

Thermodynamic Assessment of the Si-Ta and Si-W Systems

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The knowledge of phase diagram and thermodynamic properties of the Si-Ta and Si-W systems is of technical importance for metallic contacts between Ta, W, and SiC in electrical and electronic devices. The phase diagram and thermodynamic properties of the Si-Ta and Si-W systems were assessed using the CALPHAD approach with available experimental data. The intermetallic compounds of the two systems were modeled as stoichiometric ones. A set of self-consistent thermodynamic parameters were obtained and the calculated phase equilibria were found to be in reasonable agreement with most experimental data. The calculated enthalpies of formation of the silicides in the Si-Ta and Si-W systems were compared with the reported values. The enthalpies of mixing of liquid at 2000 K in similar Si-transition metal systems were used for comparison in order to judge the rationality of the calculations. The assessed thermodynamic descriptions of the Si-Ta and Si-W binary systems will serve as part of the thermodynamic database for the Si-C-M (M: Ta and W) alloys.

Keywords phase diagram, Si-Ta, Si-W, thermodynamic assessment

1. Introduction

SiC has been investigated as a wide band gap semiconductor for more than three decades. Quality contacts between SiC and metals are important for both performance and durability of electronic devices which are capable of operation at elevated temperatures. Many metals, especially transition metals are investigated to manufacture good Schottky/ohmic contacts with SiC.^[1,2] The interface structures might affect the electrical properties of the contacts because a certain degree of solid state reaction between metals and SiC gives rise to the product layer formation at the interface. Usually, silicides play a positive role to decrease the contact resistivity due to their considerable

thermal stability, oxidation resistance, high thermal and electrical conductivity.^[3]

The reaction at the interface of Ta/SiC bonding joints forms Ta carbides at the initial stage. Further reaction with increasing bonding time produces binary Ta silicides and a ternary compound Ta₅Si₃C.^[4] Carbon is consumed to produce vacancies at the interface of Ta multilayer films on the SiC substrate, which transforms Schottky to ohmic contacts in high-temperature metal/semiconductor nonhomogeneous joints.^[5] Tungsten is a high-melting point material and has a relatively low work function (4.55 eV). It has the potential to be used to fabricate SiC-based devices because of the higher thermodynamic stability of W silicides, which would lead to greater resistance to oxidation in high-temperature applications, and less probability of decomposition in composite structures.^[6]

In order to better understand the interfacial reactions between SiC and metal films in various electronic industrial applications, knowledge of thermodynamics and phase diagrams of related systems is strongly desired. Schlesinger^[3] performed a critical review of the thermodynamics of solid transition metal silicides using more than 160 references on both modeling and experimental studies. The increased interest of SiC and related transition metals has led to research work on the formation of stable or metastable phases in the ternary Si-C-metal systems.^[7-9] More recently, a series of thermodynamic studies have been performed using the Calculation of Phase Diagrams (CALPHAD) method on transition metal-Si systems such as Pt-Si,^[10] Ni-Si,^[11] Co-Si,^[12] and V-Si.^[13]

Phase diagrams of both the Si-Ta and Si-W systems have been compiled by Massalski et al.^[14] Vahlas et al. reported the optimized Si-Ta and Si-W phase diagrams.^[15] Their evaluation was mainly based on phase diagram data and thermodynamic measurements. Stoichiometric intermetallic compounds and liquid phase were included in their assessment. Their work resulted in a relatively good description of

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phase diagrams. However, more experimental data have been reported subsequently and their optimized parameters of the Si-Ta system are problematic in that the liquid becomes unstable at temperatures above 3000 K. A similar problem is also seen in their assessment of the Si-W system. Therefore, it is necessary to reassess both the Si-Ta and Si-W binary systems to obtain reliable thermodynamic parameters for thermodynamic extrapolations to ternary systems. In this paper, the phase relations and thermodynamic properties of both the Si-Ta and Si-W binary systems are assessed using the CALPHAD approach.

