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THE SOLUBILITY OF HYDROGEN IN TANTALUM

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THE SOLUBILITY OF HYDROGEN IN TANTALUM

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The solubility of hydrogen in tantalum in equilibrium with the hydride has been measured by a resistometric technique. Alloys ranged in composition from 0.5 to 10 at.% H. The solvus line is given by the equation $\ln C = 6.0 - 2150/RT$. The heat of solution of 2150 cal/mole is lower than that for Nb (2750 cal/mole) and V (3900 cal/mole). Ternary Ta-O-H alloys (containing 0.6 at.% oxygen in solid solution) had a solvus line for hydrogen no different from the Ta-H binary system, a behavior similar to that of the Nb-H system. The Ta-D solvus is closely the same as that for hydrogen in tantalum. Thermal cycling up and down through the solvus temperature increases the "apparent" solvus temperature slightly (a few °K). A thermal hysteresis occurs on cooling and heating, a hysteresis explained in terms of mechanical constraint of the matrix on the nucleation and growth of the precipitate. Growth of the hydrides depends on long-range diffusion. Trapping of hydrogen by oxygen is believed to be responsible for low diffusivities and the long times needed to achieve equilibrium. The contribution of hydrogen and deuterium in solid solution to the residual resistivity of tantalum is $0.51 \mu\Omega \text{ cm per at.}\%$, a value lower than that for either vanadium and niobium.

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INTRODUCTION

Alloys of hydrogen in the metals have been extensively investigated in recent years not only because of their technological importance, but also because of their intellectual interest. Some of the metals absorb a relatively small amount of hydrogen and do not form hydrides; among these are copper, nickel, gold, silver, and iron. Other metals of structural importance such as vanadium, niobium, tantalum, and titanium have large solubility for hydrogen in the solid state and readily form hydrides at low temperature. For some of these systems, the solubility has been determined rather conclusively, but for others, considerable discrepancy exists between various studies. The Ta-H system is one showing great variability, so this study was undertaken to examine these differences. After a brief introduction into the general features of the bcc systems with hydrogen, a more detailed statement will be made about the goals of the work.

The Ta-H Alloy System

The general features of the tantalum-hydrogen system at low temperatures have been worked out by Ducastelle, Caudron, and Costa using x-ray and resistivity measurements.¹ The phase diagram which they draw is shown in Figure 1. Above 300°K an α solid solution exists in which hydrogen is soluble

nearly to a 1/1 ratio. Below that temperature the phase diagram is controlled by the β phase, Ta_2H , which exists over a reasonably wide temperature range below room temperature. The low-composition side of the β phase was first worked out by Waite, Wallace, and Craig much earlier;² their work is in reasonably good accord with the later work shown in Figure 1. In addition, Waite et al. had determined the solvus line showing equilibrium between the α phase and the β phase below room temperature using specific heat measurements. Other investigators, using a variety of physical measurements also made determinations of the solvus line. Measurements of anomalies in the heat capacity curve were used by Kelley.³ An internal friction effect which occurs with the formation of hydrides during cooling was used by Cannelli and Mazzolai.⁴ A magnetic resonance technique using the proton resonance was used by Pedersen, Krogdahl, and Stokkeland.⁵ Optical observations of hydride precipitation and dissolution were used by Owen and Scott.⁶ They also used a macroscopic shape change related to hydride precipitation -- a technique they termed the "Poynting Method." Recently other observations based on resistivity methods were published by Matsuyama, Dohi and Hisano.⁷ Finally, a thermo-chemical method was used by Veleckis and Edwards.⁸ Many of these results show good self-consistency, but some are at wide variance with others. Many

of the data just described are plotted in Figure 2. The wide variation of the reported solvus lines is evident. One of the goals of the present work was to examine this solvus line in detail using electrical resistivity measurements and taking great precautions to ascertain that the system was in reasonable equilibrium at all times.

The V-H Alloy System

Alloys of hydrogen with vanadium have been examined much more extensively than the tantalum hydrogen system. The phase diagram is also controlled at low temperatures by a hydride V_2H . Again, the metal absorbs a large concentration of hydrogen at high temperatures, and the solid solution is in equilibrium with the hydride at lower temperatures. The solvus line has also been investigated extensively by a number of experimental techniques. Electrical resistivity measurements were used by Westlake⁹ and by Chang.¹⁰ An internal friction technique was used by Chang and Wert,¹¹ by Owen and Scott,⁶ and by Cannelli and Mazzolai.¹² Owen and Scott also used their "Poynting" method and visual observations. All of these results are in fairly good agreement, as the data in Figure 3 show, but some systematic differences clearly exist. These differences were shown by Chang and Wert probably to be caused by differences in oxygen concentration of alloys used by the various investigators.¹¹

A systematic study of the role of oxygen, nitrogen, and carbon on the solvus line for hydrogen in vanadium was a part of the study of Chang and Wert. Their results for oxygen-doped material are summarized in Figure 4, together with some of the results of the other investigators. A quantitative thermodynamic analysis was given by Chang and Wert based on the supposition that clusters of hydrogen with individual oxygen, nitrogen, or carbon atoms affect the equilibrium between the α phase and the hydride V_2H . Their analysis showed that the most predominant clusters for carbon and nitrogen were the pairs C-H and N-H, but that higher order clusters of composition around $O-H^3$ were the most common for specimens containing oxygen. Whether this interpretation is precisely correct, there is no doubt that the presence of the immobile interstitials such as oxygen, nitrogen, and carbon can greatly affect the observed solvus temperature.

