FIRST-PRINCIPLES CALCULATIONS AND THERMODYNAMIC MODELING
OF THE HF-RE BINARY SYSTEM WITH EXTENSION
TO THE NI-HF-RE TERNARY SYSTEM

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ABSTRACT

This thesis describes the thermodynamic modeling of the Hf-Re binary system and prediction of the Ni-Hf-Re ternary system. Hafnium and rhenium are both alloying elements in the nickel-based superalloys which are extensively used in the aerospace industry due to high creep and oxidation resistance. Nickel-based superalloys typically contain many alloying materials in addition to Hf and Re; therefore, a comprehensive understanding of the complex phase equilibria of this multi-component system becomes necessary. However, an empirical approach is both time consuming and costly. A more efficient approach is the CALPHAD (CALculation of PHAse Diagrams) method where a complete thermodynamic database is predicted through the summation of the thermodynamic properties of individual phases. In the absence of experimental data, first-principles calculations can be used to predict thermochemical data.

The Hf-Re binary system has three intermetallic compounds, two of which show solubility ranges. SQS (Special Quasirandom Structure) calculations are performed on the bcc and hcp solid solution phases to predict the enthalpies of mixing. SQS calculations are also performed on the Hf-Zr and Re-Zr binary systems, the latter of which strongly resembles the Hf-Re system. RDF (Radial Distribution Function) analysis is used to investigate symmetry preservation of the parent structures.

The Ni-Hf-Re ternary system is predicted by combining the thermodynamic descriptions of the three constituent binary systems: Hf-Re, Hf-Ni, and Re-Ni. The latter
two systems have been previously modeled. An experimental isothermal section at 1173 K is included.
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CHAPTER 1 INTRODUCTION

1.1 NICKEL-BASED SUPERALLOYS

Nickel-based superalloys are designed to withstand high temperature applications often in excess of 0.7 of the absolute melting temperature. The major alloying components are aluminum and titanium at typically less than 10 percent of the total concentration, and the alloy forms a two-phase equilibrium microstructure, gamma (γ) and gamma-prime (γ’). The elevated-temperature strength and resistance to creep deformation is largely attributed to the γ’ phase, the fraction of which depends on chemical composition and temperature. With increasing temperature, the fraction of γ’ decreases at a given chemical composition. Other alloying elements such as hafnium and rhenium are added to stabilize the γ’ phase. Hafnium is a carbide former with a tendency to precipitate at grain boundaries and reduce grain boundary sliding. Rhenium further improves the creep strength by promoting rafting and increasing lattice misfit. Rhenium also reduces the overall diffusion rate in Ni-based superalloys. By understanding the effect of alloying elements on the phase stability in multi-component nickel-based systems, we can design materials with carefully selected alloy compositions for optimal performance.
1.2 MOTIVATIONS

Traditionally, alloy design can be a time-consuming and costly process with numerous trial and errors to achieve the optimal composition. The presence of undesirable phases negatively impacts the phase stability of these multi-component systems and thereby reduces alloy performance. A more efficient approach to investigate phase equilibria is through the CALPHAD (CALculation of PHAse Diagrams) method, which computationally predicts the thermodynamic descriptions of multi-component systems from constituent binary and ternary systems. More details on this method will be given in the next chapter.

Modeling has many benefits over experimental alloy design. Many alloying materials are rare in nature and therefore costly to obtain. Hf has an average concentration of 5.8 ppm while Re, as one of the rarest element, has an average concentration of 0.5-1 ppb. Neither Hf nor Re occur as free elements and require rigorous extraction methods for the raw materials. Environmental concerns and pollution associated with production methods will only escalate as world population increases and demand grows. By understanding the thermodynamic properties of individual elements through modeling, more prevalent occurring elements can be use to substitute the rare elements and lower production costs.
1.3 OUTLINE

This thesis will consist of seven chapters. Chapter 2 will detail the methodologies behind first-principles calculations and thermodynamic modeling by means of the CALPHAD approach. Chapter 3 will focus on Hf-Re modeling with experimental phase equilibria data and first-principles thermochemical data. SQS (Special Quasirandom Structure) calculations for disordered phases and RDF (Radial Distribution Function) analysis for symmetry investigation will be examined for Hf-Re, Hf-Zr, and Re-Zr binary systems. Chapter 4 and Chapter 5 will briefly discuss the Hf-Ni and Ni-Re binary systems. In Chapter 6, the three constituent binary systems, Hf-Re, Hf-Ni, and Ni-Re, will be combined to form the Ni-Hf-Re ternary system. An experimental isothermal section at 1173K will be included in the modeling. Chapter 7 concludes this thesis and suggests future work.
CHAPTER 2 COMPUTATIONAL METHODOLOGY

2.1 INTRODUCTION

Typically, phase equilibria and thermochemical data for ternary systems are more scarce compared to their binary counterparts. However, the thermodynamic descriptions of a ternary system can be extrapolated from constituent binary systems. This thesis aims to predict the phase stability and properties of the Hf-Re binary system by means of the CALPHAD technique [1] and to combine the three binary constituents Hf-Re, Hf-Ni, and Ni-Re into the ternary Hf-Ni-Re system. In this method, the Gibbs energy functions of individual phases as a function of temperature, pressure, and composition are optimized with experimental parameters. In the absence of experimental data, first-principles calculations have been shown to adequately predict thermochemical properties of phases. First-principles calculations are based on the DFT (Density Functional Theory) and only require atomic positions. In systems with limited experimental data, first-principles calculations can be very useful in providing modeling parameters. This chapter will outline the underlying principles of first-principles calculations and thermodynamic modeling via the CALPHAD technique. Details of the calculation parameters will also be provided.
2.2 DENSITY FUNCTIONAL THEORY

There are two types of thermodynamic data available in literature: phase equilibria data and thermochemical data. Phase equilibria data such as liquidus, solidus, and phase boundaries describe the relationship between two or more phases in a system, and is more plentiful in literature. Thermochemical data including enthalpy, entropy, heat capacity, and activity pertain only to a single phase and are much less frequently available. A system can be reproduced with only phase equilibria data; however, the model would not be unique because different Gibbs energy functions can give the same phase diagram. By supplementing thermochemical data from first-principles calculations, a more accurate model can be given.

DFT can be used to predict thermochemical data to constrain Gibbs energy functions. DFT is based on the quantum mechanical theory of electrons and is used to determine the total energy of a crystalline solid with only the atomic number and atomic coordinates. These calculations are referred to as first-principles calculations, or ab initio as they are performed independent of experimental or empirical data. This approach allows insight into phases that have not been investigated experimentally or are difficult to investigate such as metastable phases or extrapolation of lower order systems into higher order.

The time-independent Schrodinger equation is limited to describing a single particle at a specific time and is presented by the wavefunction of the system. From such, the total energy of the system can be calculated as follows:
\[ \hat{H}\Psi = E\Psi \]  

(2.1)

where \( \hat{H} \) is the Hamiltonian operator, \( \Psi \) is the wavefunction, and \( E \) is the total energy of the system. However, this equation cannot be applied to more than one electron, which means it cannot be applied to even the simplest repeating unit (a single primitive cell). To rectify this limitation, a method was developed to describe the density of electrons rather than the wavefunction itself [2-3] assuming that the density uniquely describes the properties of the system and the wavefunction. The total energy can then be written as:

\[ E_T = E[\rho(\vec{r})] \]  

(2.2)

where \( \rho(\vec{r}) \) is the density of electrons. The electronic ground state of a system can be found by minimizing \( E_T \). The energy of the system consists of several parts:

\[ E[\rho] = T_0[\rho] + V_{\text{ext}}[\rho] + V_{\text{Hartree}}[\rho] + E_{\text{xc}}[\rho] \]  

(2.3)

where \( T_0 \) is the kinetic energy of the electrons, \( V_{\text{ext}} \) is the potential energy of the ions interacting with the electrons, \( V_{\text{Hartree}} \) is the Coulombic interaction between a single electron with the rest of the system, and \( E_{\text{xc}} \) is the exchange correlation energy which include electron interactions with each other in the system. Approximations for \( E_{\text{xc}} \) such as the local density approximation (LDA) and the generalized gradient approximation (GGA) are used since the exact form is unknown.

The total energies predicted from first-principles calculations cannot be directly included in CALPHAD modeling because the reference states are not defined. Rather, enthalpies of mixing are used using the pure elements as reference states:
\[
\Delta H_{A_iB_j}^{\text{mix}} = E_{A_iB_j} - \frac{x}{x+y} E_A - \frac{y}{x+y} E_B
\]  

(2.4)

where \( \Delta H_{A_iB_j}^{\text{mix}} \) is the enthalpy of mixing for the solid solution and the \( E \) terms are the total energies from first-principles calculations.

### 2.3 SPECIAL QUASIRANDOM STRUCTURE

Although first-principles calculations apply well to crystalline solids with periodic boundary conditions, disordered phases such as substitutional solid solutions with random configurations are more difficult to represent. Three methods were previously used to mimic the random structures: the supercell method, the coherent potential approximation method [4] and the cluster expansion method [5]. However, these methods all have limitations as to computing power or accuracy. SQS (Special Quasirandom Structure) was developed by Zunger [6] and has the advantage of accurately mimicking the interactions of random solution with only a few atoms, generally between 4 and 32. As the atoms are allowed to relax, they locally disturb the structure away from equilibrium and allow local relaxation to occur.

The ordered structure used for SQS should have similar interactions compared to a random solid structure. Interactions between the nearest neighbors have more contribution to the total energy than more distant neighbors. In binary systems, each site \( i \) is assigned a spin variable of -1 if the site is occupied by A atoms or +1 if it is occupied by B atoms. The sites are grouped into "figures" \( f = (k,m) \) where \( k = 1, 2, 3, ... \)
representing points, pairs, triplets, or so on of atoms to the $m^{th}$ nearest neighbor. The correlation functions $\bar{\Pi}_{k,m}$ represent the average of the products of the spin variables of figure $k$ at a distance of $m$. The optimum SQS is one which satisfies:

\[(\bar{\Pi}_{k,m})_{SQS} \approx (\bar{\Pi}_{k,m})_{R}\]  

(2.5)

where $(\bar{\Pi}_{k,m})_{SQS}$ is the correction function of the SQS and $(\bar{\Pi}_{k,m})_{R}$ is the correlation function of a random structure.

