Thermodynamics of the Phase Formation of the Titanium Silicides

R. J. Kematick and C. E. Myers*

Chemistry Department and Materials Research Center, Binghamton University–SUNY, Binghamton, New York 13902-6016

Vaporization thermodynamics in the titanium–silicon binary system has been studied by a Knudsen effusion–mass spectrometer technique. The equilibrium vapor pressure of silicon gas over two-phase mixtures of $TiSi_2$ + TiSi, TiSi + Ti_5Si_4, and Ti_5Si_4 + Ti_5Si_3 has been measured over a temperature range of ca. 1700–2050 K, and the vapor pressure of titanium gas was measured over a two-phase mixture of Ti_5Si_4 + Ti_5Si_3. Standard enthalpy and entropy changes for the appropriate dissociation reactions, within the temperature ranges of the experiments, were determined from the temperature dependence of the measured vapor pressures. Estimated thermal functions were combined with the vapor pressure data and used in a third-law evaluation of the standard enthalpies of formation at 298 K of the intermediate compounds. The results obtained are $^1/_3TiSi_2$, −53.5 ± 5 kJ; $^1/_2TiSi$, −71.5 ± 5 kJ; $^1/_9Ti_5Si_4$, −75.9 ± 5 kJ; $^1/_8Ti_5Si_3$, −78.1 ± 5 kJ. The results obtained in this work are compared with previous estimates and measurements of the thermodynamics of phase formation of the titanium silicides.

Introduction

Silicides of the transition and refractory metals have a number of properties of potential interest in materials applications. Their good thermal stability and oxidation resistance at high temperature have resulted in application as corrosion-resistant coatings and high-temperature furnace elements.[1] Transition-metal silicides also find application in electronic device technology, where low electrical resistivity and chemical compatibility with silicon substrates have resulted in the use of silicide materials in contacts and interconnects for integrated circuitry.[2] A number of transition-metal disilicides, most especially $TiSi_2$, have become interesting candidate materials for interconnect applications in integrated circuitry. In addition to $TiSi_2$, the Ti–Si system[3] also contains the intermediate compounds TiSi, Ti_5Si_4, Ti_5Si_3, and Ti_3Si.

Silicide materials, including $TiSi_2$, are often deposited on silicon substrates by means of chemical vapor deposition (CVD) techniques. In a typical process a mixture of gaseous $TiCl_4$, H_2, and Ar is passed over a heated silicon substrate. Under appropriate conditions reaction to form the disilicide will occur on bare silicon but will not occur on a silicon oxide-coated surface.[4] Thus, under these conditions, selective growth can be achieved on a patterned substrate. In the thermochemical modeling of vapor deposition processes (such

models typically include thermochemistry, kinetics, and mass transport), it has been noted that the real problem is not computer capacity but a lack of data.[5] Prediction of the solid phases that will form under a given set of CVD process variables requires accurate thermodynamic data for all likely product phases. In particular, an approach often adopted is a free energy minimization calculation, which requires high-temperature free energy of formation data for the reactants and likely products. Engqvist and co-workers[4] have shown that the products predicted for a given set of CVD process conditions depend crucially on the thermodynamic data employed in the thermochemical model. For deposition from a $TiCl_4/H_2/Ar$ gaseous mixture onto a silicon substrate at temperatures between 600 and 1400 K at total pressures between 10^{-2} and 10^2 Pa with $H_2/TiCl_4$ ratios between 10^{-2} and 10^5, a data set developed by Engqvist et al. and a set developed by Valhas and co-workers[6] both predicted the observed product, $TiSi_2$. However, data from a standard thermochemical compilation,[7,8] which is based on the direct reaction calorimetry data,[9] and estimated heat capacities,[10] gave a completely different result; $TiCl_3$ is predicted at low temperatures and $TiSi_2$ is predicted to be unstable with respect to disproportionation into TiSi and Si above 700 K which is not in accord with the accepted Ti–Si phase diagram.[3]

⊗ Abstract published in *Advance ACS Abstracts,* November 1, 1995.

(1) Meier, G. H. In *High Temperature Ordered Intermetallic Alloys II*; Stoloff, N. S., Koch, C., Lie, C. T., Izumi, O., Eds.; Materials Research Society Symposium Proceedings 81, Materials Research Society: Pittsburgh, 1985; p 15.

