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Influence of interstitial oxygen on hydrogen solubility in metals

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Abstract

A comparison of hydrogen solubility and enthalpy of solution of hydrogen was performed for metal–oxygen binary solid solutions. Oxygen addition into titanium, hafnium and vanadium decreased the hydrogen solubility at a fixed pressure, while the hydrogen solubility in zirconium, niobium and tantalum first increased with the oxygen content and then decreased. For the group IV metals, oxygen provided a negative effect on the enthalpy of solution of hydrogen. For the group V metals, the enthalpy of solution of hydrogen first increased with the oxygen content and then decreased. Partial thermodynamic functions of hydrogen in metal–oxygen–hydrogen ternary solid solutions were estimated using a dilute solution model. The oxygen effect on the partial molar quantities was complicated and depended on the metal. The changes in the partial molar quantities with the composition of the solution were discussed in terms of vibrational, dilatometric, and configurational contributions. © 1999 Published by Elsevier Science S.A. All rights reserved.

Keywords: Hydrogen solubility; Titanium; Zirconium; Hafnium; Vanadium; Niobium; Tantalum; Oxygen

1. Introduction

The IV and V group metals, titanium, zirconium, hafnium, vanadium, niobium and tantalum have unique characteristics, which fit them for various applications in nuclear engineering. However, the main obstacle to their use has been their great affinity for various gases such as oxygen and hydrogen. For the IV and V group metals, the solubility and the phase diagrams have been extensively studied for the metal–hydrogen binary systems [1–23]. Although sorption of the gaseous elements seems to influence the hydrogen solubility, little information is available for the effects of interstitial non-metal elements on the hydrogen solubility. In our previous study [24–33], the hydrogen solubility has been measured for metals containing non-metal elements such as oxygen and nitrogen.

Oxygen is the most important non-metal elements among impurities interstitially dissolved into the metals. In order to elucidate the effect of interstitial oxygen on hydrogen solubility in the group IV and V metals, a comparison of the hydrogen solubility data and a statistical thermodynamic analysis were carried out.

2. Hydrogen solubility and enthalpy of solution

Hydrogen solubility in pure group IV and V metals and the interstitial solid solutions having a homogeneous alpha phase with hcp or bcc structure has been studied. All the data for hydrogen solubility in pure metals and solid solutions were found to obey Sievert's law:

$$C_H = K_H \times P_{H_2}^{1/2}.$$

In this equation, C_H is the hydrogen content in atom ratio (H/M), P_{H_2} the equilibrium hydrogen pressure in Pa, and K_H the Sievert's constant. As shown in Figs. 1 and 2, the temperature dependence of the Sievert's constant K_H was expressed as:

$$\ln K_H = A + B/T$$

where T is the temperature in K, and A and B are constants. The enthalpy of solution of hydrogen ΔH (kJ g·atom^{-1}) was evaluated from the B value. The values of A, B and ΔH for pure metals and solid solutions are summarized in Tables 1 and 2.

The changes in the Sievert's constant and the enthalpy of solution of hydrogen with the composition of the solid solution are compared in Table 2. It is found from this table that the effects of interstitial oxygen on the solubility and on the enthalpy of solution of hydrogen are almost similar among the metals in the same group. As evidenced

