Thermodynamic modeling of the Th–U, Th–Zr and Th–U–Zr systems

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The thermodynamic assessments of the Th–U, Th–Zr binary and Th–U–Zr ternary systems were carried out by using the CALPHAD (Calculation of Phase Diagrams) method on the basis of the experimental data including phase equilibria and thermodynamic properties. The Gibbs free energies of the liquid, bcc, fcc, hcp, αU and βU phases were described by the subregular solution model with the Redlich–Kister equation, and that of the δ phase in the Th–U–Zr ternary system was described by the sublattice model. The thermodynamic parameters of each phase in the Th–U–Zr system were also evaluated by combining the experimental data of the phase equilibria with the parameters in three binary systems. The calculated phase equilibria are in good agreement with the experimental data.

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1. Introduction

Th–U mixed fuel has been researched mainly on oxides, carbides, molten salts and alloys for many years, in order to utilize the abundant thorium resource for breeder reactors [1]. Zr is a kind of important additional element for U–Th mixed fuel, because Zr is the only metal known to form extensive solid solutions with both Th and U [2]. Some previous studies have showed that the U–Th–Zr alloys hydrides are the candidate materials for a mixed fuel[1–3]. In order to develop new nuclear materials, it is necessary to understand the phase equilibria in the U–Th–Zr system.

The CALPHAD method, which is a powerful tool to cut down on both Th and U[2]. Some previous studies have showed that the U–Th–Zr alloys hydrides are the candidate materials for a mixed fuel[1–3]. In order to develop new nuclear materials, it is necessary to understand the phase equilibria in the U–Th–Zr system. The CALPHAD method, which is a powerful tool to cut down on cost and time during development of materials [4], effectively provides a clear guideline for materials design. As a result, it is of great essence to establish the thermodynamic database for the Th–U–Zr ternary system. In this paper, as a part of thermodynamic database of Th–U base alloy systems, the thermodynamic descriptions for the phase equilibria in the Th–U–Zr ternary system were carried out by means of the CALPHAD method.

2. Thermodynamic model

The information of stable solid phases and the used models in the U–Th–Zr system [5] are listed in Table 1.

2.1. Solution phases

The Gibbs free energies of the liquid, bcc, fcc, hcp, αU and βU phases are described by the subregular solution model, the expression of the Gibbs free energy for φ phase in the U–Th–Zr system is as follows:

\[ G_m^\phi = \sum_{i=Th,U,Zr}^n G_i^\phi x_i + RT \sum_{i=Th,U,Zr}^n x_i \ln x_i + \frac{\delta}{2} \sum_{i=Th,U,Zr}^n x_i x_j \ln \frac{x_i x_j}{x_i x_j} \]  

where \( G_m^\phi \) is the molar Gibbs free energy of pure component \( i \) in the respective reference state with the φ phase, which is taken from the SGTE pure element database [6]. \( R \) is the gas constant, and \( T \) is the absolute temperature. The \( x_i \) denotes the mole fractions of component \( i \). The term \( \delta G_m^\phi \) is the excess energy, which is expressed in the Redlich–Kister polynomials [7] as

\[ \delta G_m^\phi = L_{Th,U,Zr}^\phi x_i x_j + L_{Th,Zr}^\phi x_i x_j + L_{Th,U}^\phi x_i x_j + L_{Th,U,Zr}^\phi x_i x_j + L_{Th,Zr}^\phi x_i x_j + L_{Th,U,Zr}^\phi x_i x_j \]  

where \( L_{Th,U,Zr}^\phi \) and \( L_{Th,Zr}^\phi \) are the interaction energies in binary and ternary systems, respectively, which are expressed in the following forms:

\[ L_{ij}^\phi = a_{ij} + b_{ij}(x_i - x_j) + c_{ij}(x_i - x_j)^2 \]  

where \( m_{ij}^\phi \) is the molar volume of \( x_i - x_j \) and

\[ m_{ij}^\phi = a + bT \]  

\[ L_{Th,U,Zr}^\phi = a_{Th,U,Zr}^\phi + b_{Th,U,Zr}^\phi x_i x_j + c_{Th,U,Zr}^\phi x_i x_j + d_{Th,U,Zr}^\phi x_i x_j \]  

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\[ n_{j_{\text{th},\text{U},\text{Zr}}} = a' + b'T \]

where the parameters of \( a, b, c \) and \( d' \), \( b' \) were evaluated based on the experimental data in binary and ternary systems, respectively.