2. Experimental

2.1 The Si-Ta System

Kieffer et al.^[16] systematically studied the equilibrium diagram and crystal structures of the compounds of the Si-Ta system. On the basis of metallographic analysis of various alloys, four intermediate phases: TaSi₂, Ta₅Si₃, Ta₂Si, and Ta_{4.5}Si were observed. Brewer et al.^[17] confirmed three solid phases by metallographic analysis. However, the stoichiometry of Ta_{4.5}Si was not firmly established in their work. Brewer and Krikorian^[18] suggested that Ta_{4.5}Si was a metastable crystalline phase, which was later confirmed by Deardorff et al.^[19] A new compound, Ta₃Si, was further identified by x-ray diffraction (XRD).^[19,20]

Kocherzhinskii et al.^[21] carefully measured the phase diagram of the Si-Ta system using metallographic, XRD, and differential thermal analysis (DTA) techniques. The liquidus data between 25 and 60 at.% Si are very consistent with the results of Kieffer et al.^[16] In addition to TaSi₂, Ta₂Si, Ta₃Si, they reported the existence of Ta₅Si₃ in two crystal structures: α Ta₅Si₃ (Cr₅B₃-type) at low temperatures and β Ta₅Si₃ (W₅Si₃-type) at high temperatures. The phase transition from α Ta₅Si₃ to β Ta₅Si₃ occurred at about 2433 K. Based on the work of Ref 16-21, Schlesinger^[22] evaluated the phase diagram and thermodynamic properties of the Si-Ta system. The crystal structures of the compounds of the binary system, which are included in this optimization, are summarized in Table 1. The experimental phase diagram data^[16,21] are employed in the present optimization.

The solubility of Si in Ta was determined by Kocherzhinskii et al.^[21] to be about 7 at.% Si at the eutectic

temperature of 2533 K. No other experimental data were available on either liquidus or solidus of the Ta-rich terminal solution. Most experimental work showed that the solubility of Ta in Si was negligible.^[16-21]

By means of direct-reaction calorimetry, Robins and Jenkins^[23] measured the enthalpies of formation of α Ta₅Si₃ (−39.7 kJ/mol) and TaSi₂ (−14.4 kJ/mol) at ambient temperature. Myers and Searcy^[24] determined the Gibbs energies of formation ($\Delta_f G$) of four compounds using Knudsen effusion cells. Using solid state EMF cells, Levine and Kolodney^[25] measured $\Delta_f G$ of α Ta₅Si₃ and Ta₂Si. The Neumann-Kopp rule to extrapolate the results to the ambient temperature was used in both studies. Niessen and Boer^[26] estimated the enthalpies of formation from a cellular model and their results for the intermediate compounds in the range of $x_{\text{Si}} < 0.5$ agree reasonably with the results of Ref 24 and 25. Discrepancy in the enthalpy of formation of TaSi₂ between Ref 24 and 26 is significant. The experimental values of Robins and Jenkins^[23] were not included in the present optimization due to their significant deviations from those of others.^[24-26]

No thermodynamic data of the liquid phase have been reported for this system.

2.2 The Si-W System

The phase diagram on the Si-W system was measured by Kieffer et al.^[27] using thermal, microscopic, and XRD measurements. Later, Maksimov and Shamrai^[28] determined the phase diagram using a combination of metallographic and XRD methods. Their results agree mostly with those of Kieffer et al.,^[27] except the liquidus between 40 and ~60 at.% Si. Kocherzhinskii et al.^[29] also investigated this system; however, their results are not consistent with those of Ref 27 and 28. They reported much lower temperatures of invariant reactions in the Si-rich region. A complete evaluation of the Si-W phase diagram was performed by Naidu et al.^[30] mainly based on the work of Ref 28. In the present optimization, three eutectic reactions at 1663, 2283, and 2453 K^[28] are considered.

Two intermediate compounds are reported: WSi₂ and W₅Si₃. They congruently melt at 2433 and ~2593 K, respectively.^[28] WSi₂ is a stoichiometric compound, while W₅Si₃ was suggested as a nonstoichiometric one with a homogeneity range from 52 to 62.5 at.% W at 2283 K.^[30] Due to lack of reliable experimental data, both WSi₂ and W₅Si₃ are treated as stoichiometric compounds in the present optimization. The crystal structures of the compounds in the binary W-Si system are also summarized in Table 1.

The solubility of Si in W was suggested to be 5.5 at.% Si at the eutectic temperature of 2453 K, whereas the solid solubility of W in (Si) is negligible.^[28,30]

The thermodynamic properties of the Si-W system have been investigated by several groups.^[23,26,31-34] Kematich^[33] studied the Si-W system by mass spectrometry. The equilibrium vapor pressures of silicon gas over two phase mixtures of WSi₂ + W₅Si₃ and W₅Si₃ + W have been measured over an approximate temperature range of 1700 to 2050 K. The enthalpies of formation are estimated as −26.2 kJ/(g atom)

