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LETTER

An investigation on the thermodynamic stability of V_6Si_5

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The V–Si system has been assessed by Smith [1, 2], and results were collected in recently published binary phase diagram handbook [3]. The thermodynamic optimizations for the system were also performed by Luoma [4], Rand and Saunders [5]. However, the thermodynamic stability of V_6Si_5 is still in question. Using the method of solid state diffusion, Hallais et al. [6] noted that formation of V_6Si_5 could not be achieved below 1000 °C. By means of bulk V–Si diffusion couples, Milanese et al. [7] found that there is a nucleation barrier for the formation of V_6Si_5 at 1150 °C. Based on the electromotive force (emf) measurement, Eremenko et al. [8] realized that the difficulty of achieving an equilibrium state of V–Si alloys containing the phase V_6Si_5 is indeed overdrawn. Using activity data deduced from the Knudsen cell-mass spectrometry, Storms and Myers [9] indicated the eutectoid decomposition temperature ($V_6Si_5 \Leftrightarrow V_5Si_3 + VSi_2$) as 1160 ± 100 K. This temperature was mistakenly regarded to be 1433 K (1160 °C) in subsequent assessment [2] and thermodynamic optimizations [4, 5]. Here we prepared several alloys in the relevant composition ranges to investigate the thermodynamic stability of V_6Si_5. Additionally, a combined first-principles/CALPHAD (CALculation of PHAse Diagrams) approach is adopted to predict the decomposition temperature and a new set of thermodynamic parameters for vanadium silicides is obtained.

Two alloys ($V_{41}Si_{59}$ and $V_{73}Si_{27}$, in atomic percent) were prepared by arc-melting under argon, with 99.9% purity V and 99.99% purity Si. The alloy $V_{41}Si_{59}$ was annealed for 2 weeks at both 1000 °C and 700 °C. This temperature range covers the upper and the lower limits of the extrapolated decomposition temperature of V_6Si_5 [9]. The decomposition temperature is calculated to be 573 °C from the Gibbs energy functions assessed by Smith [2]. Therefore, another piece of the alloy $V_{41}Si_{59}$ was heat-treated at 500 °C for one month. The alloy $V_{73}Si_{27}$ was put into the same batch at 1000 °C, with a desire to check the possible contamination of interstitial elements. Every alloy was sealed in evacuated silica tubes under vacuum of 10^{-3} bar and then water-quenched after annealing.

To our surprise, the alloys $V_{41}Si_{59}$ annealed at 1000 °C, 700 °C and 500 °C show a two-phase mixture of V_6Si_5 and VSi_2, according to X-ray powder diffraction (Fig. 1). This result indicts that the decomposition temperature of V_6Si_5 is below 500 °C. As the diffraction pattern of the alloy $V_{73}Si_{27}$ show that we obtained V_3Si plus the tetragonal $D8_m$ V_5Si_3 which will transform to the hexagonal $D8_8$ with the addition of C, B, N and O [10], therefore, the contamination of interstitial elements is excluded in present experiments.

In order to further determine the relative stability of V_6Si_5 in the $T = 0$ K ground state, the state-of-art first-principles projector augmented plane-wave (PAW) calculations were applied to all intermetallic compounds of V–Si system using Vienna ab initio simulation package (VASP) [11, 12], together with the Perdew–Burke–Ernzerhof [13] generalized gradient approximation for the exchange-correlation potential. A plane-wave cutoff energy was set to be 400 eV. k-point meshes for Brillouin zone sampling were constructed using the Monkhorst–Pack [14] scheme,

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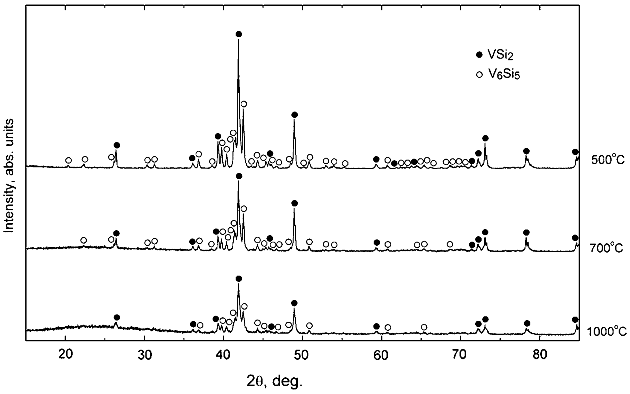

