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ARTICLE

Thermodynamic Calculation on the Formation of Titanium Hydride

Jing-wei Zhao[a*], Hua Ding[a], Xue-feng Tian[a], Wen-juan Zhao[a], Hong-liang Hou[b]

a. School of Materials and Metallurgy, Northeastern University, Shenyang 110004, China
b. Beijing Aeronautical Manufacturing Technology Research Institute, Beijing 100024, China

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A modified Miedema model, using interrelationship among the basic properties of elements Ti and H, is employed to calculate the standard enthalpy of formation of titanium hydride TiH_x ($1\leq x\leq 2$). Based on Debye theories of solid thermal capacity, the vibrational entropy, as well as electronic entropy, is acquired by quantum mechanics and statistic thermodynamics methods, and a new approach is presented to calculate the standard entropy of formation of TiH_2. The values of standard enthalpy of formation of TiH_x decrease linearly with increase of x. The calculated results of standard enthalpy, entropy, and free energy of formation of TiH_2 at 298.16 K are −142.39 kJ/mol, −143.0 J/(mol·K) and −99.75 kJ/mol, respectively, which is consistent with the previously-reported data obtained by either experimental or theoretical calculation methods. The results show that the thermodynamic model for titanium hydride is reasonable.

Key words: Titanium hydride, Thermodynamic calculation, Modeling, Enthalpy, Entropy

I. INTRODUCTION

Titanium has a good hydrogen-absorbing capacity of 9.2×10^{22} H/cm^3 at a given temperature and hydrogen pressure. In recent years, the hydrogenation characteristics of titanium have been investigated due to the potential of this metal and its alloys as hydrogen storage materials [1-5]. Since the available thermodynamic data of Ti-H system were reported by Mueller *et al.* [6], some experimental or calculated data have become available. Kubaschewski presented a critical review of the thermodynamics of hydrogen in all the titanium alloys [7]. By using McQuillan's data [8] on a relationship between the equilibrium pressure of hydrogen and the hydrogen content in titanium, Arita and Someno determined the standard free energy, enthalpy, and entropy of formation of titanium hydride [9]. Arita *et al.* measured the equilibrium relationship between the hydrogen gas pressure and the hydrogen content in Ti, and a quasi-chemical approach of statistical mechanics was used to obtain values of thermodynamic properties of the Ti-H system [10]. By using interrelationships based on certain thermodynamic constraints and other models, Wang presented a review to evaluate the consistencies among the reported values [11].

TiH_2 is a metallic hydride formed by the reaction $Ti(s)+H_2(g)\rightarrow TiH_2(s)$. Because of its high stability in air, TiH_2 is always taken as a useful supply source of pure hydrogen [12-14]. Its thermodynamic properties, such as standard enthalpy, entropy, and free energy, are important physical quantities for TiH_2, and these have receiving much attention [9,15-17]. Several experimental methods have been used to obtain the thermodynamic data of TiH_2 [10,11,18]. Nevertheless, thermodynamic experiment is sometimes influenced by some factors that there are many technical difficulties in obtaining the thermodynamic parameters of TiH_2 by means of experimental approach.

In view of the practical application of Ti-based alloys for hydrogen storage, a thermodynamic study of the Ti−H system is of importance and can be vital to understanding the physico-chemical behavior of these alloys. In this work, a method for calculating titanium hydride thermodynamic parameters is introduced, which makes it easy to obtain calculation parameters and provides a quick way to calculate the thermodynamic data. A modified Miedema [19-21] model, using interrelationship among the basic properties of elements Ti and H, is employed to calculate the standard enthalpy of formation of titanium hydride TiH_x ($1\leq x\leq 2$). A new approach, with quantum mechanics and statistic thermodynamics methods, is presented to calculate the vibrational entropy S_v and electronic entropy S_e, and the standard entropy of titanium hydride TiH_2 is obtained by $S^{\ominus}_{TiH_2}=S_v+S_e$. All the calculation results are compared with other reports.