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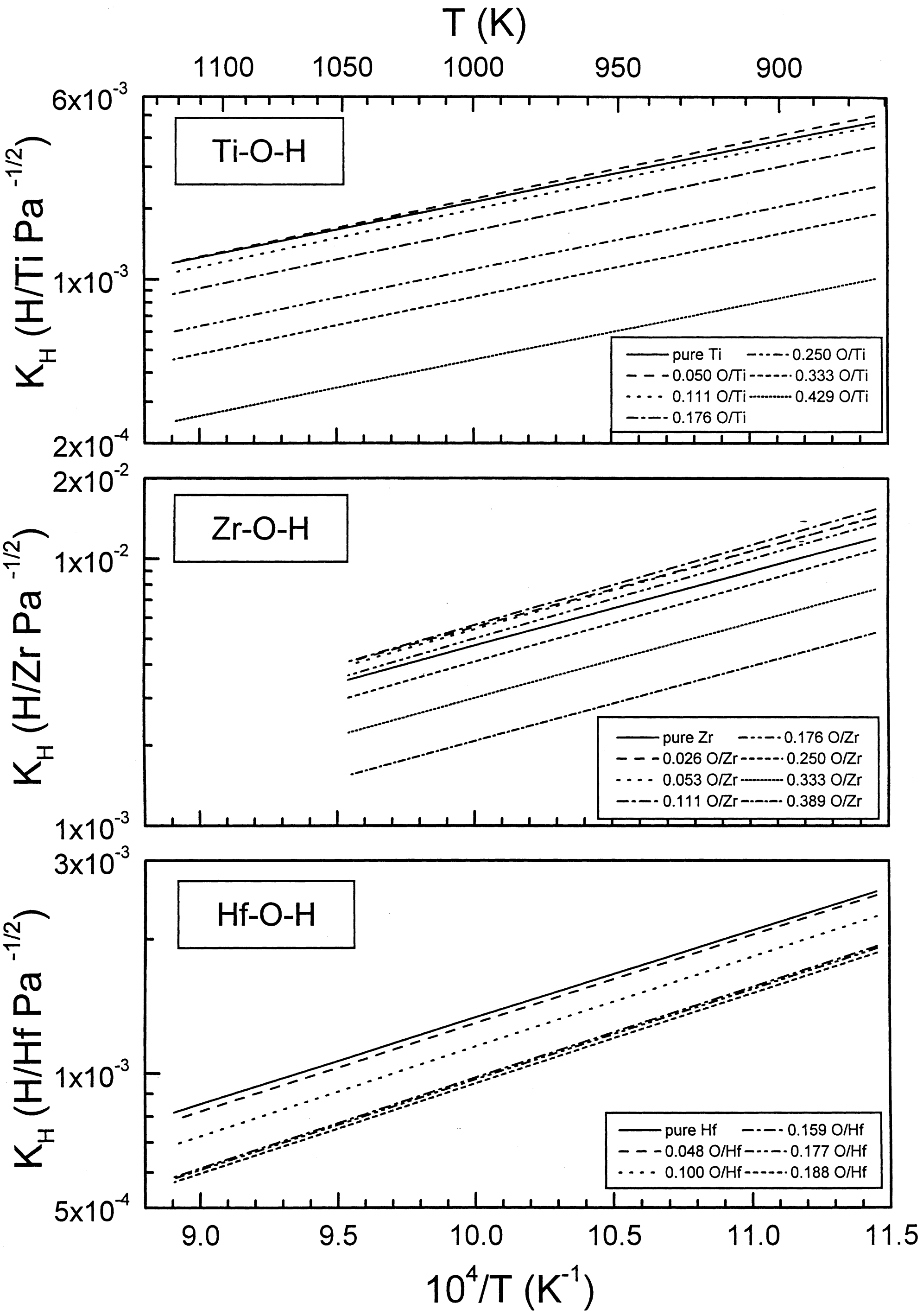

Fig. 1. Temperature dependence of Sievert's constant K_H for hydrogen in pure metals and oxygen solid solutions for the group IV metals.

by Fig. 1, oxygen addition into titanium and hafnium decreases the hydrogen solubility at a fixed pressure, whereas the hydrogen solubility in zirconium first increases with oxygen content, and then decreases at a higher oxygen content. The enthalpy of solution of hydrogen for the oxygen solid solution is lower than that for the pure metal and shows a minimum, as shown in Table 2. For the metals in the group V, the hydrogen solubility in vanadium decreased with increasing oxygen content, while the hydrogen solubility in niobium and tantalum first increased and passed through maximum values. For the metals in group V, the enthalpy of solution of hydrogen first increased with the oxygen content and then decreased.

3. Statistical thermodynamic analysis

Various spectroscopic studies have been performed previously on hydrogen and oxygen in group IV and V metals [34]. It appears from the literature data that in the