Fig. 1 X-ray diffraction patterns of the alloys $V_{41}Si_{59}$ annealed at 1000 °C, 700 °C for 2 weeks and 500 °C for 1 month. Two-phase mixture of VSi_2 + V_6Si_5 was found in phase identification

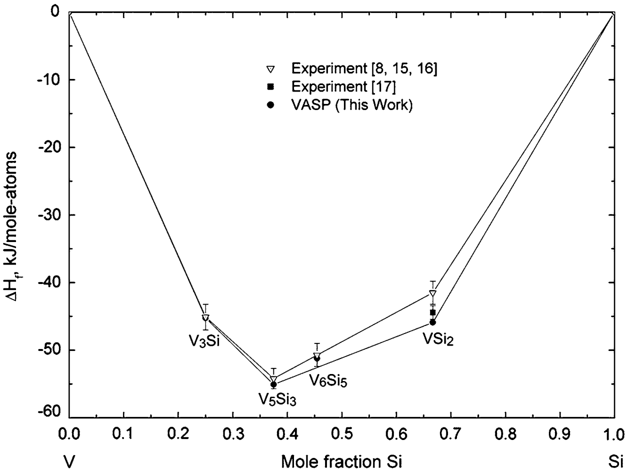

Fig. 2 First-principles calculated enthalpies of formation for the compounds in the V–Si system, compared with the experimental data of Eremenko et al. [8, 15, 16] and O'Hare et al. [17]

and extensive tests were performed (using from 5 × 5 × 5 to 15 × 15 × 15 grids). Both the unit cell sizes and the ionic coordinates were fully relaxed to find the stable state. The total energy differences were converged to within 0.1 kJ/mole-atoms.

The $T = 0$ K enthalpy of formation (per atom) of the V_pSi_q can be calculated from the following equation:

$$\Delta H_f(V_pSi_q) = E(V_pSi_q) - (1 - x)E(V) - xE(Si) \tag{1}$$

where $E(V)$, $E(Si)$ and $E(V_pSi_q)$ are the calculated zero-temperature total energies (per atom) of Bcc V, Diamond Si and the corresponding intermetallic phase, respectively, each relaxed to its equilibrium geometry. Here, $x = q/(p + q)$ is the atomic fraction of Si in these vanadium silicides.

The calculated enthalpies of formation (ΔH_f) are compared with experimental data at room temperature (Fig. 2). Except for VSi_2, first-principles calculated formation enthalpies agree well with the values measured by Eremenko et al. [8, 15, 16] using emf method. Recently, O'Hare et al. [17] remeasured the enthalpy of formation of VSi_2 by means of fluorine combustion calorimetry. The measured value of O'Hare et al. [17] is very close to the present first-principles calculation. As shown in Fig. 2, first-principles calculated ΔH_f of V_6Si_5 falls above the tie-line between those of V_5Si_3 and VSi_2. This indicates that V_6Si_5 is thermodynamically unstable at $T = 0$ K and its decomposition temperature is higher.

Due to the formidable computational work at finite-temperature and slow kinetics at low temperatures, an efficiently combined first-principles/CALPHAD hybrid method, which was well illustrated in Al–Sr system by Wolverton et al. [18], is employed to estimate the decomposition temperature of V_6Si_5. The Gibbs free energy for compound V_pSi_q is modeled as (J/mole-atoms)

$$G^{V_pSi_q} = (1 - x)^oG_V + x^oG_{Si} + a + bT \tag{2}$$

where ${}^oG_V$ and ${}^oG_{Si}$ is the molar Gibbs energy of pure V and Si in their stable structure at room temperature [19]. Accepting the parameters for liquid phase evaluated by Luoma [4], we optimized the parameters a and b for VSi_2, V_6Si_5 and V_5Si_3 respectively using the information on the congruent melting points and the invariant reactions [2]. The calculated enthalpies of formation at $T = 0$ K are set as the starting values for parameter a and limited to vary within ±1 kJ, which is the typical accuracy of first-principles calculations. All parameters generated in this work are listed in Table 1.