(2) Murarka, S. P. *Silicides for VLSI Applications*; Academic Press Inc.: Orlando, FL, 1983.

(3) Murray, J. L. In *Binary Alloy Phase Diagrams,* 2nd ed.; Massalski, T. B., Ed.; American Society for Metals: Metals Park, OH, 1990; pp 3367–3371.

(4) Engqvist, J.; Myers, C.; Carlsson, J.-O. *J. Electrochem. Soc.* **1992**, *139*, 3197–3205 and references therein.

(5) Bernard, C. *High Temp. Sci.* **1990**, *27*, 131–142.

(6) Vahlas, C.; Chevalier, P. Y.; Blanquet, E. *Calphad* **1989**, *13*, 273.

(7) Barin, I.; Knacke, O., Eds. *Thermochemical Properties of Inorganic Substances*; Springer: Berlin, 1973. Barin, I.; Knacke, O.; Kubaschewski, O., Eds., *Thermochemical Properties of Inorganic Substances, Supplement*; Springer: Berlin, 1977.

(8) Knacke, O.; Kubaschewski, O.; Hesselman, K., Eds.; *Thermochemical Properties of Inorganic Substances,* 2nd ed., Springer: Berlin, 1991.

(9) Robins, D. A.; Jenkins, I. *Acta. Met.* **1955**, *3*, 598–604.

(10) Kubaschewski, O. In *Atomic Energy Review*; Special Issue 9, Komarek, K., Ed.; Intl. Atomic Energy Agency: Vienna, 1983; p 3.

The thermodynamics of the Ti−Si has been reviewed critically by Schlesinger.[11] Previous thermodynamic experiments have primarily been calorimetric measurements of standard enthalpies of formation. Heat-capacity data for the intermediate compounds are incomplete and of questionable reliability, as are standard entropies. Prior experimental measurements of free energy changes of high-temperature reactions involving the titanium silicides were rejected in favor of the calorimetric data, but the latter are not in agreement. The free energy values needed for the modeling of high-temperature CVD reactions, i.e., for the prediction of CVD "phase diagrams", have been calculated mainly from the available (but limited) calorimetric enthalpy, entropy, and heat capacity data. In many instances,[4,12] modelers have found it necessary to "adjust" the thermodynamic functions of the silicide phases to obtain consistency with observed results of CVD experiments and/or the binary phase diagram. The present study was initiated to provide free energy of phase formation data at elevated temperatures which may be applied in CVD modeling without the need for standard molar entropy data for the silicide phases. From the results, free energy changes for high-temperature vaporization reactions involving the titanium silicides were determined. By means of reasonable assumptions regarding the heat capacity and entropy functions, standard enthalpies of formation of the silicides were calculated and compared to data from previous measurements which were largely obtained by calorimetric methods.

Experimental Technique

Bulk titanium silicide samples were prepared by arc melting weighed mixtures of elemental titanium (99.9+% Ti, metals basis, Alfa Products) and silicon (99.9999% Si, metals basis, Alfa Products) on a water cooled copper hearth under an argon atmosphere. Compositional analyses were not performed, so compositions mentioned herein are nominal. Sample weight losses were observed to be small (<1%) during the arc melting process. The "as-cast" buttons were crushed in a tool steel mortar, subjected to vacuum annealing experiments to ensure complete reaction, and X-ray powder diffraction experiments to confirm the phase mixtures present. The observed X-ray diffraction patterns were compared to patterns computed from published structural data.[13] The sample preparation procedures resulted in samples with compositions demonstrably in the Ti_5Si_3 + Ti_5Si_4, Ti_5Si_4 + TiSi, and TiSi +$TiSi_2$ two-phase regions: for samples in a given two-phase region, all observed diffraction peaks could be assigned to one or the other of the two phases, and the relative intensities conformed to the calculated diffraction patterns. Since, at fixed temperature and at equilibrium, the thermodynamic activities and hence the partial pressures of titanium and silicon will be fixed and independent of composition in the respective two-phase mixtures, it is sufficient for the purposes of this study to demonstrate that the two phases are present. Samples of nominal compositions of 59, 55, and 40 mol % Ti were then selected for the vaporization experiments.