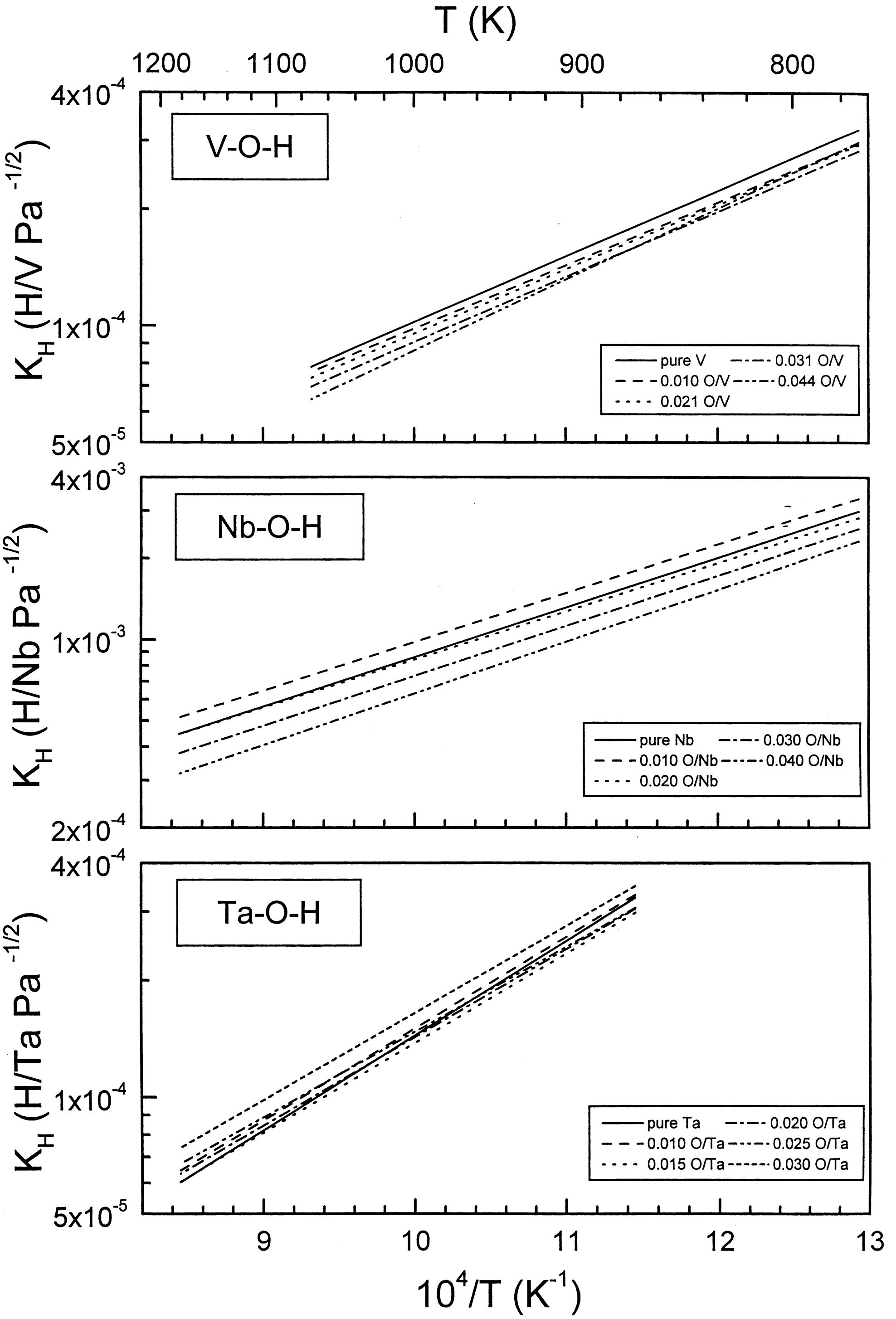

Fig. 2. Temperature dependence of Sievert's constant K_H for hydrogen in pure metals and oxygen solid solutions for the group V metals.

metal lattice oxygen is located on octahedral sites, whereas tetrahedral sites are highly favored to receive hydrogen. Assuming that hydrogen atoms have access to tetrahedral interstitial sites in the oxygen solid solutions of group IV and V metals, we have proposed the following solubility equation [29]:

$$\ln (C_H T^{7/4}/(\beta - C_H)P_{H_2}^{1/2}A_{H_2}) = -(H_H - E^d)/kT + S_H/k$$

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, $-E^d$ the one half of the dissociation energy of the hydrogen molecule, k the Boltzmann constant, and A_{H_2} the value related to partition functions of hydrogen gas. The value of β is the number of interstitial sites of given kind available to hydrogen per metal atom. For the hcp group IV metals,

Table 1
Literature data for the parameters of Sievert's law A and B and heat of solution ΔH for hydrogen

Metal	Range (°C)	A	B	ΔH (kJ g·atom^{-1})	Reference
Ti	600–850	−11.6	5450	−45.3	Present study
	480–900	−11.6	5640	−46.9	[1]
	350–800	−12.0	6090	−50.6	[2]
	500–800	−13.1	6340	−52.7	[3]
	370–850	−12.1	6090	−50.6	[4]
	420–840	−11.6	5350	−44.5	[5]
Zr	600–775	−11.8	6440	−53.5	Present study
	500–900	−12.5	6980	−58.0	[6]
	450–600	−12.4	7110	−59.2	[7]
	480–950	−10.7	5450	−45.3	[8]
	700–1000	−9.3	3910	−32.5	[9]
	450–750	−11.6	6260	−52.1	[10]
	400–900	−11.0	6240	−51.9	[11]
	500–800	−11.8	7700	−64.0	[3]
	480–760	−12.1	6570	−54.6	[5]
Hf	600–850	−11.1	4480	−37.2	Present study
	251–872	−11.2	4520	−37.6	[12]
	450–635	−10.9	4180	−34.8	[5]
	235–845	−10.6	4330	−36.0	[13]
V	500–800	−13.1	3910	−32.5	Present study
	–	–	–	−31.0	[14]
	–	–	–	−29.0	[14]
	–	–	–	−28.1	[14]
	20–55	−15.3	4030	−33.5	[15]
Nb	500–900	−11.3	4240	−35.2	Present study
	3–80	−11.5	4030	−33.5	[15]
	1200–2000	−13.2	4905	−40.8	[16]
	320–500	−16.9	5411	−45.0	[17]
	650–800	−13.8	3032	−25.2	[18,19]
	800–1000	−12.1	3592	−29.9	[20]
Ta	600–900	−14.5	5630	−46.8	Present study
	38–211	−13.0	4300	−36.0	[21]
	(−78)–240	−14.6	4770	−39.6	[22]
	40–80	−13.5	418	−34.8	[15]
	150–1000	−12.7	4320	−35.9	[23]

$\beta = 2$ and for the bcc group V metals, $\beta = 6$. Applying the above equation to our solubility data, the partial thermodynamic quantities were estimated.

