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Journal of Nuclear Materials 247 (1997) 328–332

journal of nuclear materials

Study on the Nb–O–H ternary system

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Abstract

The hydrogen solubility in pure niobium and niobium–oxygen solid solutions was measured in the temperature range of 500–900°C at a hydrogen pressure below 10^4 Pa using a modified Sieverts apparatus. The niobium–oxygen solid solutions had oxygen contents from 0.01 to 0.04 O/Nb atom ratio and showed a homogeneous bcc phase. All the hydrogen solubility data for the niobium–oxygen solid solutions were found to obey Sieverts' law. The hydrogen solubility first increased with increasing oxygen content in niobium and then decreased. The variation in the enthalpy of solution of hydrogen with the oxygen content indicated a maximum at about 0.01 O/Nb atom ratio. Partial molar thermodynamic quantities of hydrogen were derived by a solution model. The partial molar enthalpy and the partial molar excess entropy first increased and then decreased with the oxygen content. The changes in the quantities with the oxygen content were discussed in terms of sums over vibrational, lattice dilatational and configurational contributions. © 1997 Elsevier Science B.V.

1. Introduction

The niobium–hydrogen binary system has been extensively studied by several authors [1–6]. A little information of hydrogen solubility is available for a dilute solution of the niobium–hydrogen system and there are insufficient data for the influence of interstitial elements on the hydrogen solubility in niobium. Oxygen is one of the most important non-metal element among impurities interstitially dissolved into the niobium metal lattice.

In the present study, the niobium–oxygen–hydrogen ternary system has been therefore examined to elucidate the influence of interstitial oxygen on the hydrogen solubility in niobium. The effect of interstitial oxygen was discussed on the basis of partial molar quantities derived from experimental data.

2. Experimental

The niobium–oxygen solid solutions were prepared by dissolving known amounts of oxygen gas (99.999%, in purity) into a single crystal niobium disk (Goodfellow Cambridge Limited, 99.999 wt% in purity, 12 mm ∅ × 2 mm). Oxidation of the niobium disk was performed in a constant volume system and the oxidized niobium was subsequently annealed at a temperature of 1000°C for an annealing period of 200 h in a vacuum of 10^{-6} Pa. The niobium–oxygen solid solutions thus prepared were homogeneous solid solutions with a bcc structure. The oxygen contents of the solid solutions were 0.010, 0.020, 0.030 and 0.040 O/Nb atom ratios. Hydrogen gas (initial purity, 99.999%) was purified by passing through a liquid nitrogen trap and used for solubility measurement. Hydrogen solubility in the niobium–oxygen solid solutions was measured at temperatures between 500 and 900°C at a pressure below 10^4 Pa in a modified Sieverts UHV apparatus. The correction of thermal transpiration and hot volume effects was carried out for all the data obtained in the present study.

3. Results and discussion

The hydrogen solubility CH in pure niobium and niobium–oxygen solid solutions was proportional to the square root of the hydrogen pressure P_{H_2} all the data of the hydrogen solubility obeyed Sieverts' law: $C_H = K_H \times P_{H_2}^{1/2}$ where K_H the Sieverts' constant. Fig. 1 shows the change in the Sieverts' constant K_H with temperature. As indi-

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PII S0022-3115(97)00057-3

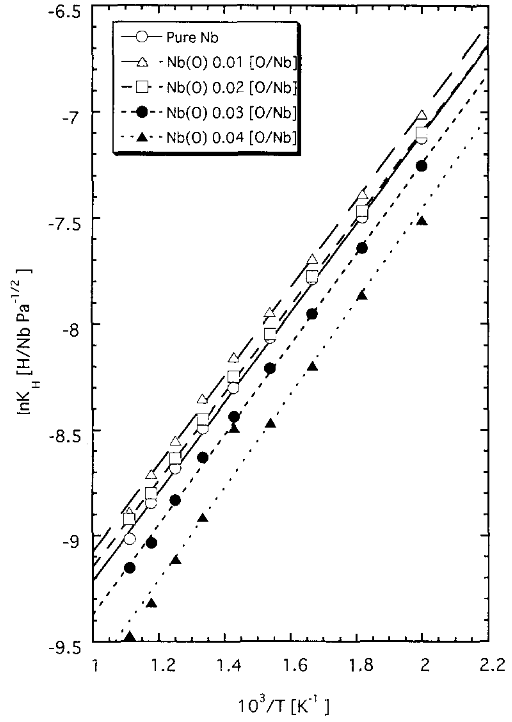

Fig. 1. Temperature dependence of Sieverts' constant K_H for pure niobium and niobium–oxygen solid solutions.