The Nb-H System

Alloys of hydrogen with niobium also show large solubility above room temperature. For this system, however, the equilibrium of the α solid solution is not with the type of hydride found in tantalum and vanadium. Rather in this case, the hydride is the monohydride NbH. The solvus line has been investigated by many experimenters. X-ray diffraction and thermo-

analysis were employed by Walter and Chandler to study many aspects of the phase diagram.¹³ Internal friction methods have been used by Thompson, Buck and Wert,¹⁴ and by Baker and Birnbaum.¹⁵ Electrical resistivity measurements were used by Westlake,¹⁶ by Westlake and Ockers,¹⁷ and by Holmquist¹⁸ to study the low temperature part of the solvus line. These results are only in fair agreement with each other and the origin of the discrepancies which exist are not well understood. Although the different experimenters undoubtedly had different levels of oxygen impurity, no systematic features have been identified which show that the equilibrium between the α and β phases is affected by the presence of oxygen. In fact, the data of Westlake¹⁶ and of Westlake and Ockers,¹⁷ shown in Figure 5, tend to prove that oxygen has no effect on the solvus line.

One of the striking features of the Nb-H system is the hysteresis which accompanies cooling and heating through the temperature region around the solvus temperature for a given composition. A typical example of this hysteresis is shown from the thesis of Holmquist, see Figure 6. During the first cooling, precipitation starts at temperature $T_1(1)$, and the hydride begins to redissolve at a temperature $T_2(1)$ on heating. Heating and cooling curves coincide only at higher temperatures greater than some temperature T_3 . During successive thermal cycles, Holmquist¹⁸ found that the hysteresis loop tended to close somewhat, but some hysteresis always remained. Similar

hysteresis effects were observed by Westlake¹⁶ for this system; Westlake has found that extremely slow cooling rates are required, especially for low hydrogen concentrations, to ensure that reasonable thermal equilibrium is achieved at all temperatures. Suppositions about the origin of this thermo-hysteresis will be described in a later paragraph.

Summary of the Ta-H, the V-H and the Nb-H Observations

The observations described for these three alloy systems show several major features. First, a wide variety of experimental methods can be used to detect the onset of precipitation during cooling of a solid solution. These results give generally fair agreement with each other, but differences between different investigators are far outside the internal consistency of individual studies. These may be due to unknown differences in the chemistry of the alloys, to the effects of unknown quantities of impurities, or to the lack of establishment of thermal equilibrium in individual cases.

The second striking effect is the existence of large hysteresis between observations made during cooling and heating through the solvus temperature. Vanadium shows almost no hysteresis, but both niobium and tantalum are found to exhibit this effect. Its explanation has generally been thought to lie in the large amount of internal plastic deformation which accompanies the formation of hydrides in these metals. The

metal hydride is about 10% less dense than the metal matrix and part of the resulting strain is taken up by generation of dislocations in the matrix when the hydride precipitates form. These dislocations have been strikingly observed by Schober¹⁹ in niobium during precipitation of fine scale hydrides at low temperatures and by Chang¹⁰ in precipitation of huge plates of vanadium hydrides at much higher concentrations near room temperature. These dislocations have also been observed in the titanium-hydrogen system by Paton, Hickman, and Leslie.²⁰

A theory to explain the effects of the surrounding matrix on a hydride plate which nucleates and grows has been proposed by Paton et al. They proposed that the normal free energy change which would accompany the formation of massive unrestrained hydrides is modified by elastic and plastic contributions to the enthalpies. The hysteresis of the cooling and heating cycle could be explained on the inability of the system to reabsorb all of the dislocations punched out by the precipitates as they form upon cooling. Paton and co-workers initially developed this theory to explain large changes in apparent solubility of hydrogen in titanium which accompanied the addition of aluminum. They proposed that the aluminum modified the ability of the hydrides to punch out dislocations and thus modified the apparent solvus temperature. The same argument could apply to the systems with tantalum, vanadium, or niobium if alloy elements such as oxygen, carbon, or nitrogen

commonly found in these systems were also to alter the ability of the matrix to resist plastic deformation. No detailed theory of this effect has yet been published for the systems, however.