II. THERMODYNAMIC MODEL

A. Standard enthalpy model

The Miedema model is a semi-empirical approach, by which the standard enthalpy of formation of binary alloy can be easily predicted according to the basic properties of components (such as atomic volume V, electronegativity ϕ^*, and electron density n_{ws}). Wigner-Seitz atomic cells [22] are assumed in the Miedema model, in which every cell includes both an atomic nu-

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[*] Author to whom correspondence should be addressed. E-mail: jwzhaocn@gmail.com, Tel.: +86-24-83687746

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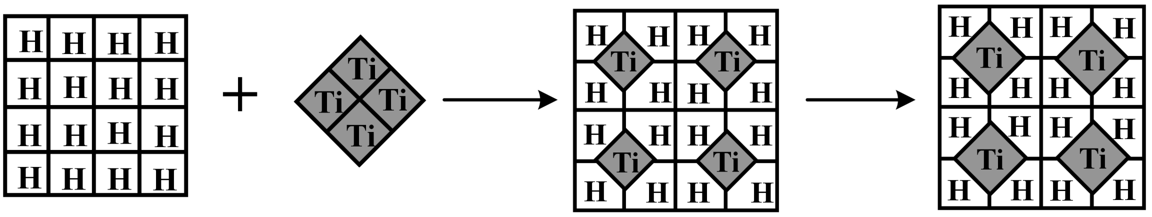

(a) (b) (c)

FIG. 1 The Winger-Seitz atomic model of Ti and H (a) before combination, (b) mechanical mixture, (c) chemical compound.

cleus and an electron. The two-dimension atomic cell models of Ti and H are shown in Fig.1(a). When the mechanical mixture is formed (Fig.1(b)), the total volume stays invariant before and after mixing which leads to the value of standard enthalpy of formation being zero. However, because the electron density of Ti is different from that of H, the electron density at cell boundary will self-adjust so as to reduce the binding energy which causes the electron density to be a minimum value. For $(n_{ws})_{\rm H}<(n_{ws})_{\rm Ti}$, as illustrated by Fig.1(c), the volume of H will decrease while the volume of Ti increases after the chemical compound is formed. The difference of electronic densities Δn_{ws} between Ti and H offers a positive value of $Q\left[(n_{ws})_{\rm H}^{1/3}-(n_{ws})_{\rm Ti}^{1/3}\right]^2$ for the standard enthalpy of formation of titanium hydride, where Q is an empirical constant. Moreover, because the electronegativity of Ti ($\phi^*_{\rm Ti}$=3.8 V) is different from that of H ($\phi^*_{\rm H}$=5.2 V), element H is inclined to gain electrons from Ti, which results in the free energy at the cell boundary decreasing. The difference between Ti and H electronegativities $\Delta\phi^*$ offers a negative value of $-P(\phi^*_{\rm H}-\phi^*_{\rm Ti})^2$ for the standard enthalpy of formation of titanium hydride, where P is an empirical constant.

For the Ti-H system, the standard enthalpy of formation of one molar gaseous H into solid Ti is defined by [19]

$$\begin{aligned}\Delta H^{\ominus}_{\rm H\rightarrow Ti} &= f_0\frac{c_{\rm H}Ac_{\rm Ti}B}{c_{\rm H}V_{\rm H}^{2/3}A+c_{\rm Ti}V_{\rm Ti}^{2/3}B} \qquad (1)\\ A &= 1+\mu_{\rm H}c_{\rm Ti}(\phi^*_{\rm H}-\phi^*_{\rm Ti})\\ B &= 1+\mu_{\rm Ti}c_{\rm H}(\phi^*_{\rm Ti}-\phi^*_{\rm H})\end{aligned}$$

where $c_{\rm H}$ and $c_{\rm Ti}$ are the molar fractions of H and Ti, $\mu_{\rm H}$ and $\mu_{\rm Ti}$ are the proportional constants, $\phi^*_{\rm H}$ and $\phi^*_{\rm Ti}$ are the electronegativities of H and Ti, $V_{\rm H}$ and $V_{\rm Ti}$ are the molar volumes of H and Ti, respectively, and f_0 is obtained as

$$f_0=2PV_{\rm H}^{2/3}V_{\rm Ti}^{2/3}\cdot\left\{\frac{Q/P[(n_{ws})_{\rm H}^{1/3}-(n_{ws})_{\rm Ti}^{1/3}]^2}{(n_{ws})_{\rm Ti}^{-1/3}+(n_{ws})_{\rm H}^{-1/3}}-\frac{(\phi^*_{\rm H}\phi^*_{\rm Ti})^2+a(R/P)}{(n_{ws})_{\rm Ti}^{-1/3}+(n_{ws})_{\rm H}^{-1/3}}\right\} \qquad (2)$$

where $(n_{ws})_{\rm H}$ and $(n_{ws})_{\rm Ti}$ are the electron densities at the Winger-Seitz atomic cells boundary of H and Ti, respectively, P and Q are empirical constants, the empirical constant, a, assumes values of 0.73 and 1 for liquid and solid alloys, respectively, and R is a non-zero constant.

