Thermodynamic re-assessment of the Hf-Si binary system

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Abstract. In view of the latest experimental information of Hf-Si binary system, and with the use of the thermodynamic software package Pandat, the Hf-Si phase diagram was re-assessed. A set of self consistent data for the Gibbs energy expressions of all the phases of the system was obtained. The calculated results were compared with the experimental data of the phase equilibrium relations of the system and the formation enthalpies of the intermetallic compounds \(\text{Hf}_2\text{Si}, \text{Hf}_5\text{Si}_3, \text{Hf}_3\text{Si}_2, \text{Hf}_5\text{Si}_4, \text{HfSi}\) and \(\text{HfSi}_2\). The theoretical prediction can reproduce the experimental information very well.

1. Introduction

With the development of aviation technology, aeroengine requires a higher thrust weight ratio and work efficiency [1]. At present, the service temperature of widely used Ni based single crystal superalloy has reached 1150°C, which is 85% of the melting point of the alloy and is close to the limit of its operating temperature [2]. Therefore, it is very important to develop a new high temperature structural material for higher temperature applications. In recent years, because of its high melting point (about 1750°C), low density (6.6~7.2 g/cm³), and good high temperature strength and room temperature fracture toughness, the Nb/Mo-Si based ultra high temperature alloy has attracted more and more attention [3]. However, the low oxidation resistance of the alloy has become a major barrier to its application [6]. The addition of Hf can promote the formation of \(\gamma(\text{Nb},\text{X})_5\text{Si}_3\) (\(\text{X}\) is the substitutional element of Nb, such as Mo) and improve the oxidation resistance of the alloy at high temperature [7]. The researches showed that in the alloys without Hf, the primary silicide is \(\alpha(\text{Nb},\text{X})_5\text{Si}_3\). And there are two kinds of eutectic structures, namely \(\text{Nbss/}\alpha(\text{Nb},\text{X})_5\text{Si}_3\) and \(\text{Nbss/}\gamma(\text{Nb},\text{X})_5\text{Si}_3\). The addition of \(\sim 2\) at% Hf promoted the formation of primary \(\gamma(\text{Nb},\text{X})_5\text{Si}_3\) and increased the content of \(\text{Nbss/}\gamma(\text{Nb},\text{X})_5\text{Si}_3\) eutectic; When the Hf content increased to \(4\) at% and \(8\) at%, the formation of the \(\alpha(\text{Nb},\text{X})_5\text{Si}_3\) was completely suppressed, and the silicide in the alloy existed only in the form of \(\gamma(\text{Nb},\text{X})_5\text{Si}_3\) [3]. Therefore, it is of great practical significance to study the thermodynamic features of the Hf-Si systems.

The Hf-Si phase diagram was first evaluated by Gokhale and Abbaschian [9] based on the work of Brukl [10], mainly including the solid solutions \(\beta\text{Hf}_{25}\) (bcc_A2), \(\delta\text{Hf}_{25}\) (hcp_A3), \(\text{Si(diamond}_{25}\) and liquid (L), as well as the stoichiometric compounds \(\text{Hf}_2\text{Si}, \text{Hf}_5\text{Si}_3, \text{Hf}_3\text{Si}_2, \text{Hf}_5\text{Si}_4, \text{HfSi}\) and \(\text{HfSi}_2\), as shown in figure 1 (a), in which the \(\beta\text{Hf}_{25}\) phase was not included. The \(\delta\text{Hf}_{25}\) phase was first determined by Karpinsky and Esseyv [11], but it was considered to be stabilized by interstitial impurities. Later, Bewlay et al found that \(\text{Hf}_3\text{Si}_2\) was still in the alloy, even if it was smelted repeatedly with very pure raw materials [12]. The phase diagram of the Hf-Si binary system evaluated by Zhao et al. [13], which was mainly based on the results of Brukl [10], and all the liquid phase compositions
involved in invariant reactions were not the same as results of Gokhale and Abbaschian \cite{9}. Yang et al. \cite{14} also assessed the phase diagram of Hf-Si system \cite{14}. As shown in figure 1(b), for the peritectic reaction \( L + H_{5}Si_{3} \leftrightarrow Hf_{2}Si \), the liquid composition is at \(-21\% Si\), which is the consistent with the research results by Bewlay et al. \cite{12} instead of 17.9\% calculated by Zhao et al. \cite{13}. In addition, Yang et al. believed that the equilibrium temperature of \( Hf_{5}Si_{3} \) is almost up to 1925°C, and their research considered that the liquid phase compositions of most invariant reactions are different from Zhao et al. \cite{5}. Recently, Gigolotti et al. \cite{15} further determined the liquid phase compositions and temperatures of the invariant reactions of the Hf-Si system. Based on the evaluation of all the reported results, the thermodynamic parameters of all the phases of the Hf-Si system were optimized in the present work.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{The Hf-Si binary phase diagram: (a) evaluated by Gokhale and Abbaschian \cite{9}; and (b) evaluated by Yang et al \cite{14}.}
\end{figure}