Multiple relaxation schemes are used for SQS calculations to find the minimum energy without losing symmetry of the parent structure. For bcc solid solutions, there is only one initial degree of freedom, the lattice parameter $a$. However, for hcp structures, there are two degrees of freedom, namely the lattice parameter $a$ and the ratio of the lattice parameters $c/a$. The relaxation schemes used in this work are:

a  VOLUME RELAXATION

In volume relaxation, only the lattice parameters are relaxed while the internal angles of the structures are preserved. Relative atom positions are fixed within the supercell and the ratio of the lattice parameters remains constant.

b  VOLUME AND SHAPE RELAXATION

For volume and shape relaxation, both the lattice parameters and the shape of the cell are relaxed including the internal angles of the structure and the ratio of the
lattice parameters. However, the relative atom positions are still fixed. This scheme is performed after the volume relaxation.

c  **ION RELAXATION**

Ion relaxation is performed after volume and shape relaxation in which the atom positions are relaxed but the lattice parameters and the shape of the cell remain fixed. The ratio of the lattice parameters also does not change.

d  **FULL RELAXATION**

Full relaxation is performed as a last relaxation step after both volume and shape relaxation and ion relaxation. The lattice parameters, the internal angles of the structure, and the relative atom positions are all allowed to relax. For this method, the ratio of the lattice parameters is also relaxed.

In some cases, the local relaxation in SQS’s might be so large as to distort the original structure; therefore the relaxation scheme with the lowest energy without losing symmetry should be chosen for CALPHAD optimization. Ion relaxation and full relaxation schemes are not always possible for some structures.

### 2.4 RADIAL DISTRIBUTION FUNCTION

To investigate whether symmetry of the parent structure is preserved, RDF (Radial Distribution Function) analysis is performed on the relaxation schemes. In this
method, the nearest neighbors of an atom of the relaxed structure, typically no more than 8, are compared to the ideal parent structure. The relative positions of the intensity peaks give an idea of how well the symmetry is preserved through different relaxation schemes.

2.5 CALPHAD MODELING

The Gibbs energy function of an individual phase can be described as with an enthalpy and an entropy term:

\[ G = H - TS \]  \hfill (2.6)

with the polynomial form as a function of temperature as:

\[ G - H^{SER} = a + bT + cT\ln T + dT^2 + eT^3 + fT^{-1} \]  \hfill (2.7)

where \( H^{SER} \) is enthalpy at 298.15 K and 1 atm, or SER (stable element reference) as defined by SGTE (Scientific Group Thermodata Europe) and the variables a-f are fitting parameters determined from the enthalpy of formation, entropy, and heat capacity. Eq. 2.7 works well with plenty of experimental data and the modeling for pure elements have been widely accepted [7]. In the case of limited experimental data, as for stoichiometric compounds, the Neumann-Kopp rule can be applied, where the heat capacity of the compound is approximated as the sum of the heat capacities of the elements:

\[ G_{A_iB_j} = x_A \delta G_A^{SER} + x_B \delta G_B^{SER} + a + bT \]  \hfill (2.8)
where \( G_{A_iB_j} \) is the molar Gibbs energy of the phase \( A_iB_j \), \( ^oG_A^{SER} \) and \( ^oG_B^{SER} \) are the molar Gibbs energies of components A and B, respectively, and a and b are fitting parameters corresponding to the enthalpy and entropy of formation of the compound, respectively.

The compound energy formulism [8] is often used for solution phases. For a two-sublattice model \((A, B)_1(C, D)_j\) describing a mixture of A-, B-, C-, and D-type atoms, there are four ideal “endmembers” \((A_jC_j, A_jD_j, B_jC_j, B_jD_j)\). The energy of the solution phase is a mixture of the energies of the endmembers. The molar Gibbs energy of the phase is described as:

\[
G_m = ^oG_m + ^{\text{ideal}}\Delta G_{\text{mix}} + ^{xs}\Delta G_{\text{mix}}
\]  
(2.9)

where \(^oG_m\) is the Gibbs energy due to the mechanical mixing of the endmembers, \(^{\text{ideal}}\Delta G_{\text{mix}}\) is the Gibbs energy due to the ideal mixing of atoms within each sublattice, and \(^{xs}\Delta G_{\text{mix}}\) is the excess Gibbs energy due to interactions between atoms within each sublattice. The first term in Eq. 2.9 is given as:

\[
^oG_m = y^I_A y^I_C ^oG_{A:C} + y^I_A y^I_D ^oG_{A:D} + y^I_B y^I_C ^oG_{B:C} + y^I_B y^I_D ^oG_{B:D}
\]  
(2.10)

where \(y^I_A\) is the site fraction of A in the first sublattice and \(^oG_{A:C}\), \(^oG_{A:D}\), \(^oG_{B:C}\), and \(^oG_{B:D}\) are the Gibbs energy of each endmember. The ideal mixing term is given as:

\[
^{\text{ideal}}\Delta G_{\text{mix}} = iRT(y^I_A \ln y^I_A + y^I_B \ln y^I_B) + jRT(y^I_C \ln y^I_C + y^I_D \ln y^I_D)
\]  
(2.11)

Finally, the excess Gibbs energy is given as a Redlich-Kister polynomial [9]:
\[ x^s \Delta G_{\text{mix}} = y_A^I y_B^I \left( y_C^I \sum_{k=0}^k k L_{A,B,C}^I (y_A^I - y_B^I)^k \right) + y_C^I \sum_{k=0}^k k L_{A,B:CD}^I (y_C^I - y_D^I)^k \] (2.12)

\[ + y_C^I y_B^I \left( y_A^I \sum_{k=0}^k k L_{A:CD}^I (y_C^I - y_B^I)^k \right) + y_B^I \sum_{k=0}^k k L_{B:CD}^I (y_C^I - y_D^I)^k \]

where \( k L_{A,B,C}^I \) is the \( k^{th} \) order mixing parameter between A and B in the first sublattice with C in the second sublattice. When only \( 0^L \) interaction parameter is used, the phase is said to be a regular solution; with both \( 0^L \) and \( 1^L \) interaction parameters, sub-regular solution; and with \( 0^L, 1^L, \) and \( 2^L \) interaction parameters, sub-sub-regular solution. Typically in CALPHAD modeling, up to \( 2^L \) interaction parameters are used due to available experimental data. An over-parameterized modeling has no physical meaning.

### 2.6 Calculation Details

All first-principles calculations are carried out using the Vienna ab-initio Simulation Package (VASP) [10]. Calculations employ the projector augmented wave (PAW) method [11-12] and the generalized gradient approximation (GGA) as implemented by Perdew, Burke, and Erzhenfest [13]. A plane wave energy cutoff of 300 eV and a k-point mesh of at least 5,000 per reciprocal space atom are used for all calculations. For the pure elements and intermetallic compound calculations, all degrees of freedom for the structure are allowed to relax to obtain the minimum energy. Multiple relaxation schemes as described in Section 2.3 are used for SQS calculations to maintain parent structure symmetry.
CALPHAD optimization of Gibbs energy parameters is performed in the PARROT module of the ThermoCalc software. Hf$_{21}$Re$_{25}$ is treated as a stoichiometric compound. HfRe$_2$ and Hf$_5$Re$_{24}$ are described with two- and three-sublattice models, respectively. The Hf-Ni-Re ternary system is built from the three constituent binary systems, Hf-Re, Hf-Ni, and Ni-Re. An experimental isothermal section of the ternary system is included in the modeling.

2.7 CONCLUSION

Thermodynamic modeling of ternary and higher order systems depend on the constituent binary systems where both thermochemical and phase equilibria data are more plentiful. In the absence of experimental data, first-principles calculations are used to predict the thermochemical data.

This thesis describes the thermodynamic modeling of the Hf-Re binary system. First-principles calculations of the enthalpies of mixing of the compounds and SQS calculations of the bcc and hcp solid solutions are used to optimize the Gibbs energy functions. The calculated Hf-Re system is combined with Hf-Ni and Ni-Re from literature to predict phase equilibria in the ternary system.
REFERENCES


CHAPTER 3 THE HF-RE BINARY SYSTEM

3.1 INTRODUCTION

The bulk of this work will focus on the Hf-Re binary system. Experimental phase equilibria data is coupled with first-principles thermochemical data to model the Hf-Re system. This chapter will include a review of available literature data, followed by first-principles calculations and thermodynamic modeling by means of the CALPHAD technique.

3.2 LITERATURE REVIEW

The Hf-Re binary system has been experimentally investigated by Savitskii [1-2] and Taylor [3] in the 1960s. Both authors agree that Hf has two polymorphs, the low temperature stable structure is hcp and transforms into the bcc structure at higher temperatures. Re also has hcp structure, which is stable up to the melting temperature. Savitskii found three intermetallic structures: Hf₅Re₂₄, HfRe₂, and Hf₃Re₂, all with limited solubility. Taylor also found three intermetallic structures, χ-Hf₅Re₂₄, ε-HfRe₂, and φ-HfRe, both χ and ε-HfRe₂ show greater homogeneity range. Out of the three intermetallic compounds, Savitskii and Taylor disagree about the crystal structure of the φ phase: Savitskii found an unknown Hf₃Re₂ structure and Taylor found a tetragonal HfRe. Further analysis by Cenzual [4] indicates that φ is a rhombohedral Hf₂₁Re₂₅.
structure containing MgZn$_2$-type columns. This is agreed by Levy [5] through first-principles calculations. Table 3-1 lists crystal structure data of the three intermetallic compounds taken from the Pauling File [6].