Table 1 Crystal structure data of the intermetallic compounds in the Si-Ta and Si-W systems

| Compound | Pearson Symbol | Space Group | Prototype | Reference |
|--|----------------|---------------|--------------------------------|-----------|
| Ta ₃ Si | <i>tP32</i> | <i>P42/n</i> | Ti ₃ P | [20] |
| Ta ₂ Si | <i>tI12</i> | <i>I4/mcm</i> | Al ₂ Gu | [16] |
| β Ta ₅ Si ₃ | <i>tI32</i> | <i>I4/mcm</i> | W ₅ Si ₃ | [21] |
| α Ta ₅ Si ₃ | <i>tI32</i> | <i>I4/mcm</i> | Cr ₅ B ₃ | [21] |
| TaSi ₂ | <i>hP9</i> | <i>P6222</i> | CrSi ₂ | [16] |
| W ₅ Si ₃ | <i>tI32</i> | <i>I4/mcm</i> | W ₅ Si ₃ | [27] |
| WSi ₂ | <i>tI6</i> | <i>I4/mmm</i> | MoSi ₂ | [27] |

Table 2 Summary of the phase diagram and thermodynamic data in the Si-Ta and S-W systems

| Type of data | Reference | Experimental method | Quoted mode |
|-----------------------------|-----------|-------------------------|--------------------------------|
| <i>The Si-Ta system</i> | | | |
| Liquidus (0-100 at.% Si) | [16] | Metallography, TA | Used for checking the modeling |
| | [21] | Metallography, DTA, XRD | Used |
| Enthalpy of formation | [23] | Reaction calorimetry | Not used |
| | [24] | Knudsen effusion cells | Used |
| | [25] | Solid state emf cells | Used for checking the modeling |
| | [26] | Cellular model | Used |
| <i>The Si-W system</i> | | | |
| Liquidus (0-100 at.% Si) | [27] | Metallography, TA, XRD | Used for checking the modeling |
| | [28] | Metallography, TA, XRD | Used |
| Enthalpy of formation | [29] | DTA, XRD | Not used |
| | [23] | Calorimetry | Used for checking the modeling |
| | [26] | Cellular model | Not used |
| | [31] | Knudsen effusion cells | Not used |
| | [32] | Knudsen effusion cells | Not used |
| | [34] | Solid state emf cells | Used |

TA, thermal analysis

for WSi_2 and -17.2 kJ/(g atom) for W_5Si_3 , Fujiwara et al.^[34] determined the standard enthalpies of formation of WSi_2 and W_5Si_3 at 298 K by the electromotive force (EMF) method. Their results agree with the data of Ref 33. The experimentally measured enthalpy of formation values^[33,34] are included in the present optimization.

The phase diagram and thermodynamic data in both the Si-Ta and Si-W systems used in the present evaluation are summarized in Table 2.

3. Thermodynamic Model

The Gibbs energy function ${}^\circ G_i^\Phi(T) = G_i^\Phi(T) - H_i^{\text{SER}}$ (298.15 K) is expressed by an equation of this form:

$${}^\circ G_i^\Phi(T) = a + b \cdot T + c \cdot T \cdot \ln T + d \cdot T^2 + e \cdot T^3 + f \cdot T^{-1} + g \cdot T^7 + h \cdot T^{-9} \quad (\text{Eq 1})$$

where H_i^{SER} (298.15 K) is the molar enthalpy of the element i at 298.15 K and 1 bar in its standard element reference (SER) state, and T is the absolute temperature. The last two terms in Eq 1 are used only for outside the ranges of the melting point.

In the present work, the Gibbs energy functions of Ta, W, and Si are taken from the SGTE (Scientific Group Thermodata Europe) dataset compiled by Dinsdale.^[35]

The liquid phase is described by a completely disordered solution model. The equation for its Gibbs energy is expressed as:

$$G_m^{\text{liquid}} = x_A {}^\circ G_A^{\text{liquid}} + x_B {}^\circ G_B^{\text{liquid}} + RT(x_A \ln x_A + x_B \ln x_B) + {}^{\text{ex}} G_m^{\text{liquid}} \quad (\text{Eq 2})$$

The ${}^{\text{ex}} G_m^{\text{Liquid}}$ is the excess Gibbs energy of the liquid phase, which is described by the Redlich-Kister polynomial^[36]:

$${}^{\text{ex}} G_m^{\text{liquid}} = x_A x_B \sum_{i=0}^n L_i^{\text{liquid}} (x_A - x_B)^i \quad (\text{Eq 3})$$

$$L_i^{\text{liquid}} = (a_i - b_i T) \quad (\text{Eq 4})$$

Here the value a_i and b_i are the parameters to be optimized in the model. Generally, we use the simple equation with four model parameters:

$${}^E G_m = x_A x_B [(a_0 + b_0 T)(x_A - x_B)^0 + (a_1 + b_1 T)(x_A - x_B)^1] \quad (\text{Eq 5})$$

The Ta and W solid solutions are also modeled as completely disordered solutions. The Gibbs energy of these solid solutions is also described using similar equations as Eq 2 and 3.