2. Evaluation of the available information
According to the previous phase diagram, Gigolotti et al. prepared 30 samples with very pure Hf (\( \geq 99.8 \) wt.%) and Si (\( \geq 99.999 \) wt.%) in an arc furnace, and measured the constituent phases by means of scanning electron microscope (SEM) and X-ray diffraction (XRD) \cite{15}. There are six intermetallic compounds \( Hf_{5}Si_{3}, Hf_{3}Si_{2}, Hf_{2}Si, Hf_{5}Si_{4}, HfSi \) and \( HfSi_{2} \) in the phase diagram. The composition of the liquid phase and the temperature of each invariant reactions were re-determined.

The results of available studies including all the measured, the evaluated and the calculated data, are listed in table 1, so as to make a comparison. The crystallographic data of the solid phases in this system are list in the table 2.

From table 1 it can be seen that the calculated results are not well agree with the experiments. It is necessary to re-optimized the Hf-Si binary system according to the latest experimental data \cite{15}. Table 2 is the crystallographic parameters of each phase in the system \cite{16-22}.

3. Thermodynamic models
In the Hf-Si binary system, there exist three solution phases liquid, \( \alpha Hf(hcp_A3) \) and \( \beta Hf(bcc_A2) \), six intermetallic phases \( Hf_{2}Si, Hf_{3}Si_{3}, Hf_{6}Si_{2}, Hf_{5}Si_{4}, HfSi \) and \( HfSi_{2} \), and one pure substance phase Si(diamond_A4).

The solubility of Si in Hf is relatively small (about 1\% Si), whether it is in \( \alpha Hf(hcp_A3) \) or \( \beta Hf(bcc_A2) \). Therefore, the solubility of Si in Hf is neglected in some literatures. In the present work, the value of 1\% Si is adopted. The solubility of Hf in Si(diamond_A4) is negligible and the latter is considered to be a pure substance phase. All the intermetallic phases are strict stoichiometric compounds without any reported solubility range. The enthalpy of formation of the intermetallic compounds of Hf-Si binary system are listed in table 3.
Table 1. Research results of the invariant reactions in the Hf-Si binary system.