### 2.2. Intermetallic phase with composition homogeneity range

The \( \delta \) phase in the U–Zr system is a intermetallic phase with compositional homogeneity range in the experimental [5] and calculated [8] phase diagrams. In the assessment of Chevalier et al. [8], the \( \delta \) phase is described as the formula \((U, Zr)_2 (U, Zr)_2\) by the two-sublattice model [9]. According to the experimental data of the U–Th–Zr system [10], there is a large solubility of Zr in the \( \delta \) phase. However, there is no experimental information about the model of the \( \delta \) phase, in the present work, the \( \delta \) phase in the Th–U–Zr system is treated as the formula \((U, Zr)_2 (U, Zr)_2\), \((U, Zr)_2 (U, Zr)_2\). The Gibbs free energy of formation per mole of formula unit \((U, Zr)_2 (U, Zr)_2\), \((U, Zr)_2 (U, Zr)_2\), \((U, Zr)_2 (U, Zr)_2\), \((U, Zr)_2 (U, Zr)_2\) can be expressed as the following equation referring to the pure elements:

\[
C_m^\delta = y_1^U y_2^U a_1^U + y_1^U y_2^Zr a_1^Zr + y_1^Zr y_2^U a_1^U + y_1^Zr y_2^Zr a_1^Zr + y_1^U y_2^U a_2^U + y_1^U y_2^Zr a_2^Zr + y_1^Zr y_2^U a_2^U + y_1^Zr y_2^Zr a_2^Zr
\]

\[
+ 2 \times RT(\sum_{j=1}^{U,Zr} y_1^j \ln y_1^j + \sum_{j=1}^{U,Zr} y_2^j \ln y_2^j) + \sum_{j=1}^{U,Zr} y_j^U y_j^U + \sum_{j=1}^{U,Zr} y_j^Zr y_j^Zr + \sum_{j,k=1}^{U,Zr} y_j^U y_k^Zr y_j^Zr y_k^U + \sum_{j,k=1}^{U,Zr} y_j^U y_k^U y_j^Zr y_k^Zr + \sum_{j,k=1}^{U,Zr} y_j^U y_k^Zr y_j^U y_k^Zr + \sum_{j,k=1}^{U,Zr} y_j^Zr y_k^U y_j^U y_k^Zr + \sum_{j,k=1}^{U,Zr} y_j^Zr y_k^Zr y_j^U y_k^U)
\]

\[ (7) \]

where \( y_1^U \) and \( y_2^U \) are respectively the site fractions of element \( i (i = U \) or Zr\) and \( j (j = U, Zr) \) in sublattices I and II; the parameters \( a_i^j \) represents the Gibbs free energy of the compound \( \delta \) phase when the first sublattice is occupied by element \( i (i = U \) or Zr\) and the second sublattice is occupied by element \( j (j = U, Zr) \) in the first sublattice, when the second sublattice is occupied by element \( k (k = Th, U \) or Zr\); \( a_{ijk} \) is the \( i-j-k \) interaction parameter \( (i = U, Zr) \) in the second sublattice, when the first sublattice is occupied by element \( i (i = U \) or Zr\).

### 3. Experimental information

#### 3.1. The Th–U system

The phase diagram of the Th–U system consists of five solution phases (\( \alpha \)-Th (fcc), \( \beta \)-Th (bcc), \( \alpha \)U, \( \beta \)U, \( \gamma \)U). The phase diagram in the Th–U system was investigated by many researchers [11–17], and then reviewed by Perterson [18]. No intermetallic compound was found in this system, and the solubilities of U in the \( \alpha \)Th and \( \beta \)Th phases are significant, whereas the solubilities of Th in the \( \alpha \)U, \( \beta \)U and \( \gamma \)U phases are extremely low. Many researchers found that there exists a wide liquid miscibility gap above 1375 °C [11,13,16]. Carlson also estimated the critical temperature of the miscibility gap to be 1650 °C [11]. The phase diagram of the Th–U system reviewed by Perterson [18] is shown in Fig. 1.

In addition, Luening et al. [17] measured the low temperature heat capacities of two dilute Th–U alloys in an adiabatic calorimeter over the temperature range from 1.5 to 5 K. And Niessen et al. [19] predicted that the enthalpies of solution at infinite dilution are 15 kJ/mol (liquid U dissolved in liquid Th) and 19 kJ/mol (liquid

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**Table 1**

The stable solid phases and the used models in the Th–U, Th–Zr and Th–U–Zr systems.