All of the intermetallic phases are modeled as stoichiometric compounds based on the available thermodynamic properties. Their Gibbs energy functions are written as:

$$G_m^{\text{M}_p\text{Si}_q} - \frac{p}{p+q} {}^\circ G_M^{\text{bcc}} - \frac{q}{p+q} {}^\circ G_{\text{Si}}^{\text{dia}} = A + B \cdot T \quad (\text{Eq 6})$$

$(M = \text{Ta}, \text{W})$

where ${}^\circ G_{\text{Ta}}^{\text{bcc}}$, ${}^\circ G_{\text{W}}^{\text{bcc}}$, and ${}^\circ G_{\text{Si}}^{\text{dia}}$ are the molar Gibbs energy of the pure elements, which were taken from the database compiled by Dinsdale.^[35] A and B in Eq 6 are the parameters to be optimized in the present work.

4. Evaluation of the Parameters

The PARROT program in the Thermo-Calc software was used to optimize the parameters in the models.^[37] The software works by minimizing the weighted summation of the squares of the differences between experimental and calculated values by using the least square method. The relative weight factor of experimental data was given based on the claimed uncertainty in the original literature.

The parameters of the liquid phase in Eq 3-5 were optimized using the experimental liquidus data, which mostly came from the work of Kocherzhinskii et al.^[21] for the Si-Ta system, and Maksimov and Shamrai^[28] for the Si-W system. They were first evaluated through the

equilibrium data between the liquid and pure components, as well as the enthalpy of mixing of liquid in similar transition-metal-Si binary systems such as V-Si,^[13] Nb-Si,^[38] and Cr-Si,^[39] and Mo-Si.^[40] When a_0 in Eq 5 was preliminarily obtained from the above data, b_0 was added to describe the liquidus lines. Stable silicides Ta₃Si, Ta₂Si, αTa₅Si₃, βTa₅Si₃, TaSi₂, and W₅Si₃ are adopted in the present work. The αTa₅Si₃ and βTa₅Si₃ were treated as the same phase in the first step. The parameters of the solid phases were evaluated using the enthalpies of formation of the silicides.^[24-26,31-34] The terminal solid solution phases (Ta) and (W) were optimized with the experimental data on the liquidus and solid solubility.

5. Results and Discussion

5.1 The Si-Ta System

All the model parameters in the Si-Ta system obtained in the present work are listed in Table 3. The calculated Si-Ta phase diagram from the optimized parameters is given in Fig. 1 together with the experimental data.^[16,21] Three parameters (a_0 , b_0 , and a_1) are used for the liquid phase. A regular solution model is used to describe the (Ta) solid solution, considering a lack of related experimental data. The enthalpy of melting of Ta^[41] was used to evaluate the limit liquidus at the dilute solution. Table 4 compares the

calculated and measured invariant equilibria. It can be seen that the calculated invariant reactions are consistent with the values given by Kocherzhinskii et al.^[21] with the largest difference of 7 K except for the temperature of the eutectic reaction, $L \leftrightarrow \text{TaSi}_2 + \alpha\text{Ta}_5\text{Si}_3$, which is higher by 31 K than the measured value. Lots of attention was paid to this reaction during the optimization. If the reaction temperature was forced to be within 5 K of the experimental value, the TaSi₂ phase would become unstable at low temperatures and

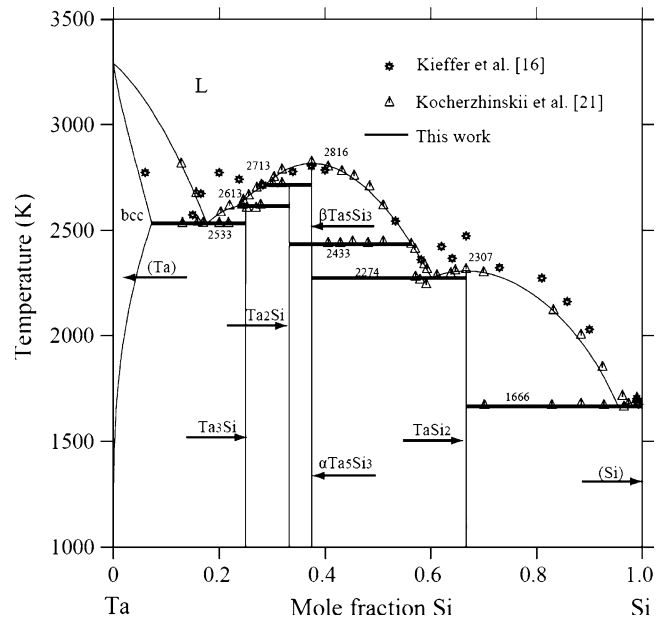


Fig. 1 Calculated Si-Ta phase diagram in comparison with the experimental data^[16,21]

