ELSEVIER

Journal of Nuclear Materials 247 (1997) 244–248

journal of nuclear materials

Influence of interstitial oxygen and nitrogen on hydrogen solubility in vanadium

Shinsuke Yamanaka *, Yukio Kashiwara, Hironori Sugiyama, Masahiro Katsura

Department of Nuclear Engineering, Graduate School of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565, Japan

Abstract

Measurement of hydrogen solubility was carried out in the temperature range 500–800°C at a hydrogen pressure below 10^4 Pa using a modified Sieverts apparatus. The compositions of the vanadium–nitrogen bcc solid solutions were 0.010 and 0.021 N/V. All the hydrogen solubility data for the vanadium–nitrogen solid solutions followed Sieverts' law. The presence of nitrogen increased the hydrogen solubility and gave the small negative effect on the enthalpy of solution. The change in partial molar enthalpy and the partial molar excess entropy with the nitrogen content of solid solution were derived from the experimental data and were compared with the results of vanadium–oxygen solid solutions through discussion in terms of vibrational, lattice dilatational and configurational contributions. © 1997 Elsevier Science B.V.

1. Introduction

For applications of vanadium to hydrogen handling systems such as a fusion reactor, it is of the utmost importance to clarify the hydrogen behavior in vanadium. The solubility and the phase diagram are well known for the V–H binary system [1–5]. Although the sorption of other active gases such as oxygen and nitrogen appears to affect its solubility, only limited information is available for the influence of interstitial elements on the hydrogen solubility in vanadium [6].

In our previous work [7], thermodynamic studies have been performed on the vanadium–oxygen–hydrogen ternary system and the presence of interstitial oxygen was found to influence the hydrogen solubility in vanadium. In the present work, the influence of nitrogen has been studied and the results obtained were compared with the oxygen effect.

2. Experimental

The vanadium–nitrogen solid solutions were prepared by nitridation of vanadium single crystal (Goodfellow Cambridge, 99.999% in purity) in the form of a disk (20 mm ∅ × 2 mm) in a constant volume system and subsequent annealing in a vacuum below 10^{-6} Pa at 1000°C for 200 h. The compositions of vanadium–nitrogen solid solutions were 0.010 and 0.021 N/V atom ratio. Hydrogen (99.999% in purity) gas was further purified with hot titanium sponges and then used for solubility measurement.

The hydrogen solubility in vanadium–nitrogen solid solutions was studied using a modified Sieverts' UHV apparatus. The solubility was evaluated from the change in pressure with dissolution of hydrogen gas into the solid solution at constant volume. The measurement was performed at a temperature of 500–850°C at a pressure lower than 10^4 Pa by a constant volume method.

3. Results and discussion

The hydrogen solubility in vanadium–nitrogen was closely proportional to the square root of the equilibrium hydrogen pressure. This indicates that all the solubility data for the vanadium–nitrogen solid solution closely obey Sieverts' law: $C_H = K_H \times P_{H_2}^{1/2}$, where C_H is the hydrogen content in atom ratio, P_{H_2} the equilibrium hydrogen pressure in Pa and K_H the Sieverts' constant. The temperature dependence of Sieverts' constant obtained for vanadium–nitrogen is shown in Fig. 1. From Fig. 1, it is found that

---

* Corresponding author. Tel.: +81-6 789 7887; fax: +81-6 873 3696; e-mail: yamanake@nucl.eng.osaka-u.ac.jp.