The invariant reactions are listed in Table 3.2. There are considerable differences between the two phase diagrams. The $\beta\text{Hf} \leftrightarrow \alpha\text{Hf} + \varphi$ eutectoid reaction occurs at approximately the same composition, but with a temperature difference of 50 K. The liquid $\leftrightarrow \beta\text{Hf} + \varphi$ eutectic reaction has a 150 K temperature difference and 5% composition difference. The peritectic liquid $+ \text{HfRe}_2 \leftrightarrow \varphi$ reaction has a temperature difference of 165 K and almost 10% composition difference. The major dissimilarities are near the Re-rich side of the phase diagram. For the $\varepsilon$-HfRe$_2$ phase, Taylor observed a congruent melting reaction while Savitskii observed a peritectic reaction. For the $\chi$ phase, Taylor observed an eutectic reaction liquid $\leftrightarrow \alpha\text{Re} + \text{Hf}_5\text{Re}_{24}$ and a peritectic reaction liquid $+ \text{HfRe}_2 \leftrightarrow \text{Hf}_5\text{Re}_{24}$ while Savitskii only observed a peritectic reaction liquid $+ \gamma\text{Re} \leftrightarrow \text{Hf}_5\text{Re}_{24}$. The differences in temperature were because the homogenizing treatments of the alloys in the Russian studies were carried out at far too low a temperature, the highest being only 1500 °C for Re-rich alloys against 2750 °C as used by Taylor. Therefore, Taylor’s experimental data are used for CALPHAD modeling.

### 3.3 First-principles Calculations

First-principles calculations are performed on the pure elements and intermetallic compounds, and SQS calculations are performed on the bcc and hcp solid solutions for
Hf-Re to calculate the enthalpies of formation and enthalpies of mixing, respectively. Since Zr, similar to Hf, is hcp at lower temperatures and bcc at higher temperatures; SQS calculations of Hf-Zr and Re-Zr are also carried out for comparison. Symmetry preservation is checked through RDF analysis.

3.3.1

3.3.2  PURE ELEMENTS

Pure elements predictions of lattice parameters and total energies are compared to experimental data and previously published first-principles calculations (with GGA pseudopotential) [7] in Table 3-3 and 3-4 for Hf and Re, respectively. The calculated lattice parameters show good agreement with experimental data and published calculations, less than 1% in most cases and less than 3.5% for hcp Hf.

3.3.3

3.3.4  INTERMETALLIC COMPOUNDS

Table 3-5 lists the predicted lattice parameters for Hf$_{21}$Re$_{25}$, HfRe$_2$, and Hf$_5$Re$_{24}$ compared to experimental data. All show less than 0.5% error. The calculated lattice parameter for Hf$_{21}$Re$_{25}$, a rhombohedral structure, cannot be compared with experimental data because Taylor predicted a tetragonal structure.

Out of the three intermetallic compounds, $\varphi$-Hf$_{21}$Re$_{25}$ shows very limited solubility and is thus treated as a stoichiometric compound. Figure 3.1 shows a
crystallographic representation of the structure. The molar Gibbs energy for this phase is as follows:

$$ G_m = x_{Hf} G_{Hf}^0 + x_{Re} G_{Re}^0 + a + bT $$

Here, $x_{Hf}$ is 21, $x_{Re}$ is 25, and $a$ is the enthalpy of formation.

Both $\varepsilon$-HfRe$_2$ and $\chi$-Hf$_5$Re$_{24}$ have greater homogeneity range, thus cannot be treated as stoichiometric compounds. Figures 3.2 and 3.3 show the crystallographic arrangements of $\varepsilon$-HfRe$_2$ and $\chi$-Hf$_5$Re$_{24}$, respectively. $\varepsilon$-HfRe$_2$ is represented with a two-sublattice model (Hf, Re)$_1^1$(Hf, Re)$_2^1$ with substitutional mixing of Re on the first site and Hf on the second site. There are four endmembers: HfHf$_2$, HfRe$_2$, ReHf$_2$, ReHf$_2$. The molar Gibbs energy function is:

$$ G_m = y_{Hf}^1 y_{Hf}^I oG_{HfHf_2} + y_{Hf}^I y_{Re}^I oG_{HfRe_2} + y_{Re}^I y_{Hf}^I oG_{ReHf_2} + y_{Re}^I y_{Re}^I oG_{ReRe_2} $$

$$ +RT[y_{Hf}^I \ln(y_{Hf}^I) + y_{Re}^I \ln(y_{Re}^I) + y_{Hf}^I \ln(y_{Hf}^I) + y_{Re}^I \ln(y_{Re}^I)] + G_{m}^{\varepsilon} $$

where $^oG_{HfHf_2}$ represents the mechanical mixing of the HfHf$_2$ endmember and is defined in a similar fashion to Eq. 3.1. The lattice parameters and enthalpies of formation are predicted for each of the four endmembers and are listed in table 3-6. Out of the four endmembers, the stable structure HfRe$_2$ has the lowest enthalpy of formation.

$\chi$-Hf$_5$Re$_{24}$ is represented with a three-sublattice model Re$_{24}^I(Hf, Re)_{10}^I(Hf, Re)_{24}^{III}$. However, there is only substitutional mixing on the second and third sublattice with four
endmembers: \( \text{Re}_{24}\text{Hf}_{10}\text{Hf}_{24}, \text{Re}_{24}\text{Hf}_{10}\text{Re}_{24}, \text{Re}_{24}\text{Re}_{10}\text{Hf}_{24}, \text{Re}_{24}\text{Re}_{10}\text{Re}_{24}. \) The molar Gibbs energy function is:

\[
G_m = y_{\text{Re}}^{\text{I}} y_{\text{Hf}}^{\text{II}} y_{\text{Hf}}^{\text{III}} G_{\text{Re}_{24}\text{Hf}_{10}\text{Hf}_{24}} + y_{\text{Re}}^{\text{I}} y_{\text{Hf}}^{\text{II}} y_{\text{Re}}^{\text{III}} G_{\text{Re}_{24}\text{Hf}_{10}\text{Re}_{24}} + y_{\text{Re}}^{\text{I}} y_{\text{Re}}^{\text{II}} y_{\text{Hf}}^{\text{III}} G_{\text{Re}_{24}\text{Re}_{10}\text{Hf}_{24}} + y_{\text{Re}}^{\text{I}} y_{\text{Re}}^{\text{II}} y_{\text{Re}}^{\text{III}} G_{\text{Re}_{24}\text{Re}_{10}\text{Re}_{24}} + y_{\text{Re}}^{\text{I}} RT \left[ y_{\text{Hf}}^{\text{II}} \ln(y_{\text{Hf}}^{\text{II}}) + y_{\text{Re}}^{\text{II}} \ln(y_{\text{Re}}^{\text{II}}) + y_{\text{Hf}}^{\text{III}} \ln(y_{\text{Hf}}^{\text{III}}) + y_{\text{Re}}^{\text{III}} \ln(y_{\text{Re}}^{\text{III}}) \right] + G_{m}^{xs}
\]

The lattice parameters and enthalpies of formation for each endmember are listed in table 3-7. Although the endmember \( \text{Re}_{24}\text{Hf}_{10}\text{Hf}_{24} \) has a lower enthalpy of mixing than the ideal structure, \( \text{Re}_{24}\text{Hf}_{10}\text{Re}_{24} \), it lies above the convex hull in figure 3.4.

### 3.3.5 SPECIAL QUASIRANDOM STRUCTURES

For bcc and hcp solid solutions, SQS calculations are performed as described in Chapter 2. A 16-atom supercell structure was used for both bcc [8] and hcp [9] structures at 25%, 50%, and 75% Re compositions. Multiple relaxation methods are done for both structures.

### 3.3.6

### 3.3.7 RADIAL DISTRIBUTION FUNCTION ANALYSIS

To ensure that symmetry of the parent structure is preserved, RDF analysis is performed on all SQS calculations. Figures 3.5 and 3.6 show the RDF results of 25%,
50%, and 75% Re for bcc and hcp structures respectively. For bcc SQS, symmetry is maintained through volume and shape relaxation when compared to the ideal bcc structure. For the hcp structure however, symmetry is only maintained through volume relaxation and breaks down completely after volume and shape relaxation. For hcp structures, there are two independent variables, a and the c/a lattice parameter ratio. For volume relaxation, since the internal angles are fixed, the c/a ratio is preserved. However, for volume and shape relaxation, c/a is allowed to relax, thus explains the symmetry breakdown. The enthalpies of mixing can be determined from Eq. 2.4 and are listed in table 3-8. The bcc enthalpy of mixing is negative for all Re compositions because there is greater solubility of Re in bcc Hf. The hcp enthalpy of mixing is positive for all Re compositions indicating very small solubility Hf in hcp Re and Re in hcp Hf.

For comparison purposes, SQS are calculated for the bcc and hcp solid solutions of Hf-Zr and Re-Zr binary systems. Re-Zr has phases analogous to the Hf-Re systems as Zr is directly above Hf in the periodic table. The RDF’s for both systems are listed in Appendix A.

3.4 THERMODYNAMIC MODELING

The pure elements phase descriptions are taken from version four of the SGTE PURE database. The enthalpies of mixing data from SQS calculations allows for a more accurate description of the bcc and hcp solid solution phases rather than using arbitrary
interaction parameters. The predicted enthalpies of formation and enthalpies of mixing are substituted for the a term in Eq. 2.8.

The liquid phase is treated as a subregular solution with an L1 term. The bcc solid solution is treated as a subregular solution and the hcp solid solution is treated as a regular solution. The Hf$_{21}$Re$_{25}$ phase is treated as stoichiometric compound. HfRe$_2$ has a two-sublattice model with 4 endmembers and Hf$_3$Re$_{24}$ has a three-sublattice model with 4 endmembers. By using sublattice models, the solubility range could be modified. A calculated phase diagram is shown in Figure 3.7.