cated in Fig. 1, the temperature dependence of Sieverts' constant can be represented by ln $K_H = A + B/T$ where A and B are constants and T is the temperature in K. The enthalpy of solution of hydrogen ΔH (kJ/mol) was evaluated from the B value. In Table 1, the values of A, B and ΔH are summarized.

The hydrogen solubility in pure niobium obtained in the present study agreed with the literature data [1–6]. The reported values for the enthalpy of solution estimated from the solubility measurements range from −34 to −40 kJ/mol [1–6]. Kleppa et al. [3] have performed microcalorimetry on the niobium-hydrogen system and reported the enthalpy value of −36.4 kJ/mol for a dilute solution at 713 K. The value of −35.2 kJ/mol obtained in the present study is consistent with the enthalpies of solution in the literature.

Table 1

Parameters of Sieverts' law A and B and enthalpy of solution ΔH for pure niobium and niobium–oxygen solid solutions

Composition (Nb/O atom ratio)	A	B	ΔH (kJ/mol)
0	−11.3	4240	−35.2
0.010	−11.1	4170	−34.7
0.020	−11.2	4120	−34.3
0.030	−11.5	4280	−35.6
0.040	−11.8	4430	−36.8

It is found from Fig. 1 that the hydrogen solubility at first increases with the oxygen content of the niobium–oxygen solid solution and then decreases at a higher oxygen content. The enthalpy of solution of hydrogen goes through a maximum and then decreases with increasing oxygen content, as shown in Table 1. In our previous study [7], the hydrogen solubility in vanadium–oxygen solid solutions has been examined and the oxygen addition gave almost the same trend in the hydrogen solubility as niobium. Dantzer et al. [8] have reported that oxygen in tantalum reduced both the hydrogen solubility and the enthalpy of solution at 713 K. The hydrogen solubility in the Nb–O solid solutions obtained in the present study revealed a similar trend for the tantalum–oxygen solid solutions reported by Dantzer et al. [8].

Tetrahedral (displaced-tetrahedral) interstitial site occupancies of hydrogen establish in the bcc niobium lattice. At equilibrium, the chemical potential of hydrogen in the gas phase is equal to that of hydrogen in the solid solution. The following solubility equation was obtained from a simple model and applied to the experimental data:

$$\ln\left(\frac{C_H T^{7/4}}{6P_{H_2}^{1/2}A_{H_2}}\right) = -\frac{\left(H_H - E^d_{H_2}\right)}{kT} + \frac{S_H}{k}. \qquad (1)$$

In Eq. (1), H_H and S_H are the partial molar enthalpy and the partial molar excess entropy of hydrogen referred to the standard state of hydrogen atoms at rest in a vacuum.

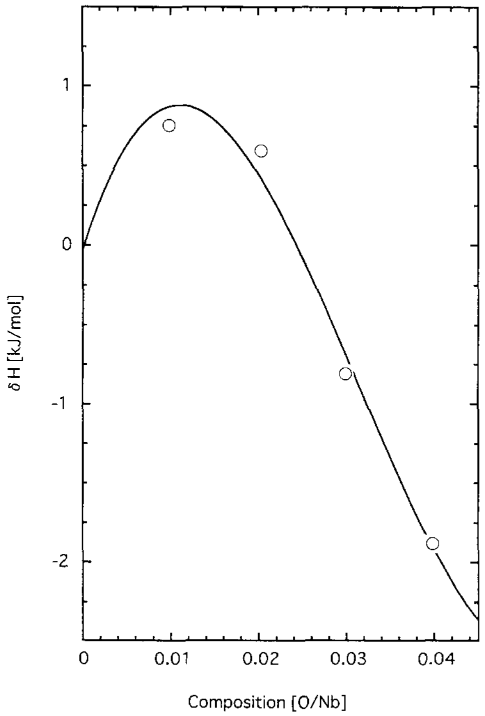

Fig. 2. Change in δH value with the composition of solid solution.