PII S0022-3115(97)00098-6

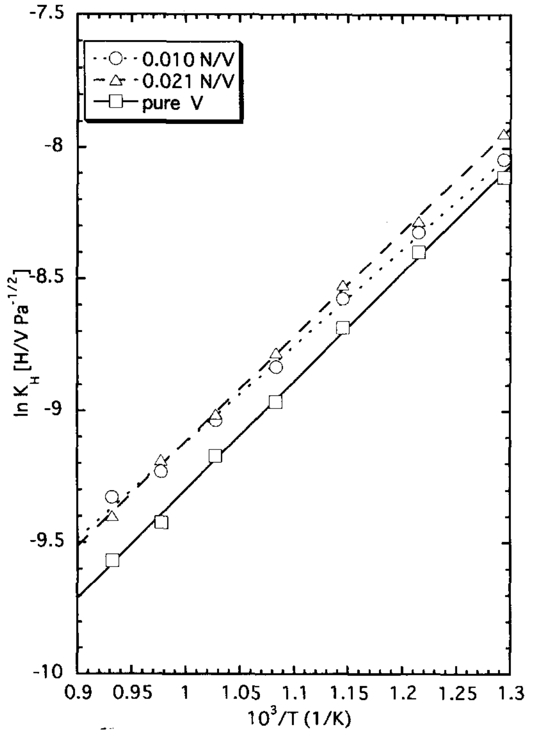

Fig. 1. Temperature dependence of Sieverts' constant K_H for hydrogen in pure vanadium and vanadium–nitrogen solid solution.

there exist, linear relationships between the natural logarithm of Sieverts' constant and reciprocal temperature expressed by, $\ln K_H = A + B/T$, where T is the temperature in K and A and B are constants. The values of A, B and ΔH obtained for vanadium–nitrogen solid solutions are given in Table 1, together with the results for vanadium–oxygen solid solutions [7]. The solubility of hydrogen increases with the nitrogen content in vanadium, and the enthalpy of solution appreciably decreases as the nitrogen content increases, as shown in Fig. 1 and Table 1.

The changes in the Sieverts' constant and in the enthalpy of solution with the composition of vanadium–oxygen and vanadium–nitrogen solid solutions are shown in Figs. 2 and 3. As can be seen in Figs. 2 and 3, the effect on the solubility and the enthalpy of solution strongly depends on the type of interstitial element. It is obvious form Figs. 2 and 3 that the hydrogen solubility increases and the enthalpy of solution slightly decreases with addition of nitrogen into vanadium. In contrast to the vanadium–nitrogen solid solution, the hydrogen solubility in the vanadium–oxygen solid solution first increases with the oxygen content and then decreases above an oxygen content of 0.01 O/V. The enthalpy of solution shows a pronounced maximum at a O/V ratio of 0.01. It is likely that the interstitial nitrogen attractively interacts with hydrogen in vanadium.

Table 1
Parameters of Sieverts' law A and B and enthalpy of solution ΔH

Composition (atom ratio)	A	B	ΔH (kJ/mol)
Pure V	−13.1	3910	−32.5
0.010 O/V	−13.0	3770	−31.4
0.021 O/V	−13.1	3840	−31.9
0.031 O/V	−13.2	3890	−32.3
0.044 O/V	−13.6	4240	−35.3
0.010 N/V	−13.1	3910	−32.5
0.021 N/V	−13.0	3940	−32.7

Oxygen and nitrogen in vanadium bcc lattice are located on octahedral sites, whereas tetrahedral sites are highly favored to receive hydrogen atoms. In ternary vanadium–oxygen–hydrogen and vanadium–nitrogen–hydrogen ternary solid solutions, the tetrahedral occupation of hydrogen and the octahedral occupation of oxygen and nitrogen were experimentally confirmed by spectroscopic measurements. There is a little information on the sizes of hydrogen, oxygen and nitrogen interstitially dissolved into vanadium. The presence of oxygen and nitrogen in an octahedral site is inferred to affect the state and configuration of hydrogen atoms in adjacent tetrahedral sites. This means that the addition of interstitial element into vanadium may result in a change in hydrogen solubility.

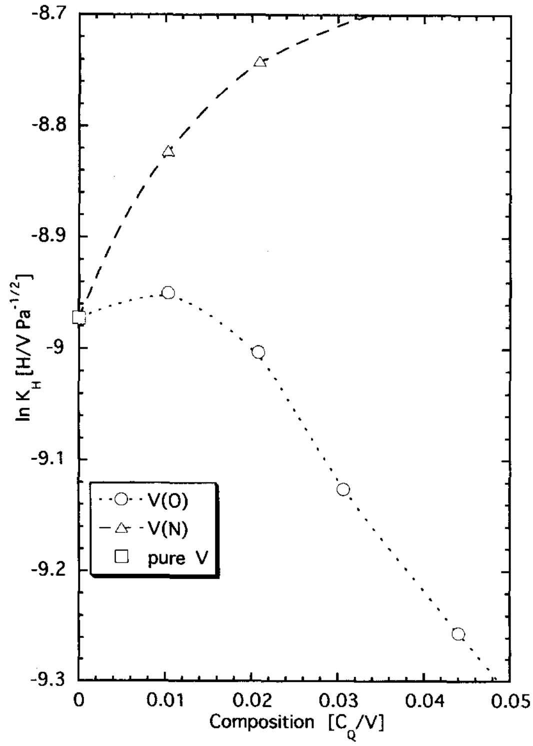

Fig. 2. Change in Sieverts' constant K_H with the composition of solid solution (650°C).