The liquid, bcc, and hcp phase interaction parameters are given as:

$$^0L_{\text{liquid}} = -78,800$$ (3.4)

$$^1L_{\text{liquid}} = -13,300$$ (3.5)

$$^0L_{\text{bcc}} = -71,500$$ (3.6)

$$^0L_{\text{hcp}} = 16,000$$ (3.7)

$$^0L_{\text{hcp}} = 109,000$$ (3.9)

The Ψ-Hf$_{21}$Re$_{25}$ Gibbs energy function is:

$$^0G_{\text{Hf}_{21}\text{Re}_{25}} = 21G_{\text{Hf}} + 25G_{\text{Re}} - 1,848,000 + 47.0T$$ (3.10)

The Gibbs energy functions for the four ε-HfRe$_2$ endmembers are:

$$^0G_{\text{HfHf}_2} = G_{\text{Hf}} + 2G_{\text{Hf}} + 93,420$$ (3.11)
The Gibbs energy functions for the four endmembers of the $\chi$-Hf$_5$Re$_{24}$ phase are:

\begin{align}
0G_{HfRe_2} &= G_{Hf} + 2G_{Re} - 118,300 \\
0G_{ReHf_2} &= G_{Re} + 2G_{Hf} + 191,400 \\
0G_{ReRe_2} &= G_{Re} + 2G_{Re} + 77,460
\end{align}

The Gibbs energy functions for the four endmembers of the $\chi$-Hf$_5$Re$_{24}$ phase are:

\begin{align}
0G_{Re_{24}Hf_{10}Hf_{24}} &= 24G_{Re} + 10G_{Hf} + 24G_{Hf} - 1,546,000 \\
0G_{Re_{24}Hf_{10}Re_{24}} &= 24G_{Re} + 10G_{Hf} + 24G_{Re} - 1,478,000 + 46.8T \\
0G_{Re_{24}Re_{10}Hf_{24}} &= 24G_{Re} + 10G_{Re} + 24G_{Hf} - 339,000 \\
0G_{Re_{24}Re_{10}Re_{24}} &= 24G_{Re} + 10G_{Re} + 24G_{Re} + 261,000
\end{align}

3.5 CONCLUSION

The Hf-Re binary has been modeled with experimental phase equilibria data and calculated thermochemical data from first-principles. The enthalpies of mixing for the bcc and hcp solid solutions were calculated with SQS. There are three intermetallic compounds in the system. Enthalpies of formation for the endmembers were calculated with first-principles.
REFERENCES


Table 3-1 Crystal structure data for Hf-Re intermetallic compounds

<table>
<thead>
<tr>
<th>Structure</th>
<th>Chemical Formula</th>
<th>Structure Type (Prototype)</th>
<th>Pearson Symbol</th>
<th>Space Group</th>
<th>Space Group Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>φ</td>
<td>Hf$<em>{21}$Re$</em>{25}$</td>
<td>Zr$<em>{21}$Re$</em>{25}$</td>
<td>hR276</td>
<td>R3c</td>
<td>167</td>
</tr>
<tr>
<td>ε</td>
<td>HfRe$_2$</td>
<td>MgZn$_2$</td>
<td>hP12</td>
<td>P6$_3$/mmc</td>
<td>194</td>
</tr>
<tr>
<td>χ</td>
<td>Hf$<em>5$Re$</em>{24}$</td>
<td>Ti$<em>3$Re$</em>{24}$</td>
<td>cI58</td>
<td>I43m</td>
<td>217</td>
</tr>
</tbody>
</table>

Table 3-2 Invariant reactions for Hf-Re

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Type</th>
<th>T (K)</th>
<th>Composition (Re)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>βHf ↔ αHf + Hf$_3$Re$_2$</td>
<td>Eutectoid</td>
<td>1523</td>
<td>13 wt.%</td>
<td>[2]</td>
</tr>
<tr>
<td>βHf ↔ αHf + HfRe</td>
<td>Eutectoid</td>
<td>1573</td>
<td>12 at.%</td>
<td>[3]</td>
</tr>
<tr>
<td>liquid ↔ βHf + Hf$_3$Re$_2$</td>
<td>Eutectic</td>
<td>2373</td>
<td>17-18 wt.%</td>
<td>[2]</td>
</tr>
<tr>
<td>liquid ↔ βHf + HfRe</td>
<td>Eutectic</td>
<td>2113</td>
<td>23.5 at.%</td>
<td>[3]</td>
</tr>
<tr>
<td>liquid + HfRe$_2$ ↔ Hf$_3$Re$_2$</td>
<td>Peritectic</td>
<td>2553</td>
<td></td>
<td>[2]</td>
</tr>
<tr>
<td>liquid + HfRe$_2$ ↔ HfRe</td>
<td>Peritectic</td>
<td>2718</td>
<td>50.5 at.%</td>
<td>[3]</td>
</tr>
<tr>
<td>liquid + Hf$<em>5$Re$</em>{24}$ ↔ HfRe$_2$</td>
<td>Peritectic</td>
<td>3123</td>
<td>66.0-69.0 wt.%</td>
<td>[2]</td>
</tr>
<tr>
<td>liquid ↔ HfRe$_2$</td>
<td>Congruent</td>
<td>3433</td>
<td>62.0-67.5 at.%</td>
<td>[3]</td>
</tr>
<tr>
<td>liquid + HfRe$_2$ ↔ Hf$<em>5$Re$</em>{24}$</td>
<td>Peritectic</td>
<td>3359</td>
<td>82.5 at.%</td>
<td>[3]</td>
</tr>
<tr>
<td>liquid + γRe ↔ Hf$<em>5$Re$</em>{24}$</td>
<td>Peritectic</td>
<td>3248</td>
<td>82.7 at.%</td>
<td>[2]</td>
</tr>
<tr>
<td>liquid ↔ αRe + Hf$<em>5$Re$</em>{24}$</td>
<td>Eutectic</td>
<td>3203</td>
<td>91.5 at.%</td>
<td>[3]</td>
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</tbody>
</table>
### Table 3-3 Pure Hf total energy and lattice parameters

<table>
<thead>
<tr>
<th>Structure</th>
<th>Total Energy (eV/atom)</th>
<th>% Diff.</th>
<th>Lattice Parameter</th>
<th>% Diff.</th>
<th>c/a</th>
<th>% Diff.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>bcc</td>
<td>-9.7764</td>
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<td>3.5385</td>
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<td></td>
<td></td>
<td>This work</td>
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<tr>
<td></td>
<td>-9.6562</td>
<td>1.24%</td>
<td>3.538</td>
<td>0.01%</td>
<td></td>
<td></td>
<td>[7]</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>3.545</td>
<td>0.18%</td>
<td></td>
<td></td>
<td>[3]</td>
</tr>
<tr>
<td>hcp</td>
<td>-9.9449</td>
<td></td>
<td>3.3005</td>
<td>1.5797</td>
<td></td>
<td></td>
<td>This Work</td>
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<tr>
<td></td>
<td>-9.8320</td>
<td>1.15%</td>
<td>3.200</td>
<td>3.14%</td>
<td>1.580</td>
<td>0.02%</td>
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<td>3.1969</td>
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<td>1.5823</td>
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### Table 3-4 Pure Re total energy and lattice parameters

<table>
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<th>Structure</th>
<th>Total Energy (eV/atom)</th>
<th>% Diff.</th>
<th>Lattice Parameter</th>
<th>% Diff.</th>
<th>c/a</th>
<th>% Diff.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>bcc</td>
<td>-12.0966</td>
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<td>3.1068</td>
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<td></td>
<td>-11.9107</td>
<td>1.56%</td>
<td>3.125</td>
<td>0.58%</td>
<td></td>
<td></td>
<td>[7]</td>
</tr>
<tr>
<td>hcp</td>
<td>-12.4036</td>
<td></td>
<td>2.7696</td>
<td></td>
<td>1.6144</td>
<td></td>
<td>This Work</td>
</tr>
<tr>
<td></td>
<td>-12.2334</td>
<td>1.39%</td>
<td>2.785</td>
<td>0.55%</td>
<td>1.615</td>
<td>0.04%</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>2.7611</td>
<td>0.31%</td>
<td>1.6148</td>
<td>0.02%</td>
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</tbody>
</table>
Table 3-5 Intermetallic compound lattice parameters

<table>
<thead>
<tr>
<th>Structure</th>
<th>Lattice Parameter a (Å)</th>
<th>Lattice Ratio c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This work</td>
<td>[3]</td>
</tr>
<tr>
<td>Hf₂₁Re₂₅</td>
<td>15.120</td>
<td></td>
</tr>
<tr>
<td>HfRe₂</td>
<td>5.259</td>
<td>5.2470</td>
</tr>
<tr>
<td>Hf₅Re₂₄</td>
<td>9.742</td>
<td>9.7126</td>
</tr>
</tbody>
</table>

Table 3-6 HfRe₂ endmember calculations

<table>
<thead>
<tr>
<th>Structure</th>
<th>Enthalpy of Formation (kJ/mole)</th>
<th>Lattice Parameter a (Å)</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>HfHf₂</td>
<td>93.423</td>
<td>5.708</td>
<td>1.673</td>
</tr>
<tr>
<td>HfRe₂</td>
<td>-118.34</td>
<td>5.259</td>
<td>1.641</td>
</tr>
<tr>
<td>ReHf₂</td>
<td>191.42</td>
<td>5.467</td>
<td>1.603</td>
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<tr>
<td>ReRe₂</td>
<td>77.462</td>
<td>5.087</td>
<td>1.624</td>
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</tbody>
</table>

Table 3-7 Hf₅Re₂₄ endmember calculations

<table>
<thead>
<tr>
<th>Structure</th>
<th>Enthalpy of Formation (kJ/mole)</th>
<th>Lattice Parameter a (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re₂₄Hf₁₀Hf₂₄</td>
<td>-1567.7</td>
<td>10.28</td>
</tr>
<tr>
<td>Re₂₄Hf₁₀Re₂₄</td>
<td>-1478.0</td>
<td>9.742</td>
</tr>
<tr>
<td>Re₂₄Re₁₀Hf₂₄</td>
<td>-339.88</td>
<td>10.10</td>
</tr>
<tr>
<td>Re₂₄Re₁₀Re₂₄</td>
<td>261.09</td>
<td>9.572</td>
</tr>
</tbody>
</table>
Table 3-8 SQS enthalpy of mixing

<table>
<thead>
<tr>
<th>Structure</th>
<th>Composition</th>
<th>Enthalpy of Mixing (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bcc</td>
<td>25% Re</td>
<td>-9.85</td>
</tr>
<tr>
<td></td>
<td>50% Re</td>
<td>-24.55</td>
</tr>
<tr>
<td></td>
<td>75% Re</td>
<td>-25.40</td>
</tr>
<tr>
<td>hcp</td>
<td>25% Re</td>
<td>20.35</td>
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<tr>
<td></td>
<td>50% Re</td>
<td>27.22</td>
</tr>
<tr>
<td></td>
<td>75% Re</td>
<td>20.80</td>
</tr>
</tbody>
</table>
Figure 3-1 Hf$_{21}$Re$_{25}$ crystal structure
Figure 3-2 HfRe2 Crystal Structure
Figure 3-3 Hf$_5$Re$_{24}$ crystal structure
Figure 3-4 Hf-Re convex hull
Figure 3-5 Hf-Re bcc RDF
Figure 3-6 Hf-Re hcp RDF
Figure 3-7 Calculated Hf-Re phase diagram
CHAPTER 4 THE HF-NI BINARY SYSTEM

4.1 INTRODUCTION

Hf as a common alloying element in the nickel-based superalloys has attracted much attention. Thus, the Hf-Ni binary system has been extensively investigated, both experimentally and computationally. A literature review of the system will be presented here. The Hf-Ni ThermoCalc database file is taken from literature and no further modeling has been done on the system in this work.