The influences of interstitial oxygen on the hydrogen solubility in the group IV and V metals were analyzed in terms of differences in the partial molar thermodynamic functions between pure metal and solid solution:

$$\delta H = H_{\mathrm{H}} - H_{\mathrm{H}}{}^{\circ} \text{ and } \delta S = S_{\mathrm{H}} - S_{\mathrm{H}}{}^{\circ}$$

where H_{H} and S_{H} are the values for the oxygen solid solutions and $H_{\mathrm{H}}{}^{\circ}$ and $S_{\mathrm{H}}{}^{\circ}$ for pure metals. The experimental values of δH and δS as a function of the oxygen content are indicated in Figs. 3–6. As shown in Figs. 3 and 4, the experimental δH value goes through a minimum value for the group IV metals, but goes through a maximum value for the group V metals. The magnitude of the enthalpy change is dependent on the metals. Oxygen in the group IV metals monotonically decrease the δS value, as obvious in Fig. 5. It is found from Fig. 6 that for the group V metals, the effect of oxygen addition on the δS value are more complicated than that for the group IV metals. The magnitude of the entropy change depends on the metal.

The partial molar enthalpy and the partial molar excess entropy appear to be expressed as the sum of contributions from various degrees of freedom. We can write the enthalpy and entropy difference, δH and δS, as:

$$\delta H = \delta H^{\mathrm{v}} + \delta H^{\mathrm{d}} + \delta H^{\mathrm{c}} \text{ and } \delta S = \delta S^{\mathrm{v}} + \delta S^{\mathrm{d}} + \delta S^{\mathrm{c}}$$

where δH^{v} and δS^{v} are the differences in vibrational contribution between the alloy and pure zirconium, δH^{d} and δS^{d} the lattice dilatation terms, and δH^{c} and δS^{c} the configurational terms. The results for the analysis are shown in Figs. 3–6. The method for the analysis was reported in detail elsewhere [29].

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:

$$\delta H^{\mathrm{v}} = \sum [(h\nu_i - h\nu_i{}^{\circ})/2 + h\nu_i/(\exp(h\nu_i/kT) - 1) - h\nu_i{}^{\circ}/(\exp(h\nu_i{}^{\circ}/kT) - 1)]$$

$$\delta S^{\mathrm{v}} = \sum [-k \ln\{(1 - \exp(-h\nu_i/kT))/(1 - \exp(-h\nu_i{}^{\circ}/kT))\}$$

Table 2
Parameter of Sievert's law *A* and *B*, and heat of solution ΔH for hydrogen

Alloy	Oxygen content (O/M)	*A*	*B*	ΔH (kJ g·atom^{-1})
Ti–O	0.000	−11.6	5450	−45.3
	0.050	−11.8	5680	−47.2
	0.111	−11.9	5680	−47.2
	0.176	−12.1	5670	−47.1
	0.250	−12.4	5590	−46.5
	0.333	−12.7	5620	−46.7
	0.429	−13.2	5500	−45.7
Zr–O	0.000	−11.8	6440	−53.5
	0.026	−11.8	6600	−54.9
	0.053	−12.0	6780	−56.4
	0.111	−12.1	6920	−57.6
	0.176	−12.2	6900	−57.4
	0.250	−12.2	6700	−55.7
	0.333	−12.3	6490	−54.0
	0.389	−12.6	6420	−53.4
Hf–O	0.000	−11.1	4480	−37.2
	0.048	−11.2	4550	−37.8
	0.100	−11.4	4630	−38.5
	0.469	−11.6	4670	−38.8
	0.177	−11.6	4660	−38.7
	0.188	−11.6	4640	−38.5
V–O	0.000	−13.1	3910	−32.5
	0.010	−13.0	3770	−31.4
	0.021	−13.1	3840	−31.9
	0.031	−13.2	3890	−32.3
	0.044	−13.6	4240	−35.3
Nb–O	0.000	−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
Ta–O	0.000	−14.5	5630	−46.8
	0.010	−14.3	4550	−45.3
	0.015	−14.2	5320	−44.2
	0.020	−14.1	5240	−43.6
	0.025	−13.9	5060	−42.1
	0.030	−13.9	5170	−43.0

$$+ h\nu_i/(\exp(h\nu_i/kT) - 1)/T$$
$$- h\nu_i^\circ/(\exp(h\nu_i^\circ/kT) - 1)/T]$$

where ν_i ($i = 1$–3) is the vibrational frequency of hydrogen in the oxygen solid solution and ν_i° is the vibrational frequency of hydrogen in pure metal. For the group IV metals, the vibrational frequency of hydrogen is $\nu_1 = \nu_2 = \nu_3$. On the other hand, for the group V metals, the frequencies for the nondegenerate and doubly degenerate modes of vibration of hydrogen are ν_1 and $\nu_2 (= \nu_3)$. The vibrational frequency of hydrogen appears to change with addition of interstitial oxygen into the metal lattice. On the assumption that a decrease in the vibrational frequencies of ν_i with the oxygen content is expressed by:

$$\nu_i = \nu_i^\circ \times (1 - C_\mathrm{O}^x)$$

where C_O is the oxygen content of the solid solution in atom ratio and x is the constant, we evaluated the values of δH^v and δS^v. As shown in Figs. 3–6, the δH^v is small and negative, and δS^v is small and positive. The changes of δH^v and δS^v obtained for the group V metals were slightly larger than from those for the group IV metals.