Since the molar volume of H in Ti can be different from that of pure Ti volume because the formation of the electrostatic dipole layer occurs with a transfer of charge, in calculations of the standard enthalpy of formation of titanium hydride, it is necessary to modify the H atomic volume $V_{\rm H}$ by taking account of the values before and after charge transfer. This can be derived from

$$V_{\rm H}'^{2/3}({\rm Ti})=V_{\rm H}^{2/3}({\rm pure})[1+\mu_{\rm H}f_{\rm Ti}^{\rm H}(\phi^*_{\rm H}-\phi^*_{\rm Ti})] \qquad (3)$$

where $f_{\rm Ti}^{\rm H}$ represents the degree to which H atoms are surrounded by Ti atom neighbours. The relative volume change is proportional to the difference $\phi^*_{\rm H}-\phi^*_{\rm Ti}$ in electronegativity and to the degree to which H atoms are surrounded by dissimilar neighbours. The applicability of Eq.(3) to titanium hydride can be verified by comparing the experimentally observed volume changes upon hydride formation with those corresponding to the values of $V_{\rm Ti}^{2/3}$ and $V_{\rm H}^{2/3}$ obtained from Eq.(3). It must be kept in mind that Eq.(3) represents the volumes taking account of the values before and after charge transfer, whereas the experimentally observed volume changes will correspond to the situation after charge transfer.

The value of $f_{\rm Ti}^{\rm H}$ can be expressed as

$$f_{\rm Ti}^{\rm H}=(1-c_{\rm H}^{\rm s})\{1+8[c_{\rm H}^{\rm s}(1-c_{\rm H}^{\rm s})]^2\} \qquad (4)$$

where $c_{\rm H}^{\rm s}$ represents the surface concentrations of H atoms which can be expressed as a function of $c_{\rm H}$ and $c_{\rm Ti}$ as follows:

$$c_{\rm H}^{\rm s}=\frac{c_{\rm H}V_{\rm H}^{2/3}}{c_{\rm H}V_{\rm H}^{2/3}+c_{\rm Ti}V_{\rm Ti}^{2/3}} \qquad (5)$$

The value of $V_{\rm H}'^{2/3}$ can be obtained after some mathematical manipulation with Eq.(3)-Eq.(5).

When the values of $V_{\rm H}^{2/3}$ in Eqs.(1) and (2) are replaced by $V_{\rm H}'^{2/3}$, the modified standard enthalpy of formation can be expressed as

$$\Delta H'^{\ominus}_{\rm H\rightarrow Ti}=f_0'\frac{c_{\rm H}Ac_{\rm Ti}B}{c_{\rm H}V_{\rm H}'^{2/3}A+c_{\rm Ti}V_{\rm Ti}^{2/3}B} \qquad (6)$$

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$$f_0' = 2PV_{\text{H}}'^{2/3}V_{\text{Ti}}^{2/3} \cdot \left\{ \frac{Q/P[(n_{ws})_{\text{H}}^{1/3} - (n_{ws})_{\text{Ti}}^{1/3}]^2}{(n_{ws})_{\text{Ti}}^{-1/3} + (n_{ws})_{\text{H}}^{-1/3}} - \frac{(\phi_{\text{H}}^* - \phi_{\text{Ti}}^*)^2 + a(R/P)}{(n_{ws})_{\text{Ti}}^{-1/3} + (n_{ws})_{\text{H}}^{-1/3}} \right\} \tag{7}$$

The standard enthalpy of formation of TiH_x can be calculated by $\Delta H^{\ominus}_{\text{TiH}_x} = x\Delta H'^{\ominus}_{\text{H}\rightarrow\text{Ti}}$.