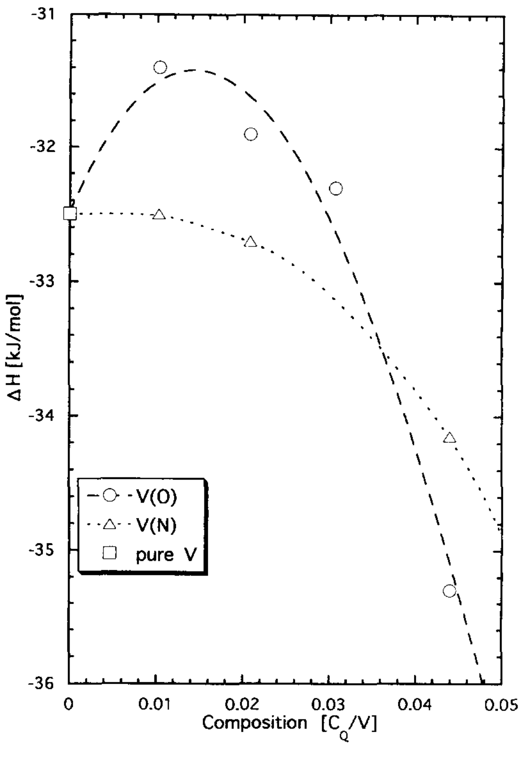

Fig. 3. Change in the enthalpy of solution ΔH with the composition of solid solution.

In order to clarify the influence of interstitial element, the solubility data for vanadium nitrogen solid solutions were analyzed by a dilute solution model proposed for the vanadium–oxygen–hydrogen ternary solution in our previous study [7]. The changes in the solubility and in the enthalpy of solution with the addition of interstitial element into vanadium lattice were discussed in terms of difference in partial molar enthalpy and excess entropy between pure metal and alloys, which are defined as $\delta H = H_H - H_H^0$ and $\delta S = S_H - S_H^0$, where 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 and H_H^0 and S_H^0 are the values for pure vanadium. Figs. 4 and 5 reveal the changes in δH and δS values for the vanadium–nitrogen solid solutions with the composition, together with those obtained for the vanadium–oxygen solid solutions. As can be seen in Figs. 4 and 5, the δH value slightly decreases with the nitrogen content, while the δS value increases with the nitrogen content. The increase in the solubility in vanadium–nitrogen solid solution is attributable mainly to an increase in δS. However, the vanadium–oxygen solid solution indicates a more complicated change in the partial molar quantities with the oxygen content.

Assuming 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 were given in the forms of $\delta H = \delta H^v + \delta H^d + \delta H^c$ 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 vanadium, δH^d and δS^d the lattice dilatation terms and δH^c and δS^c the configurational terms.

The magnitude of the vibrational terms can be estimated from the local vibrational mode of hydrogen in the solid solution. In the present study, we applied the following equations to estimate the vibrational terms:

$$\delta H^v = \Sigma\Big[\big(h\nu_i - h\nu_i^0\big)/2 + h\nu_i/\big(\exp(h\nu_i/kT) - 1\big) - h\nu_i^0/\big(\exp(h\nu_i^0/kT) - 1\big)\Big], \quad (1)$$

$$\delta S^v = \Sigma\Big[-k\ln\big\{\big(1 - \exp(-h\nu_i/kT)\big)/\big(1 - \exp(-h\nu_i^0/kT)\big)\big\} + h\nu_i/\big(\exp(h\nu_i/kT) - 1\big)/T - h\nu_i^0/\big(\exp(h\nu_i^0/kT) - 1\big)/T\Big], \quad (2)$$

where $\nu_i (i = 1\text{–}3)$ is the vibrational frequency of hydrogen in the solid solution and ν_i^0 is the vibrational frequency of hydrogen in pure metal. Frequencies for the nondegenerate and doubly degenerate modes of vibration of hydrogen on tetrahedral sites in vanadium are ν_1 and $\nu_2 (= \nu_3)$. The