Interstitial oxygen causes considerable expansion of metal lattice, which appear to offer large enthalpy change and negligible small entropy change:

$$\delta H^\mathrm{d} = -\int (V_\mathrm{H}V_\mathrm{O}/V_\mathrm{M}K_\mathrm{M}) \times (1 - \alpha T)\, \mathrm{d}C_\mathrm{O}$$

$$\delta S^\mathrm{d} = \int (V_\mathrm{H}V_\mathrm{O}/V_\mathrm{M}K_\mathrm{M}) \times \alpha\, \mathrm{d}C_\mathrm{O}.$$

In these equations, V_H and V_O are the partial molar volumes of hydrogen and oxygen in metal, and V_M and K_M are the molar volume and compressibility of metal, α is the thermal expansion coefficient of metal. Figs. 3 and 4 show the calculated δH^d values, indicating that the volume expansion due to interstitial oxygen results in a negative enthalpy change. There is no marked difference in the magnitude of δH^d between the group IV and V metals.

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 oxygen with hydrogen through metal atoms. An oxygen atom appears to modify electronic properties of an adjacent metal atom, and a hydrogen atom located in a tetrahedral cell consisting of four metal atoms is affected. The following equations proposed for hydrogen in the metal–oxygen solid solutions in our previous work [29] was applied to the ternary solid solution for estimating δH^c and δS^c values:

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

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

where

$$(P.F.)' = (\textstyle\sum \varepsilon_n N_n \exp(-\varepsilon_n/kT)) \times (1/6N_\mathrm{M})$$

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

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 metal atoms of a tetrahedral cell, N_n is the number of n-type cell and N_M is the total number of metal atoms in a solid solution. On the assumption that a metal atom is completely modified if one or more oxygen atoms occupy the first and second nearest octahedral sites, the changes in δH^c and δS^c with the oxygen content were estimated by use of a set of the cell energies ε_n and these equations. As the oxygen content increases, the theoretical configurational enthalpy term δH^c increases for both the metals in the groups IV and V, as evidenced by Figs. 3 and 4. Figs. 5 and 6 indicates that for all the metals δS^c shows a negative value and decreases with the oxygen content.