The vaporization experiments were performed using a Nuclide Model 12-90-HT mass spectrometer.[14] This is a magnetic deflection instrument in which a molecular beam

effusing from a Knudsen effusion cell at high temperature is directed into an electron impact (EI) ionization source, the positive ions formed by EI are electrostatically accelerated and brought to focus on a channeltron detector by a tunable magnetic field. A hand-operated shutter was placed in the system such that the beam effusing from the Knudsen cell could be blocked before entering the EI source, thus permitting background measurements. The temperature of the Knudsen cell was determined by sighting an optical pyrometer directly into the effusion orifice through a calibrated viewport.

The titanium silicide samples to be examined were placed in a cylindrical tungsten cup, the tungsten cup was placed inside a tungsten effusion cell, and the Knudsen cell and furnace assembly were then mounted, and the system was evacuated. Measurement of Si^+ ion intensity is complicated by the large background signal from CO^+ and N_2^+ ions forming from the residual gas in the vacuum system, all of these ions appear near mass number 28. To measure accurately the intensity due to silicon ions, the electron kinetic energy in the EI source was reduced to 12.0 V. At this setting, the instrument was found to be capable of resolving the Si^+ signal from the CO^+ background.[14] Measurements of titanium silicide ion intensity (at mass 48) were made using an electron energy of 30 eV. All data collected in this study were obtained by recording manually first the temperature indicated by the optical pyrometer, and then the mass 28 or mass 48 ion intensity with the beam shutter open, and finally the mass 28 or 48 ion intensity with the shutter blocking the effusing beam. The difference in the latter two measurements gives the Si^+ or Ti^+ ion intensity, from which the silicon or titanium vapor pressure was calculated.

In a Knudsen cell mass spectrometry experiment, the vapor pressure P_i of a given species is related to the observed ion intensity I_i via the relation $P_i = k_i I_i T$, the proportionality factor k_i must be determined by calibration. In this study, the instrument was calibrated against the solid elements. After measuring the variation of I_i versus T for Ti and Si gas over the titanium silicide samples, calibration experiments were performed by placing either elemental silicon or titanium in the same cell previously used for the silicide samples. Measurements of Si and Ti ion intensity versus T were then made for Si and Ti gas in equilibrium with the corresponding elemental solids, and the factors k_{Si} and k_{Ti} were evaluated by comparison to published vapor pressures.[15]
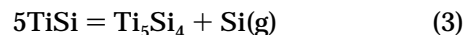
Thermodynamic Calculations

Assuming the intermediate silicide phases to be stoichiometric, the thermodynamic analysis of the vapor pressure data proceeds by considering the following vaporization reactions for the two-phase titanium−silicide mixtures:
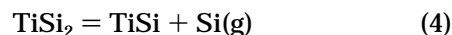
For a mixture of Ti_5Si_3 and Ti_5Si_4:

$$Ti_5Si_4 = Ti_5Si_3 + Si(g) \qquad (1)$$

$$^4/_5Ti_5Si_3 = {}^3/_5Ti_5Si_4 + Ti(g) \qquad (2)$$
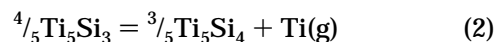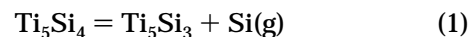
For a two-phase mixture of Ti_5Si_4 and TiSi:

$$5TiSi = Ti_5Si_4 + Si(g) \qquad (3)$$

For a two-phase mixture of TiSi and $TiSi_2$:

$$TiSi_2 = TiSi + Si(g) \qquad (4)$$

The following reference reactions are also considered:

(11) Schlesinger, M. E. *Chem. Rev.* **1990**, *90*, 607−628.

(12) Murray, J. L. In *Phase Diagrams of Binary Titanium Alloys*; Murray, J. L., Ed., American Society for Metals: Metals Park, OH, 1987.

(13) Villars, P., Calvert. L. D., Eds. *Pearson's Handbook of Crystallographic Data*; American Society for Metals: Metals Park, OH, 1985; p 2891.