B. Standard entropy model

According to statistic thermodynamics theory, the entropy of microscopic particle consists of translational, rotational, vibrational, electronic, and nuclear spin contribution. Because the nuclear state is invariant during general chemical and physical reaction process, the contribution of nuclear spin on entropy is always omitted. Debye theories [23] suggest that the solid thermal capacity is only related to vibration, so the translation, rotation, and electronic motion are not taken into account. For solid crystal lattice, it is reasonable to omit the influences of translation and rotation on entropy, but the contribution of electronic motion on entropy should be considered when calculating the value of entropy. So, the thermodynamic parameters obtained with Debye solid thermal capacity theories are approximately correct. A new method, based on Debye solid thermal capacity theories, is employed in the present work, and the method will take into account the influences of vibration and electronic motion on the entropy of formation of titanium hydride TiH_2.

Debye theories suggest that vibrational entropy S_{v} is a function of D and θ_D [23],

$$S_{\text{v}} = 4RD - 3R\ln(1 - \text{e}^{-\theta_D/T}) \tag{8}$$

where R is the gas constant, D is Debye function, θ_D is Debye temperature, and T is Kelvin temperature. Debye temperature can be calculated by $\theta_D = h\nu/k$, where h is the Planck constant, ν is resonant frequency, and k is the Boltzmann constant. Debye function D is expressed as

$$D = 3\left(\frac{T}{\theta_D}\right)^3 \int_0^{u_D} \frac{u^3}{\text{e}^u - 1}\text{d}u \tag{9}$$

where $u_D = h\nu/(kT) = \theta_D/\text{T}$.

Based on Eq.(8) and Eq.(9), the vibrational entropy S_{v} of formation of titanium hydride TiH_2 can be acquired at a given value of ν.

The electronic thermal capacity of solid crystal lattice C_{e} is defined as [24]

$$\begin{aligned} C_{\text{e}} &= \frac{\pi^2}{2}\frac{ZRT}{T_{\text{F}}^{\ominus}} \\ T_{\text{F}}^{\ominus} &= \frac{E_{\text{F}}^{\ominus}}{k} \\ E_{\text{F}}^{\ominus} &= \frac{\hbar^2}{2m_{\text{e}}}(3\pi^2 n_{\text{e}})^{2/3} \end{aligned} \tag{10}$$

where Z is the average number of free electrons each atom contains, and $T_{\text{F}}^{\ominus}$ is Fermi temperature. $E_{\text{F}}^{\ominus}$ is the Fermi energy at absolute zero. $\hbar = h/2\pi$, m_{e} is the electron mass, and n_e is free electron density. If the values of Z and n_{e} are known, the electronic thermal capacity C_{e} can be obtained from Eq.(10) after some mathematical manipulation. Also, the value of electronic entropy S_{e} can be calculated by the following equation:

$$S_{\text{e}} = \int_0^T \frac{1}{T} C_{\text{e}} \text{d}T \tag{11}$$

The value of standard entropy of TiH_2 should be the sum of vibrational entropy S_{v} and electronic entropy S_{e}, so $S^{\ominus}_{\text{TiH}_2} = S_{\text{v}} + S_{\text{e}}$. For the reaction $\text{Ti(s)} + \text{H}_2\text{(g)} \rightarrow \text{TiH}_2\text{(s)}$, the standard entropy of formation of TiH_2 can be acquired as

$$\Delta S^{\ominus}_{\text{TiH}_2} = S^{\ominus}_{\text{TiH}_2} - S^{\ominus}_{\text{Ti}} - S^{\ominus}_{\text{H}_2} \tag{12}$$

where $S^{\ominus}_{\text{Ti}}$ and $S^{\ominus}_{\text{H}_2}$ are the values of standard entropy of Ti and H_2 at 298.16 K, respectively.

III. RESULTS AND DISCUSSION

In the present calculation of standard enthalpy of formation of titanium hydride, it is necessary to know the electronegativity parameter ϕ_{H}^* of hydrogen metal, the cell boundary electron density $(n_{ws})_{\text{H}}^{1/3}$ in metallic hydrogen, the corresponding molar volume V_{H}, and the constant R. If ϕ_{H}^* is expressed in volts, n_{ws} is expressed in empirical density units (d.u.) and $\Delta H^{\ominus}_{\text{TiH}_x}$ is expressed in kJ/mol, then $P=12.3$, $Q/P=9.4$, and $R/P=3.9$. The value assumed for ϕ^* in the standard enthalpy model agrees quite well with the position of hydrogen in Pauling's electronegativity scale [25]. The value of n_{ws} agrees well with the value for the interstitial electron density in hydrogen metal, derived in the self-consistent band structure calculations by Moruzzi *et al.* [26], and with the average relation existing between empirical cell boundary densities and calculated interstitial electron densities [27]. The assumed molar volume of hydrogen metal ($V_{\text{H}}=1.7\ \text{cm}^3$) is that derived from experiments on the pressure dependence of the enthalpy of formation of hydrides of metals which is slightly smaller than the theoretically predicted molar volume V_{H} of metallic hydrogen of 1.85 cm^3 [26,28]. The values of input parameters for the standard enthalpy model are tabulated in Table I.

