta T} S_c(T') dT' - \Delta T S\left(T + \frac{1}{2}\Delta T\right) . \quad (5b)$$

Reducing to

$$S\left(T + \frac{1}{2}\Delta T\right) = \frac{1}{\Delta T} \int_T^{T+\Delta T} S_c(T') dT' - \frac{V}{\Delta T} . \quad (6)$$

The last integral is easily evaluated since $S_c(T)$ has been fit to a ninth degree polynomial between 77 K and 316 K.

The quantity L/A or the form factor is needed in order to compute the electrical and thermal conductivity. With the sample mounted in the thermal conductivity holder the probe separation L cannot be visually measured due to the stainless steel radiation shield surrounding the sample. The separation L was measured indirectly by measuring the sample resistivity in a form factor holder that permitted the sample to be removed with voltage probes attached to the sample. The sample diameter and the distance between voltage probes of the form factor holder were measured by a traveling microscope. If the resistivity is constant for a given temperature, then the probe separation in the thermal conductivity holder can be determined from the resistance between probes in the thermal conductivity holder and the sample cross sectional area A . The resistance in the form factor holder and in the thermal conductivity holder were measured after the sample had been cooled to 77 K and warmed back to the triple point of water. The resistance was also measured at 296 K in a water bath since it was possible that the resistivity could have an anomaly at either temperature.

The initial cooling rate from 300 K was 40 K per hour. Approximately 30 hours were required to reach liquid nitrogen temperature. The sample was heated at 3 K per hour. All measurements in this research were taken as the sample was being warmed in order to avoid possible supercooling. A uniform and standard procedure was adopted for measuring electrical resistivity and thermal properties. The cryostat was only

filled when the sample temperature was being raised. Two hours elapsed after the temperature was changed, before an electrical resistivity measurement was made or an initial reading of thermal offsets for thermal conductivity was recorded. Before the final reading of a data point, two and one-half hours were allowed for a steady state condition to be established after a thermal gradient was applied.

C. Apparatus

The apparatus used in this research was built and calibrated by Jung to measure the transport properties of high purity vanadium.¹² The apparatus is shown in Fig. 3 and in Fig. 4. An important feature of this apparatus is the thermal shielding employed. Three radiation shields are used to minimize heat leaks by radiation. At high temperatures radiation loss can be dominant because of the T^4 radiation law.

The stainless steel shield surrounding the sample is wound with a heater at the lower end. If the thermoconductivity of the shield has the same temperature dependence as the sample, then the adjacent surfaces of the shield and sample will be at the same temperature when the temperature of the shield heater is matched to the temperature of the gradient heater by a controller. Thermal conduction in the wire leads is reduced by thermally anchoring the sample leads to the stainless steel shield. The temperature gradient in the wires is then greatly reduced. Conduction by gas is reduced by maintaining a pressure lower than 10^{-6} Torr with an oil diffusion pump.

Figure 3. Block diagram of the apparatus used in this research.

Figure 4. Diagram of thermal conductivity holder.

The ambient temperature of the upper thermocouple clamp was measured by a Au-0.03% Fe vs chromel differential thermocouple referenced to the liquid nitrogen bath. Sample temperature gradient was also measured by a Au-0.03% Fe vs chromel differential thermocouple with junctions at the bottom and top clamp. Sample voltage connections were made with #40 copper wire. The thermocouple and voltage leads were thermally anchored at the bath temperature before leaving the sample holder.

Calibration of the ambient temperature thermocouple (upper clamp) was performed by measurement of the thermocouples emf as a function of the bath temperature and the temperature of the clamp. The nitrogen bath temperature was calculated using the data of Corruccini,²⁴ as a function of the bath vapor pressure. The temperature of the clamp was measured by a platinum resistance thermometer. A function was derived by least squares to describe the ambient temperature.

The sample gradient thermocouple was not directly calibrated, but was calculated from the polynomial fit of the ambient thermocouple. Jung has discussed the fitting of the thermocouples and an analysis of the temperature errors is given.¹²

Prior to the measurement of hydrogen doped sample, the electrical resistivity, thermal conductivity, and Seebeck coefficient of SRM 34 electrolytic iron were measured. As the measurements were indistinguishable from Jung's measurements of the sample,¹² Jung's calibration was used.

III. RESULTS

A. Electrical Resistivity

The electrical resistivities of the vanadium samples are plotted in Fig. 5. An increase in resistivity in samples containing a greater concentration of hydrogen than present in VH1 is observed above 190 K. Abrupt changes in slope occur for samples VH54 and VH260 occur at temperatures that correspond to the solvus temperature for the given concentration of hydrogen. The temperatures observed for formation of a hydride are 272 K for sample VH260 and 230 K for VH54.

The shape and behavior of the resistivities are found to be in agreement with previous work by Westlake⁶ and by Chang and Wert.⁸ Transition temperatures correspond to the solvus curve of Chang and Wert but not to the curve of Westlake as reproduced in Fig. 1.

Samples were thermally cycled from 300 K to 77 K several times. A resistivity increase of a maximum of 0.3% was observed. No thermal cycling effects have been reported previously of the resistivity of vanadium. Westlake has reported a similar thermal cycling effect for niobium-hydrogen alloys.²⁵

B. Thermal Conductivity

Thermal conductivity of six samples of vanadium are plotted in Fig. 6. The three samples labelled VH1 show the relative shift of measured conductivity for samples of varying interstitial concentrations. The measurements of VH1 are those of Jung.¹² A discontinuity in slope

Figure 5. Temperature dependence of the electrical resistivity of the three hydrogen doped samples compared to a sample containing less than 1 wt ppm hydrogen (VH1). The solvus temperature of VH330 is above 300 K.

