CONF

MASTER

RECEIVED BY OSTI MAY 12 1986

CONF 86-1401-1-1

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

LA-UR--86-1401

DE86 010197

TITLE A RE-EXAMINATION OF THE NEPTUNIUM-HYDROGEN SYSTEM

AUTHOR(S) J. W. Ward, MS-13
W. Bartscher
J. Rebizant

SUBMITTED TO Properties and Applications of Metal Hydrides,
Maubuisson, France, May-25-30, 1986

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.

By acceptance of this article the publisher recognizes that the U S Government retains a nonexclusive royalty-free license to publish or reproduce the published form of this contribution or to allow others to do so, for U S Government purposes

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U S Department of Energy

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

1350

A RE-EXAMINATION OF THE NEPTUNIUM-HYDROGEN SYSTEM

JOHN W. WARD,* WILHELM BARTSCHER and JEAN REBIZANT

Commission of the European Communities, Joint Research
Centre, Karlsruhe Establishment, European Institute for
Transuranium Elements, Postfach 2266, 75 Karlsruhe (FRG)

Summary

New P-C-T studies have been made on the NP + H system, using ultra-pure double-electrorefined metal. Measurements were carried out over six orders of magnitude in pressure, from 0.0005 to 70 bar. The solubility of hydrogen was found to be very low. Metal-dihydride plateaus were flat, the two-phase boundary extremely sharp; this occurred at the unusual value $H/Np = 2.13$. The dihydride lattice expanded upon addition of hydrogen, also in contrast to other trivalent rare-earth and actinide hydrides. A rather narrow cubic/hexagonal two-phase region was found (only on dehydriding), together with an even narrower hexagonal phase region. The effect of the beta-gamma transition at 576°C could be seen both in the curvature of the phase boundary and the partial molal enthalpy values.

Entropies of formation were found to be nearly constant. The data below 576°C can be described by the equation $\ln P(\text{bar}) = 13.297 - 13233/T(K)$, giving values, adjusted for the reaction $0.93 Np + H_2 = 0.93 NpH_{2.13}$: $\Delta H_f(NpH_{2.13}) = 118.3 \text{ kJ/mol}$ (28.27 kcal/mol), and $\Delta S_f(NpH_{2.13}) = 118.4 \text{ J/mol-K}$ (28.3 cal/mol-K). Integral heats and entropies are calculated for the entire system, and the unusual phase behavior is discussed in terms of the electronic structure.

1. Introduction

Considerable diversity and complexity is found in the early actinide hydrogen systems Th + H, Pa + H and U + H [1]. Thorium forms a simple dihydride, but also a complex near-tetrahydride Th_4H_{15} with 16 thorium atoms per unit cell, which becomes a superconductor at low temperatures. Protactinium exhibits even more complex hydriding behavior [2,3], forming both a C15 Laves phase and an A15 $\beta-UH_3-x$ structure above 500°C, as well as an apparently stable bcc $\alpha-UH_3-x$ structure with wide stoichiometry range at lower temperatures. The uranium-hydrogen system has been well-studied, forming normally the A15 beta-phase compound, with its stoichiometric, metallic and magnetic; the alpha-structure is quite unstable and exists only at low temperatures.

* On Professional Research and Teaching Leave, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

Then it is somewhat of a surprise that the neptunium-hydrogen system suddenly reverts to rare-earth-like chemistry -- doubly so because band structure calculations predict maximum 5f-electron character in neptunium and its intermetallic compounds [4]. Orthorhombic Np exists to 553K, the tetragonal beta-phase to 848K, and the bcc gamma-phase to the melting point at 913K. One might expect the incommensurate nature of the metal-dihydride interface to affect the phase boundary and the thermodynamic data for each of these phases, and this indeed can be seen in the results given here.