Substituting the values shown in Table I into Eq.(3) and Eq.(4), the value of $V_{\text{H}}'^{2/3}$ can be calculated by

$$\begin{aligned} V_{\text{H}}'^{2/3} = {} & -2.2264{c_{\text{H}}^{\text{s}}}^5 + 6.6792{c_{\text{H}}^{\text{s}}}^4 - 6.6792{c_{\text{H}}^{\text{s}}}^3 + \\ & 2.2264{c_{\text{H}}^{\text{s}}}^2 - 0.2783c_{\text{H}}^{\text{s}} + 1.6983 \end{aligned} \tag{13}$$

For the TiH_x, substituting $c_{\text{H}} = x/(x+1)$ and $c_{\text{Ti}} = 1/(x+1)$ into Eq.(5), the value of c_{H}^{s} can be ob-

TABLE I The values of input parameters for the standard enthalpy model with a=1, P=12.3, Q/P=9.4, and R/P=3.9.

Elements	ϕ^*/V	$V^{2/3}$/(cm^2/mol)	$(n_{ws})^{1/3}$/(d.u.)$^{1/3}$	μ
Ti	3.80	4.83	1.52	0.10
H	5.20	1.42	1.50	0.14

TABLE II The calculated results of $\Delta H^{\ominus}_{\mathrm{TiH}_x}$ (in unit of kJ/mol).

x	$\Delta H^{\ominus}_{\mathrm{TiH}_x}$	x	$\Delta H^{\ominus}_{\mathrm{TiH}_x}$
1.0	−71.58	1.7	−121.32
1.1	−78.73	1.75	−124.85
1.2	−85.86	1.8	−128.36
1.3	−92.99	1.85	−131.88
1.4	−100.10	1.9	−135.38
1.5	−107.19	1.95	−138.89
1.6	−114.26	2.0	−142.39

tained by

$$c^s_{\mathrm{H}} = \frac{1.42x}{1.42x + 4.83} \tag{14}$$

Substituting the values shown in Table I into Eq.(6), the value of $\Delta H^{\ominus}_{\mathrm{TiH}_x}$ can be obtained after some mathematical manipulation,

$$\begin{aligned} \Delta H^{\ominus}_{\mathrm{TiH}_x} &= x\Delta H'^{\ominus}_{\mathrm{H}\to\mathrm{Ti}} \\ &= -525.311x\frac{c_{\mathrm{H}}c_{\mathrm{Ti}}V'^{2/3}_{\mathrm{H}}CD}{c_{\mathrm{H}}V'^{2/3}_{\mathrm{H}}C + 4.83c_{\mathrm{Ti}}D} \qquad (15) \\ C &= 1 + 0.196c_{\mathrm{Ti}} \\ D &= 1 - 0.14c_{\mathrm{H}} \end{aligned}$$

and the value of $\Delta H^{\ominus}_{\mathrm{TiH}_x}$ can be calculated by combining Eqs.(13), (14), and (15).

The calculated values of $\Delta H^{\ominus}_{\mathrm{TiH}_x}$ are tabulated in Table II. It can be seen that the values of $\Delta H^{\ominus}_{\mathrm{TiH}_x}$ decrease with increasing of x. Figure 2 indicates a linear relationship between $\Delta H^{\ominus}_{\mathrm{TiH}_x}$ and x. It can be seen from Fig.2 that the calculated results in this work agree well with those reported in Refs.[9,10,29] (obtained by experimental methods), but there is some deviation from the results of Ref.[30] (obtained by theoretical calculation).

For calculating the vibrational entropy S_{v}, Zhang's data [31] of resonant frequency ν are used in the present work. The calculation results based on Eqs.(8) and (9) are tabulated in Table III.