Table 3 Model parameters for the phases in the Si-Ta and Si-W systems(a)

| | |
|---|-----------------------|
| Liquid: (Ta,Si) ₁ | |
| $^0L_{\text{Ta,Si}}^{\text{liquid}}$ | $= -194925.2 + 26.8T$ |
| $^1L_{\text{Ta,Si}}^{\text{liquid}}$ | $= 33280$ |
| bcc (Ta): | |
| $^0L_{\text{Ta,Si}}^{\text{bcc}}$ | $= -103500$ |
| Ta ₃ Si: | |
| $^0G(\text{Ta}_3\text{Si}) - \frac{3}{4}^0G_{\text{Ta}}^{\text{bcc}} - \frac{1}{4}^0G_{\text{Si}}^{\text{dia}}$ | $= -42947.8 + 1.1T$ |
| Ta ₂ Si: | |
| $^0G(\text{Ta}_2\text{Si}) - \frac{2}{3}^0G_{\text{Ta}}^{\text{bcc}} - \frac{1}{3}^0G_{\text{Si}}^{\text{dia}}$ | $= -52781.4 + 0.92T$ |
| αTa ₅ Si ₃ : | |
| $^0G(\alpha\text{Ta}_5\text{Si}_3) - \frac{5}{8}^0G_{\text{Ta}}^{\text{bcc}} - \frac{3}{8}^0G_{\text{Si}}^{\text{dia}}$ | $= -52262.4 - 0.82T$ |
| βTa ₅ Si ₃ : | |
| $^0G(\beta\text{Ta}_5\text{Si}_3) - \frac{5}{8}^0G_{\text{Ta}}^{\text{bcc}} - \frac{3}{8}^0G_{\text{Si}}^{\text{dia}}$ | $= -51581.2 - 1.1T$ |
| TaSi ₂ : | |
| $^0G(\text{TaSi}_2) - \frac{1}{3}^0G_{\text{Ta}}^{\text{bcc}} - \frac{2}{3}^0G_{\text{Si}}^{\text{dia}}$ | $= -41100 - 3.0T$ |
| Liquid: (W,Si) ₁ | |
| $^0L_{\text{W,Si}}^{\text{liquid}}$ | $= -158254.6 + 19.8T$ |
| $^1L_{\text{W,Si}}^{\text{liquid}}$ | $= 15300$ |
| bcc (W): | |
| $^0L_{\text{W,Si}}^{\text{bcc}}$ | $= -38724.2$ |
| W ₅ Si ₃ : | |
| $^0G(\text{W}_5\text{Si}_3) - \frac{5}{8}^0G_{\text{W}}^{\text{bcc}} - \frac{3}{8}^0G_{\text{Si}}^{\text{dia}}$ | $= -18121.7 - 8.65T$ |
| WSi ₂ : | |
| $^0G(\text{WSi}_2) - \frac{1}{3}^0G_{\text{W}}^{\text{bcc}} - \frac{2}{3}^0G_{\text{Si}}^{\text{dia}}$ | $= -26713.2 - 7.51T$ |

(a) In J/(mol of atom); temperature (T) in Kelvin. The Gibbs energies for the pure elements are from the SGTE compilation^[35]

Table 4 Comparison between the calculated and measured invariant equilibria in the Si-Ta binary system