The A_{H_2} is the value related to partition functions of hydrogen gas, $-2E^d_{H_2}$ is the dissociation energy of the hydrogen molecule and k the Boltzmann constant.

The influences of interstitial oxygen on the hydrogen solubility in niobium were discussed on the basis of the differences in the partial molar thermodynamic functions between pure niobium and oxygen solid solutions defined as: $\delta H = H_H - H^0_H$ and $\delta S = S_H - S^0_H$ where H^0_H and S^0_H are the values for pure niobium. The changes in the values of δH and δS with the oxygen content of solid solution were estimated from the experimental data, as shown in Figs. 2 and 3. From Figs. 2 and 3, both the experimental δH and δS values are found to go through maximum values and then decrease with increasing oxygen content. Dantzer et al. [8] have reported that oxygen addition into tantalum with an amount of 0.031 O/Ta brings about the partial molar enthalpy decrease of 3.8 kJ/mol and reduces the partial molar entropy by about 4 J/mol K. The values of δH and δS obtained in the present study are comparable to the enthalpy and entropy changes for tantalum–oxygen–hydrogen ternary by Dantzer et al.

In order to elucidate the effect of interstitial oxygen on the hydrogen solubility, we assumed that the partial molar enthalpy and the partial molar excess entropy can be written by the sum of contributions from various degrees of freedom: the enthalpy and entropy difference δH and δS are expressed as, $\delta H = \delta H^v + \delta H^d + \delta H^c$ and $\delta S = \delta S^v + \delta S^d + \delta S^c$ where δH^v and δS^v are the differences in vibrational contribution between the solid solutions and pure niobium, δH^d and δS^d the lattice dilatation terms and δH^c and δS^c the configurational terms. The results for the theoretical analysis of partial molar quantities are shown in Figs. 4 and 5, together with the experimental values.

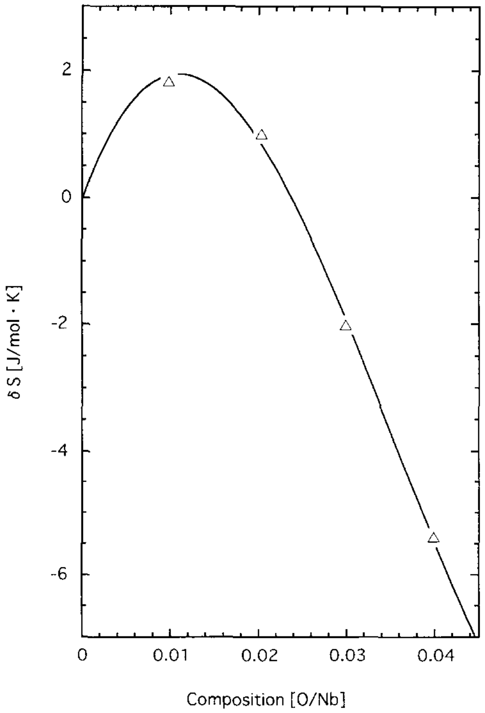

Fig. 3. Change in δS value with the composition of solid solution.

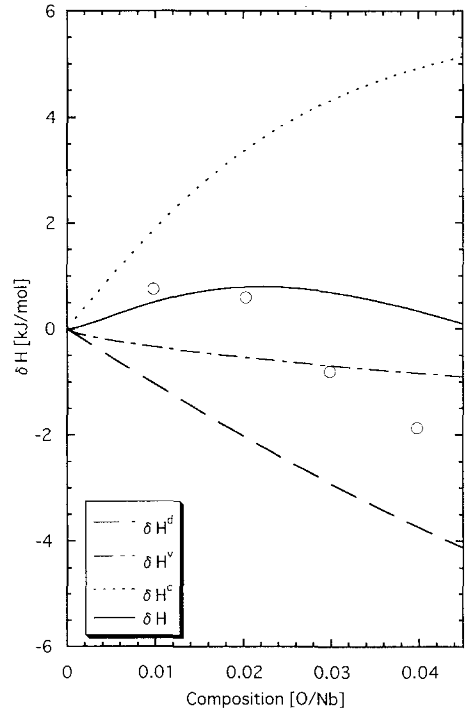

Fig. 4. Theoretical analysis of δH value. O: experimental values.