The vibrational entropy of TiH_2 at 298.16 K is obtained by $S_{\mathrm{v}}=\sum\limits_i S_{\mathrm{v}i}$=18.09 J/(mol·K).

As is known, the titanium hydride TiH_2 has a face centered cubic (fcc) lattice structure with a lattice constant of 0.444 nm. In each crystal lattice, there are four Ti atoms and eight H atoms. Because each Ti and H atom contains two and one free electrons, respectively, the total free electrons contained in every crystal lattice is N=4×2+8×1=16, and the average number of free electrons each atom contains should be Z=16/12=1.333. Because the crystal lattice volume $V=(4.44\times10^{-10})^3$ m^3, the free electron density can be obtained by $n_{\mathrm{e}}=N/V=1.828\times10^{29}$ m^{-3}. Based on Eq.(10), the Fermi energy at absolute zero and Fermi temperature are $E^{\ominus}_F=1.883\times10^{-18}$ J and $T^{\ominus}_{\mathrm{F}}$=136449 K, respectively, the electronic thermal capacity of TiH_2 can be calculated as $C_{\mathrm{e}}=4.008\times10^{-4}T$ J/K. According to Eq.(11), the value of S_{e} at 298.16 K can be acquired as S_{e}=0.12 J/(mol·K). Therefore, the standard entropy of TiH_2 at 298.16 K is $S^{\ominus}_{\mathrm{TiH}_2}=S_{\mathrm{v}}+S_{\mathrm{e}}$=18.21 J/(mol·K).

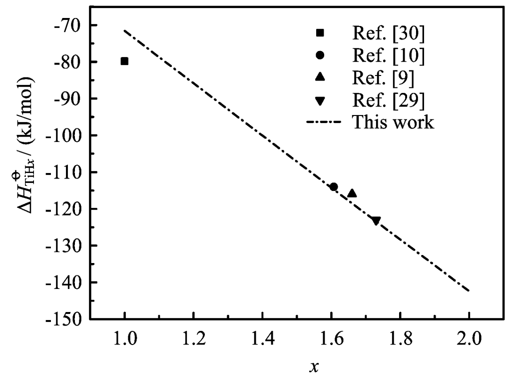

FIG. 2 Comparison of standard enthalpy of formation of TiH_x.

TABLE III The calculated results of vibrational entropy. $S_{\mathrm{v}i}$ in unit of J/(mol·K)

$\tilde{\nu}_i$/cm^{-1}	$v_i/(10^{13}\mathrm{s}^{-1})$	θ_{Di}/K	D_i	$S_{\mathrm{v}i}$
484.4377	1.453	697.80	0.380	15.17
1521.0368	4.563	2190.29	0.046	1.55
1590.5987	4.772	2291.20	0.041	1.37

For the reaction $\mathrm{Ti(s)+H_2(g)\rightarrow TiH_2(s)}$, the standard entropy of formation of TiH_2 can be calculated as in the following:

$$\begin{aligned} \Delta S^{\ominus}_{\mathrm{TiH}_2} &= S^{\ominus}_{\mathrm{TiH}_2} - S^{\ominus}_{\mathrm{Ti}} - S^{\ominus}_{\mathrm{H}_2} \\ &= 18.21 - 30.63 - 130.58 \\ &= -143.0 \ \ \mathrm{J/(mol{\cdot}K)} \end{aligned} \tag{16}$$

The standard enthalpy and entropy of formation of TiH_2 are tabulated in Table IV and compared with those reported in Refs.[10,11,29,31-33]. The value of $\Delta H^{\ominus}_{\mathrm{TiH}_2}$ obtained in this work (−142.39 kJ/mol) lies between that of Dantzer *et al.* (−137 kJ/mol) [32] and Zhang *et al.* (−148 kJ/mol) [31]. $\Delta S^{\ominus}_{\mathrm{TiH}_2}$ from this work (−143.0 J/(mol·K)) is close to that of Arita *et al.* (−145 J/(mol·K)) [10] and San-Martin *et al.* (−142 J/(mol·K)) [33]. For comparison, the reported

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TABLE IV Comparison of standard enthalpy and entropy of formation of TiH$_2$, $\Delta H^{\ominus}_{\mathrm{TiH_2}}$ in kJ/mol, $\Delta S^{\ominus}_{\mathrm{TiH_2}}$ in J/(mol·K).