| Invariant reaction | Reference | Composition of the respective phase, at.% Si | | | Temperature, K |
|--|-----------|--|------|------|----------------|
| | | | | | |
| $L \leftrightarrow (\text{Ta}) + \text{Ta}_3\text{Si}$ | This work | 17.7 | 25 | 7 | 2533 |
| | [21] | 17 | 25 | ~7 | 2533 |
| $L + \text{Ta}_2\text{Si} \leftrightarrow \text{Ta}_3\text{Si}$ | This work | 23.4 | 33.3 | 25 | 2613 |
| | [21] | 22 | 33.3 | 25 | 2613 |
| $L + \beta\text{Ta}_5\text{Si}_3 \leftrightarrow \text{Ta}_2\text{Si}$ | This work | 28.6 | 37.5 | 33.3 | 2713 |
| | [21] | 28 | 37.5 | 33.3 | 2713 |
| $\beta\text{Ta}_5\text{Si}_3 \leftrightarrow \alpha\text{Ta}_5\text{Si}_3$ | This work | ... | 37.5 | ... | 2433 |
| | [21] | ... | 37.5 | ... | 2433 |
| $L \leftrightarrow \beta\text{Ta}_5\text{Si}_3$ | This work | ... | 37.5 | ... | 2816 |
| | [21] | ... | 37.5 | ... | 2823 |
| $L \leftrightarrow \text{TaSi}_2 + \alpha\text{Ta}_5\text{Si}_3$ | This work | 60.2 | 66.7 | 37.5 | 2274 |
| | [21] | 62 | 66.7 | 37.5 | 2233 |
| $L \leftrightarrow \text{TaSi}_2$ | This work | ... | 66.7 | ... | 2307 |
| | [21] | ... | 66.7 | ... | 2313 |
| $L \leftrightarrow (\text{Si}) + \text{TaSi}_2$ | This work | 95.4 | 100 | 66.7 | 1666 |
| | [21] | ~99 | ~100 | 66.7 | 1673 |

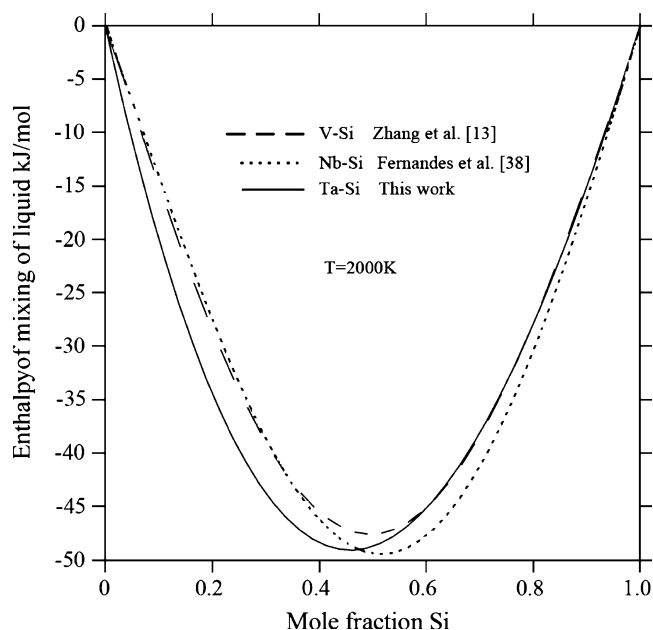


Fig. 2 Enthalpy of mixing of liquid in the Si-Ta system at 2000 K in comparison with that of the V-Si system^[13] and Nb-Si system^[38]

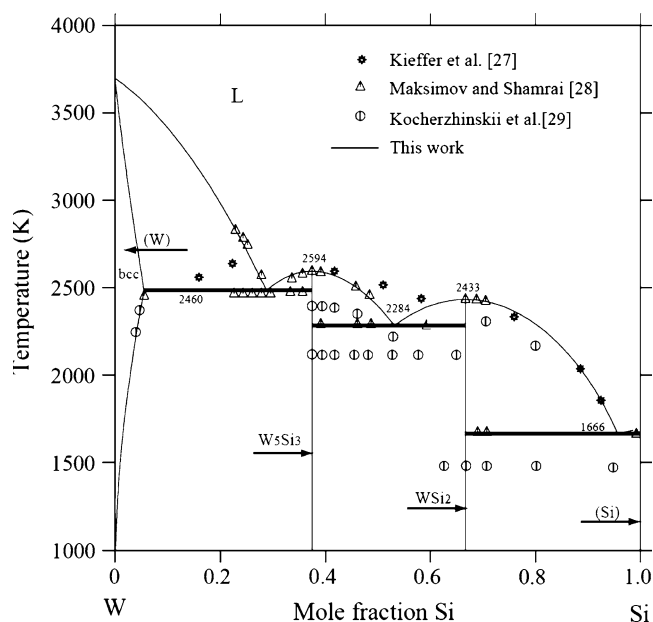


Fig. 4 Calculated Si-W phase diagram in comparison with the experimental data^[27-29]