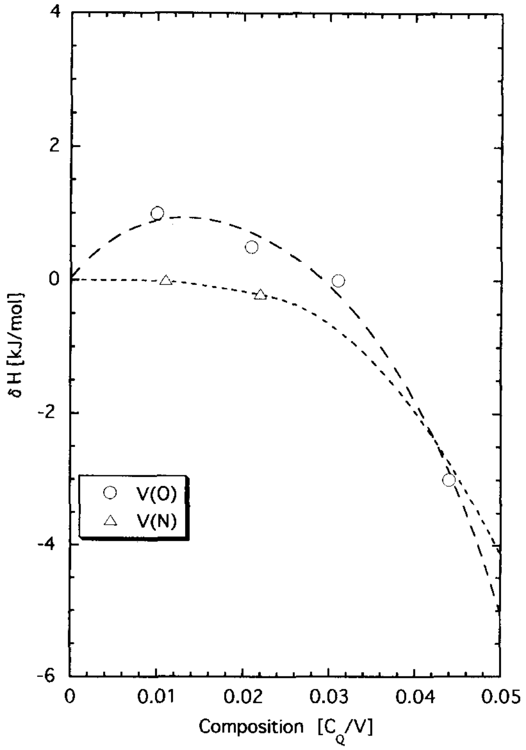

Fig. 4. Change in the δH value with the composition of solid solution.

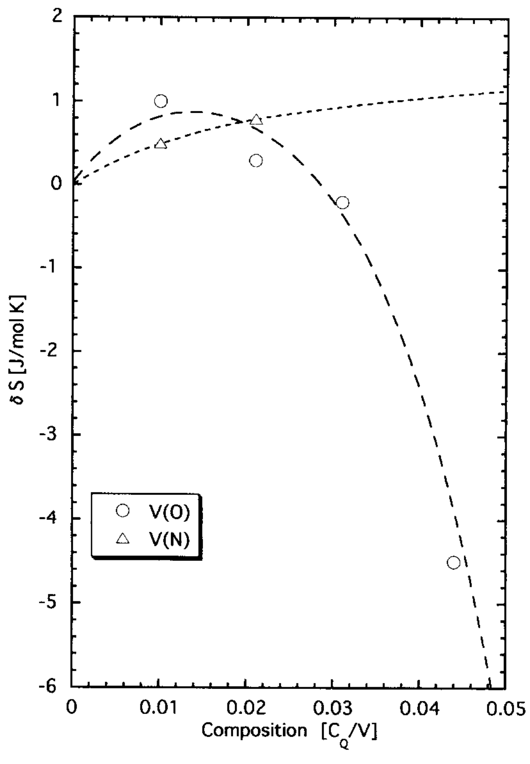

Fig. 5. Change in the δS value with the composition of solid solution.

vibrational frequency of hydrogen appears to vary owing to change with addition of interstitial element into the bcc lattice. Margel et al. [8] have performed inelastic neutron scattering measurements and found that slight difference in the vibrational energy of hydrogen was observed among $NbH_{0.0055}$, $NbO_{0.011}H_{0.003}$ and $NbN_{0.004}H_{0.010}$. Oxygen or nitrogen addition into niobium reduces the vibrational energy for doubly degenerate mode, but no marked change is not observed for non-degenerate mode. These experimental findings suggest that the vibrational energy levels of hydrogen in a bcc metal are slightly perturbed by dissolved interstitial element. On the assumption that for vanadium–nitrogen solid solutions a decrease in the vibrational frequencies of ν_2 and ν_3 with the nitrogen content is expressed by the following empirical equation:

$$\nu_i = \nu_i^0 \times \left(1 - C_N^{0.6}\right), \tag{3}$$

where C_N is the nitrogen content of the solid solution in atom ratio, we evaluated the values of δH^v and δS^v using $\nu_2^0 = \nu_3^0 = 4.11 \times 10^{13}\ s^{-1}$ and $T = 923$ K. As shown in Figs. 6 and 7, the δH^v is small and negative and δS^v is small and positive. The values of δH^v and δS^v obtained for vanadium–nitrogen solid solutions were slightly different from those for vanadium–oxygen solid solutions.