4.2 LITERATURE REVIEW

The Hf-Ni binary system has been updated by Wang [1] using diffusion couple method and electron probe microanalysis data technique and modeled by means of the CALPHAD technique.

Hcp Hf is stable at low temperatures and transforms into bcc structure at high temperatures. Ni is soluble in hcp Hf up to 1.3 at.% and up to 8.4 at.% in bcc Hf. Ni has fcc structure. Hf is soluble in Ni up to 1.3 at.%. There are nine intermetallic phases, HfNi₅, Hf₂Ni₇, Hf₃Ni₉, Hf₆Ni₂₁, Hf₃Ni₇, Hf₇Ni₁₀, Hf₉Ni₁₁, HfNi, and Hf₂Ni, all but Hf₂Ni are treated as stoichiometric compounds. Among them, Hf₂Ni shows limited homogeneity range at higher temperatures, Hf₈Ni₂₁ and Hf₃Ni₇ are only stable at higher temperatures, both HfNi and Hf₃Ni₃ have two polymorphs, and Hf₂Ni₇, HfNi, and Hf₂Ni
melt congruently. Figure 4-1 shows the calculated phase diagram of Hf-Ni, redrawn with database from Wang et.al [4].

4.3 CONCLUSION

The Hf-Ni binary system is updated by Wang [1] by means of the CALPHAD technique. The ThermoCalc database file is taken from the authors and will be combined with the Hf-Re and Ni-Re binary systems.
REFERENCES

Figure 4-1 Hf-Ni phase diagram from literature
CHAPTER 5 THE NI-RE BINARY SYSTEM

5.1 INTRODUCTION

Rhenium is another common alloying element in the nickel-based superalloys. In the present work, the Ni-Re binary database is taken from literature and no further modeling has been done on the system.

5.2 LITERATURE REVIEW

Ni-Re has been previously modeled by Huang [1]. Zacherl [2] updated the pure element descriptions using version four of the SGTE SSUB pure element database. Ni-Re is a simple binary system with no intermetallic compounds. There is extended solubility of Re in fcc Ni up to 0.2 at.% and of Ni in hcp Re up to 0.2 at.%. Error!

Reference source not found. shows a calculated phase diagram redrawn with database from Zacherl [2].

5.3 CONCLUSION

The Ni-Re binary system has been previously modeled with the CALPHAD technique. The database is taken from literature to be combined with Hf-Re and Hf-Ni to form the Ni-Hf-Re ternary system.
REFERENCES


Figure 5-1 Ni-Re phase diagram from literature
CHAPTER 6 THE HF-NI-RE TERNARY SYSTEM

6.1 INTRODUCTION

All three constituent binary systems, Hf-Re, Hf-Ni, and Ni-Re, of the Hf-Ni-Re ternary system have been modeled. There is one experimental isothermal section at 1173 K which will be discussed in the next section. The ternary system can now be constructed by combining the three binary systems.

6.2 LITERATURE REVIEW

Wang [1] investigated the phase equilibria of the Hf-Ni-Re system at 1173 K by means of diffusion triple technique and electron microprobe analysis. Five binary intermetallics, (HfNi$_3$, Hf$_7$Ni$_{10}$, Hf$_9$Ni$_{11}$, HfNi, and Hf$_2$Ni) and two ternary intermetallics ($\alpha$ and $\beta$) are found in the Hf-Ni-Re diffusion triple annealed at 1173 K. The $\alpha$ phase consists of 40%-46% Hf, 30%-36% Ni, and 17%-25% Re with unknown structure. The $\beta$ phase consists of 66%-70% Hf, 4%-6% Ni, and 22%-30% Re, again with unknown structure. The Hf-Re side of the diagram does not exhibit any compounds.

6.3 THERMODYNAMIC MODELING
The database files of Hf-Re, Hf-Ni, and Ni-Re are combined into Hf-Ni-Re. An isothermal section is shown in Figure 6-1 with no ternary compounds. When taking the two ternary compounds into consideration and modeling them as stoichiometric compounds, a different isothermal section is shown in Figure 6-2. Here, the enthalpies of formation for α is estimated to be -50 kJ/atom and -40 kJ/atom for β. The Hf-Re side of the diagram shows the three intermetallic compounds in equilibrium with the two ternary compounds. At 1173K, all three Hf-Re compounds should be stable.

The difference between the experimental isothermal section and the modeled ternary isothermal is mainly due to the 3 Hf-Re compounds. With diffusion triple techniques, local equilibrium are sometimes never reached thus will not show up on phase diagrams. To obtain an exact modeling of the experimental isothermal section, the ternary compounds would need enthalpies of formation of at least -100 kJ/mole-atom, which are quite unreasonable assumptions. The Gibbs energy descriptions of the two ternary compounds α and β are given as follows:

\[
\delta G_\alpha = 50G_{Hf} + 30G_{Ni} + 20G_{Re} - 4,000,000 \quad (6.1)
\]

\[
\delta G_\beta = 70G_{Hf} + 5G_{Ni} + 25G_{Re} - 5,000,000 \quad (6.2)
\]

6.4 CONCLUSION
Isothermal sections at 1173K are shown, one without ternary compounds and one with ternary compounds. The calculated ternary phase diagram show the Hf-Re intermetallic compounds in equilibrium with the ternary compounds.
REFERENCES

Figure 6-1: Ni-Hf-Re Isothermal section at 1173K without ternary compounds.
Figure 6-2 Ni-Hf-Re Isothermal section at 1173K including ternary compounds.
CHAPTER 7 CONCLUSION AND FUTURE WORK

7.1 CONCLUSION

The Hf-Re binary system has been modeled with experimental phase equilibria data and calculated first-principles thermochemical data. SQS calculations for bcc and hcp solid solutions are used to predict enthalpies of mixing. The lattice parameters and enthalpies of formation for three intermetallic compounds are also predicted. The Gibbs energy functions for are given for the three intermetallic compounds. The interaction parameters of liquid, bcc, and hcp are also given.

Hf-Re, Hf-Ni, and Ni-Re are combined to form the Hf-Ni-Re ternary system. There is one experimental isothermal section at 1173K which show two ternary compounds. The two ternary compounds are treated as stoichiometric and enthalpies of formation are estimated. A calculated isothermal section at 1173K is shown for the ternary system.

7.2 FUTURE WORK

Future works include calculating the entropies of formation from the Debye model and perform ternary SQS calculations for bcc, hcp, and fcc solid solutions. Those parameters will provide better fitting parameters for CALPHAD modeling. Also, ternary
compounds need to investigated more fully. The Ni-Hf-Re ternary system will be integrated into the Ni-based superalloy database.
A.1 HF-RE SETUP FILE

GOTO_MODULE DATABASE_RETRIEVAL
SWITCH_DATABASE PURE4
DEFINE_ELEMENTS HF RE
REJECT PHASES FCC_A1
GET_DATA
LIST_SYSTEM CONSTITUENT

GOTO_MODULE GIBBS_ENERGY_SYSTEM
ENTER_PHASE PHI,, 2 21 25 HF; RE; NO NO
ENTER_PHASE EPSILON,, 2 1 2 HF RE; HF RE; NO NO
ENTER_PHASE CHI,, 3 24 10 24 RE; HF RE; HF RE; NO NO

GOTO_MODULE PARROT
ENTER_PARAMETER G(LIQUID,HF,RE;0) 298.15 V1+V2*T; 6000.00 NO
ENTER_PARAMETER G(LIQUID,HF,RE;1) 298.15 V3+V4*T; 6000.00 NO
ENTER_PARAMETER G(LIQUID,HF,RE;2) 298.15 V5+V6*T; 6000.00 NO
LIST_PHASE_DATA LIQUID

ENTER_PARAMETER G(BCC_A2,HF,RE;0) 298.15 V11+V12*T; 6000.00 NO
ENTER_PARAMETER G(BCC_A2,HF,RE;1) 298.15 V13+V14*T; 6000.00 NO
ENTER_PARAMETER G(BCC_A2,HF,RE;2) 298.15 V15+V16*T; 6000.00 NO
LIST_PHASE_DATA BCC_A2

ENTER_PARAMETER G(HCP_A3,HF,RE;0) 298.15 V21+V22*T; 6000.00 NO
ENTER_PARAMETER G(HCP_A3,HF,RE;1) 298.15 V23+V24*T; 6000.00 NO
ENTER_PARAMETER G(HCP_A3,HF,RE;2) 298.15 V25+V26*T; 6000.00 NO
LIST_PHASE_DATA HCP_A3