$\Delta H^{\ominus}_{\mathrm{TiH_2}}$	$\Delta S^{\ominus}_{\mathrm{TiH_2}}$	Method
−123	−126	Experimental [29]
−137	−142	Experimental [32,33]
−148	−149	Calculated [31]
−165	−174	Experimental and Calculated [11]
−179	−145	Experimental and Calculated [10]
−142.39	−143.0	Calculated in this work

results obtained by Wang *et al.* [11] and Stull *et al.*[29] are also listed in Table IV. Since too many details, such as the exact obtaining and processing of experimental data, were included in the methods presented by Wang *et al.* [11] and Stull *et al.* [29], there are many technical difficulties in obtaining the thermodynamic parameters of TiH$_2$ by means of their experimental approach. However, some influencing factors on the formation of TiH$_2$ are simplified in the present model, and the results obtained in the present work show a greater difference from the reported data from Refs.[11,29].

The standard Gibbs free energy of formation of titanium hydride TiH$_2$ can be obtained by

$$\begin{aligned}\Delta G^{\ominus}_{\mathrm{TiH_2}} &= \Delta H^{\ominus}_{\mathrm{TiH_2}} - T\Delta S^{\ominus}_{\mathrm{TiH_2}}\\ &= -142.39 + 298.16 \times 143.0 \times 10^{-3}\\ &= -99.75 \ \ \mathrm{kJ/mol} \qquad (17)\end{aligned}$$

Because $\Delta G^{\ominus}_{\mathrm{TiH_2}}$ is related to the equilibrium hydrogen pressure $P_{\mathrm{H_2}}$ [34,35] by

$$\ln P_{\mathrm{H_2}} = \frac{\Delta G}{R}\frac{1}{T} \qquad (18)$$

where $P_{\mathrm{H_2}}$ is the equilibrium hydrogen pressure and R is the gas constant. Substituting the values of $\Delta G^{\ominus}_{\mathrm{TiH_2}}$=−99.75 kJ, R=8.314 J/(mol·K), and T=298.16 K into Eq.(18), the values of ln$P_{\mathrm{H_2}}$ and $P_{\mathrm{H_2}}$ can be obtained as ln$P_{\mathrm{H_2}}$=−40.24, $P_{\mathrm{H_2}}$=3.34×10^{-13} Pa which agree well with the reported data obtained by Zhang *et al.* (ln$P_{\mathrm{H_2}}$=−47.38, $P_{\mathrm{H_2}}$=2.7154×10^{-16} Pa, and ln$P_{\mathrm{H_2}}$=−29.77, $P_{\mathrm{H_2}}$=1.2075×10^{-8} Pa at 273.16 K and 373.16 K, respectively) [31].

Overall, the consistency between the results obtained in this work and the reported data from Refs.[11,31,32,33] is satisfactory, which shows the effectiveness of the thermodynamic model for titanium hydride employed in this work.

IV. CONCLUSION

A modified Miedema model, using interrelationship among the basic properties of elements Ti and H, is employed to calculate the standard enthalpy of formation of titanium hydride TiH$_x$ (1≤x≤2). A new approach, based on Debye theories of solid thermal capacity, is presented to calculate the standard entropy of formation of titanium hydride TiH$_2$. The values of standard enthalpy of formation of TiH$_x$ decrease linearly with increasing of x, and agree well with the data from Arita [9,10] and Stull [29] obtained by experimental methods. The values of vibrational and electronic entropy of TiH$_2$ acquired in the present work are S_{v}=18.09 J/(mol·K) and S_{e}=0.12 J/(mol·K), respectively, and the standard entropy of TiH$_2$ at 298.16 K is $S^{\ominus}_{\mathrm{TiH_2}}$=18.21 J/(mol·K). The calculated results of standard enthalpy $\Delta H^{\ominus}_{\mathrm{TiH_2}}$, entropy $\Delta S^{\ominus}_{\mathrm{TiH_2}}$, and free energy $\Delta G^{\ominus}_{\mathrm{TiH_2}}$ of formation of TiH$_2$ at 298.16 K are −142.39 kJ/mol, −143.0 J/(mol·K), and −99.75 kJ/mol, respectively, which show satisfactory consistency with the reported data from Refs.[10,31-33]. The results show that the thermodynamic model of titanium hydride is reasonable.

V. ACKNOWLEDGMENT

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