Interstitial elements such as oxygen and nitrogen cause considerable expansion of vanadium bcc lattice. The lattice

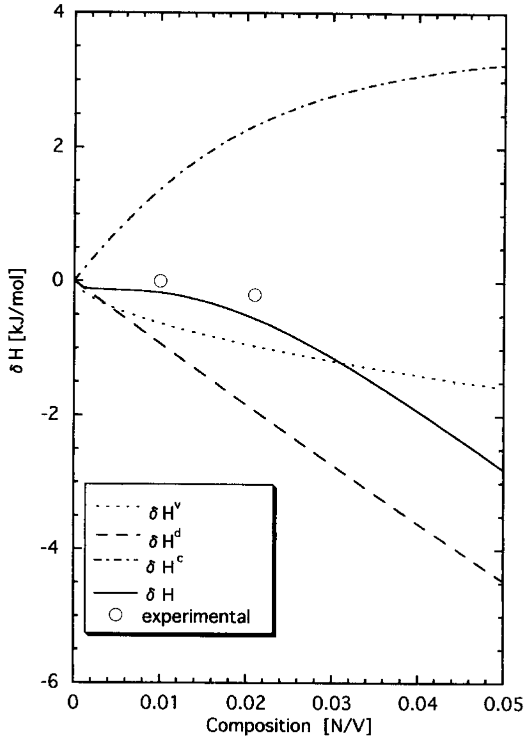

Fig. 6. Theoretical analysis of δH value.

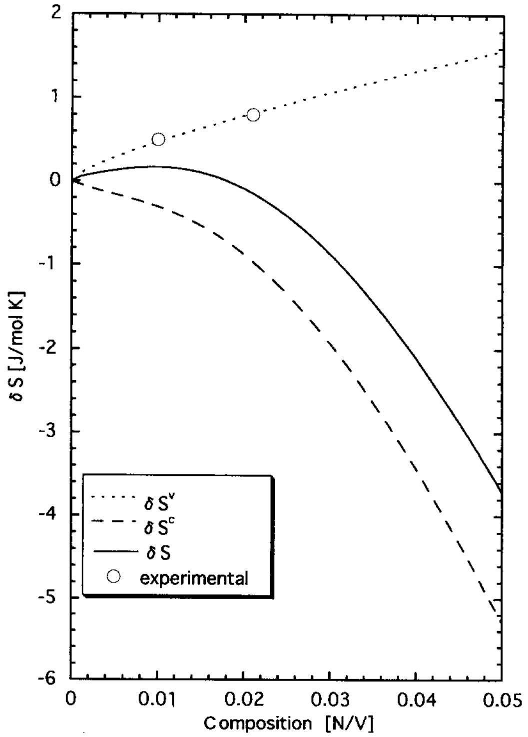

Fig. 7. Theoretical analysis of δS value.

strain resulting from interstitial solute gives large enthalpy change:

$$\delta H^{\mathrm{d}} = -\int (V_{\mathrm{H}} V_{\mathrm{N}} / V_{\mathrm{V}} K_{\mathrm{V}}) \times (1 - \alpha T) \, \mathrm{d}C_{\mathrm{N}}, \qquad (4)$$

$$\delta S^{\mathrm{d}} = \int (V_{\mathrm{H}} V_{\mathrm{N}} / V_{\mathrm{V}} K_{\mathrm{V}}) \times \alpha \, \mathrm{d}C_{\mathrm{N}}. \qquad (5)$$

In these equations, V_{H} and V_{N} are the partial molar volumes of hydrogen and nitrogen in vanadium and V_{V} and K_{V} are the molar volume and compressibility of vanadium, α is the thermal expansion coefficient of vanadium. The partial molar volumes of hydrogen and nitrogen were evaluated from the reported values of lattice parameters of the vanadium–nitrogen solid solutions. The partial molar volume of nitrogen in vanadium was found to be smaller than that of oxygen. The calculated δH^{d} values are indicated in Fig. 6. As evidenced by Fig. 6, the volume expansion due to interstitial nitrogen results in a negative enthalpy change. The magnitude of enthalpy change was smaller for nitrogen than for oxygen. The value of δS^{d} was not estimated because of the small value of the thermal expansion coefficient of the solid solutions.