The role of the immobile interstitials such as oxygen may indeed simply be to strengthen the matrix, but the ability of interstitials to form immobile clusters and thus alter the thermodynamic equilibrium is an attractive possibility. The existence of clusters of N-H and O-H as well as H-H pairs in niobium has been amply demonstrated by Baker and Birnbaum.¹⁵ They found that hydrogen could presumably not exist as single H atoms as long as oxygen or nitrogen atoms were around to trap them; the binding energy of 0.1 ev measured for these systems is much larger than kT at low temperatures and thermodynamic equilibrium would be much in favor of formation of clusters until the oxygen or nitrogen atoms were saturated. Since the enthalpies of solution of the hydrides are also around 0.1 to 0.2 ev, the thermodynamic balance is a very delicate one; and, the determination of the probable role of oxygen, nitrogen, or carbon is not an easy one. At the very least, it is clear that this trapping is strong enough to alter appreciably the diffusion rate of hydrogen; hence, extremely slow cooling and heating rates are required to ensure the establishment of equilibrium at all temperatures. The possibility that hydrogen could be trapped by lattice defects

has also been pointed out by Oriani in his analysis of data on diffusion of hydrogen in iron and steel.²¹

The present investigation also had the goal of determining the solvus line in tantalum which had been degassed of nitrogen and oxygen. In particular, the role of oxygen in affecting the equilibrium solvus line and the rate of approach to equilibrium was to be studied in detail.

The Metal-Deuterium Systems

Inconsistencies exist between the several metals concerning the effect of differences in isotopic mass on the phase equilibrium. In vanadium, the solvus line for deuterium has been determined by Westlake and Ockers²² using resistivity methods and by Cannelli and Mazzolai²³ using internal friction techniques. The results of these two investigations agree quite well and show that deuterium is about twice as soluble as hydrogen in vanadium at a given temperature, although the heat of solutions is roughly the same. In niobium, Holmquist¹⁸ and Westlake and Ockers¹⁷ have found no isotope effect upon addition of hydrogen and of deuterium to that metal, Figure 5. The two reported measurements for tantalum are conflicting. Pryde and Tsong have found no isotope effect on the solvus in tantalum from equilibrium pressure and electrical resistance measurements.²⁴ On the other hand, Cannelli and Cantelli²⁵ have found, for lower concentrations, a distinct difference in the

solvus between hydrogen and deuterium using internal friction measurements, Figure 7. Again, they found deuterium to be more soluble than hydrogen. An additional goal of the present investigation was to verify the one or the other of these observations.

Summary

This investigation thus had the following goals:

1. To establish the solubility limit in oxygen-free tantalum as a function of temperature.
2. To investigate the general features of hysteresis of hydride formation and dissolution in this system.
3. To investigate the effect of oxygen on the solvus line.
4. To ascertain whether or not the Ta-H solvus is the same as that for Ta-D.

EXPERIMENTAL PROCEDURE

Specimen Preparation

The tantalum was Materials Research Corporation rods of marz grade purity. The chemical analysis furnished by the supplier is given in Table I. After cleaning in a solution $\text{HF}:\text{HNO}_3:\text{H}_2\text{O}$, the 1/4 inch rods were swaged to 45 mil. wires. They were then cold-rolled to 10 mil foils and cleaned. Strips of foils were annealed in vacuum at 2400°C for 4 to 5 hours typically. The foils were heated during this treatment by the joule heat of a dc current in a vacuum better than 5×10^{-7} torr. The recrystallized foils had a typical grain size of 1/2 to 1 mm in diameter.

The gases hydrogen, deuterium and oxygen were of research purity grade. Specimens containing only hydrogen or deuterium were prepared by reacting the foils with known amounts of gas introduced at 1300°C . The temperature was then slowly decreased and the absorption of the gas by the foils was followed by the decrease in gas pressure. When the pressure reached 0.1% of the initial value, the foils were cooled to room temperature.

Specimens containing both oxygen and hydrogen were prepared in two steps. Oxygen was first added by reacting the foils with a known quantity of gas at 1500°C for 1 hour. The foils were then radiation cooled to room temperature and

Table I. Supplier's Analysis of Tantalum Starting Material
(All values are in weight ppm.)

O	8.0	Cr	0.1
N	2.0	Mn	0.03
C	10.0	Fe	1.0
Na	0.1	Cu	0.2
Mg	0.2	Zn	0.5
Al	0.2	Se	< 1.0
Si	0.3	Nb	5.0
P	0.2	Te	< 2.0
S	0.6	W	10.0
Cl	0.6	Pt	< 1.0
K	0.01	Au	< 2.0
Ca	0.3	Th	< 0.3
V	0.1	U	< 0.4

All others non-detected to 0.1 ppm

the vacuum was brought back to a value better than 5×10^{-7} torr. They were then reheated to 1300°C and a known volume of hydrogen was introduced. The regular procedure was then followed. However in this case the reaction was sluggish and a certain amount of hydrogen was not absorbed. The difference between the initial and final pressure readings was used to calculate the exact amount of hydrogen absorbed.

Since the solubility of oxygen in tantalum is not well known at room temperature, the assumption of an oxygen solid solution had to be verified. A sample containing 6000 ppm oxygen was prepared and cooled to room temperature at a rate four times slower than the typical rate used during subsequent hydrogen doping. The sample was then thinned and observed in the electron microscope. No trace of a second phase was found.