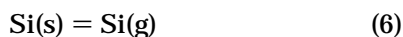(14) Myers, C. E.; Kematick, R. J. *J. Electrochem Soc.* **1987**, *133*, 720−724.

(15) Chase Jr., M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *JANAF Thermochemical Tables*, 3rd ed.; American Chemical Society: Washington DC, and American Institute of Physics: New York, 1986.

$$Ti(\alpha) = Ti(g) \qquad (5)$$

$$Si(s) = Si(g) \qquad (6)$$

Standard enthalpy and entropy changes ($\Delta_r H^\circ{}_T$ and $\Delta_r S^\circ{}_T$) for vaporization reactions 1−4 can be determined at the median experimental temperature from least squares fits of $\ln K_r$ versus $1/T$. Using these $\Delta_r H^\circ{}_T$ and $\Delta_r S^\circ{}_T$ values, a free energy change $\Delta_r G^\circ{}_T$ for each of the reactions 1−4 can be computed at the appropriate median temperature. Standard enthalpy changes at 298 K ($\Delta_r H^\circ{}_{298}$) for reactions 1−4 then be derived from the high-temperature free energies of reaction by the third-law method, i.e.

$$\Delta_r G^\circ{}_T = \Delta_r H^\circ{}_{298} - T \Delta_r \Phi'{}_T$$

where $\Delta_r \Phi'{}_T$ is the change in the "free energy function" for the reaction and

$$\Delta_r \Phi' = -\Delta_r \left(\frac{G^\circ{}_T - H^\circ{}_{298}}{T} \right) =$$

$$\Delta_r S^\circ{}_{298} + (\Delta_r S^\circ{}_T - \Delta_r S^\circ{}_{298}) - \left(\frac{\Delta_r H^\circ{}_T - \Delta_r H^\circ{}_{298}}{T} \right)$$

The evaluation of $\Phi'{}_T$ functions requires estimation of heat capacity functions and standard molar entropy for each of the silicide phases. Heat capacity curves above 298 K were constructed for each of the silicide phases by summing the heat capacity curves of elemental solid titanium (alpha) and silicon (i.e., Kopp's rule). The standard molar entropy value for Ti_5Si_3 has been determined experimentally by Sychev;[16] standard molar entropies for the remaining phases were estimated by linear interpolation between the values for Ti_5Si_3 and pure solid Si.

After computing the standard enthalpy change at 298 K for each of the reactions 1−4, the standard enthalpy of formation of the silicide phases (Ti_5Si_3, Ti_5Si_4, TiSi, and $TiSi_2$) were found by a Hess law combination of reactions 1−6. Data for the pure elements as needed were taken from standard compilations.[15]

Results and Discussion

X-ray diffraction patterns were obtained at different stages for the various samples, e.g., after arc-melting (as-cast), after vacuum annealing procedures, and in the residues of the mass spectrometer experiments. No phases other than those identified as titanium silicides were observed in annealed samples or in residues. The stability of the SiO molecule is such[15] that oxygen impurities are removed in vacuum annealing, and the tantalum radiation shields in the furnace section of the mass spectrometer act as a getter for both oxygen and nitrogen. For samples which contained the $TiSi_2$ phase, the only structure type observed for this phase was the C54 *Strukturbericht* type (Pearson designation *oF24*). X-ray powder diffraction patterns of as-cast samples in the composition range between Ti_5Si_3 and TiSi often could not be indexed as mixtures of reported Ti−Si structure types. These samples were pulverized, transferred to tungsten containers, and subjected to vacuum
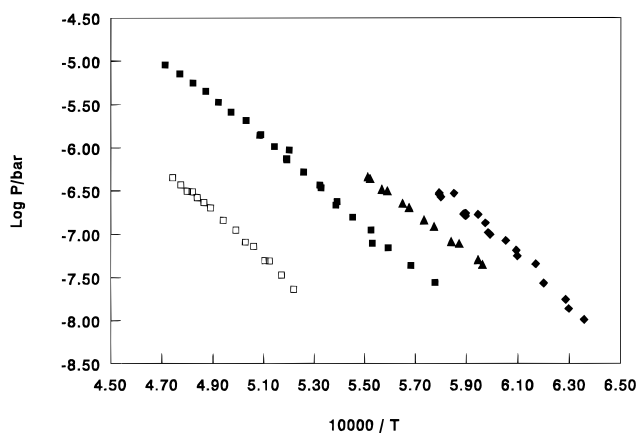
(16) Sychev, N. I.; Gel'd, P. V.; Kalishevich, G. I. *Russ. J. Phys. Chem.* **1980**, *54*, 125−127.