The vibrational terms were evaluated from the local vibrational mode of hydrogen in the solid solution:

$$\delta H^v = \Sigma \left[\frac{h\nu_i - h\nu_i^0}{2} + \frac{h\nu_i}{\exp(h\nu_i/kT) - 1} + \frac{h\nu_i^0}{\exp(h\nu_i^0/kT) - 1} \right], \tag{2}$$

$$\delta S^v = \Sigma \left[-k \ln \left\{ \frac{1 - \exp(h\nu_i/kT)}{1 - \exp(h\nu_i^0/kT)} \right\} + \frac{1}{T} \left\{ \frac{h\nu_i}{\exp(h\nu_i/kT) - 1} - \frac{h\nu_i^0}{\exp(h\nu_i^0/kT) - 1} \right\} \right] \tag{3}$$

In Eqs. (2) and (3), ν_i ($i = 1$–3) is the vibrational frequency of hydrogen in niobium–oxygen solid solution, ν_i^0 is the vibrational frequency of hydrogen in pure metal, and frequencies for the non-degenerate and doubly degenerate modes of vibration of hydrogen are ν_1 and ν_2 ($= \nu_3$). Oxygen in niobium slightly perturbs the vibrational energy levels of hydrogen [9]. Oxygen addition results in the

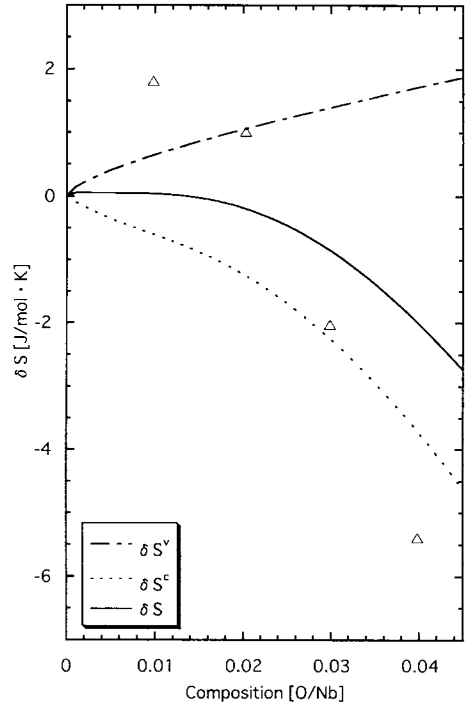

Fig. 5. Theoretical analysis of δS value. △: experimental values.

decrease of the vibrational energy for doubly degenerate mode, but no marked change for non-degenerate mode. Assuming that the change in the vibrational frequencies of ν_2 and ν_3 as a function of the oxygen content is given by $\nu_i = \nu_i^0 \times (1 - C_O^{0.67})$ where C_O is the oxygen content of the solid solution in atom ratio, we evaluated the values of δH^v and δS^v using $\nu_2^0 = \nu_3^0 = 4.04 \times 10^{13}$ s^{-1} and $T =$ 973 K. It is found from Figs. 4 and 5 that the δH^v is small and negative and δS^v is small and positive.

Oxygen addition causes the expansion of the niobium bcc lattice and consequently changes the partial molar quantities of hydrogen: δH^d and δS^d. The following equations approximately express the dilatational contribution:

$$\delta H^d = -\int \frac{V_H V_O}{V_{Nb} K_{Nb}} (1 - \alpha T)\, dC_O, \qquad (4)$$

$$\delta S^d = -\int \frac{V_H V_O}{V_{Nb} K_{Nb}} \alpha\, dC_O, \qquad (5)$$

where V_H and V_O are the partial molar volumes of hydrogen and oxygen in niobium, V_{Nb} and K_{Nb} are the molar volume and compressibility of niobium and α is the thermal expansion coefficient of metal. The theoretical δH^d values are shown in Fig. 4, indicating that the volume expansion due to interstitial oxygen yields a large negative enthalpy change. Since the value of δS^d appears to be negligibly small due to a small value of thermal expansion coefficient of niobium, the δS^d term was not estimated theoretically.