Resistivity Measurements

The classical four lead method was used. Current and potential leads made of outgassed Ta wire were spotwelded on a 5 inch foil. Temperatures were measured by two copper-constantan thermocouples spotwelded on the top and bottom of the specimens outside the potential leads. Two windings around copper cylinders in which the specimens were mounted permitted adjustment of cooling and heating rates by joule effect. This setup permitted constancy of temperature along the foil to less than 1°K between the two extremities of the

specimens. A current of about 0.5 ampere was supplied by a 6 volt battery. The voltage drop across a known resistance (0.100 Ω) and across the sample was measured on a digital voltmeter with a sensitivity of .1 μv .

EXPERIMENTAL RESULTS

Hydrogen Solubility in Pure Tantalum

The compositions of hydrogen used in the present experiment were in the range 0.5 at.% to 10 at.%. The solvus temperatures for this range of compositions were expected to lie between 175°K and 300°K. Therefore, an initial measurement was made for a purified specimen containing no hydrogen to determine the shape of the curve of resistance as a function of the temperature. Data obtained on cooling and heating are drawn in Figure 8. As can be seen, no hysteresis is observed on cooling and heating. The curve, nearly a straight line, is slightly concave downward since the Debye temperature for pure tantalum is about 240°K.¹ This temperature increases with hydrogen content, however in the following, cooling curves of solid solutions are approximated as straight lines within experimental error. The data points plotted in Figure 8 are only about one-half of the data obtained in this run; the rest have been omitted for purposes of clarity in drawing the line. The same procedure is adopted for similar curves reported in this section.

Measurements of the solvus temperature were made for six compositions spaced over the range. In the early stages of the experiment, the temperature was reduced at a modest rate, about 1°K per minute. Numerous observations were made

which could not be easily interpreted in terms of a simple solvus line. During the course of the investigation, the results of the experiments of Westlake and Ockers on niobium became available, and the possibility of too-rapid cooling became apparent.¹⁷ Consequently, a second set of observations were made in which the cooling rate was extremely low, about 2°K per hour. This cooling rate gave quite different results from the early observations and are internally consistent among the specimens. A measurement for the specimen containing 1.5 at.% H is shown in Figure 9. During the first cooling, the resistance decreases linearly with the temperature until a temperature $T_1(1)$ is reached. Below that temperature, the resistance decreases linearly but with a steeper temperature dependence. At a temperature of 160°K cooling is stopped and the temperature is slowly raised. The resistance increase upon warming is also approximately linear with temperature until some temperature $T_2(1)$ is reached; then the line becomes steeper and remains nearly linear to some temperature T_3 where it intersects the first cooling line. The resistance then retraces the cooling line to room temperature. A second cooling shows the same hysteresis, but in this instance, the temperature T_1 is a few degrees higher. Thus, the steeper part of the cooling curve is shifted about 2° or 3° higher in temperature. The heating curve on the second cycle is identical to that on the first cycle. Successive cycling shows

cooling and heating curves indistinguishable from the second cycle. Thus, we have several temperatures of interest. Temperature $T_1(1)$ is considered to be the temperature of formation of the first hydride precipitate for this composition. During the cooling below T_1 the hydride forms continuously. After turning around at 160°K, the hydride must begin to dissolve; but, the dissolution is not complete until the temperature T_3 is reached. The significance of temperature T_2 seems not certain and is discussed later. The temperature $T_1(2)$ on the second cooling is considered to be the precipitation temperature for formation of hydride in the presence of residual dislocations presumed to be punched out during the first cooling.

The existence of hysteresis makes one wonder whether or not the cooling and heating rates of 2°K per hour are slow enough for this composition. Consequently, several types of investigations were made to check this point. During the first cooling, a specimen was held at a temperature slightly below $T_1(1)$ for twelve hours. The resistance remained constant during this constant temperature anneal. Furthermore, the resistance remained constant on the first heating at a temperature of 201°K -- this is slightly above $T_1(1)$ -- for an anneal of eight hours. Thus, it is assumed that a resistance reading is characteristic of the temperature with the cooling and heating rates used. For this specimen and other specimens

the temperature $T_1(1)$ is considered to be the "solvus temperature."

A similar set of observations was obtained for a specimen containing 4 at.% H; the results are summarized in Figure 10. On the first cooling a linear temperature dependence of the resistance is found until the temperature $T_1(1)$ is reached. Below that temperature the curve for this alloy is not straight but is convex upward. The heating curve does not retrace the cooling curve but again shows a hysteresis; in this instance without any breaks until T_3 is reached. Above that temperature the resistance line retraces the original cooling line. On the second cooling the onset of precipitation occurs at some temperature $T_1(2)$ higher than the first. Below that temperature the cooling curve lies under the first, but approaches the line for the first curve as the temperature falls below 150°K. Again, the heating curve retraces the first. To show the result of continued cycling, this sample was then cycled seven times between 77°K and 293°K by immersing it successively into a dewar of liquid nitrogen. A cooling curve was then made on the tenth cycle; in this instance, precipitation started at a temperature $T_1(10)$ which was only 2°K higher than on the second cooling. Thus, for this specimen the difference between one and ten cycles is not more than 5°K.