Figure 1. Measured vapor pressures over Ti−Si alloys: (■) $Ti_5Si_4 = Ti_5Si_3 + Si(g)$; (□) $^4/_5 Ti_5Si_3 = {}^3/_5 Ti_5Si_4 + Ti(g)$; (▲) $5TiSi = Ti_5Si_4 + Si(g)$; (◆) $TiSi_2 = TiSi + Si(g)$.

annealing for at least 24 h at temperatures of 1300 °C or higher. After the vacuum annealing experiments, the diffraction patterns corresponded to the anticipated two-phase mixtures of $Ti_5Si_3 + Ti_5Si_4$ or $Ti_5Si_4 + TiSi$. The TiSi phase was always observed in the FeB-type structure (Pearson designation *oP8*). X-ray results were obtained that indicate a transition between the low- and high-temperature forms of Ti_5Si_4. The low-temperature form[17] is isostructural with Zr_5Si_4, and we have prepared it by vacuum annealing of a nominal Ti_5Si_4 sample at 1550 °C. The high-temperature form has been prepared by further annealing of Ti_5Si_4 at 1700 °C. The experimental powder diffraction pattern of the high-temperature form matches approximately with a pattern calculated assuming a Sm_4Ge_5 type structure,[17] but the transition temperature seems higher than previously reported. The phase transition, according to results of our annealing/X-ray diffraction experiments, occurs in the vicinity of 1950 K.

The results of the vapor pressure measurements are presented in the log P vs $1/T$ plots in Figure 1. Least-squares treatment of the vapor pressure data yielded the standard enthalpy, entropy, and free energy changes for the high-temperature vaporization reactions 1−4 as presented in Table 1. The third-law treatment of the data at the midpoint of the temperature range for each of the individual vaporization reactions yielded the standard enthalpy changes at 298 K, also presented in Table 1. The vapor pressure measurements made over a $Ti_5Si_3 + Ti_5Si_4$ mixture undoubtedly crossed the transition temperature of Ti_5Si_4, and the high-temperature form of Ti_5Si_4 was in fact observed by X-ray diffraction in the residues cooled quickly from above 1950 K. Thus, in the strict sense, the enthalpy of the phase transition should be included in the $\Delta_f H^\circ{}_{298}$ calculations. However, since the transition enthalpy is not likely to exceed 5 kJ/(g at.) (the enthalpy of transition for the $\alpha \rightarrow \beta$ transition of titanium metal is 4.172 kJ/mol[15]), the effect is lost in the scatter of the data. The enthalpy of formation values at 298 K of the intermediate silicide phases, determined by a Hess law combination of reactions 1−4 are presented in Table 2, together with data previously reported in the literature. Since the conversion of the high-temperature free energy changes (obtained from the vapor pressure

(17) Nickl, J.; Sprenger, H. *Z. Metallk.* **1969**, *60*, 136−139.

Table 1. Thermodynamic Parameters for Vaporization Reactions

	$\Delta_r H^\circ{}_T$/kJ	$\Delta_r S^\circ{}_T$(K/J)	T/K	T_{mid}/K	$\Delta_r G^\circ{}_{T_{mid}}$/kJ	$\Delta_r H^\circ{}_{298}$/kJ
$Ti_5Si_4 = Ti_5Si_3 + Si(g)$	472.1	127.6	1731−2122	1926	226.3	508.5
$^4/_5Ti_5Si_3 = 3/5\ Ti_5Si_4 + Ti(g)$	508.4	120.0	1916−2109	2012	267.0	564.1
$5\ TiSi = Ti_5Si_4 + Si(g)$	423.7	113.7	1677−1814	1746	225.3	481.7
$TiSi_2 = TiSi + Si(g)$	493.9	163.1	1572−1726	1649	224.9	467.4

