Journal of Alloys and Compounds 253–254 (1997) 167–170

Solubility of hydrogen and deuterium in bcc uranium–titanium alloys

G.L. Powell*, J.R. Kirkpatrick

Oak Ridge Y-12 Plant[1], *Lockheed Martin Energy Systems, Inc., Oak Ridge, TN 37831-8096, USA*

Abstract

For the body-centered-cubic uranium–titanium alloy system, hydrogen and deuterium solubility measurements have been made on 12 alloy specimens ranging in composition from pure uranium to pure titanium and over a temperature range of 900–1473 K. The results are described in closed form by an analytical model within a standard error of 3%. The Einstein temperature (1680 K), and thus the isotope effect, was independent of alloy composition. The solubility and the enthalpy of solution were strongly dependent on alloy composition, more so at low titanium concentrations.

Keywords: Solubility; Uranium–titanium alloys

1. Introduction

The uranium–titanium alloy system has a high temperature (~900 °C) region in which the body-centered-cubic (bcc) phase extends unbroken across the composition range from pure uranium to pure titanium [1]. Over this alloy composition range, the solubility of hydrogen in these alloys, represented as the equilibrium constant (k, the ratio of the H concentration to the square-root of the H_2 pressure, the Sievert's constant), varies by almost three orders of magnitude [2,3]. This hydrogen solubility can be measured near infinite dilution without serious experimental interference from factors such as hydride formation, slow surface and diffusion kinetics, or trapping effects. In this paper, the measurement of the solubility of hydrogen and of deuterium in this alloy system, at infinite dilution, is reported for 12 alloy compositions covering the composition range from pure uranium to pure titanium. The resulting measurements are described by the bound proton model [4–8] for the purpose of precisely describing the measurements in closed form and determining the dependence of effect of alloy composition on the parameters of the model.

2. Theory

In the context of the bound proton model [4–6], the hydrogen solubility (k) is described as

$$\begin{aligned}\ln(k) = {} & \ln(N) + \ln(1 + A\mathrm{e}^{-B/T}) - 3\ln(1 - \mathrm{e}^{-C/T}) \\ & + (E - 3C/2)/T - 0.5\ln(LT^{7/2}/(1 - \mathrm{e}^{-J/T})) \\ & - M/2T \qquad (1)\end{aligned}$$

where $N=3$ or $N=6$ is the number of hydrogen sites per bcc metal atoms, C ($C_D = C_H/2^{0.5}$) is the Einstein temperature, E is the ground state energy relative to atomic hydrogen at rest, the last two terms together are the free energy function for H_2 (or, with different parameters, the free energy function for D_2) [6], and the term containing A and B (the A,B term) is an approximation for all Boltzmann states not explicitly included in the three dimensional harmonic oscillator model for hydrogen in its site. From hydrogen solubility data obtained from alloys over a range of compositions, the alloy compositional dependence of these parameters may be determined [7].

3. Experimental

The method and equipment for measuring of hydrogen and deuterium solubility in these uranium alloys near infinite dilution was that described in detail for uranium–niobium alloys [4,5]. The measurements reported here were made near infinite dilution with typically 1% accuracy on 12 alloy specimens representing titanium compositions (x) in mole fraction of 0.000, 0.018, 0.036, 0.060, 0.080,

---

*Corresponding author.

[1] Managed by Lockheed Martin Energy Systems, Inc., for the U.S. Department of Energy under contract DE-AC05-84OR21400.

0925-8388/97/$17.00
PII S0925-8388(96)03093-9

0.147, 0.185, 0.242, 0.335, 0.597, 0.850 and 1.000. Low titanium alloy specimens were typically 0.5–0.7 moles alloy. For the alloys having higher titanium compositions (i.e., higher hydrogen solubilities), the quantity of alloy was decreased in order that the hydrogen adsorbed by the alloy did not drop to immeasurably low levels. For these high composition alloys, isotherms were measured as a function of hydrogen mole ratio in the range of 0.01–0.05 mole ratio to extrapolate k to infinite dilution. Similar measurements were made for deuterium, except for the titanium compositions 0.060 and 0.185. The temperature range for these solubility measurements extended from the lesser of the liquidus temperature (1406 K for uranium) or 1473 K down to the solvus line for phase separation that ranged from 1173 K for the composition of U_2Ti to temperatures as low as 900 K for $x = 0.850$.