The first extensive studies on the Np - H system were reported by Mulford and Wiewandt [5], using a glass Sieverts-type apparatus. Samples were contained in a fused silica bulb, enclosed in a massive silver block. The measuring thermocouple was external, but calibrated against a test thermocouple in the sample position. Studies were carried out in the range 373-898K. For the Np-NpH_{2-x} region flat reproducible plateaus were found, both on hydriding and dehydriding. The solubility of hydrogen in the metal was judged to be small. An anomalous apparent increase in hydrogen content of the NpH_{2+x} phase boundary with temperature was noted, in contradiction to expected behavior. The location of this phase boundary near $\text{H/Np} = 2.15$ is also quite anomalous. Beyond the composition $\text{H/Np} \approx 2.7$ an hexagonal phase was found in the X-ray data, with attendant pressure hysteresis upon hydriding and dehydriding. Hexagonal-cubic plateaus were not found, but inferred from the data. The hexagonal phase was identified by X-ray. Finally, the lattice parameters of the cubic NpH_{2+x} phase were found to increase with addition of hydrogen, whereas all other known rare-earth hydrides and the hydrides of plutonium and americium exhibit the opposite behavior.

In a more recent and somewhat abbreviated study [6], Mintz et al have questioned some of the results of Mulford and Wiewandt [5], particularly the increase in hydrogen content at the phase boundary with increasing temperature, and also the behavior of the partial molal enthalpies and entropies for the cubic phase; their analysis of the P vs $1/T$ curves published by Mulford and Wiewandt showed ΔH values apparently independent of composition, and ΔS values decreasing with increasing H/Np . Both these results are in contradiction to conventional thermodynamics.

The metal-dihydride plateaus reported by Mintz et al [6] were not flat, and a considerable solubility could be implied, for example at 610°C. Much larger heats and entropies of formation were from their data; partial molal enthalpies decreased with increasing composition, and partial molal entropies became less negative, in contrast to the Pu + H system, where entropies were found to be quite constant [7]. An approximately constant phase boundary (over the range studied) was found, again at about H/Np = 2.15. Cubic/hexagonal plateaus were again not found, but the hexagonal hydride was identified by X-ray diffraction.

The considerable disagreement between these two studies indicated the need for a confirming measurement. Therefore, a fortunate situation was the recent production of limited quantities of ultra-pure, double-electrorefined neptunium metal at Los Alamos National Laboratory, and the existence of a sophisticated semi-automated Sievert-type apparatus dedicated to the study of radioactive materials at the Institute for Transuranium Elements (EURATOM) in Karlsruhe, West Germany.

2. Experimental methods

2.1 Materials and analysis

The neptunium metal supplied by Los Alamos had a purity better than 99.6%. Major contaminants were Ag(5ppm), Al(25ppm), Ca(100ppm), Pu(15ppm), and O₂(40ppm). Other impurities were below the detection limits of spark-source mass spectrometry. Approximately 0.5 gm samples were loaded, in a dry nitrogen atmosphere, into the equipment. High purity (99.9997) hydrogen and high purity (99.999%) argon, obtained from Messer Griesheim, were further purified by passage through in-line Oxisorb[®] traps.

2.2 Equipment and procedures

The experimental apparatus has been described previously [2]. In addition to the quartz cell for work below one bar, a new gold-lined cell was constructed for diffusion-free studies at high pressures and temperatures, as shown in Fig. 1. The 0.5 mm gold inner cup is sealed permanently in the cool area at the first joint, and a normal copper Mini-Conflat seal is used for loading; thus hydrogen gas is never in

contact with hot steel. Samples were loaded into a single-crystal tungsten crucible, in direct contact with the internal thermocouple. As noted earlier in studies with the protactinium-hydrogen system, this becomes extremely important at very low pressures, where the hydrogen gas no longer carries temperature information efficiently from the cell wall to the sample. This effect has been seen below about 10 torr, and in these experiments the differential between outer and inner thermocouples reached 28°C at the lowest pressures of measurement. Therefore, any very low pressure hydriding studies utilizing an external thermocouple should be suspect. Both the quartz and metal cells were carefully calibrated with hydrogen over the entire temperature range of the measurements, to obtain formulae for precise apparent volumes.

Studies were performed at several temperatures, from 364 to 628°C (neptunium melts at 640°C). Most of the pressure measurements were made along hydriding and dehydriding isotherms, adding and subtracting gas in small increments. Dehydriding values were also obtained in temperature ramp experiments. A fixed quantity of hydrogen was introduced to the system, which was then ramped by the computer (usually overnight) through the selected temperatures of measurement.