| Invariant reaction | T (℃)   | Reaction type | L/α      | X_Si    | Experiment methods | Reference |
|-------------------|---------|---------------|----------|---------|--------------------|-----------|
| L↔βHf (bcc)       | 2231±20 | Melting point |          |         | Evaluated          | [9]       |
| 2218              |         |               |          |         | Experimental       | [10]      |
| βHfss↔αHfss       | 1743    | Allotropic    |          |         | Evaluated,Calculated | [9]     |
| βHfss+Hf3Si↔αHfss | 1770    | Peritectoid   | <1       |         | Evaluated,Calculated, Experimental,Calculated | [9] [10] |
| L↔βHfss+ Hf2Si    | 1831±5  | Eutectic      | ~12      |         | Experimental       | [15]      |
|                  |         |               | 12±1     |         | Calculated/Experimental | [9]     |
|                  | 1828    |               | 11.1     |         | Calculated         | [13]      |
|                  | 1827    |               | 12       |         | Calculated         | [14]      |
|                  | 1828    |               | ~12      |         | Calculated         | This work |
| L + Hf3Si2↔Hf3Si  | 2083±12 | Peritectic    | 27       |         | Calculated/Experimental | [9]     |
| L + Hf3Si3 ↔Hf3Si | 2360    | Peritectic    | ~32.50   |         | Experimental       | [15]      |
|                  | 2086    |               | 17.9     |         | Calculated         | [13]      |
|                  | 2092    |               | 21       |         | Experimental       | [14]      |
|                  | 2360    |               | 30.6     |         | Calculated         | This work |
| L + Hf3Si2 ↔Hf3Si3| 2440    | Peritectic    | ~37      |         | Experimental       | [15]      |
|                  | 2357    |               | 27.7     |         | Calculated         | [13]      |
|                  | 2355    |               | 30.30    |         | Calculated         | [14]      |
|                  | 2440    |               | 35.5     |         | Calculated         | This work |
| Hf3Si3↔Hf3Si + Hf5Si2 | 1925±25 | Eutectoid | 37.5 |         | Calculated         | [13]      |
|                  | 1925    |               |          |         | Calculated         | [14]      |
|                  | 1925    |               |          |         | Calculated         | This work |
| L ↔Hf3Si2         | 2480±20 | Congruent     | ...      |         | Calculated/Experimental | [9]     |
|                  | 2480    |               |          |         | Calculated         | [13]      |
|                  | 2463    |               |          |         | Calculated         | [14]      |
|                  | 2480    |               |          |         | Calculated         | This work |
| L + Hf3Si3 ↔Hf3Si4| 2315    | Peritectic    | ~49      |         | Experimental       | [15]      |
|                  | 2320±15 |               | ~46.5    |         | Calculated/Experimental | [9]     |
|                  | 2313    |               | 54.60    |         | Calculated         | [13]      |
|                  | 2321    |               | 50.90    |         | Calculated         | [14]      |
|                  | 2315    |               | 49.2     |         | Calculated         | This work |
| L + Hf3Si4 ↔HfSi  | 2110    | Peritectic    | ~52.5    |         | Experimental       | [15]      |
|                  | 2142±15 |               | ~51.5    |         | Calculated/Experimental | [9]     |
|                  | 2133    |               | 62.80    |         | Calculated         | [13]      |
|                  | 2145    |               | 58.30    |         | Calculated         | [14]      |
|                  | 2142    |               | 55.2     |         | Calculated         | This work |
| L + HfSi ↔HfSi2   | 1543±8  | Peritectic    | ~70      |         | Calculated/Experimental | [9]     |
|                  | 1543±8  |               | ~69      |         | Calculated/Experimental | [9]     |
|                  | 1546    |               | 80.8     |         | Calculated         | [13]      |
|                  | 1541    |               | 76.2     |         | Calculated         | [14]      |
|                  | 1745    |               | 70.1     |         | Calculated         | This work |
| L ↔HfSi2 + SiSS  | 1330±8  | Eutectic      | ~91      |         | Calculated/Experimental | [9]     |
|                  | 1330±8  |               | 91.5±1   |         | Calculated/Experimental | [9]     |
|                  | 1325    |               | 90.80    |         | Calculated         | [13]      |
|                  | 1330    |               | 89.30    |         | Calculated         | [14]      |
|                  | 1329    |               | 87.4     |         | Calculated         | This work |
| L ↔Si             | 1414    | Melting point | ⋯        |         | Calculated         | [9]       |
|                  | 1430    |               |          |         | Experimental       | [10]      |
### Table 2. The crystallographic data of the Hf-Si binary system.

| Phase | Structure type | Space group | Pearson symbol | Lattice parameters, nm | References |
|-------|----------------|-------------|----------------|------------------------|------------|
| βHf(bcc_A2) | W | Im3m | cl2 | a: 3.226, b: 0, c: 0 | [16] |
| αHf(hcp_A3) | Mg | P6_3/mmm | hP2 | a: 0.33330, b: 0.66670, c: 0.25000 | [16] |
| HfSi | Al2Cu | I4/mcm | t112 | a: 0, b: 6.553, c: 0.25000 | [16] |
| Hf2Si3 | Mn3Si3 | P6_3/mmc | hP16 | a: 0.33330, b: 0.66670, c: 0.25000 | [16] |
| Hf2Si2 | U3Si2 | I4/mmb | tP10 | a: 0, b: 0.37000, c: 0.17000 | [16,20] |
| Hf2Si4 | Zr5Si4 | P41212 | tP36 | a: 0.17300, b: 0.17300, c: 0.21500 | [16,20] |
| HfSi | BFe | Pnma | oP8 | a: 0.17800, b: 0.25000, c: 0.12400 | [16,20] |
| HfSi2 | ZrSi2 | Cmcm | oC12 | a: 0.10600, b: 0.25000, c: 0.25000 | [16,20] |
| Si(diamond_A4) | C (diam) | Fd3m | cF8 | a: 3.567, b: 0, c: 0 | [21,22] |
Table 3. The enthalpy of formation of intermetallic compounds of Hf-Si binary system at 25°C (298 K)