The δH^c and δS^c terms represent the degeneracy of the configurational energy and entropy of hydrogen owing to the electronic interaction of oxygen with hydrogen through niobium. In our previous study [10], a cell model was proposed for hydrogen in the IV group metal–oxygen solid solutions and the δH^c and δS^c values were estimated.

On the assumption that octahedral oxygen modifies electronic properties of an adjacent niobium atom and hydrogen atom is located in a tetrahedral cell consisting of four niobium atoms, we developed the cell model for the niobium–oxygen–hydrogen solid solution. A type of the cell is distinguished with the number of niobium atoms modified by non-metal element atoms in neighboring octahedral sites. An n-type cell ($n = 0$–4) is defined as having n modified metal atoms. The number of n-type cell N_n is expressed by $N_n = 6N_M {}_4C_n(1-x)^{4-n}x^n$ where N_M is the total number of metal atoms in a solid solution ($N_M = \Sigma N_n/6$) and x is the ratio of the total number of modified metal atoms to the N_M. Thus, the δH^c and δS^c are written as

$$\delta H_c = \frac{(\mathrm{P.F.})'}{(\mathrm{P.F.})}, \qquad (6)$$

$$\delta S_c = \frac{(\mathrm{P.F.})'}{T(\mathrm{P.F.})} + k \ln(\mathrm{P.F.}). \qquad (7)$$

$$(\mathrm{P.F.})' = \left[\Sigma \varepsilon_n N_n \exp\left(-\frac{\varepsilon_n}{kT}\right)\right] \times \frac{1}{6N_M}.$$

$$(\mathrm{P.F.}) = \left[\Sigma N_n \exp\left(-\frac{\varepsilon_n}{kT}\right)\right] \times \frac{1}{6N_M}.$$

In Eqs. (6) and (7), ε_n is the energy required to insert a hydrogen atom into a n-type cell for the fixed reference level. In order to develop the relationship of the x value with the oxygen content C_O, we assume that a niobium atom is completely modified if one or more oxygen atoms occupy the first and second nearest octahedral sites. Since the number of the first nearest octahedral sites is 6 and the number of the second nearest octahedral sites is 12, the variation in x with C_O is given as follows: $x = 1 - (1 - C_O)^{18}$.

As shown in Figs. 4 and 5, the changes in δH^c and δS^c with the oxygen content are estimated, using a set of the cell energies ε_n and the Eqs. (6) and (7). The theoretical configurational enthalpy term δH^c increases with the oxygen content, as evidenced by Fig. 4. It is found from Fig. 5 that δS^c shows a small negative value at a low oxygen content, but at a higher oxygen content it decreases rapidly with the oxygen content.

In Figs. 4 and 5, the theoretical curves of δH and δS are indicated by solid lines. It should be noted that the theoretical curves well express the tendency for the changes in the experimental δH and δS values with the oxygen content of solid solution. The increase in the δS value at an oxygen content of 0.01 O/Nb appears to be of importance for the change in the hydrogen solubility in the niobium–oxygen solid solution. However, the magnitude of the positive change in the partial molar excess entropy cannot be explained only by the vibrational contribution. Therefore, further analysis on other contributions such as dual site occupancies of hydrogen is needed for understanding the influence of interstitial oxygen on hydrogen behavior in niobium more clearly.

4. Conclusions

The study on the hydrogen solubility in pure niobium and niobium oxygen solid solutions with an oxygen content of 0.010–0.040 O/Nb has been performed in the temperature range of 500–900°C at a hydrogen pressure below 10^4 Pa using a modified Sieverts UHV apparatus. All the hydrogen solubilities for the niobium–oxygen solid solutions followed Sieverts' law. The hydrogen solubility first increased and then decreased with increasing oxygen content in niobium. The change in the enthalpy of solution of hydrogen with the oxygen content indicated a maximum at about 0.01 O/Nb atom ratio. Partial molar enthalpy and partial molar excess entropy derived from the experimental solubility data first increased and passed through maximum values. The results were discussed and compared with theoretical values estimated for vibrational, lattice dilatational and configurational contributions.

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