The changes in slopes of the cooling curves for more dilute alloys are much smaller and the temperature of precipita-

tion cannot be read with good precision. However, if the data are plotted as $\Delta\rho$ vs. temperature, the curves show a sharp break. The value $\Delta\rho$ is defined by the equation

$$\Delta\rho = \rho_{\text{Ta-H}} - \rho_{\text{Ta}}$$

where $\rho_{\text{Ta-H}}$ and ρ_{Ta} are respectively the resistivities of the Ta-H alloy and the pure metal. The validity of such a plot is discussed in the appendix. A plot is shown for an alloy of 0.5 at.% H in Figure 11. The temperature $T_1(1)$ for this composition can easily be found by extrapolating the two straight lines to a point of intersection. The value of T_1 can be read off this plot to about 1°K. Of course, for such a dilute alloy one must be especially careful that the cooling rate be slow enough so that equilibrium is reached at all temperatures. This is difficult to assure with certainty, but the data, when plotted altogether, show that the value of T_1 for this alloy fits nicely with those at higher composition where supercooling is not thought to be a problem. Therefore, the cooling rate of 2°K per hour seems adequate for this alloy as well.

Measurements of resistance as a function of temperature have been made for three other alloys at 2, 3, and 10 at.%. The values of T_1 for these alloys as well as for the three just described are plotted in Figure 12. Also plotted there are the lines from several of the previous investigations. Clearly, the present results agree well with those of Cannelli and Mazzolai⁴ and of Waite, Wallace, and Craig.² The present

results disagree markedly from those obtained by Owen and Scott.⁶ The same data plotted as in Arrhenius' plot shows the present data to fit a nice straight line, Figure 13. The equation of that line is the following:

$$\ln C(\text{at.}\%) = 6.04(+0.014) - \frac{2150(+60)}{RT}$$

We thus assume that the solvus line obeys an exponential with an enthalpy of solution of 2150 cal/mole.

Hydrogen Solubility in Oxygen-Doped Tantalum

The effect of dissolved oxygen on the temperature of the solvus line was examined for two compositions of hydrogen. The alloys contained 6000 at. ppm oxygen in solid solution. The hydrogen concentrations were 0.63 at.% H (6300 at. ppm) and 2.62 at.% H (26,200 at. ppm). For these specimens great care was taken to make sure that the cooling rate was slow enough to ensure equilibrium at all temperatures. The samples were slowly cooled at a rate of 12°K per hour to a temperature about 10°K above the temperature T_1 expected for a Ta-H alloy of the same composition. Specimens were then cooled in steps of 2°K and held at each temperature until the resistance reached a constant value. The cooling rate never exceeded 2°K per hour in the 10°K interval above the estimated T_1 . Below the break-point T_1 measured for the two alloys, the time needed to reach equilibrium was much longer; for the alloy of 2.62 at.%, the time was 6 hours for temperatures slightly below

T_1 and for the alloy containing 0.63 at.% H the time was about 40 hours. Because of the long time involved in reaching equilibrium at lower temperatures, the complete hysteresis loop was not measured; only the cooling curves were measured in the vicinity of T_1 . The cooling curve for the alloy containing 6000 ppm oxygen and 26,200 ppm hydrogen is shown in Figure 14. The break-point T_1 is rather sharp; it can clearly be determined to within 1° or 2°K . The cooling curve for the alloy containing 6300 ppm of hydrogen is not shown, but the temperatures T_1 are plotted in Figure 15 on the Arrhenius plot. One sees that both points fit right on the line for the oxygen-free tantalum which was determined in this work. Thus, there seems to be no influence of oxygen on the solvus temperature, although the time required to reach equilibrium is much increased by the presence of oxygen.

Deuterium Solubility in Pure Tantalum

The temperature of the solvus for two alloys of tantalum containing 1 and 4 at.% deuterium were measured by the procedure just described. Since the diffusion coefficient of deuterium in tantalum is known to be smaller than that of hydrogen at the same temperature, the cooling procedure was the slow-process just described for the Ta-O-H alloys. In this instance, the time required to reach apparent equilibrium just below T_1 for the alloy containing 1 at.% was about 2

hours and for the alloy containing 4 at.% about 1 hour. Again, the cooling curves showed nice sharp breaks and the temperature T_1 could be determined to within a 1° or 2°K . The results of these two experiments are plotted on an Arrhenius plot in Figure 16. Data fit nicely on the solvus line obtained for tantalum containing hydrogen of mass 1. These results are quite different, however, from those reported by Cannelli and Cantelli.²⁵ Apparently, the effective cooling rate of less than 1°K per hour in the present experiment was sufficiently slow to permit equilibrium to be established for this slow diffusing isotope, whereas the cooling rate of 12°K per hour used by Cannelli and Cantelli was not slow enough. There seems no reason to believe that the electrical resistance measurements of the present study and the internal friction measurements of the earlier study should give inherently different results.

Influence of the Cooling Rate

A complete set of alloys has been examined using heating and cooling rates much faster than those described in the previous measurements, rates of the order of 1°K per minute. The value of T_1 obtained for alloys of composition 4% is closely the same as that obtained with the slower cooling rates, but alloys of lower composition gave results departing significantly from the observations quoted above. Not all of

the observations will be described in detail since the measurements are clearly non-equilibrium, but some of the results will be presented.

