CONF-960855--1

Y/DZ-1185/R1

Y-12

OAK RIDGE Y-12 PLANT

LOCKHEED MARTIN

SOLUBILITY OF HYDROGEN AND DEUTERIUM IN bcc-URANIUM-TITANIUM ALLOYS

G. L. Powell

Development Division

J. R. Kirkpatrick

Oak Ridge National Laboratory

DEC 20 1996

OSTI

Date of Issue: August 5, 1996

International Symposium on Metal Hydrogen Systems,
Fundamentals and Applications
Les Diablerets, Switzerland
August 25-30, 1996

MASTER

Prepared by the
Oak Ridge Y-12 Plant
Oak Ridge, Tennessee 37831
managed by
LOCKHEED MARTIN ENERGY SYSTEMS, INC.
for the
U. S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

MANAGED BY
LOCKHEED MARTIN ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

UCN-13672 (26 6-95)

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

COPYRIGHT NOTICE

The submitted manuscript has been authored by a contractor of the U.S. Government under contract DE-AC05-84OR21400. Accordingly, the U.S. Government retains a paid-up, nonexclusive, irrevocable, worldwide license to publish or reproduce the published form of this contribution, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, or allow others to do so, for U.S. Government purposes.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

SOLUBILITY OF HYDROGEN AND DEUTERIUM IN bcc-URANIUM-TITANIUM ALLOYS

G. L. Powell and J. R. Kirkpatrick^a, Oak Ridge Y-12 Plant*, Lockheed Martin Energy Systems, Inc.,
Oak Ridge, Tennessee 37831-8096

^aOak Ridge National Laboratory, Lockheed Martin Research Corporation, Oak Ridge, Tennessee

ABSTRACT

For the bcc-U-Ti alloy system, H and D solubility measurements have been made on 12 alloy specimens ranging in composition from pure U to pure Ti and temperature range bounded by 900 K to 1500 K. The results are described by a model within a standard error of 3%.

INTRODUCTION

The U-Ti alloy system has a high temperature (~900°C) region in which the bcc phase extends unbroken across the composition range from pure U to pure Ti/1/. Over this 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 H₂ pressure, varies by almost three orders of magnitude. It 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 the context of the bound proton model/2-5/, k is described as

$$\ln(k) = \ln(N) + \ln(1 + Ae^{-B/T}) - 3\ln(1 - e^{-C/T}) + (E - 3C/2)/T - 0.5\ln(LT^{7/2}/(1 - e^{-J/T})) - M/2T \quad (I)$$

where $N = 3$ or 6 is the number of H 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

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

together is the free energy function for H_2 (or, with different parameters, the free energy function for D_2)/4/, and the term containing A and B is an approximation for Boltzman states not explicitly included in the harmonic oscillator model for H in its site.

EXPERIMENTAL

H solubility measurements/2-4/ were made at infinite dilution with 1% accuracy on 12 alloy specimens representing Ti compositions in mole fraction of 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. Similar measurements were made for D except for the Ti compositions 0.060 and 0.185. The temperature range for these solubility measurements extended from the lesser of the liquidus temperature (1406 K for U) 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 Ti composition 0.850.

RESULTS

Preliminary analyses indicated that eq. I would describe each alloy 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 Ti composition with $N = 6$ since the A,B term was very small at the low temperature extremes, and the desired slope and magnitude of eq. I could not be simultaneously achieved. To describe the alloy effect, a more global model was employed for which $N=3$, $B=3600$ K, $C_H=1680$ K. A and E were optimized using all the $\ln(k_H)$ data with the following form $Q(x)$ to describe the alloy (x) dependence of A and E.

$$Q(x) = a\{x - 1/g \ln(\cosh[g(x-b)])\}/2 + c\{1/g \ln(\cosh[g(x-b)]) - 1/g \{\ln(\cosh[g(x-d)])\}/2 + e\{1/g \ln(\cosh[g(x-d)]) + x\}/2 + f \quad (II)$$

Eq. II describes 3 linear segments that are smoothly connected. For A, 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, $a=28957.2$, $b=0.02406$, $c=8179.18$, $d=0.28692$, $e=4833.22$, $f=29358.8$, $g=15.4827$, fit standard error=32.1. Using the above parameters, the data for D was fit 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 was 3%.

CONCLUSIONS

The Einstein temperature (C) is not a function of alloy composition. The ground state energy (E) varies from 28908 K ($A=16.73$) for U to 35462 K ($A=2.71$) for Ti, a change of -0.56 eV. Inflections occur at U-0.19Ti ($E=31189$, $A=4.27$) and U0.29Ti ($E=31927$ K, $A=2.81$). The contribution from thermally excited states also grew markedly as the concentration of titanium approached zero. This large increase in hydrogen solubility in U resulting from small additions of Ti is consistent with the observation that there is total transfer of valence electrons from Ti to U at concentrations below that of U_2Ti /6/. The A, B term is apparently due to electronic factors.

REFERENCES

1. M. Hansen, "Constitution of Binary Alloys," McGraw-Hill, New York, p.1238 (1958)
2. G. L. Powell, **J. Phys. Chem.** **80**, 375 (1976).
3. G. L. Powell, **J. Phys. Chem.** **83**, 605 (1979).
4. R. Lässer and G. L. Powell, **Phys. Rev. B** **34**, 578 (1986).
5. G. L. Powell and R. Lässer, **Z. Phys. Chem. NF** **163**, 47 (1989).
6. W. P. Ellis and G. L. Powell, **Surf. Sci.** **115**, L165 (1982).

Distribution

International Symposium on Metal Hydrogen Systems, Fundamentals and Applications

Louis Schlapbach

Oak Ridge National Laboratory

J. R. Kirkpatrick

Oak Ridge Y-12 Plant

A. K. Lee/DOE-OSTI (2)

G. L. Powell

K. F. Simon/W. E. Smith

Y-12 Central Files - (RC)