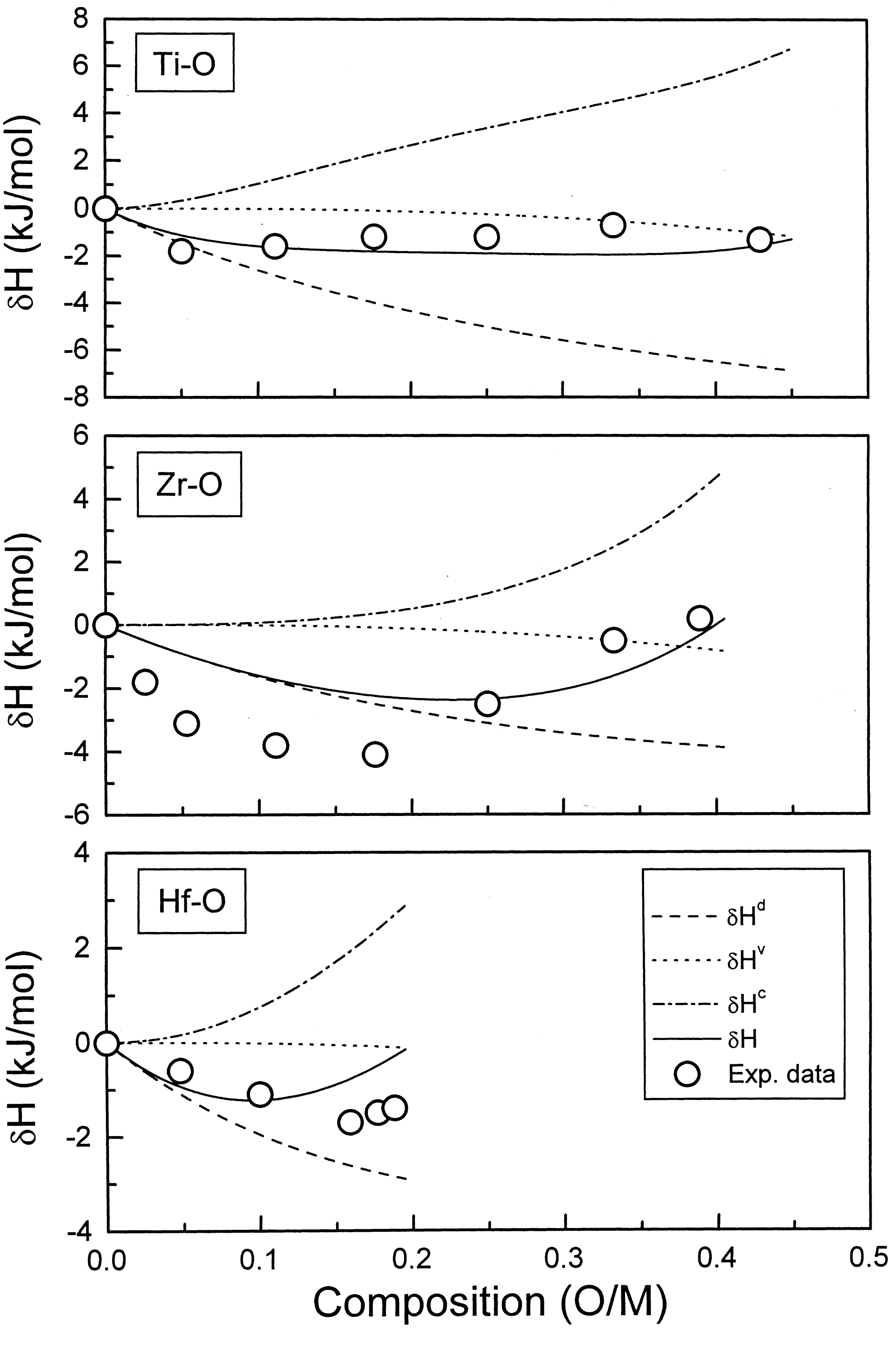

Fig. 3. Change in the δH value with the oxygen content for the group IV metals.

As obvious in Figs. 3 and 5, the theoretical curves for the group IV metals are in good agreement with the experimental δH and δS values. Although the theoretical curves for the group V metals indicated in Figs. 4 and 6 express the tendency for the changes in the experimental δH and δS values with oxygen addition, the difference between the calculated values and the experimental ones is larger, vanadium, niobium and tantalum.

It should be noted that there exists a good correlation between δH^c values and physico-chemical properties of (Ti, Zr, Hf)–O binary solid solution such as partial molar enthalpy of oxygen, congruent melting point and axial ratio c/a. The marked increase of δH^c at a higher oxygen content appears to be associated with the changes in the characteristics of metal atoms in the (Ti, Zr, Hf)–O solid solutions. The thermodynamic analysis suggests that for

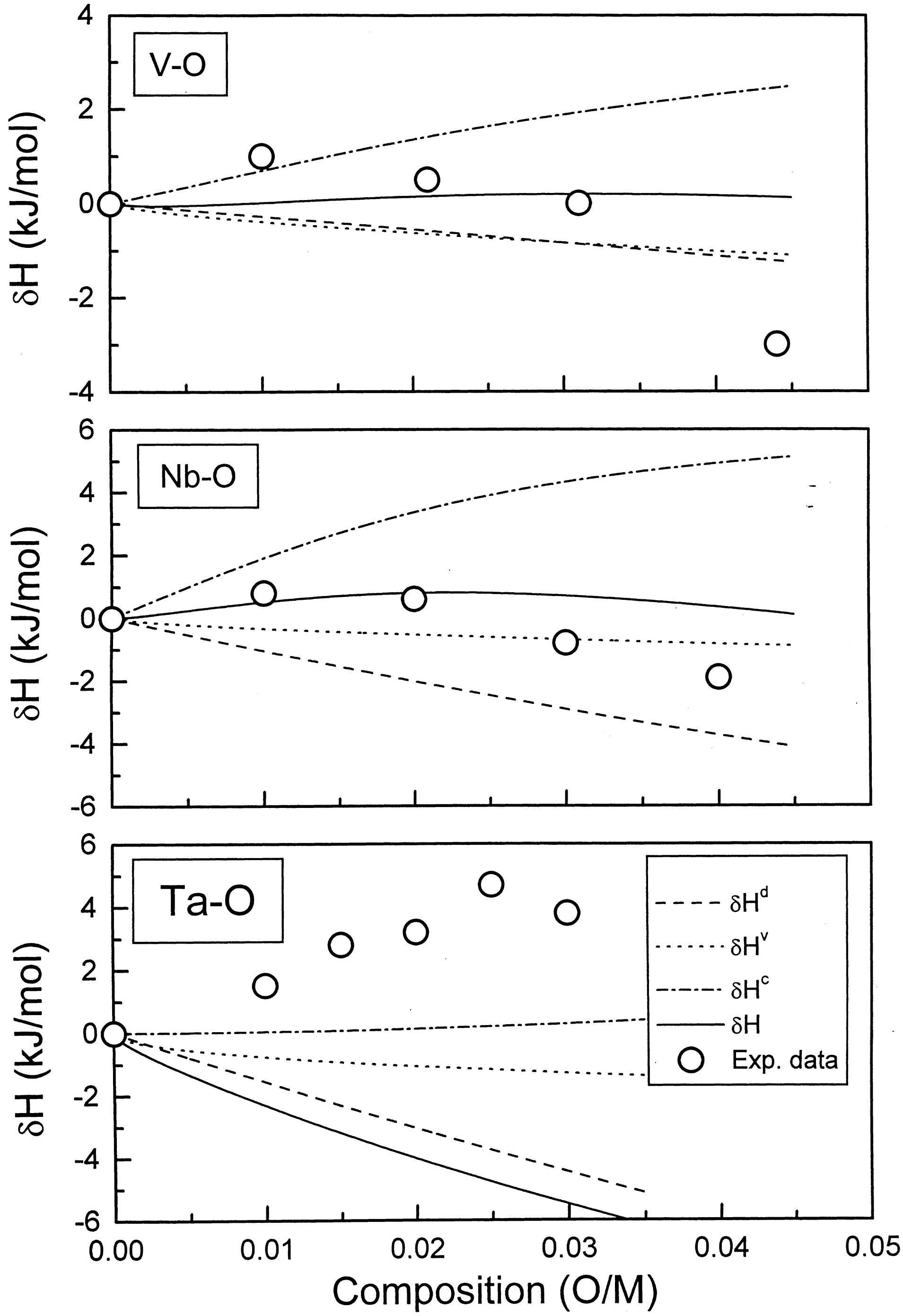

Fig. 4. Change in the δH value with the oxygen content for the group V metals.