A typical result is that shown in Figure 17 for an alloy containing 6000 ppm oxygen and 6300 ppm hydrogen. This heating curve shows a hysteresis similar to that described in Figure 9, except that the temperature T_2 (the first break-point upon heating) is higher than that of T_1 . On the second heating and cooling, the temperatures T_1 and T_2 are the same; but both are higher than either T_1 and T_2 on the first cycle. These results are strikingly similar to the hysteresis loops observed by Holmquist as drawn in Figure 6.¹⁸

Other alloys studied under these conditions of cooling were Ta containing 6000 ppm oxygen and 26,200 ppm hydrogen and Ta containing deuterium or hydrogen of compositions 1 at.% or higher. The detailed hysteresis loops are not shown for these alloys but they are similar to those of Figure 17. The values of T_1 for the several experiments carried out are plotted in Figure 18 and are compared with the results obtained for Ta-D alloys by Cannelli and Cantelli.²⁵ For compositions below 2 at.% the present measurements agree well with their line for deuterium. For compositions of 3% and 4% hydrogen the results fall between the two curves; this indicates that precipitation is easy enough in the Ta-H system that even this faster cooling rate is nearly slow enough to permit equilibrium

to be achieved at the solvus temperature.

This set of observations shows again that deuterium and hydrogen have the same apparent solvus line at this faster cooling rate but that the rate is too rapid for equilibrium to be achieved for both systems.

DISCUSSION

This set of observations is concerned with four principal features of the phase diagram:

1. The solvus line for hydrogen in tantalum.
2. The solvus line for deuterium in tantalum.
3. The effect of oxygen on the kinetics of precipitation and the equilibrium solvus line.
4. The hysteresis in the precipitation and dissolution of the hydride.

The solvus line for the phase diagram of hydrogen dissolved in pure metals usually obeys a simple exponential law

$$C = C_0 e^{-\Delta H_s/RT}$$

The heat of solution ΔH_s for the hydride is about 2150 calories per gram atom of hydrogen in tantalum. This value is lower than that for hydrogen in either niobium or in vanadium.

The solubility lines for all three of these metals are drawn in Figure 19. Vanadium has the least solubility at these low temperatures and the highest heat of solution, about 3900 calories per gram atom.¹¹ Niobium is intermediate; it has a heat of solution of about 2750 calories per gram atom.¹⁶ If these lines are extrapolated to $1/T = 0$, the values of C_0 thus obtained are about the same for tantalum and niobium; vanadium has a value more than twice that size. Values of C_0 ΔH_s for the three are tabulated in Table II. Differences in

Table II. Solubility Constants for Hydrogen
Dissolved in V, Nb and Ta

Metal	C_o	ΔH_s
V	1050 at.%	3900 cal/mole
Nb	365	2750
Ta	400	2150

$$C = C_o e^{-\Delta H_s/RT}$$

in C_0 may be caused by possible differences in the α phase itself by differences in the β phases.

Examination of the solubility line in Figure 13 and consideration of the overall solvus line in Figure 1 does not permit any conclusions to be drawn about the influence of ordering reactions in the β phase observed near room temperature by Saba and co-workers.²⁶ Some slight changes in the solvus line ought to be observed but the compilations of measurements one can make for the tantalum-hydrogen system is not accurate enough to show any possible deviations from a simple Arrhenius behavior.

The present observations on the solubility of deuterium in tantalum were made for only 2 specimens. However the data points obtained in these measurements fitted so well on the solvus line for hydrogen that no point seemed served by continuing measurements to alloys of other compositions. The alloys of tantalum and deuterium thus behaved the same way as do alloys out of niobium with hydrogen and deuterium; the solvus line is the same for both isotopes. It does differ from the effect for vanadium where the solubility of deuterium is considerably higher than the solubility of hydrogen at the same temperature.

Striking effects on the kinetics of precipitation may be observed by altering the rate of cooling through the solvus temperature. For alloys in the composition range of 2% or lower,

cooling rates of 1° or 2°K per hour seem sufficient to permit equilibrium to be achieved at all temperatures near the solvus temperature. However, when the cooling rate is increased to values in the vicinity of 1°K per minute, considerable undercooling is observed for these dilute alloys. This is apparent from comparisons of the data plotted in Figure 13 and in Figure 18. At higher compositions, above 4 at.%, the supercooling even at the faster cooling rate is insignificant. The present measurements cannot decide whether this is an effect of higher diffusion rates at higher temperatures or of differences in scale of the precipitate size.