ENTER_PARAMETER G(PHI,HF;RE;0) 298.15
21*GHSERHF+25*GHSERRE+V31+V32*T;
6000.00 NO
LIST_PHASE_DATA PHI

ENTER_PARAMETER G(EPSILON,HF:HF;0) 298.15
GHSERHF+2*GHSERHF+V41+V42*T;
6000.00 NO
ENTER_PARAMETER G(EPSILON,HF:RE;0) 298.15
GHSERHF+2*GHSERRE+V43+V44*T;
6000.00 NO
ENTER_PARAMETER G(EPSILON,RE:HF;0) 298.15
GHSERRE+2*GHSERHF+V45+V46*T;
6000.00 NO
ENTER_PARAMETER G(EPSILON,RE:RE;0) 298.15
GHSERRE+2*GHSERRE+V47+V48*T;
6000.00 NO

ENTER_PARAMETER G(EPSILON,HF,RE;HF;0)298.15 V51+V52*T; 6000.00 NO
ENTER_PARAMETER G(EPSILON,HF,RE;RE;0)298.15 V53+V54*T; 6000.00 NO
ENTER_PARAMETER G(EPSILON,HF:HF,RE;0) 298.15 V55+V56*T; 6000.00 NO
ENTER_PARAMETER G(EPSILON,RE:HF,RE;0) 298.15 V57+V58*T; 6000.00 NO
LIST_PHASE_DATA EPSILON

ENTER_PARAMETER G(CHI,RE:HF:HF;0) 298.15
24*GHSERRE+10*GHSERHF+24*GHSERHF+V61+V62*T; 6000.00 NO
ENTER_PARAMETER G(CHI,RE:HF:RE;0) 298.15
24*GHSERRE+10*GHSERHF+24*GHSERRE+V63+V64*T; 6000.00 NO
ENTER_PARAMETER G(CHI,RE:RE:HF;0) 298.15
24*GHSERRE+10*GHSERRE+24*GHSERHF+V65+V66*T; 6000.00 NO
ENTER_PARAMETER G(CHI,RE:RE:RE;0) 298.15
24*GHSERRE+10*GHSERRE+24*GHSERRE+V67+V68*T; 6000.00 NO

ENTER_PARAMETER G(CHI,RE:HF,RE:HF;0) 298.15 V71+V72*T; 6000.00 NO
ENTER_PARAMETER G(CHI,RE:HF,RE:RE;0) 298.15 V73+V74*T; 6000.00 NO
ENTER_PARAMETER G(CHI,RE:HF:HF,RE;0) 298.15 V75+V76*T; 6000.00 NO
ENTER_PARAMETER G(CHI,RE:RE:HF,RE;0) 298.15 V77+V78*T; 6000.00 NO
LIST_PHASE_DATA CHI

SET_INTERACTIVE
A.2 HF-RE POP FILE

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$\$$ Taylor 1963 $\$$

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****************
$\$$ LIQUID 100-500 $\$$

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$\$$ LIQUID + HCP_A3 $\$$

TABLE 100
CREATE_NEW_EQUILIBRIUM @@,1
LABEL A3LH
CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE LIQUID=ENTERED 1
CHANGE_STATUS PHASE HCP_A3=ENTERED 1
SET_CONDITION P=1E5 N=1 X(RE)=@1 T=@2
EXPERIMENT DGM(LIQUID)>-1E-3:1E-3
EXPERIMENT DGM(HCP_A3)>-1E-3:1E-3
EXPERIMENT DGM(BCC_A2)<-1E-3:1E-3
EXPERIMENT DGM(PHI)<-1E-3:1E-3
EXPERIMENT DGM(EPSILON)<-1E-3:1E-3
EXPERIMENT DGM(CHI)<-1E-3:1E-3

TABLE_VALUES
0.945 3151
0.949 3194
0.947 3248
TABLE_END

$$ LIQUID + BCC\_A2 $$

TABLE 200

CREATE_NEW_EQUILIBRIUM @@,1

LABEL A3LB

CHANGE_STATUS PHASE *=DORMANT

CHANGE_STATUS PHASE LIQUID=ENTERED 1

CHANGE_STATUS PHASE BCC\_A2=ENTERED 1

SET_START_CONSTITUTION liquid

SET_CONDITION P=1E5 N=1 X(RE)=@1 T=@2

EXPERIMENT DGM(LIQUID)>-1E-3:1E-3

EXPERIMENT DGM(HCP\_A3)<-1E-3:1E-3

EXPERIMENT DGM(BCC\_A2)>-1E-3:1E-3

EXPERIMENT DGM(PHI)<-1E-3:1E-3

EXPERIMENT DGM(EPSILON)<-1E-3:1E-3

EXPERIMENT DGM(CHI)<-1E-3:1E-3

TABLE_VALUES

0.148 2121

0.122 2124

0.098 2210

0.072 2210

TABLE_END

$$ LIQUID + PHI $$

TABLE 300
CREATE_NEW_EQUILIBRIUM @@,1
LABEL A3LP
CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE LIQUID=ENTERED 1
CHANGE_STATUS PHASE PHI=ENTERED 1
SET_START_CONSTITUTION liq
SET_CONDITION P=1E5 N=1 X(RE)=@1 T=@2
EXPERIMENT DGM(LIQUID)>-1E-3:1E-3
EXPERIMENT DGM(HCP_A3)<-1E-3:1E-3
EXPERIMENT DGM(BCC_A2)<-1E-3:1E-3
EXPERIMENT DGM(PHI)>-1E-3:1E-3
EXPERIMENT DGM(EPSILON)<-1E-3:1E-3
EXPERIMENT DGM(CHI)<-1E-3:1E-3
TABLE_VALUES
0.423 2118
0.349 2122
0.248 2118
0.497 2519
TABLE_END

$$ LIQUID + EPSILON $$
TABLE 400
CREATE_NEW_EQUILIBRIUM @@,1
LABEL A3LE
CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE LIQUID=ENTERED 1
CHANGE_STATUS PHASE EPSILON=ENTERED 1
SET_CONDITION P=1E5 N=1 X(RE)=@1 T=@2
EXPERIMENT DGM(LIQUID)>-1E-3:1E-3
EXPERIMENT DGM(HCP_A3)<-1E-3:1E-3
EXPERIMENT DGM(BCC_A2)<-1E-3:1E-3
EXPERIMENT DGM(PHI)<-1E-3:1E-3
EXPERIMENT DGM(EPSILON)>-1E-3:1E-3
EXPERIMENT DGM(CHI)<-1E-3:1E-3

TABLE_VALUES
0.537 2720
0.598 2731
0.547 2806
0.618 2917
0.798 3344

TABLE_END

$$ LIQUID + CHI $$

TABLE 500
CREATE_NEW_EQUILIBRIUM @@,1
LABEL A3LC
CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE LIQUID=ENTERED 1
CHANGE_STATUS PHASE CHI=ENTERED 1
SET_CONDITION P=1E5 N=1 X(RE)=@1 T=@2
EXPERIMENT DGM(LIQUID)>-1E-3:1E-3
EXPERIMENT DGM(HCP_A3)<-1E-3:1E-3
EXPERIMENT DGM(BCC_A2)<-1E-3:1E-3
EXPERIMENT DGM(PHI)<-1E-3:1E-3
EXPERIMENT DGM(EPSILON)<-1E-3:1E-3
EXPERIMENT DGM(CHI)>-1E-3:1E-3
TABLE_VALUES
0.898 3133
0.896 3190
TABLE_END

*******************************************************************************

$$ SINGLE PHASE 1, 1100-1300 $$

*******************************************************************************

$$ HCP_A3 $$

CREATE_NEW_EQUILIBRIUM 1,1
LABEL A3H
CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE HCP_A3=FIXED 1
SET_CONDITION P=1E5 X(RE)=0.972 T=2861
EXPERIMENT DGM(LIQUID)<-1E-3:1E-3
EXPERIMENT DGM(HCP_A3)>-1E-3:1E-3
EXPERIMENT DGM(BCC_A2)<-1E-3:1E-3
EXPERIMENT DGM(PHI)<-1E-3:1E-3
EXPERIMENT DGM(EPSILON)<-1E-3:1E-3
EXPERIMENT DGM(CHI)<-1E-3:1E-3

$$ BCC_A2 $$
TABLE 1100
CREATE_NEW_EQUILIBRIUM @@,1
LABEL A3B
CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE BCC_A2=FIXED 1
SET_CONDITION P=1E5 X(RE)=@1 T=@2
EXPERIMENT DGM(LIQUID)<-1E-3:1E-3
EXPERIMENT DGM(HCP_A3)<-1E-3:1E-3
EXPERIMENT DGM(BCC_A2)>-1E-3:1E-3
EXPERIMENT DGM(PHI)<-1E-3:1E-3
EXPERIMENT DGM(EPSILON)<-1E-3:1E-3
EXPERIMENT DGM(CHI)<-1E-3:1E-3
TABLE_VALUES
0.099 1874
0.074 1870
0.124 2085
TABLE_END

$$ EPSILON $$

TABLE 1200
CREATE_NEW_EQUILIBRIUM @@,1
LABEL A3E
CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE EPSILON=FIXED 1
SET_CONDITION P=1E5 X(RE)=@1 T=@2
EXPERIMENT DGM(LIQUID)<-1E-3:1E-3
TABLE VALUES
0.649 1472
0.638 2617
0.638 2753
0.672 2763
0.666 2767
0.648 2763
0.646 2992
0.670 3110
TABLE_END

$\text{CHI}$

TABLE 1300
CREATE_NEW_EQUILIBRIUM @ @, 1
LABEL A3C
CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE CHI=FIXED 1
SET_CONDITION P=1E5 X(RE)=@1 T=@2
EXPERIMENT DGM(LIQUID)<-1E-3:1E-3
EXPERIMENT DGM(HCP_A3)<-1E-3:1E-3
EXPERIMENT DGM(BCC_A2)<-1E-3:1E-3
EXPERIMENT DGM(PHI)<-1E-3:1E-3
EXPERIMENT DGM(EPSILON)<-1E-3:1E-3
EXPERIMENT DGM(CHI)>-1E-3:1E-3