the group IV metals the configurational and dilatometric contributions are important in influencing the partial molar quantities of hydrogen.

The δH^{c} change with oxygen addition differs from the group V metals to the group V metals. Though we have attempted to account for the change in δH^{c} on the basis of the properties of (V, Nb, Ta)–O solid solutions, the influence of interstitial oxygen is not yet fully interpreted for the group V metals. The increase in the δS value appears to be of importance for the change in the hydrogen solubility in the oxygen solid solution of the group V metals. 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 the other contributions such as dual site occupancies of hydrogen is needed for understanding the influence of

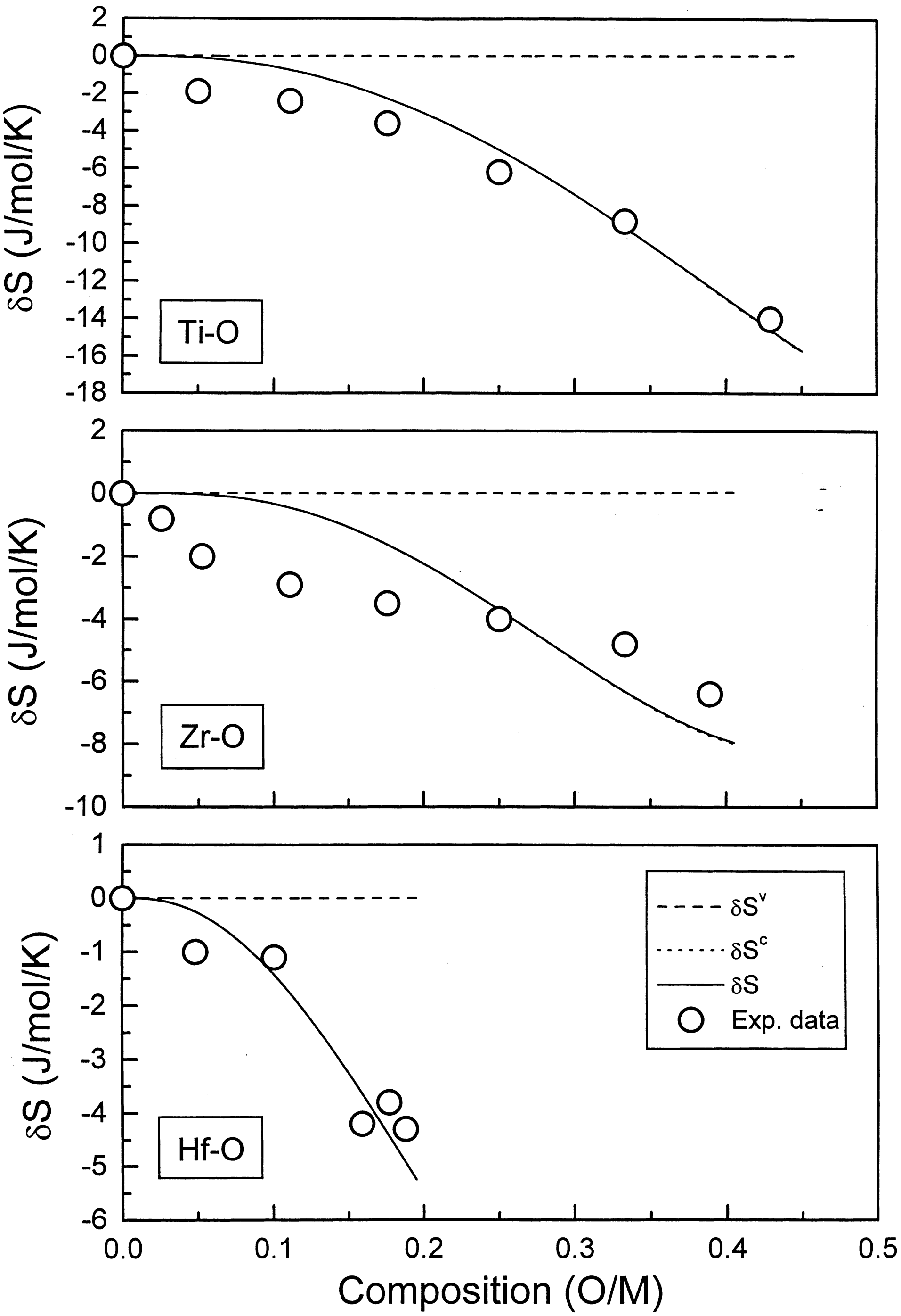

Fig. 5. Change in the δS value with the oxygen content for the group IV metals.

interstitial oxygen on hydrogen behavior in the group V metal more clearly.