4. Results

The solubility data for hydrogen and deuterium in these uranium–titanium alloys are shown in Fig. 1. The isotope effect is small and typical of bcc uranium alloys [4,5]. The difference $(\ln (k_H) - \ln (k_D))$ between the results for hydrogen and for deuterium yields values for the $C_H = 1680$ K for each of the alloys. Preliminary analyses indicated that Eq. (1) would describe data for individual alloys with a precision comparable to the measurement precision for $N = 3$, $B = 3600$ K, and $C = 1680$ K, with A and E optimized for a particular alloy. Difficulty was encountered in fitting high titanium composition alloys with $N = 6$, since the A,B term was very small at the low temperature extremes and the desired slope and magnitude of Eq. (1) could not be simultaneously achieved by varying only E. The model tended to make parameter A negative imparting negative curvature to the results, which lead to a relatively poor fit. To describe the alloy effect, a more global model was employed for which $N = 3$, $B = 3600$ K, $C_H = 1680$ K. $A(x)$ and $E(x)$ were optimized using Jandel TABLECURVE software to process all of the $\ln (k_H)$ data for all of the alloys with the following function $Q(x)$ to describe the alloy composition (x) dependence of parameters $A(x)$ and $E(x)$.

$$
\begin{aligned}
Q(x) = {} & a\{x - 1/g \ln(\cosh[g(x - b)])\}/2 \\
& + c\{1/g \ln(\cosh[g(x - b)])\} \\
& - 1/g\{\ln(\cosh[g(x - d)])\}/2 \\
& + e\{1/g \ln(\cosh(g(x - d)]) + x\}/2 + f \qquad (2)
\end{aligned}
$$

Eq. (2) describes 3 linear segments that are smoothly connected. For $A(x)$, the parameters were $a = -1131.1221$, $b = -0.031043$, $c = 17.2527$, $d = 0.296235$, $e = 0.37877$, $f = 9.969$, $g = 17.5788$, fit standard error $= 0.595$. For $E(x)$, $a = 28957.2$, $b = 0.02406$, $c = 8179.18$, $d = 0.28692$, $e = 4833.22$, $f = 29358.8$, $g = 15.4827$, fit standard error $= 32.1$ K. Fig. 2 shows a plot of these equations with the alloy compositions used in the fit superimposed as symbols. Using the above parameters, the data for deuterium was fit

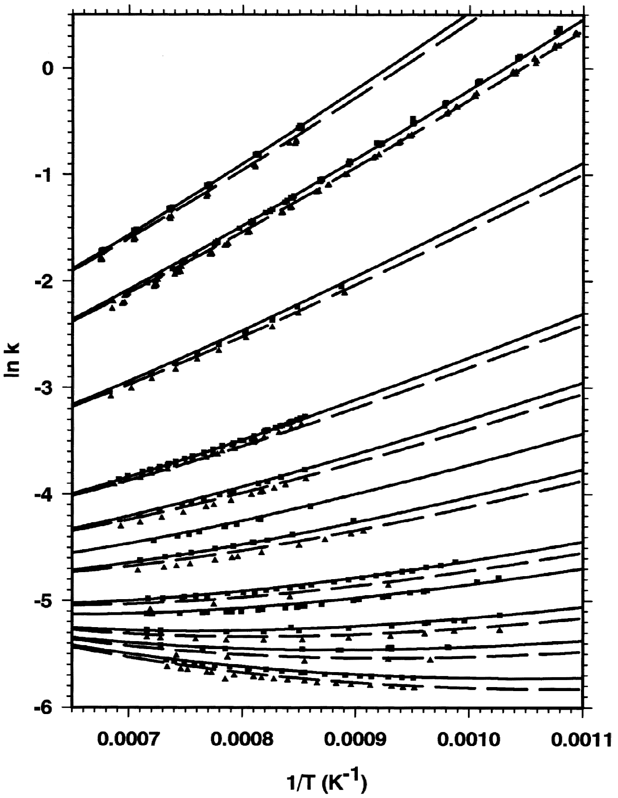

Fig. 1. Hydrogen and deuterium solubility (k in units of moles H per square-root hydrogen pressure in atmospheres) data for bcc uranium–titanium alloys. Squares, H data; triangles, D data; solid lines, H model; dashed lines, D model. Alloy compositions from bottom to top as mole fraction titanium: 0.000, 0.018, 0.036, 0.060, 0.080, 0.147, 0.185, 0.242, 0.335, 0.597, 0.850 and 1.000.