For tantalum containing deuterium the kinetics are a little different. Deuterium diffuses more slowly in tantalum than does hydrogen. Over the temperature range of the present measurement the difference is about 3 to 5 times slower; see the lower two curves of Figure 20.^{27,28} Thus rates of cooling necessary to avoid supercooling are even slower for the deuterium alloys than for the hydrogen alloys. Unfortunately for the interpretation of the observations made by Cannelli and Cantelli, their cooling rates for the hydrogen and deuterium alloys span this crucial gap and they are misled into believing that the solvus line for deuterium in tantalum is different from that for hydrogen in tantalum; see Figure 10 of their paper.²⁵ Further credence for this interpretation of their data may be seen by considering the alloy of highest composition in their

measurements; this alloy contained about 8% deuterium. (See their highest point in Figure 10 of their paper.) It departs from linearity of their six alloys of lower composition and tends toward their line for hydrogen in tantalum. Thus it shows the same behavior as is seen in Figure 18 of the present work.

The data for diffusion coefficients of hydrogen and deuterium in vanadium and niobium in Figure 20 give a hint of one reason that supercooling may be less important in vanadium than it is in niobium and tantalum.²⁹ Diffusion coefficient at a given temperature, say 200°K, for vanadium is nearly four orders of magnitude higher in vanadium than in tantalum. Thus equilibrium should be much easier to achieve in that system. Niobium presumably should be intermediate between the two, but Westlake and Ockers have shown the same difficulty of preventing supercooling in those alloys that are found in the present study for tantalum.¹⁷ Consequently nucleation of the β phase and the fineness of dispersion of the resultant hydride may also play a significant role in supercooling.

Additions of oxygen in solid solution do not appear to affect the equilibrium solvus line for hydrogen in tantalum, see Figure 15. However, the rate of approach to equilibrium is altered significantly by the presence of oxygen; much slower cooling rates are required to prevent supercooling when oxygen is present. This might be caused by the hardening effect of

oxygen which could alter the thermodynamics of precipitation of the hydride in the tantalum matrix. More likely, though, it is caused by the trapping effect of oxygen for hydrogen, with a consequent slowing of the diffusion rate. The binding energy of a hydrogen atom to an oxygen atom has not been measured for tantalum, but values of about 2000 cal/mole are reported for both niobium and vanadium.^{11,15} Assuming that binding energy is about the same in tantalum, a hydrogen atom dissolved in tantalum would spend a considerable fraction of its time bound to an oxygen atom at these low temperatures. Thus long-range diffusion through the crystal could be markedly affected by the presence of oxygen. This could account for the much longer times required for achievement of equilibrium in these oxygen-containing alloys.

The final feature requiring explanation is the presence of hysteresis on cooling and heating. Because of the extra difficulty of explanation involved for non-equilibrium cooling; i.e., fast cooling and heating rates, consideration will be given only to curves obtained on slow cooling and heating. The comments to be made are similar to those made by Westlake¹⁶ but the ideas have been developed further after conversations with Westlake. An examination of a typical curve such as that in Figure 9 shows the following features. Upon the first cooling, the resistance decreases linearly until the solvus line is reached; this is presumed to be $T_1(1)$. At this point hydride

is presumed to form as the hydrogen leaves the solid solution. Since the precipitate is much less dense than the matrix, the volume difference must be accommodated by elastic and plastic strains. Elastic strains cannot accommodate the total volume difference, so dislocations must be punched out during the growth of the hydride precipitate. The hydride precipitates continuously as the temperature is further lowered. On heating from the lower temperature, small changes in particle size will reverse the sign of the elastic stress; this can be accomplished by very small changes in the hydrogen concentration in the solid solution. This behavior explains why the curve c in Figure 9 tends to be roughly parallel to curve a. Above $T_2(1)$, dissolution of the hydride is only possible by the collapse of dislocation loops and ultimately by generation of dislocation loops of opposite sign. This would explain why curve d tends to be parallel to curve b. Complete dissolution of the hydride occurs at T_3 .

Precipitation occurs on a second cooling at a temperature $T_1(2)$ higher than $T_1(1)$. This can be explained by the fact that some dislocations left after the first cycle would act as nucleation sites for the hydride on the second cooling. Thus on the second cycle less supercooling is needed. Below $T_1(2)$ the same mechanism as discussed above is applicable. If the hydrides are roughly in the same geometrical configuration on successive coolings, the heating curve for all cycles

should be approximately the same. The absence of effect of O on the solubility limit under equilibrium conditions supports the theory formulated by Holmquist.¹⁸ His results showed that solution strengthening by an interstitial had no effect on hydride formation. Thus the increase in macroscopic flow stress does not affect the plastic work during hydride nucleation and growth. This is consistent with the fact that dislocation loops must be punched in an essentially perfect crystal during the first cooling.

CONCLUSIONS

The resistometric method used is an appropriate technique by which hydride precipitation and dissolution can be detected. Nearly equilibrium conditions are essential for an accurate determination of the solubility limit of hydrogen in tantalum. Several interesting features emerge in the determination of the solvus line.

1. The heat of solution ΔH_s for the hydride is 2150 calories per gram atom in a composition range of 0.5 to 10 at.%. It is lower than in the Nb-H and V-H systems where the heat of solution is respectively 2750 and 3900 calories per gram atom.
2. There is no isotope effect on the solvus line.
3. Oxygen impurities in solid solution up to 6000 ppm do not affect the solubility limit of hydrogen in tantalum.
4. Considerable undercooling is observed by changing the cooling rates. Under equilibrium conditions long-range diffusion appears to be the governing factor on precipitation and growth.
5. The rate of approach to equilibrium is slower for deuterium than for hydrogen. In the temperature range considered the diffusivity of deuterium was 3 to 5 times smaller than that of hydrogen.