TABLE_VALUES
0.879 2761
0.857 2761
0.847 2993
0.830 3007
0.875 3111

TABLE_END

*************************
$$ TWO PHASE 2100-2600 $$
*************************
$$ HCP_A3 + BCC_A2 $$

TABLE 2100
CREATE_NEW_EQUI @,1
LABEL A3HB
CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE HCP_A3=ENTERED 1
CHANGE_STATUS PHASE BCC_A2=ENTERED 1
SET_CONDITION P=1E5 N=1 X(RE)=@1 T=@2
EXPERIMENT DGM(LIQUID)<-1E-3:1E-3
EXPERIMENT DGM(HCP_A3)>-1E-3:1E-3
EXPERIMENT DGM(BCC_A2)>-1E-3:1E-3
EXPERIMENT DGM(PHI)<-1E-3:1E-3
EXPERIMENT DGM(EPSILON)<-1E-3:1E-3
EXPERIMENT DGM(CHI)<-1E-3:1E-3

TABLE_VALUES
0.099 1577
0.076 1577
0.052 1877
0.009 1877

TABLE_END

$$\text{HCP}_A3 + \phi$$

TABLE 2200
CREATE_NEW_EQUILIBRIUM @@,1
LABEL A3HP
CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE HCP_A3=ENTERED 1
CHANGE_STATUS PHASE PHI=ENTERED 1
SET_CONDITION P=1E5 N=1 X(RE)=@1 T=@2
SET_START_CONSTITUTION phi
SET_START_CONSTITUTION hcp
EXPERIMENT DGM(LIQUID)<-1E-3:1E-3
EXPERIMENT DGM(HCP_A3)>-1E-3:1E-3
EXPERIMENT DGM(BCC_A2)<-1E-3:1E-3
EXPERIMENT DGM(PHI)>-1E-3:1E-3
EXPERIMENT DGM(EPSILON)<-1E-3:1E-3
EXPERIMENT DGM(CHI)<-1E-3:1E-3

TABLE_VALUES
0.051 1476
0.051 1530
TABLE_END

$$ BCC_A2 + PHI $$

TABLE 2300
CREATE_NEW_EQUILIBRIUM @@,1
LABEL A3BP
CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE BCC_A2=ENTERED 1
CHANGE_STATUS PHASE PHI=ENTERED 1
SET_CONDITION P=1E5 N=1 X(RE)=@1 T=@2
SET_START_CONSTITUTION bcc
SET_START_CONSTITUTION phi
EXPERIMENT DGM(LIQUID)<-1E-3:1E-3
EXPERIMENT DGM(HCP_A3)<-1E-3:1E-3
EXPERIMENT DGM(BCC_A2)>-1E-3:1E-3
EXPERIMENT DGM(PHI)>-1E-3:1E-3
EXPERIMENT DGM(EPSILON)<-1E-3:1E-3
EXPERIMENT DGM(CHI)<-1E-3:1E-3
TABLE_VALUES
0.125 1573
0.150 1874
0.124 1870
0.475 1943
0.426 2025
0.399 2022
0.199 2024
0.424 2083

TABLE_END

$$ PHI + EPSILON $$

TABLE 2400
CREATE_NEW_EQUILIBRIUM @@,1
LABEL A3PE
CHANGE_STATUS PHASE *'=DORMANT
CHANGE_STATUS PHASE PHI'=ENTERED 1
CHANGE_STATUS PHASE EPSILON'=ENTERED 1
SET_CONDITION P=1E5 N=1 X(RE)='@ 1 T='@ 2
EXPERIMENT DGM(LIQUID)<-1E-3:1E-3
EXPERIMENT DGM(HCP_A3)<-1E-3:1E-3
EXPERIMENT DGM(BCC_A2)<-1E-3:1E-3
EXPERIMENT DGM(PHI)>-1E-3:1E-3
EXPERIMENT DGM(EPSILON)>-1E-3:1E-3
EXPERIMENT DGM(CHI)<-1E-3:1E-3

TABLE_VALUES
0.618 2069
0.549 2319
0.509 2519
0.597 2556
0.620 2620
0.538 2623
0.519 2623
0.546 2666

TABLE_END

$$ \text{EPSILON} + \text{CHI} $$

TABLE 2500

CREATE_NEW_EQUILIBRIUM @@,1

LABEL A3EC

CHANGE_STATUS PHASE *=DORMANT

CHANGE_STATUS PHASE EPSILON=ENTERED 1

CHANGE_STATUS PHASE CHI=ENTERED 1

SET_CONDITION P=1E5 N=1 X(RE)=@1 T=@2

EXPERIMENT DGM(LIQUID)<-1E-3:1E-3

EXPERIMENT DGM(HCP_A3)<-1E-3:1E-3

EXPERIMENT DGM(BCC_A2)<-1E-3:1E-3

EXPERIMENT DGM(PHI)<-1E-3:1E-3

EXPERIMENT DGM(EPSILON)>-1E-3:1E-3

EXPERIMENT DGM(CHI)>-1E-3:1E-3

TABLE_VALUES

0.798 2020
0.699 2019
0.746 2764
0.797 3011
0.697 3014

TABLE_END
$$ \text{HCP}_A3 + \text{CHI} $$

TABLE 2600

CREATE_NEW_EQUILIBRIUM @@,1

LABEL A3HC

CHANGE_STATUS PHASE *=DORMANT

CHANGE_STATUS PHASE HCP_A3=ENTERED 1

CHANGE_STATUS PHASE CHI=ENTERED 1

SET_CONDITION P=1E5 N=1 X(RE)=@1 T=@2

EXPERIMENT DGM(LIQUID)<-1E-3:1E-3

EXPERIMENT DGM(HCP_A3)>-1E-3:1E-3

EXPERIMENT DGM(BCC_A2)<-1E-3:1E-3

EXPERIMENT DGM(PHI)<-1E-3:1E-3

EXPERIMENT DGM(EPSILON)<-1E-3:1E-3

EXPERIMENT DGM(CHI)>-1E-3:1E-3

TABLE_VALUES

0.973 2064
0.949 2060
0.947 2861
0.921 2861
0.905 3008
0.898 3011
0.945 3087
0.906 3094
0.898 3094

TABLE_END
$\textit{INVARIANT EQUILIBRIA 21-26}$

$\textit{HCP_A3 + BCC_A2 + PHI}$

CREATE_NEW_EQUILIBRIUM 21,1

LABEL A321

CHANGE_STATUS PHASE HCP_A3=FIXED 1
CHANGE_STATUS PHASE BCC_A2=FIXED 1
CHANGE_STATUS PHASE PHI=FIXED 1

SET_CONDITION P=1E5
SET_START_VALUE Y(BCC_A2,HF)=0.88
SET_START_VALUE Y(BCC_A2,RE)=0.12
SET_START_VALUE y(HCP_A3,HF)=0.99
SET_START_VALUE y(HCP_A3,RE)=0.01
SET_START_VALUE T=1580
SET_CONDITION P=1E5
EXPERIMENT T=1573:10
EXPERIMENT X(HCP_A3,RE)=0.008:0.005
EXPERIMENT X(BCC_A2,RE)=0.120:0.010
EXPERIMENT X(PHI,RE)=0.5:0.010

$\textit{LIQUID + BCC_A2 + PHI}$

CREATE_NEW_EQUILIBRIUM 22,1

LABEL A322

CHANGE_STATUS PHASE LIQUID=FIXED 1
CHANGE_STATUS PHASE BCC_A2=FIXED 1
CHANGE_STATUS PHASE PHI=FIXED 1
SET_CONDITION P=1E5
SET_START_VALUE T=2150
SET_START_VALUE Y(BCC_A2, HF)=.87
SET_START_VALUE Y(BCC_A2, RE)=.13
SET_START_VALUE Y(LIQUID, HF)=.76
SET_START_VALUE Y(LIQUID, RE)=.24
EXPERIMENT T=2113:15
EXPERIMENT X(BCC_A2, RE)=0.125:0.010
EXPERIMENT X(LIQUID, RE)=0.235:0.010
EXPERIMENT X(PHI, RE)=0.5:0.010

$$ \text{LIQUID} + \text{PHI} + \text{EPSILON} $$
CREATE_NEW_EQUILIBRIUM 23,1
LABEL A323
CHANGE_STATUS PHASE LIQUID=FIXED 1
CHANGE_STATUS PHASE PHI=FIXED 1
CHANGE_STATUS PHASE EPSILON=FIXED 1
SET_CONDITION P=1E5
SET_START_VALUE T=2750
SET_START_VALUE Y(EPSILON, HF)=0.38
SET_START_VALUE Y(EPSILON, RE)=0.62
SET_START_VALUE Y(EPSILON, HF#2)=0.38
SET_START_VALUE Y(EPSILON, RE#2)=0.62
SET_START_VALUE Y(LIQUID, HF)=0.60
SET_START_VALUE Y(LIQUID, RE)=0.4
SET_START_VALUE T=2750
EXPERIMENT T=2718:15
EXPERIMENT X(EPISODE,RE)=0.620:0.010
EXPERIMENT X(PE,RE)=0.505:0.010

$$\text{CONGRUENT MELTING EPSILON}$$
CREATE_NEW_EQUILIBRIUM 24,1
LABEL A324
CHANGE_STATUS PHASE LIQUID=FIXED 1
CHANGE_STATUS PHASE EPSILON=FIXED 1
SET_CONDITION P=1E5
SET_CONDITION X(EPISODE,RE)-X(LIQUID,RE)=0
SET_START_VALUE T=3450
SET_START_VALUE Y(EPISODE,HF)=0.32
SET_START_VALUE Y(EPISODE,RE)=0.68
SET_START_VALUE Y(EPISODE,HF#2)=0.32
SET_START_VALUE Y(EPISODE,RE#2)=0.68
SET_START_VALUE Y(LIQUID,HF)=0.32
SET_START_VALUE Y(LIQUID,RE)=0.68
EXPERIMENT T=3443:20
EXPERIMENT X(EPISODE,RE)=.325:0.010
EXPERIMENT X(LIQUID,RE)=0.325:0.010