<table>
<thead>
<tr>
<th>Systems</th>
<th>Phase</th>
<th>Prototype</th>
<th>Strukturbericht designation</th>
<th>Modeling phase</th>
<th>Used models</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th–U</td>
<td>(βTh, γU)</td>
<td>W</td>
<td>A2</td>
<td>(Th, U)</td>
<td>Subregular solution model</td>
</tr>
<tr>
<td>αTh</td>
<td>Cu</td>
<td>A1</td>
<td>(Th, U)</td>
<td>Subregular solution model</td>
<td></td>
</tr>
<tr>
<td>βU</td>
<td>Cu</td>
<td>A1</td>
<td>(Th, U)</td>
<td>Subregular solution model</td>
<td></td>
</tr>
<tr>
<td>αZr</td>
<td>Mg</td>
<td>A3</td>
<td>(Th, Zr)</td>
<td>Subregular solution model</td>
<td></td>
</tr>
<tr>
<td>Th–Zr</td>
<td>(βTh, βZr)</td>
<td>W</td>
<td>A2</td>
<td>(Th, Zr)</td>
<td>Subregular solution model</td>
</tr>
<tr>
<td>αZr</td>
<td>Mg</td>
<td>A3</td>
<td>(Th, Zr)</td>
<td>Subregular solution model</td>
<td></td>
</tr>
<tr>
<td>Th–U–Zr</td>
<td>(βTh, βZr, γU)</td>
<td>W</td>
<td>A2</td>
<td>(Th, U, Zr)</td>
<td>Subregular solution model</td>
</tr>
<tr>
<td>αZr</td>
<td>Mg</td>
<td>A3</td>
<td>(Th, U, Zr)</td>
<td>Subregular solution model</td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 1.** The phase diagram of the Th–U system reviewed by Perterson [18].
Th dissolved in liquid U), respectively, however, no temperature dependence was given in the work of Niessen et al. [19].

3.2. The Th–Zr system

The phase diagram in the Th–Zr system consists of three solution phases (αTh (fcc), αZr (hcp) and (βTh + βZr)) and a miscibility gap of the bcc phase (βTh + βZr) at lower temperature. The phase diagram in the Th–Zr system was investigated by Gibson et al. [20] using high temperature X-ray studies. It was found that there exists a monotectoid reaction at 910 °C and a eutectoid reaction at 650 °C in the Th–Zr system, and there is a solid miscibility gap of the bcc phase above the 910 °C from 40 to 54 at.% Th. Evans et al. found that the solubility of Zr in the αTh phase is from 6.4 at.% at 900 °C to 2.9 at.% at 550 °C. Gibson et al. [20] estimated the solubility lines, but did not give the shape of liquidus lines, and gave the minimum solidus line at 1350 °C and 54 at.% Th. Based on the previous work, Massalski et al. [22] reviewed the phase diagram in the Th–Zr system and the reviewed phase diagram is shown in Fig. 2.

No experimental data on thermodynamic properties were reported, Niessen et al. [19] predicted that the enthalpies of solution at infinite dilution are 15 kJ/mol (liquid Zr dissolved in liquid Th) and 19 kJ/mol (liquid Th dissolved in liquid Zr), respectively, however, no temperature dependence was given in the work of Niessen et al. [19].

3.3. The Th–U–Zr system

The phase equilibria in the Th–U–Zr ternary system were studied by Carlson [11], however, his investigation was limited to several alloys in order to elucidate the question of the presence of a minimum on the liquidus surfaces. Badaeva et al. [10] studied phase equilibria in the Th–U–Zr system based on microstructure, X-ray diffraction analysis and hardness measurements of alloys quenched at 550, 700, 750, 800, 915, 930, 960 and 1000 °C. Badaeva and Kuznetsova [23] experimentally determined the liquidus surface, using thermal analysis with subsequent study of the microstructure, and found a solid miscibility gap in the Th–U side at high temperature. The experimental results indicated that there exists a small solubility of Th in the δ phase in the U–Zr system. However, no ternary phases and thermodynamic properties in the Th–U–Zr system were reported.

4. Optimized results and discussion

Optimization of thermodynamic parameters describing the Gibbs free energy of each phase is carried out using PARROT [24] module in the Thermo-Calc software [25], a computer program that can accept different types of data, such as phase equilibria and thermodynamic properties, in the same operation. Each piece of the selected data is given a certain weight and the weight can be changed until a satisfactory description for most of the selected data is achieved. A complete set of the thermodynamic parameters describing the Gibbs free energy of each phase in the Th–U–Zr ternary system is given in Table 2.