Figure 6. The temperature dependence of the thermal conductivity. The thermal conductivity of vanadium samples containing less than one wt ppm hydrogen, with different O+N+C concentrations is also shown. Note that thermal conductivity is larger as hydrogen concentration is increased.

is observed in VH260 at 272 K, and a possible discontinuity is observed in VH54 at 230 K, but the magnitude is within the scatter of the data. A minimum is observed in all plots at approximately 190 K.

C. Seebeck Coefficient

The Seebeck coefficient is plotted versus temperature in Fig. 7 and the data is replotted again in Fig. 8 as the product of Seebeck coefficient and temperature versus temperature. No special significance is implied by plotting $T\alpha(T)$ vs T other than emphasizing the change in the Seebeck coefficient at 230 K for VH54 and at approximately 270 K for VH260.

The position and magnitude of the anomaly observed by Mackintosh and Sill¹¹ is reproduced for comparison. Mackintosh and Sill reported that the Seebeck coefficient was positive in the temperature range 77 K to 300 K, in contrast to the negative Seebeck coefficient measured above 240 K in this research.

Figure 7. Temperature dependence of the Seebeck coefficient. The increase in the Seebeck coefficient below 200 K is proportional to the hydrogen concentration indicating that the phonon drag term may be greater than the diffusion term.

Figure 8. Product of the Seebeck coefficient and temperature versus temperature. Data is plotted in this manner to make transition apparent.

IV. CONCLUSION

Anomalous behavior has been observed in electrical resistivity and Seebeck coefficient of vanadium. Anomalies in the electrical resistivity have been shown by Westlake⁶ and by Chang and Wert⁸ to be caused by hydrogen. The electrical resistivity, thermal conductivity, and Seebeck coefficient of high purity, hydrogen free vanadium has been shown by Jung to have no anomalous behavior. We have shown that for a given hydrogen concentration, the anomalies in the electrical, thermal conductivity, and Seebeck coefficient will occur at the same temperature, the solvus temperature.

Comparison of the thermal conductivity with the electrical resistivity at the same temperature is accomplished by sight since the electrical resistivity of a particular sample is nearly identical to another from 77 K to 200 K. In this research the probe spacing was identical for electrical resistivity and thermal conductivity measurements so that the two measurements relative to each other are independent of geometry. The larger thermal conductivity observed for samples containing more hydrogen is indicative that electronic relaxation times may differ for electrical conductivity and thermal conductivity or perhaps the lattice thermal conductivity is larger. The latter is supported by the increased Seebeck coefficient below 200 K. The increase in lattice thermal conductivity would make the phonon drag term of the Seebeck coefficient larger relative to the diffusion term.

V. LITERATURE CITED

1. C. R. Hammond, in Handbook of Chemistry and Physics, edited by R. C. Weast (Chemical Rubber Co., Cleveland, Ohio, 1973).
2. B. A. Loomis and O. N. Carlson, in Reactive Metals 2, edited by W. R. Clough (New York: Interscience Publishers, 1958), p. 227.
3. W. Rostoker and A. S. Yamamoto, Trans. Am. Soc. Metals 47, 1002 (1955).
4. G. K. White and S. B. Woods, Phil. Trans. R. Soc. 251, 273 (1959).
5. J. P. Burger and M. A. Taylor, Phys. Rev. Lett. 6, 185 (1961).
6. D. G. Westlake, Trans. TMS-AIME 239, 1341 (1967).
7. G. Cannelli and F. M. Mazzolai, Appl. Phys. 1, 111 (1973).
8. H. Y. Chang and C. A. Wert, Acta Met. 21, 1233 (1973).
9. H. Suzuki and S. Miyahana, J. Phys. Soc. Japan 21, 2735 (1966).
10. D. H. Sherman, C. V. Owen, and T. E. Scott, Trans. TMS-AIME 242, 1775 (1968).
11. A. R. Mackintosh and L. Sill, J. Phys. Chem. Solids 24, 501 (1962).
12. W. D. Jung, Ph.D. thesis, Iowa State University, 1975 (unpublished).
13. T. Chiba and S. Takano, J. Phys. Soc. Japan 31, 1113 (1971).
14. S. Takano and T. Suzuki, Acta Met. 22, 265 (1974).
15. A. H. Wilson, The Theory of Metals, (Cambridge University Press, London, 1953).
16. E. H. Sondheimer, Proc. Roy. Soc. A 203, 75 (1956).
17. M. Bailyn, Phil. Mag. 5, 1059 (1960).
18. P. G. Klemens, in Thermal Conductivity, edited by R. D. Tye, (Academic Press, New York, 1969), Vol. 1, p. 1.
19. O. N. Carlson, F. A. Schmidt, and D. G. Alexander, Met. Trans. 3, 1249 (1972).

20. R. C. Svedberg, J. Vac. Sci. Tech. 8, VM41 (1971).
21. D. G. Westlake, Phil. Mag. 16, 905 (1967).
22. E. Lang and J. Bressers, Z. Metallkde. 67, 66 (1976).
23. J. W. Christian, J. P. Jan, W. B. Pearson, and I. M. Templeton, Proc. Roy. Soc. A 245, 213 (1958).
24. R. J. Corruccini, Chem. Eng. Prog. 53, 262 (1967).
25. D. G. Westlake, Trans. TMS-AIME 245, 287 (1969).

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