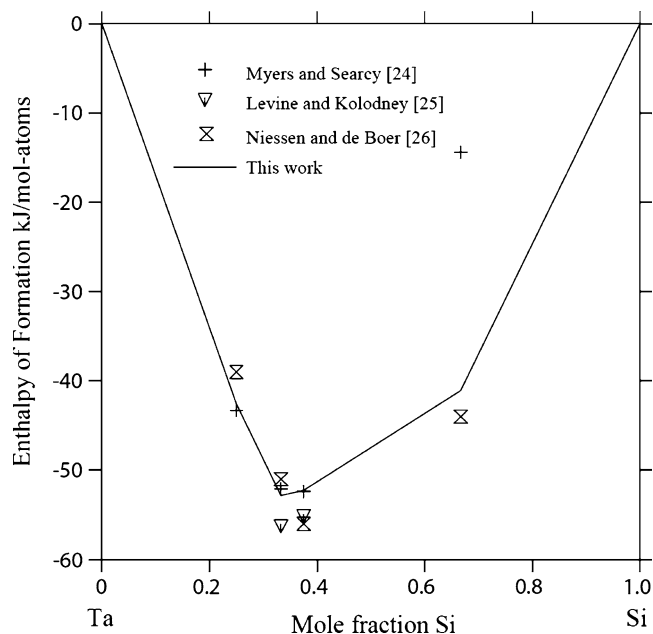


Fig. 3 Calculated enthalpy of formation of the Si-Ta intermetallic compounds at 298 K in comparison with the experimental data^[24-26]

unreasonable parameters had to be introduced to make it stable. The presently optimized parameters are the best compromise. Further experimental measurements are highly desirable.

No experimental enthalpies of mixing of the Si-Ta liquid have been reported. To check the presently calculated values, enthalpies of mixing of liquid in other Si-transition

Table 5 Comparison between the calculated and measured invariant equilibria in the Si-W binary system

| Invariant reaction | Reference | Composition of the respective phase, at.% Si | | | Temperature, K |
|---|-----------|--|------|-------|----------------|
| L ↔ (W) + W ₅ Si ₃ | This work | 5.5 | 37.5 | 28.1 | 2460 |
| | | ~5.5 | 37.5 | ~31.5 | 2453 |
| | [28] | ~5.0 | 37.5 | 32 | 2358 |
| | [29] | ~5.0 | 37.5 | 32 | 2358 |
| L ↔ W ₅ Si ₃ | This work | ... | 37.5 | ... | 2594 |
| | | ... | 37.5 | ... | ~2593 |
| | [28] | ... | 37.5 | ... | ~2593 |
| | [29] | ... | 37.5 | ... | ~2368 |
| L ↔ W ₅ Si ₃ + WSi ₂ | This work | 53.2 | 66.7 | 37.5 | 2284 |
| | | ~59.3 | 66.7 | ~40 | 2283 |
| | [28] | 53.0 | 66.7 | 37.5 | 2213 |
| | [29] | 53.0 | 66.7 | 37.5 | 2213 |
| L ↔ WSi ₂ | This work | ... | 66.7 | ... | 2433 |
| | | ... | 66.7 | ... | 2433 |
| | [28] | ... | 66.7 | ... | 2433 |
| | [29] | ... | 66.7 | ... | 2293 |
| L ↔ Si + WSi ₂ | This work | 66.7 | 100 | 95.6 | 1666 |
| | | 66.7 | ~100 | 99.2 | 1663 |
| | [28] | 66.7 | ~100 | 99.2 | 1663 |
| | [29] | 66.7 | ~100 | 97.4 | 1673 |

metal systems such as Si-V and Si-Nb were adopted for comparison. The thermodynamic parameters of the Si-V and Si-Nb binary systems assessed by Zhang et al.^[13] and Fernandes et al.^[38] were used to calculate the enthalpies of mixing of liquid at 2000 K as shown in Fig. 2 together with the results of the Si-Ta system assessed in the present work. It can be seen that the general tendency of the curve of the Si-Ta system in this work is consistent with the calculated results of