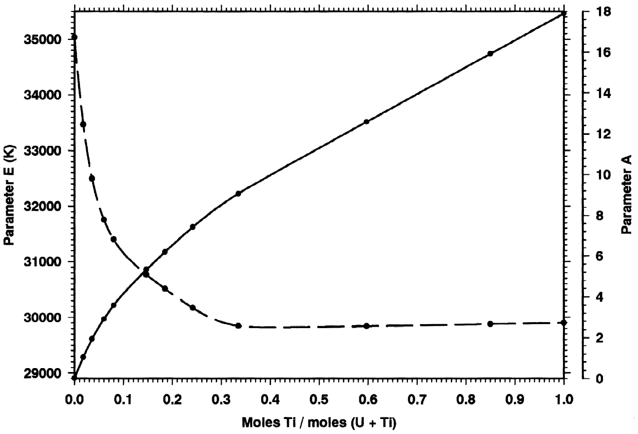

Fig. 2. Alloy compositional dependence of the model fit parameters $A(x)$ and $E(x)$. Solid curve, $E(x)$; dashed curve, $A(x)$; circles represent compositions for which solubility data was obtained.

with C as the only variable. The Einstein temperature was found to be 1680.9 K with a fit standard error of 7.9 K. The overall fit standard error for predicting k_H and k_D was 3%. The lower quality fit using $N=6$ yielded results that were qualitatively similar to those for $N=3$ given above.

5. Discussion

Eq. (1) describes the solubility of hydrogen in a metal in terms of the number of sites per metal atom, the ground state energy of hydrogen in the metal relative to that for hydrogen gas, and the contributions of the thermally populated energy states of hydrogen in the metal relative to comparable terms for hydrogen gas. The model is that of Lacher [8] with additional Boltzmann states (the A,B term) added because the Boltzmann states associated with a three dimensional harmonic oscillator are grossly inadequate to describe the observations [4–8]. The Boltzmann states and the number of sites per metal atom principally contribute to the entropy of reaction (i.e., the number of ways the system can be achieved). For hydrogen gas, this term has a strong temperature dependence at low temperatures and drives the solubility down at low temperatures. At higher temperatures, the Boltzmann states for the hydrogen in the alloy eventually contribute and, in the high temperature limit, these states have a stronger temperature dependence ($\sim T^3$) than does the gas phase ($\sim T^{7/4}$). The contribution from the vibrational Boltzmann states of hydrogen gas is minor at temperatures below 2000 K. This guarantees that the data as shown in Fig. 1 will display a positive curvature. The ground state energy is the dominant contributor to the enthalpy of the reaction and is the relationship that assures that the solubility data as shown in Fig. 1 for a series of alloy compositions are principally related by a rotation. The enthalpy of the reaction at any temperature is the negative derivative of a smooth curve through the data, for a particular alloy and hydrogen isotope, taken with respect to the inverse absolute temperature multiplied by the gas constant of choice. The positive curvature of the solubility data in Fig. 1 results in the enthalpy increasing with increasing temperature for a given alloy.

The curve fitting procedure used here independently arrived at the Einstein temperature based on the difference $\{\ln(k_H)-\ln(k_D)\}$. An integer value is then assumed for N based on symmetry considerations ($N=6$ for tetrahedral site occupancy or $N=3$ for octahedral site occupancy for bcc metals). The ground state energy (E) is then adjusted to rotate the calculated curve in proximity with the low temperature limits of the data. Here the A,B term has a very small value. Finally, the A,B parameters are adjusted interactively with E to complete the fit. For alloys such as U–0.85Ti where the bcc-phase extends to relatively low temperatures, the A,B term has little effect on the fit at the low temperature limits of the data and, thus, little effect on the value of $E(x)$. Indeed, the slope and the magnitude of the curve at a particular temperature are rigorously coupled and, for $N=6$, a value of $E(x)$ that intersects the data produces an unacceptably low value for the slope. The only way that an appropriate fit can be achieved is to lower the value of N. The global model used here effectively does that by choosing a negative value for $A(x)$, but this introduces a negative curvature at higher temperatures, and thus, a large standard error.