| Phase   | Enthalpy of formation (kJ mol⁻¹) | Reference          |
|---------|----------------------------------|--------------------|
| Hf₂Si   | -62.7                            | [23]               |
|         | -72.0                            | [24]               |
|         | -63.8                            | [13]               |
|         | -71.5                            | This work          |
| Hf₃S₃   | -70.2 ± 3.3                      | [25]               |
|         | -70.2                            | [23]               |
|         | -79.0                            | [24]               |
|         | -68.5                            | [13]               |
|         | -68.6                            | This work          |
| Hf₃Si₂  | -83.0                            | [24]               |
|         | -80.0 ± 4.7                      | [26]               |
|         | -76.8                            | [13]               |
|         | -70.3                            | This work          |
| Hf₅S₄   | -75.0                            | [13]               |
|         | -69.5                            | This work          |
| HfSi    | -71.1 ± 4.6                      | [25]               |
|         | -71.1                            | [23]               |
|         | -91.0                            | [24]               |
|         | -70.9 ± 2.0                      | [27] at 1473 ± 2 K |
|         | -73.0                            | [13]               |
|         | -68.4                            | This work          |
| HfSi₂   | -55.7 to -69.7                   | [28] - estimated from volume contraction |
|         | -75.2                            | [23]               |
|         | -74.0                            | [24]               |
|         | -69.7                            | [13]               |
|         | -65.4                            | This work          |

The molar Gibbs free energies of the solution phases were regarded as a substitutional solution with the Redlich-Kister polynomial expression:

\[
G_{Hf}^L = x_{Hf} G_{Hf}^L + x_{Si} G_{Si}^L + RT (x_{Hf} \ln x_{Hf} + x_{Si} \ln x_{Si}) + G_m^{E}
\]  

(1)

where, \(x_i\) and \(G_i^f\) represent the mole fraction and the molar Gibbs energy of element \(i\) (\(i=\text{Hf} \text{ and } \text{Si}\)) in the solution phase \(\phi\), respectively. \(R\) and \(T\) are the gas constant and temperature, respectively. The last item of the above Eq. (1) is the molar excess Gibbs energy.

The molar excess Gibbs free energy in the form of Redlich-Kister polynomial can be written as follows [29]:

\[
G_m^{E} = x_{Hf} x_{Si} \sum_n L_n^L (x_{Hf} - x_{Si})^n
\]  

(2)

The \(L_n^L\) (\(n=0, 1, 2, \ldots\)) represents the nth level interaction parameter between Hf and Si in the phase \(\phi\).

All the Hf silicides are strictly stoichiometric compounds, and the Gibbs free energy for one mole of atoms of each compound HfₘSiₙ can be described as follows:

\[
G_{Hf_\alpha Si_\beta} = x_{Hf} G_{Hf}^{nep} + x_{Si} G_{Si}^{adam} + \Delta G_f
\]  

(3)
The $\Delta G_f$ represents the molar Gibbs energy of formation of the compound and the Gibbs free energy for one mole of atoms of each compound $Hf_Si$:

$$\Delta G_f = a + bT + cT\ln T$$

(4)

where, a, b and c are the parameters to be optimized in the present work.

The pure elemental data for Hf and Si were obtained from the Scientific Group Thermodata Europe (SGTE) database [30].

4. Results and discussions

According to the phase equilibrium relations and the thermodynamic properties reported by literatures, the thermodynamic description of the Hf-Si binary system is optimized by using Pandat software package. The obtained results are listed in Table 4. These parameters can be used to reproduce most of the thermochemical properties and the phase boundary data.