The general agreement between the calculated phase diagram in this work and that of Luoma [4] is excellent (Fig. 3). The decomposition temperature of V_6Si_5 is predicted to be 460 °C which is consistent with the present experimental result. Lozova et al. [20] did not find V_6Si_5 in the presented isothermal section of the Li–V–Si system at 297 °C. Thus the real decomposition temperature of the V_6Si_5 should be between 297 °C and 460 °C. Moreover, the predicted phase stability diagram using the present parameters is in good agreement with the experimental data reported by Storms and Myers [9] (Fig. 4). This is another check of the reliability of the presently obtained parameters.

Table 1 The optimized parameters for vanadium silicides based on the output of first-principles calculations and experimental phase diagram data

Phase	Eq. (2) a (J/mole-atoms)	Eq. (2) b (J/mole-atoms·K)
VSi_2	–45913.1	3.79418
V_6Si_5	–52220.5	4.44687
V_5Si_3	–55072.0	5.35583

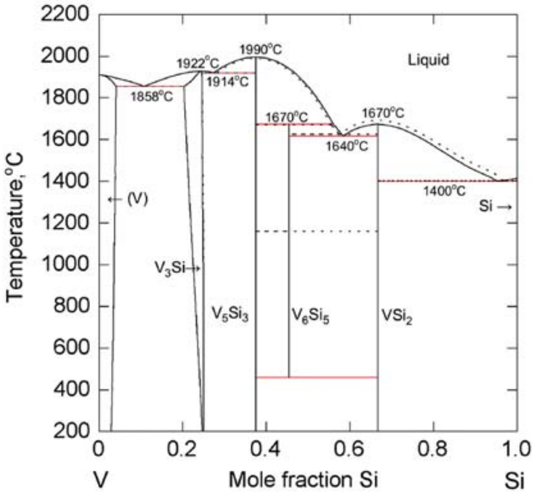

Fig. 3 Comparison between the calculated V–Si phase diagram of Luoma [4] (dash line) and the present work (solid line)

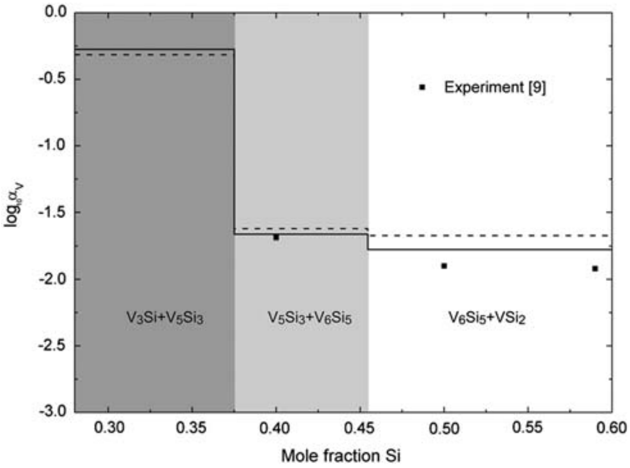

Fig. 4 Model-predicted phase stability diagram at 1650 K, compared with the experimental data of Storms and Myers [9]. (Dash line is calculated using the parameters of Luoma [4] and solid line comes from the present work). α_v is the activity of Vanadium. The reference state is bcc-V

The combined CALPHAD/first-principles approach shows its value to detect the eutectoid decomposition temperature of V_6Si_5, which is confirmed experimentally to be stable down to 500 °C. The newly obtained parameters for the vanadium silicides provide a more precise description of the thermodynamic stability of V_6Si_5.

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