Lowering N to $N=3$ yielded a global fit that was acceptable (3%), but not quite as good as the precision with which the data could be fit to individual alloy data sets (1%). Fig. 2 compares $A(x)$ with $E(x)$. Both are strongly dependent on alloy composition and both show the strongest dependence on composition at the low titanium concentrations. In a plot of the values of $E(x)$ for $N=6$ (an inferior fit), or the enthalpy determined numerically from the data for each alloy in Fig. 1 are qualitatively similar to $E(x)$ from Fig. 2. The inflections occur at the same positions and the largest changes occur at low Titanium concentrations. On the other hand, the Einstein temperature (C), is not a function of x and the large inflections seen in parameters $A(x)$ and $E(x)$ are not detectable in $C(x)=C$. $E(x)$ varies from 28908 K ($A=16.73$) for uranium to 35462 K ($A=2.71$) for titanium, a change of -0.56 eV. Inflections occur at U–0.02Ti ($E=31189$ K, $A=4.27$) and U–0.29Ti ($E=31927$ K, $A=2.81$). The contribution from thermally excited states (the A,B term) also grew markedly as the concentration of titanium approached zero.

Fig. 3 shows the magnitude and the characteristics of

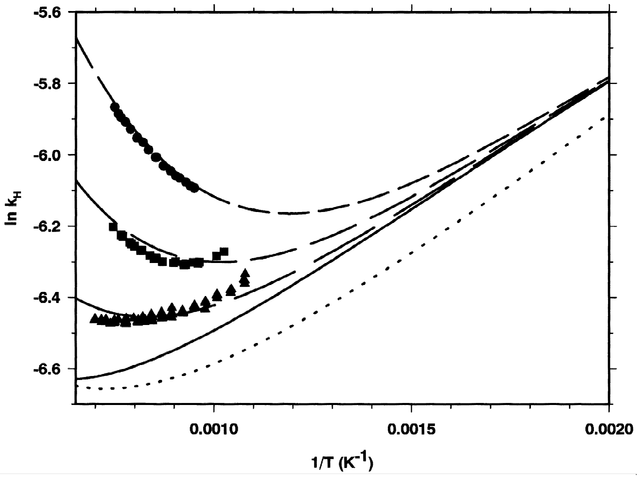

Fig. 3. The alloy effect and the contribution of the A,B term to the hydrogen solubility. Solid line, calculated hydrogen solubility based on zero ground-state-energy difference for the reaction (Eq. (1) with $C=1680$ K, $E=28517.5$ K, $A=0$), dotted line, deuterium solubility for $C=1680$ K, $E=28517.5$ K, $A=0$ (the isotope effect). Other curves, starting from the top, are hydrogen solubilities calculated from Eq. (1) with $C=1680$ K, $E=28517.5$ K, A calculated from Eq. (2) for $x=0.000$, $x=0.060$ and $x=0.850$. Points are experimental data rotated by $[28517.5\ \text{K}-E(x)]/T$ where $x=0.000$, circles; $x=0.060$, squares and $x=0.850$, triangles.

the isotope effect, and demonstrates the magnitude of the A,B term contribution at elevated temperatures. This was achieved by setting $E=28517.5$ K, the value that yields a net ground state energy change for the reaction of 0.0 K, and calculating the curve for ln (k_H) (the solid line) that indicates the contribution of the three-dimensional 1680 K harmonic oscillator only. The curve for ln (k_D) was calculated using the parameters for deuterium and $E=$ 28517.5 K The A,B term was calculated and added to the solid curve to produce the remaining curves in Fig. 3. The data for the alloys U–0.000Ti, U–0.060Ti and U–0.850Ti were superimposed on these curves by rotating each by $[28517.5\ \mathrm{K} - E(x)]/\mathrm{T}$. The positive curvature imparted to the model by the sum over the Boltzmann states of the harmonic oscillator is readily apparent as is the inadequacy of the harmonic oscillator model alone to describe the data. For pure uranium, the A,B term contributes as much as a factor of 2 to the magnitude of the hydrogen solubility at the high temperature limit. This term also contributes significantly to the temperature dependence of the enthalpy of solution over the entire compositional range.