The degeneracy of the configurational energy and entropy of hydrogen determines the terms of δH^{c} and δS^{c}, which may be ascribed to electronic interaction of nitrogen with hydrogen through vanadium. A nitrogen atom appears to modify electronic properties of an adjacent vanadium atom and a hydrogen atom located in a tetrahedral cell consisting of four vanadium atoms is affected. The following equations proposed for hydrogen in the IV group metal–oxygen solid solutions in our previous work [9] was applied to the vanadium–nitrogen–hydrogen ternary solid solution for estimating δH^{c} and δS^{c} values:

$$\delta H^{\mathrm{c}} = (\mathrm{P.F.})'/(\mathrm{P.F.}), \qquad (6)$$

$$\delta S^{\mathrm{c}} = (\mathrm{P.F.})'/(\mathrm{P.F.})/T + k \ln(\mathrm{P.F.}). \qquad (7)$$

$$(\mathrm{P.F.})' = \left(\Sigma \varepsilon_n N_n \exp(-\varepsilon_n/kT)\right) \times (1/6N_{\mathrm{M}}),$$

$$(\mathrm{P.F.}) = \left(\Sigma N_n \exp(-\varepsilon_n/kT)\right) \times (1/6N_{\mathrm{M}}).$$

In these equations, ε_n is the energy required to insert a hydrogen atom into a n-type cell ($n = 0$–4) defined as having n modified vanadium atoms of a tetrahedral cell, N_n is the number of n-type cell and N_{M} is the total number of vanadium atoms in a solid solution. On the assumption that a vanadium atom is completely modified if one or more nitrogen atoms occupy the first and second nearest octahedral sites, the relations of δH^{c} and δS^{c} to the nitrogen content were estimated by use of a set of the cell energies ε_n and Eqs. (6) and (7). The theoretical configurational enthalpy term δH^{c} increases with the nitrogen content as shown in Fig. 6. Fig. 7 indicates that δS^{c} shows a small negative value and decreases rapidly with the nitrogen content. The magnitudes of δH^{c} and δS^{c} for nitrogen were almost the same as oxygen.

It is found from Figs. 6 and 7 that the theoretical curves shown by solid lines in Figs. 6 and 7 well express the tendency for the changes in the experimental δH and δS values with nitrogen addition. It should be noted that the difference between the calculated values and the experimental ones is not large.

We have attempted to account for the influence of interstitial elements such as oxygen and nitrogen on the hydrogen solubility in vanadium. Although the influence of interstitial element is not yet fully interpreted, the present analysis suggests that the dilatometric contribution may be of importance in influencing the difference in partial molar quantities of hydrogen between nitrogen and oxygen.

4. Conclusions

In the temperature range 500–850°C at a hydrogen pressure below 10^4 Pa, the hydrogen solubility in vanadium–nitrogen solid solutions with a nitrogen content of 0.010 and 0.021 N/V was studied using a modified Sieverts UHV apparatus. All the hydrogen solubilities for the vanadium–nitrogen solid solutions followed Sieverts' law. The hydrogen solubility increased with increasing nitrogen content. The enthalpy of solution was slightly reduced with the addition of nitrogen. Partial molar enthalpy and partial molar excess entropy were derived by applying a solution model to the experimental data for the vanadium–nitrogen solid solutions, which were compared with the results for the vanadium–oxygen solid solutions. The partial molar enthalpy slightly decreased and the partial molar excess entropy increased with the nitrogen content. The changes in the partial molar quantities with the nitrogen content were discussed in terms of sums over vibrational, lattice dilatational and configurational contributions and compared with the results for vanadium–oxygen solid solutions.

References

[1] E. Veleckis et al., J. Phys. Chem. 73 (1969) 683.
[2] R. Griffiths et al., Trans. Faraday Soc. 68 (1972) 2344.
[3] T. Eguchi et al., J. Jpn. Inst. Met. 38 (1974) 1025.
[4] K. Fujita et al., J. Jpn. Inst. Met. 43 (1979) 601.
[5] O. Kleppa et al., J. Chem. Phys. 61 (1974) 4048.
[6] K. Abe et al., Proc. 2nd JIM Int. Symp. on Hydrogen in Metals, 1979, p. 157.
[7] S. Yamanaka et al., J. Alloys Compounds 231 (1995) 730.
[8] A. Magerl et al., Phys. Rev. B27 (1983) 927.
[9] S. Yamanaka et al., J. Nucl. Mater. 201 (1993) 134.