The hydrides formed under the various conditions of preparation were characterized by powder X-ray diffraction. Desired compositions were obtained by hydriding or dehydriding to a selected H/Np value, then cooling to room temperature while maintaining precise composition by withdrawing gas under computer control. Samples were protected by an inert atmosphere during handling and preparation. The lattice parameters were calculated with the LRC-2 program, using the Nelson-Riley extrapolation [8].

3. Results

3.1 Hydrogen pressures

Pressure-composition isotherms are shown in Fig. 2. In both the saturated metal region and the metal/dihydride plateau region, pressures came to equilibrium immediately, upon either addition or subtraction of hydrogen -- an indication of the high purity of the metal. Plateaus were absolutely flat for all temperatures, though some sluggishness was

noted for hydriding (not dehydriding) at 364°C upon approaching H/Np = 2.0.

Plateau pressures were very close to those reported by Mulford and Wiewandt [5] except at 425 and 364°C where their pressures were lower than ours, no doubt due to the lagging thermocouple effect discussed above. The solubility of hydrogen is clearly very low at all temperatures, reaching an H/Np value of only 0.04 at 605°C.

As can be seen in Fig. 2, the phase boundary is very sharp (also at 364°C, but only on dehydriding). The sharpness and reversibility at this corner is again evidence, in contrast to earlier studies, of the high purity of the metal. This boundary does appear to displace slightly toward higher content with increasing temperature, from H/Np = 2.11 at 364°C to 2.14 at 574°C; we attach no particular significance to this. Of more interest, however, is the reverse displacement above 574°C, where the gamma-neptunium/hydride interface is involved.

The addition/subtraction of hydrogen in the range $2.13 < \text{H/Np} < 2.6$ was generally reversible, but more sluggish on hydriding (addition) at the higher composition. Beyond this composition there was increasing hysteresis, and it was clear that, upon cooling at high pressure, a transition was occurring, the H/Np ratio finally (with time) reaching 3.0. Using the high pressure capabilities of the system, dehydriding studies were carried out, after equilibration at high pressure, at 148, 196, 255 and 310°C -- the latter requiring a starting pressure of 70 bar. As shown in Fig. 2, this method produced for the first time the hexagonal-cubic two-phase plateau region, joining smoothly to the hydriding/dehydriding data in the cubic region.

These results are summarized in the proposed phase diagram shown in Fig. 3. It is clear that not only is the hexagonal phase quite narrow, but also that both it and the two-phase region will probably disappear above 400°C, leaving finally just the solid-solution cubic phase.

3.2 X-ray diffraction results

Samples prepared as described above were analyzed at the compositions H/Np = 1.50, 2.00, 2.15, 2.30, 2.50, 2.80 and ~3.00. X-ray results are given in Table 1. The strong pattern of the hydride masks the weaker metal lines at H/Np = 1.50, as also found by Mulford and Wiewandt [5]. A lattice parameter increasing with composition is also

confirmed. Weak cubic lines observed at $H/Np = 3.0$ come from the surface, an artifact due to decomposition of the hexagonal phase at zero pressure, during the capillary preparations.

3.3 Thermodynamic results

In the thermodynamic evaluation of the P-C-T data significant differences in partial molal enthalpies and entropies, as well as the enthalpies and entropies of formation, could be detected for the first time for temperatures below and above the β to γ transition temperature of the neptunium metal at 576°C . The plateau data below 576°C are well-described by the equation

$$\ln P(\text{bar}) = 13.297 - 13233/T(\text{K}) \quad \text{Eq. 1}$$

for the formation of the dihydride, in reasonable agreement with the earlier results of Mulford and Wiewandt [5]. Since the actual single-phase composition of hydride (end of plateau) is $H/Np = 2.13$, the heats and entropies of formation, adjusted to the reaction

$$\Delta H_f (\text{Np H}_{2.13}) = 118.3 \text{ kJ/mol, and } \Delta S_f (\text{Np H}_{2.13}) = 118.4 \text{ J/mol-K.}$$