| Phase | Parameters |
|-------|------------|
| Liquid | $^0 L^1 = 200000 + 9T - 7T\ln(T)$; $^1 L^1 = 28500.2 + 7T$; $^2 L^1 = 56500.82$ |
| $\beta Hf$ | $^0 L_{\beta Hf} = -158000 - 5.2244T$; $^1 L_{\beta Hf} = -46284.7 + 8.6849T$ |
| $\alpha Hf$ | $^0 L_{\alpha Hf} = -217000 - 3.6438T$ |
| $Hf_2Si$ | $G_{Hf_2Si} = -71500 - 9.3168T + 0.333G_{HSERSi} + 0.667G_{HSERHf}$ |
| $Hf_3Si$ | $G_{Hf_3Si} = -68000 - 2.66T - 1.3803T\ln(T) + 0.375G_{HSERSi} + 0.625G_{HSERHf}$ |
| $Hf_4Si$ | $G_{Hf_4Si} = -71000 + 3.8286T - 2.2298T\ln(T) + 0.4G_{HSERSi} + 0.6G_{HSERHf}$ |
| $Hf_5Si$ | $G_{Hf_5Si} = -70150 + 2.4101T - 2.1488T\ln(T) + 0.444G_{HSERSi} + 0.556G_{HSERHf}$ |
| $HfSi$ | $G_{HfSi} = -69035 + 2.3327T - 2.0974T\ln(T) + 0.5G_{HSERSi} + 0.5G_{HSERHf}$ |
| $HfSi_2$ | $G_{HfSi_2} = -65400 - 2.4799T + 0.667G_{HSERSi} + 0.333G_{HSERHf}$ |

Figure 2 is the calculated Hf-Si binary phase diagram, in which the dotted line is the experimental results by Gigolotti et al [15]. The most obvious difference between the present optimized results and the experimental data is that for the peritectic reaction $L + Hf_5Si \rightarrow HfSi$. J.C.J.Gigolotti et al believe that the peritectic temperature of 2110 °C reported by Gigolotti et al. [15] is not measured by DTA or other experimental method. The experimental temperature of 2142 °C reported by Brukl [10] is taken into account in the present work. For the eutectic reaction $L \leftrightarrow \beta Hf(bcc_A2) + Hf_5Si$, the reaction temperature is calculated to be 1328 °C while the experimental results in the previous literatures are mostly 1330 ± 5 °C, the difference is within the experimental error range. For other reactions, whether eutectic or peritectic, the reaction temperatures have been consistent with previous experimental or computational results. The composition of Si in the liquid phase is optimized as close as possible to the latest experimental results [15], and the agreement has been greatly improved compared with the previous calculation results.
Figure 2. The calculated Hf-Si binary phase diagram compared with experimental data [15].

Figure 2 is the calculated Hf-Si binary phase diagram, in which the dotted line is the experimental results by Gigolotti et al [15]. The most obvious difference between the present optimized results and the experimental data is that for the peritectic reaction $L + \text{Hf}_5\text{Si}_4 \leftrightarrow \text{HfSi}$. J.C.J. Gigolotti et al believe that the peritectic temperature of 2110 °C reported by Gigolotti et al. [15] is not measured by DTA or other experimental method. The experimental temperature of 2142 °C reported by Brukl [10] is taken into account in the present work. For the eutectic reaction $L \leftrightarrow \beta\text{Hf}(\text{bcc A}_2) + \text{Hf}_2\text{Si}$, the reaction temperature is calculated to be 1328 °C while the experimental results in the previous literatures are mostly 1330 ± 5 °C, the difference is within the experimental error range. For other reactions, whether eutectic or peritectic, the reaction temperatures have been consistent with previous experimental or computational results. The composition of Si in the liquid phase is optimized as close as possible to the latest experimental results [15], and the agreement has been greatly improved compared with the previous calculation results.

Figure 3 is the enthalpies of formation of the intermetallic compounds at 298 K, as well as previously reported data from literatures.

Figure 3. The enthalpies of formation of the Hf–Si intermetallic compounds at 298 K [23-25].
Figures 4 and 5 are the activity and the mixing enthalpy of the liquid phase at 2800 K, respectively. By comparing the present calculations with the data reported in literatures [31], it can be seen that the consistency is relatively good.

![Figure 4](image4.png)  
**Figure 4.** The activity of Hf in liquid at 2800 K compared with literature data [31].

![Figure 5](image5.png)  
**Figure 5.** The mixing enthalpy of liquid at 2800K compared with literature data [31].

5. Conclusions

In view of the latest experimental results including the liquidus boundaries, the solid solubilities, the temperatures and compositions of the invariant reactions, and the enthalpies of formation of all of the intermetallic compounds, the Hf-Si binary system has been thermodynamically re-assessed. A set of self consistent thermodynamic data for all of the phases of the system has been obtained. Using the presently obtained thermodynamic data, the calculations can reproduce the experimental results very well. Compared with the previous calculations, the agreement between the present calculated results with the available experimental data has been greatly improved.

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