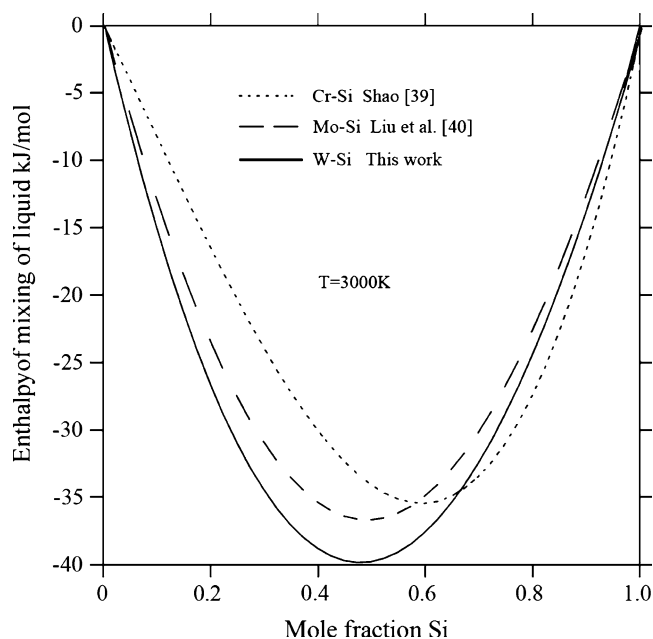


Fig. 5 Enthalpy of mixing of liquid in the Si-W system at 3000 K in comparison with the Cr-Si system^[39] and the Mo-Si system^[40]

Si-V and Si-Nb systems.^[13,38] The minimum values of the three systems are all between -45 and -50 kJ/mol.

The enthalpies of formation of the compounds in the Si-Ta system at 298 K are compared with the reported data^[24-26] in Fig. 3. The present assessment agrees well with the experimental data of Ref 25 and model predictions of Ref 26.

5.2 The Si-W System

All the model parameters in the Si-W system obtained in the present work are listed in Table 3. The calculated Si-W phase diagram from the optimized parameters is given in Fig. 4 together with the experimental data.^[27-29] Three parameters (a_0 , b_0 , and a_1) are used for the liquid, less than those of used in Ref 15. Table 5 compares the calculated invariant equilibria with the results reported in Ref 28 and 29. Considering the reliability of experimental results, the data given by Maksimov and Shamrai^[28] were adopted in the present assessment for reproducing the phase diagram. A satisfactory agreement is obtained between the calculated and experimental data^[28] with the largest difference of 7 K.

Using the thermodynamic parameters assessed by Shao^[39] and Liu et al.,^[40] enthalpies of mixing of liquid at 3000 K in the Mo-Si and Cr-Si systems were calculated and shown in Fig. 5 together with the data assessed in this work for the Si-W system. The enthalpies of mixing of the Si-W liquid show similar trends as the data of Ref 39 and 40 with the minimum value at -35 to -40 kJ/mol.

The enthalpies of formation of the Si-W system at 298 K are compared with the reported data^[23,26,31-34] as shown in Fig. 6. As mentioned above, the experimental data from

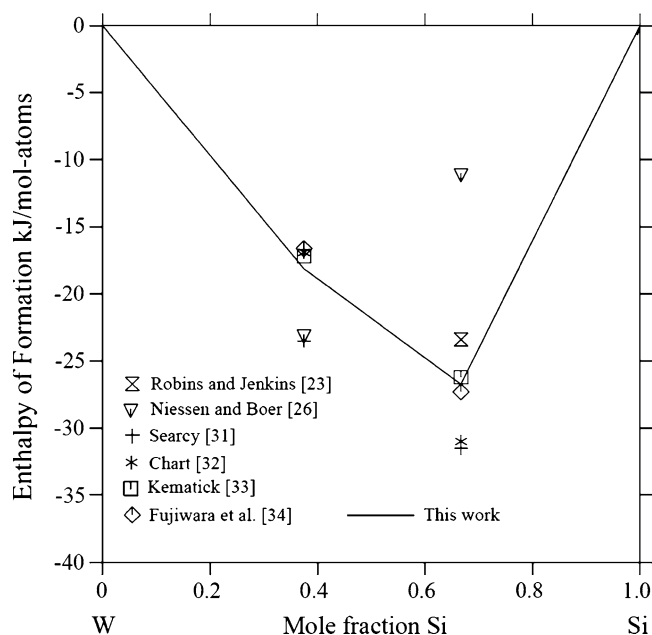


Fig. 6 Calculated enthalpy of formation of the Si-W intermetallic compounds at 298 K in comparison with the experimental data^[23,26,31-34]

Ref 33 and 34 are considered. It is clear that the calculated results agree well with the experimental data.^[33,34]

6. Conclusions

A thermodynamic assessment of the Si-Ta and Si-W systems has been performed using the CALPHAD approach. All experimental phase diagrams and thermodynamic data available for both systems have been critically evaluated. The compounds in these systems are treated as stoichiometric ones, and the terminal (Ta) and (W) solid solutions are considered as disordered solutions. Self-consistent thermodynamic parameters have been obtained. The comparison shows that most experimental thermodynamic properties and phase diagrams are reproduced.

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