4.1. The Th–U system

The calculated phase diagram of the Th–U system comparing with all experimental data used in the present optimization is

Table 2

<table>
<thead>
<tr>
<th>Parameters in each phase (J/mol)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(u) = C_{Th} + C_{Zr} + C_{U}</td>
<td>This work</td>
</tr>
<tr>
<td>C_{Th} = 24,580</td>
<td>This work</td>
</tr>
<tr>
<td>C_{U} = 48,000</td>
<td>This work</td>
</tr>
<tr>
<td>C_{Zr} = 26,092</td>
<td>This work</td>
</tr>
<tr>
<td>C_{Th} = 33,000</td>
<td>This work</td>
</tr>
<tr>
<td>C_{Zr} = 25,287</td>
<td>This work</td>
</tr>
<tr>
<td>C_{U} = 25,287</td>
<td>This work</td>
</tr>
<tr>
<td>C_{Th} = 33,000</td>
<td>This work</td>
</tr>
<tr>
<td>C_{Zr} = 30,000</td>
<td>This work</td>
</tr>
<tr>
<td>C_{U} = 20,000</td>
<td>This work</td>
</tr>
<tr>
<td>C_{Th} = 100,000</td>
<td>This work</td>
</tr>
<tr>
<td>C_{Zr} = 100,000</td>
<td>This work</td>
</tr>
</tbody>
</table>

Fig. 2. The phase diagram of the Th–Zr system reviewed by Massalski et al. [22].
shown in Fig. 3. It is seen that most of the calculated results are in agreement with Perterson’s work [18]. However, the calculated shape of the liquid miscibility gap and the solubility of U in the $\beta$Th phase differ somewhat from the Perterson’s estimation [18], which needs more experimental data to confirm the calculated results. In addition, the heat capacities in the temperature range 1.5–5 K calculated by Luengo et al. [17] cannot be used in the present assessment due to too low temperature. The calculated enthalpies of mixing of the liquid phase are small positive values in the whole composition range, which are close to the value predicated by Niessen et al. [19].

All invariant reactions and special points in the Th–U system are summarized in Table 3, with the experimental data for comparison [18]. The critical temperature of the liquid miscibility gap and the temperatures of invariant reactions are in agreement with the experimental data [18].

### 4.2. The Th–Zr system

The calculated Th–Zr phase diagram with the experimental data is shown in Fig. 4. The calculated phase diagram, especially the phase boundary of the bcc miscibility gap region ($\beta$Th + $\beta$Zr), is in agreement with the experimental data [20–22]. The calculated solidus line agrees with Gibson’s experimental data [20], but there are some differences on the liquidus line between the present calculation and the experimental data by Gibson et al. [20] and Massalski et al. [22]. The calculated enthalpies of mixing of the liquid phase are small negative values, which are smaller than the values predicated by Niessen et al. [19] and more experimental thermodynamic data were needed to improve the assessment in this system. All invariant reactions in the Th–Zr system are summarized in Table 4, with the experimental data for comparison [22].

### 4.3. The Th–U–Zr system

In the assessment of the Th–U–Zr ternary system, the thermodynamic parameters of the U–Zr binary system [8] were adopted, and the calculated phase diagram is shown in Fig. 5. The calculated isothermal sections diagrams of the Th–U–Zr ternary system at 550,
Fig. 6. The calculated isothermal section diagrams of the Th–U–Zr system at (a) 550°C, (b) 700°C, (c) 750°C, (d) 800°C, (e) 915°C, (f) 930°C, (g) 960°C and (h) 1000°C.
Table 5
The calculated invariant reactions and special points in the Th–U–Zr system in this work.

<table>
<thead>
<tr>
<th>Point</th>
<th>Reaction</th>
<th>U (at.%)</th>
<th>Zr (at.%)</th>
<th>T (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>L ↔ bcc1 + bcc2 ↔ αTh</td>
<td>85.6</td>
<td>10.1</td>
<td>83.8</td>
<td>4.8</td>
</tr>
<tr>
<td>C1</td>
<td>L ↔ L1 + L2</td>
<td>69.5</td>
<td>10.1</td>
<td>83.8</td>
<td>4.8</td>
</tr>
</tbody>
</table>

Fig. 7. The calculated liquidus projection of the Th–U–Zr system with experimental data [23].

700, 750, 800, 915, 930, 960 and 1000 °C with the experimental data [10] are shown in Fig. 6(a)–(h), where a good agreement is obtained. The calculated liquidus projection is shown in Fig. 7, where most of the calculated results are in agreement with the experimental data [23]. The calculated results indicate that there is a peritectic reaction (liquid + bcc1 + bcc2 → αTh at 1187 °C), and the lowest critical temperature of the liquid miscibility gap is 1322 °C. All invariant reactions and special points in the Th–U–Zr system are summarized in Table 5.

5. Conclusions

The phase diagrams in the Th–U and Th–Zr binary systems and Th–U–Zr ternary system were evaluated by combining the thermodynamic models with the available experimental information in literature. A consistent set of optimized thermodynamic parameters has been derived for describing Gibbs free energy for each phase, and good agreement between the calculated results and most of the experimental data is obtained.

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References