6. Much slower cooling rates are needed to reach equilibrium when oxygen impurities are present. This is probably caused by the trapping of hydrogen by oxygen and a consequent slowing of diffusion rates.
7. There is an hysteresis upon cooling and heating around the solvus temperature even under equilibrium conditions.
8. This hysteresis loop tends to close up upon successive thermal cycles but never disappears completely.
9. Strengthening the matrix with an interstitial impurity such as oxygen does not affect the precipitation temperature.

Figure 1. The low temperature section of the phase diagram for Ta-H alloys. Some uncertainty exists in the boundary of the β phase near room temperature (dotted line).

Figure 2. Reported measurements of the solvus line
for hydrogen in tantalum and equilibrium
with the phase Ta_2H .

Figure 3. Several of the measurements of solvus line
for hydrogen in vanadium.

Figure 5. The solubility of hydrogen in niobium
and equilibrium with the phase NbH.

Figure 6. The cooling-heating hysteresis for niobium-hydrogen alloys. After Holmquist.

Figure 7. The solvus lines for the Ta-H and Ta-B alloys reported by Cannelli and Mazzolai and Cannelli and Cantelli.

Figure 8. The resistance as a function of temperature for a specimen of tantalum freed of oxygen by a high temperature vacuum treatment. No hysteresis is evident in the cooling-heating cycle.

Figure 9. The cooling-heating hysteresis loop for the first and second cooling cycles of a tantalum alloy containing 1.5 at.% H. The symbols "a" through "e" are referred to later in the discussion.

Figure 10. The cooling-heating hysteresis loop for
the first and second cooling cycles for
a tantalum specimen containing 4 at.% H.

Figure 11. A plot of $\Delta\rho$ as a function of temperature
for an alloy containing 0.5% H.

Figure 12. The measured points on the solvus line for the Ta-H system measured in the present work compared to several previous measurements.

Figure 13. The observations from the present work compared with those reported earlier for the Ta-H system.

Figure 14. Part of the cooling cycle for a specimen
of Ta-O-H.

Figure 15. The two measured values of hydrogen solubility in an alloy of Ta-O-H compared to the measured solvus line for hydrogen in tantalum.

Figure 16. The two measurements of the solubility of Ta-D system compared to the measured solubility of hydrogen in tantalum from this work and to the deuterium in tantalum solvus reported by Cannelli and Cantelli.

Figure 17. The cooling-heating cycle for a specimen cooled at the rapid rate.

Figure 18. The "apparent" solvus line for the Ta-H and Ta-D binaries and the Ta-O-H ternary carried through the cooling-heating cycle at a rapid rate.

Figure 19. The solvus lines for hydrogen in tantalum, niobium and vanadium.

Figure 20. The diffusivities of hydrogen and deuterium in vanadium, niobium and tantalum. The dotted lines are extrapolations of higher temperature measurements.

Figure 21. Increase in electrical resistivity as a function of hydrogen and deuterium in solid solution in tantalum.

APPENDIX

For a single-phase solid solution of hydrogen and deuterium in tantalum, the resistivity of the alloy at any temperature is equal to the resistivity of the pure tantalum plus a constant $\Delta\rho$. This can be seen on a plot of $\Delta\rho$ vs. temperature, see Figure 11. $\Delta\rho$ is defined as

$$\Delta\rho = \rho_{\text{Ta-H}} - \rho_{\text{Ta}}$$

with $\rho_{\text{Ta-H}}$ and ρ_{Ta} being respectively the resistivity of the Ta-H alloy and that of pure Ta. Before precipitation of the hydride occurs $\Delta\rho$ is independent of the temperature. Thus hydrogen in solid solution contributes only to the residual resistivity, and not to the ideal resistivity.

This increase $\Delta\rho$ due to hydrogen and deuterium is plotted vs. concentration in Figure 21. The resistivity increase is found to be $0.51 \mu\Omega \text{ cm per at.}\%$. This value is lower than for V-H and Nb-H alloys. For Nb-H alloys Westlake¹⁶ reports a value of $0.655 \mu\Omega \text{ cm per at.}\%$ compared to $0.75 \mu\Omega \text{ cm per at.}\%$ found by Borgucci and Verdini.³⁰ For V-H alloys Westlake has found $\Delta\rho$ to be $1.12 \mu\Omega \text{ cm per at.}\%$.⁹ For Ta-H alloys Borgucci and Verdini report a value of $0.80 \mu\Omega \text{ cm per at.}\%$. It can also be seen in Figure 21 that the contribution to the residual resistivity is identical for hydrogen and deuterium. This is not the case in the vanadium systems where the value of $\Delta\rho$ is

smaller than that due to hydrogen. In the V-D system $\Delta\rho$ is approximately $0.8 \mu\Omega \text{ cm}$ per at.%.²²

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