Table 2. Standard Enthalpies of Phase Formation: $\Delta_f H^\circ{}_{298}$/kJ

	$^1/_8Ti_5Si_3$	$^1/_9Ti_5Si_4$	$^1/_2TiSi$	$^1/_3TiSi_2$	method[a]
this work	−78.1 ± 5	−75.9 ± 5	−71.5 ± 5	−53.5 ± 5	KEMS
Robins and Jenkins[9]	−72.5		−65.0	−45.0	DRC
Golutvin[18]	−76.9		−82.0	−59.8	COMB
Polyachenok et al.[19]	−72.7				IRC
Savin[20]	−76.5		−78.6	−60.2	IRC
Maslov et al.[21]	−72.4				DRC
Topor and Kleppa[22]				−57.0	MSC

[a] KEMS, Knudsen effusion mass spectrometry; DRC, direct reaction calorimetry; COMB, combustion calorimetry; IRC, indirect reaction calorimetry; MSC, metal solution calorimetry.

Table 3. Heat Capacity[a] and Entropy Parameters (J/mol K)

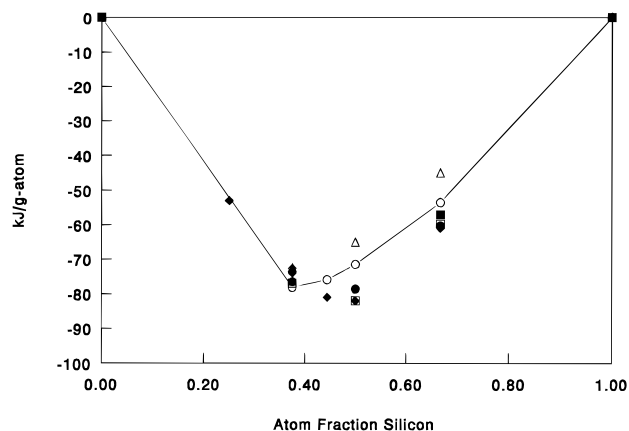|	A	B	C	D	$S^\circ{}_{298}$
Ti(α)	23.1	0.00866	7.25×10^{-7}	-6.30×10^4	30.76
Si(s)	22.8	0.00386	0.00	-3.53×10^5	18.82
$TiSi_2$(s)	68.7	0.0164	7.25×10^{-7}	-7.70×10^5	63.2
TiSi(s)	45.9	0.0125	7.25×10^{-7}	-4.16×10^5	44.4
Ti_5Si_4(s)	206	0.0587	3.62×10^{-6}	-1.73×10^6	203.3
Ti_5Si_3(s)	184	0.0549	3.62×10^{-6}	-1.38×10^6	184.5

[a] $Cp = A + BT + CT^2 + DT^{-2}$.

Figure 2. Enthalpies of formation, $\Delta_f H^\circ{}_{298}$, of titanium silicides, $Ti_{1-x}Si_x$: (○) this work; (△) Robins and Jenkins;[9] (□) Golutvin;[18] (◇) Polyachenok and Novikov;[19] (●) Savin;[20] (▲) Maslov et al.,[21] (■) Topor and Kleppa;[22] (◆) de Boer et al.[23]

Figure 3. Enthalpies of formation, $\Delta_f H^\circ{}_{298}$, of transition-metal silicides, $M_{1-x}Si_x$: (○) Ti−Si, this work; (△) V−Si;[14,24] (□) Cr−Si;[25] (◇) Mn−Si;[11] (●) Fe−Si;[11] (▲) Co-Si;[26] (■) Ni−Si.[11]

measurements) to standard enthalpy changes at 298 K is dependent on the assumptions made regarding the heat capacity functions and standard molar entropies, the functions used have been included in Table 3.