The alloy composition dependence of parameters A and E demonstrate very strong alloy composition effects, such as the compositional ranges over which the parameters have a linear dependence on alloy composition and the inflection points between these segments, that correlate between these parameters. Indeed, these alloy composition effects manifest themselves distinctly in empirically calculated enthalpies of solution at constant temperature, in a simple plot of ln (k_H) versus alloy composition at constant temperature, and even in the less precise fits such as the one for $N=6$. On the other hand, the Einstein temperature, (parameter C, which is measured with high precision because of its sensitivity to both the magnitude of the isotope effect $\{\ln (k_H) - \ln (k_D)\}$ and the temperature at which this isotope effect is a maximum) shows no dependence on alloy composition. This indicates that the chemical (electronic) forces that bond the hydrogen in the metal have little or no effect on the spring constant of the proton in its interstitial lattice site. The large increase in hydrogen solubility in uranium, resulting from small additions of titanium, is consistent with the observations based on Auger electron spectroscopy surface analysis that there is total transfer of valence electrons from titanium to uranium at concentrations below that of U_2Ti [9]. This transfer of electrons from titanium to uranium greatly enhances the chemical binding (and solubility) of hydrogen in the alloy. From the linear segments of $E(x)$, it appears that this electron transfer takes place in three distinct stages. The A,B term is apparently due to electronic factors and relates to thermally induced changes in this electronic structure. These changes are more pronounced for low titanium compositions where the enthalpy of solution is most sensitive to alloy composition.

6. Conclusions

Hydrogen and deuterium solubility measurements have been made on 12 alloy specimens from the bcc uranium–titanium alloy system ranging in composition from pure uranium to pure titanium and bounded by the temperature range of 900–1473 K. The results are described by a global model within a standard error of 3% compared to a data precision for individual alloys of 1%. The model yielded an equation that describes the solubility of hydrogen in the alloy as a function of temperature, isotope and alloy composition as closed form algebra. Parameters in the model were interpreted as the Einstein temperature (1680 K) being independent of alloy composition. The solubility and the enthalpy of solution were strongly dependent on alloy composition and indicated electronic interactions between the alloy elements that strongly influenced the solubility without influencing the isotope effect. The major observations listed above were relatively independent of the details of the model. The model, and the fit to the data, could be improved by arriving at a better description of the Boltzmann states that add to the electronic contribution to the hydrogen solubility. If the model is to describe hydrogen in tetrahedral sites in these bcc alloys, the model must be altered to allow a decrease in the number of sites per metal atom with increasing temperature. For six sites per metal atom, this model based on a ground state energy and Boltzman-type thermally populatable energy states cannot describe these experimental observations.

References

[1] M. Hansen, *Constitution of Binary Alloys*, McGraw–Hill, New York, 1958, p. 1238.
[2] M.W. Mallette and M.J. Trzeciak, *Amer. Soc. Metals, Trans. Quart., 50* (1958) 981.
[3] A D. McQuillan, *Proc. Royal Soc. Ser. A, 204* (1950) 309.
[4] G.L. Powell, *J. Phys. Chem., 80* (1976) 375.
[5] G.L. Powell, *J. Phys. Chem., 83* (1979) 605.
[6] R. Lässer and G.L. Powell, *Phys. Rev., B 34* (1986) 578.
[7] G.L. Powell and R. Lässer, *Z. Phys. Chem., NF 163* (1989) 47.
[8] J.R. Lacher, *Proc. R. Soc. London, Ser. A, 16* (1937) 525.
[9] W.P. Ellis and G.L. Powell, *Surf. Sci., 115* (1982) L165.