4. Conclusions

A comparison was made for all the hydrogen solubility data for oxygen solutions for the group IV and V metals: titanium, zirconium, hafnium, vanadium, niobium and tantalum. Oxygen addition decreased the hydrogen solubility in titanium, hafnium and vanadium. The hydrogen solubility in zirconium, niobium and tantalum first increased with the oxygen content and then decreased at a higher oxygen content. For the group IV metals, the presence of oxygen provided a negative effect on the enthalpy of solution of hydrogen. For the group V metals,

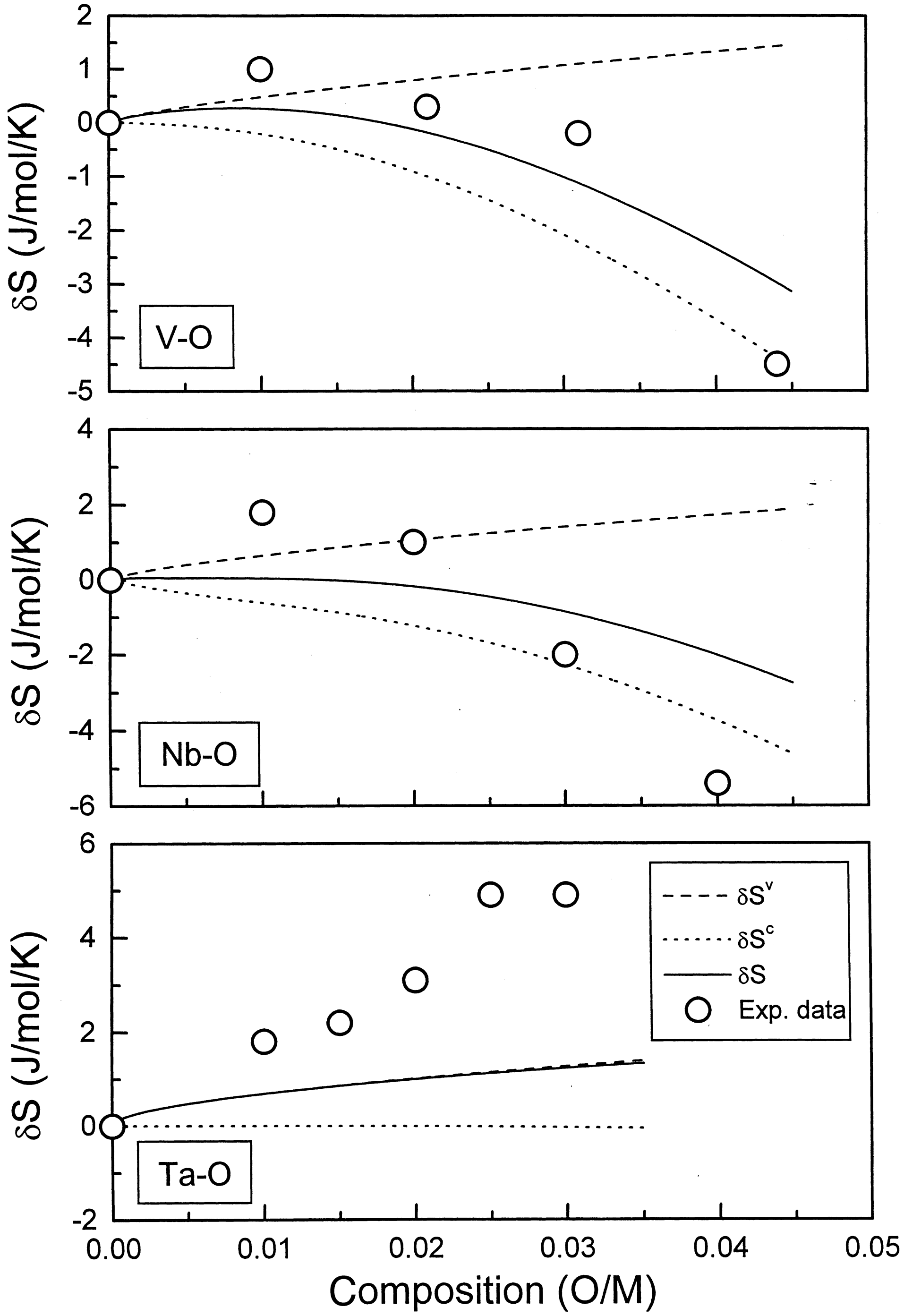

Fig. 6. Change in the δS value with the oxygen content for the group V metals.

the enthalpy of solution of hydrogen first increased with the oxygen content and then decreased.

On the basis of the dilute solution model, the hydrogen solubility data for the oxygen solid solutions of the group IV and V metals were analyzed. The partial molar enthalpy and the partial molar excess entropy were estimated for hydrogen in the ternary solid solutions. The changes in the partial quantities with the oxygen content were explained in terms of various contributions such as vibrational, dilatometric and configurational effects.

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