The plateau data above 576°C then show a slightly steeper slope. This effect can be more clearly seen in the pressure vs $1/T$ data at constant composition, as shown in Fig. 4. Slopes break at this temperature for the compositions 2.15, 2.20 and 2.30 but the effect damps out by 2.40. This probably describes a minor structural perturbation due to the metal/hydride mismatch at the interface, for the two metal phases. Nevertheless, the general "wagon-wheel effect" of the slopes with composition is clear, as also shown by Haschke [7] and therefore the calculated partial molal enthalpies decrease in regular fashion with composition, as they should, until the appearance of the hexagonal phase. These results are compared and contrasted with those of Mulford and Wiewandt [5] and Mintz et al [6] in Table 2. It can be seen, for the partial molal enthalpies, that our values are in the same range as those of Ref. 5 for temperatures representative of the $\beta\text{-Np/NpH}_x$ region, whereas for the $\gamma\text{-Np/NpH}_x$ region (but only near the phase boundary) the data of Ref. 6 are comparable.

Partial molal entropies for the cubic region are in the range 90-100 J/K mol H_2 for temperatures below 576°C , and show no apparent correlation with either Ref. 5 or Ref 6. For temperatures above 576°C

our values are about 130 J/K mol H_2 (except for $H/Np = 2.30$), again with no clear correlation with either Ref. 5 or Ref. 6.

Integral entropies and entropies of formation for NpH_2 and NpH_3 were calculated from integration of the isotherms, up to the limits $H/Np = 2$ and 3 respectively. Integration was by Simpson's method. Plots of $\Delta G^\circ f(T)$ gave straight lines. Integration of the $\ln P = f(H/Np)$ curves for the ranges $2.0 \leq H/Np \leq 2.6$ and $2.6 \leq H/Np \leq 3.0$ gave smooth results; for 148, 186, 255 and 310°C and $H/Np < 2.6$, extrapolation of the partial data to lower temperatures was made. These data are given in Table 3, again contrasted with the data from Ref. 5 and Ref. 6. The indicated confidence limits are at the 0.95 probability level. Here again, the composite results of Mulford and Wiewandt [5] are close to our values.

TABLE 1

Lattice parameters and space groups for neptunium hydrides

H/Np	Parameters (pm)	Space group	Remarks
1.50	5.3565 ± 7	Fm3m	Diffuse lines, cubic
2.00	5.3475 ± 4	Fm3m	Cubic
2.15	5.3481 ± 7	Fm3m	Cubic
2.30	5.3490 ± 5	Fm3m	Cubic
2.50	5.3516 ± 6	Fm3m	Cubic
2.80	5.3578 ± 27	Fm3m	Two-phase region, cubic + hexagonal
	a 6.5045 ± 45	P3c1	
	c 6.7086 ± 54		
3.00	a 6.5338 ± 37	P3c1	Strong hexagonal, very weak cubic
	c 6.7204 ± 43		

TABLE 2

Partial molal enthalpies and entropies of neptunium hydrides

H/Np	$\bar{\Delta}H$ (kJ/mol H_2)				$\bar{\Delta}S$ (J/K mol H_2)			
	$\leq 576^\circ C$	$> 576^\circ C$	Ref. 5	Ref. 6	$\leq 576^\circ C$	$> 576^\circ C$	Ref. 5	Ref. 6
2.15	-90.5	-124	-88.7	-124.4	-88	-131	-144	-121
2.20	-87.1	-125	-87.1	-100.4	-89	-136	-144	-100
2.30	-85.3	-125	-88.3	-46.0	-98	-115	-158	-46
2.40	-81.0	-100	-84.5		-104	-129	-166	
2.60	-70.0				-100			
2.70	-82.3				-156			
2.80	-89.0				-174			
2.90	-88.3				-173			

TABLE 3

Integral enthalpies and entropies of formation of neptunium hydrides

NpH_x	ΔH_f (kJ/mol product)			
	$\leq 576^\circ C$	$> 576^\circ C$	Ref. 5	Ref. 6
NpH_2	-112.8 ± 1.7	-122.2 ± 1.8	-117.2	-146.5
NpH_3	-156.2 ± 1.7			

NpH_x	ΔS_f (J/K mol product)			
	$\leq 576^\circ C$	$> 576^\circ C$	Ref. 5	Ref. 6
NpH_2	-114.3 ± 2.4	-125.5 ± 2.1	-121.4	-146.5
NpH_3	-177.8 ± 2.4			