A comparison of the present results with calorimetric data reported in the literature is given in Table 2 and Figure 2. It is unlikely that uncertainties in any of the data are less than ±5 kJ/mol. For a calorimetric measurement to give a reliable result, the reaction studied must proceed rapidly and completely to well-defined products. In practice, corrections are often made for lack of complete reaction. The direct reaction calorimetry data of Robins and Jenkins[9] are consistently smaller in magnitude than the results reported here; there may have been a problem incompleteness of reaction. Although Golutvin's combustion calorimetry value[18] for Ti_5Si_3 is in acceptable agreement with data reported here, his values for TiSi and $TiSi_2$ are signifi-
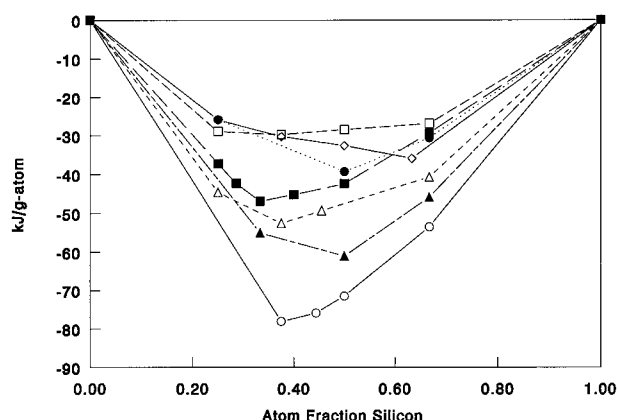
cantly greater in magnitude. A possible problem could have been formation of a silicate rather than the binary oxides. Polyachenok and Novikov[19] obtained the enthalpy of formation of Ti_5Si_3 by an indirect method with results only marginally in agreement with the present work. Savin[20] also employed an indirect method; his data for Ti_5Si_3 agree acceptably, but agreement for TiSi and $TiSi_2$ is not acceptable. Maslov et al.[21] employed direct reaction calorimetry to measure the enthalpy of formation of Ti_5Si_3, and their results, although agreeing with those of Robins and Jenkins,[9] are only marginally in agreement with the data reported here. Topor and Kleppa[22] measured the enthalpy of formation of $TiSi_2$ by metal solution calorimetry; agreement with present results is acceptable. Additional adjustment in 298 K enthalpies must be made for Topor and Kleppa's data,[22] as well as for the present results, once accurate experimental data are available for standard molar entropies and high-temperature heat capacities. The Ti−Si system has been modeled semiempirically by de Boer and co-workers.[23] Their calculations predict both Ti_5Si_4 and

(18) Golutvin, Yu. M. *Russ. J. Phys. Chem.* **1959**, *33*, 164−168.
(19) Polyachenok, L. D.; Novikov, G. I. *Obchsh. Prikl. Khim.* **1972**, *4*, 45 (cited in ref. 11).
(20) Savin, V. D. *Russ. J. Phys. Chem.* **1973**, *47*, 1423−1426.
(21) Maslov, V. M.; Neganov, A. S.; Borovinskaya, I. P.; Merzhanov, A. G. *Fiz. Goreniya Vzryva* **1978**, *14*, 73−82.
(22) Topor, L.; Kleppa, O. J. *Metall. Trans.* **1986**, *17A*, 1217−1221.
(23) de Boer, F. R.; Bloom, R.; Miedema, A. R. *Physica B+C* **1980**, *101B*, 294−319.
(24) Storms, E. K.; Myers, C. E. *High Temp. Sci.* **1985**, *20*, 87−96.

TiSi to have significantly greater stability than observed here. Generally, one can expect the highest melting point for the compound in a system which has the most negative enthalpy of formation. Figure 3 is a plot of available data for first-row transition-metal silicides; only in the case of the manganese silicides is the general rule not obeyed. In the Ti−Si system,[3] Ti_5Si_3 has the highest melting point and the most negative enthalpy of formation. Both Ti_5Si_4 and TiSi melt incongruently. It is unlikely that the trends in stability reported by be Boer et al.[23] are correct.

---

(25) Murray, G. A. Ph.D. Dissertation, State University of NY at Binghamton, 1992.
(26) Lexa, D.; Kematick, R. J.; Myers, C. E., unpublished work.

Conclusion

The thermodynamic stabilities of titanium silicide phases have been measured by means of a Knudsen effusion−mass spectrometric vapor pressure study over the $Ti_5Si_3 + Ti_5Si_4$, $Ti_5Si_4 + TiSi$, and $TiSi + TiSi_2$ two-phase regions. The standard enthalpies of formation at 298 K were obtained from a combination of the experimental data with published and estimated heat capacity and standard molar entropy data, as well as data for the elements. Result are compared to published stability data.

CM950386Q