4. Conclusions

The general plateau pressures reported by Mulford and Wiewandt [5] have been in the main substantiated, with the added refinement of a slightly different equation for the gamma region. P-C-T data reported by Mintz et al [6] appear to contain serious systematic errors, perhaps in temperature, or in apparent volume calibrations. The curvature in the

solubility region and slightly sloping plateaus indicate also a lack of metal purity. Our data show an approximately constant partial molal entropy of formation, as also occurs for plutonium [7], and a regularly increasing (more positive) partial molal enthalpy over the cubic region, in agreement with expected thermodynamics.

As noted in the introduction, neptunium and neptunium intermetallics should show large 5f electron effects. However, the metal-metal distance in the hydrides is large enough for the f-electrons to be localized. The hydrides are non-magnetic [9], simply due to a non-magnetic $\text{Np}^{3+}(5f^4)$ ground state. Nevertheless, Np-5f/H-1s interactions should be strong. In contrast to the rare-earth, plutonium and americium hydrides, the "magic minimum" metal-hydrogen distance of 2.3Å is already reached before $\text{H/Np} = 2.0$; thus the lattice must expand upon addition of more hydrogen (or change phase). But the hexagonal phase does not appear early, and in fact should disappear above 400°C. Therefore, the cubic dihydride lattice must be quite metallic and "plastic" in nature; this was born out by the appearance of the samples, which, after dozens of hydridding cycles, remained intact, with no powdering.

The sharp phase boundary at $\text{H/Np} = 2.13$ is very hard to explain. Are all the tetrahedral sites filled? Recent studies [10] indicate a cluster mechanism and actual depopulation of tetrahedral sites at higher compositions in the Pu + H system; this could be even more likely in the Np + H system, given the degree of 5f character in the electronic structure. Clearly this is a very unusual system which deserves further study. Particularly interesting would be resistivity experiments, and extensive neutron studies at various NpH_{2+x} compositions.

References

1. J. W. Ward, "Properties and Comparative Trends in Actinide-Hydrogen Systems," Ch. 1 in Handbook on the Physics and Chemistry of the Actinides, Eds. A. J. Freeman and C. Keller, Elsevier Science Publ. B. V. (1985).
2. J. W. Ward, J. M. Haschke, J. Rebizant and W. Bartscher, J. Less-Common Metals 100 (1984) 195.
3. J. M. Haschke, J. W. Ward and W. Bartscher, J. Less-Common Metals 107 (1985) 159.

4. H. H. Hill, Plutonium 1970 and Other Actinides, Ed. W. N. Miner, Nucl. Met. Series 17 AIME (1970) 2.
5. R. N. R. Mulford and T. A. Wiewandt, J. Phys. Chem. 69 (1965) 1641.
6. M. H. Mintz, Z. Hadari and M. Bixon, J. Less-Common Metals 48 (1976) 183.
7. J. M. Haschke, USDOE Rept. RFP-3099 (1981).
8. D. E. Williams, Rep. IS-1052, 1964 (U.S. Atomic Energy Commission, Washington, DC).
9. A. T. Aldred, C. Cinader, D. J. Lam and L. W. Weber, Phys. Rev. B19 (1979) 300.
10. W. Bartscher, A. Boeuf, R. Caciuffo, J. M. Fournier, J. M. Haschke, L. Manes, J. Rebizant, F. Rustichelli, J. W. Ward, Solid State Comm. 52 (1984) 619.

CAPTIONS

- Fig. 1. Diagram of the new high-pressure, high-temperature gold-lined metal cell, showing sample, thermocouple and seal details.
- Fig. 2. Pressure-composition diagram for the Np + H system. Open circles denote hydriding, solid circles dehydriding. Squares connected by dotted lines are temperature-ramp experiments.
- Fig. 3. Proposed phase diagram for the Np + H system.
- Fig. 4. Plot of pressure vs $1000/T(K)$ for five compositions $H/Np = X$. The perturbation near 575° for compositions nearer the phase boundary shows the influence of the beta-gamma metal transition on the data.