$$\text{LIQUID} + \text{EPSILON} + \text{CHI}$$
CREATE_NEW_EQUILIBRIUM 25,1
LABEL A325
CHANGE_STATUS PHASE LIQUID=FIXED 1
CHANGE_STATUS PHASE EPSILON=FIXED 1
CHANGE_STATUS PHASE CHI=FIXED 1
SET_START_VALUE T=3360
SET_START_VALUE Y(CHI,HF#2)=0.18
SET_START_VALUE Y(CHI,RE#2)=0.82
SET_START_VALUE Y(CHI,HF#3)=0.18
SET_START_VALUE Y(CHI,RE#3)=0.82
SET_START_VALUE Y(EPSILON,HF)=0.3
SET_START_VALUE Y(EPSILON,RE)=0.7
SET_START_VALUE Y(EPSILON,HF#2)=0.3
SET_START_VALUE Y(EPSILON,RE#2)=0.7
SET_START_VALUE Y(LIQUID,HF)=0.15
SET_START_VALUE Y(LIQUID,RE)=0.85
SET_CONDITION P=1E5
EXPERIMENT T=3359:15
EXPERIMENT X(CHI,RE)=0.825:0.010
EXPERIMENT X(EPSILON,RE)=0.675:0.010
EXPERIMENT X(LIQUID,RE)=0.850:0.010

$$ \text{LIQUID} + \text{HCP}_A3 + \text{CHI} $$
CREATE_NEW_EQUILIBRIUM 26,1
LABEL A326
CHANGE_STATUS PHASE LIQUID=FIXED 1
CHANGE_STATUS PHASE HCP_A3=FIXED 1
CHANGE_STATUS PHASE CHI=FIXED 1
SET_CONDITION P=1E5
SET_START_VALUE T=3250
SET_START_VALUE Y(CHI,HF#2)=0.1
SET_START_VALUE Y(CHI,RE#2)=0.9
SET_START_VALUE Y(CHI,HF#3)=0.1
SET_START_VALUE Y(CHI,RE#3)=0.9
SET_START_VALUE Y(HCP_A3,HF)=0.03
SET_START_VALUE Y(HCP_A3,RE)=0.97
SET_START_VALUE Y(LIQUID,HF)=0.08
SET_START_VALUE Y(LIQUID,RE)=0.92
EXPERIMENT T=3203:15
EXPERIMENT X(HCP_A3,RE)=0.965:0.010
EXPERIMENT X(CHI,RE)=0.895:0.010

*****************
$$ X - RAY \ 31-34 $$
*****************

$$ \ PHI \  + \ EPSILON $$
CREATE_NEW_EQUILIBRIUM 31,1
LABEL A3X1
CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE PHI=FIXED 1
CHANGE_STATUS PHASE EPSILON=FIXED 1
SET_CONDITION P=1E5 T=2624
EXPERIMENT X(RE)=0.627:0.015
$$ \text{EPSILON + CHI} $$
CREATE_NEW_EQUILIBRIUM 32,1
LABEL A3X2
CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE EPSILON=FIXED 1
CHANGE_STATUS PHASE CHI=FIXED 1
SET_CONDITION P=1E5 T=3010
EXPERIMENT X(RE)=0.672:0.015

$$ \text{EPSILON + CHI} $$
CREATE_NEW_EQUILIBRIUM 33,1
LABEL A3X3
CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE EPSILON=FIXED 1
CHANGE_STATUS PHASE CHI=FIXED 1
SET_CONDITION P=1E5 T=3007
EXPERIMENT X(RE)=0.821:0.015

$$ \text{HCP_A3 + CHI} $$
CREATE_NEW_EQUILIBRIUM 34,1
LABEL A3X4
CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE HCP_A3=FIXED 1
CHANGE_STATUS PHASE CHI=FIXED 1
SET_CONDITION P=1E5 T=3008
EXPERIMENT X(RE)=0.891:0.015
$\text{SAVITSKII 1962}$

$\text{LIQUID 3100-3500}$

$\text{LIQUID + HCP_A3}$

TABLE 3100

CREATE_NEW_EQUILIBRIUM @@,1

LABEL A2LH

CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE LIQUID=ENTERED 1
CHANGE_STATUS PHASE HCP_A3=ENTERED 1

SET_CONDITION P=1E5 N=1 \text{X(RE)}=@1 \text{T}=@2

EXPERIMENT DGM(LIQUID)>-1E-3:1E-3
EXPERIMENT DGM(HCP_A3)>-1E-3:1E-3
EXPERIMENT DGM(BCC_A2)<-1E-3:1E-3
EXPERIMENT DGM(PHI)<-1E-3:1E-3
EXPERIMENT DGM(EPSILON)<-1E-3:1E-3
EXPERIMENT DGM(CHI)<-1E-3:1E-3

TABLE_VALUES

0.803 3217
0.919 3209
0.952 3209
0.957 3262
0.970 3413

TABLE_END

$$ LIQUID + BCC_A2 $$

TABLE 3200

CREATE_NEW_EQUILIBRIUM @@,1

LABEL A2LB

CHANGE_STATUS PHASE *=DORMANT

CHANGE_STATUS PHASE LIQUID=ENTERED 1

CHANGE_STATUS PHASE BCC_A2=ENTERED 1

SET_CONDITION P=1E5 N=1 X(RE)=@1 T=@2

EXPERIMENT DGM(LIQUID)>-1E-3:1E-3

EXPERIMENT DGM(HCP_A3)<-1E-3:1E-3

EXPERIMENT DGM(BCC_A2)>-1E-3:1E-3

EXPERIMENT DGM(PHI)<-1E-3:1E-3

EXPERIMENT DGM(EPSILON)<-1E-3:1E-3

EXPERIMENT DGM(CHI)<-1E-3:1E-3

TABLE_VALUES

0.000 2613

0.027 2520

0.091 2420

TABLE_END

$$ LIQUID + PHI $$

TABLE 3300

CREATE_NEW_EQUILIBRIUM @@,1
LABEL A2LP

CHANGE_STATUS PHASE * = DORMANT

CHANGE_STATUS PHASE LIQUID = ENTERED 1

CHANGE_STATUS PHASE PHI = ENTERED 1

SET_CONDITION P = 1E5 N = 1 X(RE) = @ 1 T = @ 2

EXPERIMENT DGM(LIQUID) > -1E-3:1E-3

EXPERIMENT DGM(HCP_A3) < -1E-3:1E-3

EXPERIMENT DGM(BCC_A2) < -1E-3:1E-3

EXPERIMENT DGM(PHI) > -1E-3:1E-3

EXPERIMENT DGM(EPSILON) < -1E-3:1E-3

EXPERIMENT DGM(CHI) < -1E-3:1E-3

TABLE_VALUES
0.188 2353
0.284 2497

TABLE_END

$$ LIQUID + EPSILON $$

TABLE 3400

CREATE_NEW_EQUILIBRIUM @@, 1

LABEL A2LE

CHANGE_STATUS PHASE * = DORMANT

CHANGE_STATUS PHASE LIQUID = ENTERED 1

CHANGE_STATUS PHASE EPSILON = ENTERED 1

SET_CONDITION P = 1E5 N = 1 X(RE) = @ 1 T = @ 2

EXPERIMENT DGM(LIQUID) > -1E-3:1E-3

EXPERIMENT DGM(HCP_A3) < -1E-3:1E-3
EXPERIMENT DGM(BCC_A2)<-1E-3:1E-3
EXPERIMENT DGM(PHI)<-1E-3:1E-3
EXPERIMENT DGM(EPSILON)>-1E-3:1E-3
EXPERIMENT DGM(CHI)<-1E-3:1E-3

TABLE_VALUES

0.306 2537
0.334 2543
0.384 2536
0.579 3055

TABLE_END

$$ LIQUID + CHI $$

TABLE 3500
CREATE_NEW_EQUILIBRIUM @@,1
LABEL A2LC
CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE LIQUID=ENTERED 1
CHANGE_STATUS PHASE CHI=ENTERED 1
SET_CONDITION P=1E5 N=1 X(RE)=@1 T=@2

EXPERIMENT DGM(LIQUID)>-1E-3:1E-3
EXPERIMENT DGM(HCP_A3)<-1E-3:1E-3
EXPERIMENT DGM(BCC_A2)<-1E-3:1E-3
EXPERIMENT DGM(BCC_A2)<-1E-3:1E-3
EXPERIMENT DGM(CHI)<-1E-3:1E-3
EXPERIMENT DGM(CHI)<-1E-3:1E-3

TABLE_VALUES
0.632 3100
0.659 3212
0.772 3218
TABLE_END

*******************************************************************************

$$ SINGLE PHASE 4100-4400 $$
*******************************************************************************

$$ HCP_A3 $$
TABLE 4100
CREATE_NEW_EQUILIBRIUM @@,1
LABEL A2H
CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE HCP_A3=FIXED 1
SET_CONDITION P=1E5 X(RE)=@1 T=@2
EXPERIMENT DGM(LIQUID)<-1E-3:1E-3
EXPERIMENT DGM(HCP_A3)>-1E-3:1E-3
EXPERIMENT DGM(BCC_A2)<-1E-3:1E-3
EXPERIMENT DGM(PHI)<-1E-3:1E-3
EXPERIMENT DGM(EPSILON)<-1E-3:1E-3
EXPERIMENT DGM(CHI)<-1E-3:1E-3
TABLE_VALUES
0.995 1026
0.993 1350
0.993 1745
TABLE_END
$$ \text{PHI} $$

TABLE 4200
CREATE_NEW_EQUILIBRIUM @@,1
LABEL A2P
CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE PHI=FIXED 1
SET_CONDITION P=1E5 X(RE)=@1 T=@2
EXPERIMENT DGM(LIQUID)<-1E-3:1E-3
EXPERIMENT DGM(HCP_A3)<-1E-3:1E-3
EXPERIMENT DGM(BCC_A2)<-1E-3:1E-3
EXPERIMENT DGM(PHI)>-1E-3:1E-3
EXPERIMENT DGM(EPSILON)<-1E-3:1E-3
EXPERIMENT DGM(CHI)<-1E-3:1E-3
TABLE_VALUES
0.397 1052
0.395 1382
0.392 1758
TABLE_END

$$ \text{EPSILON} $$

TABLE 4300
CREATE_NEW_EQUILIBRIUM @@,1
LABEL A2E
CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE EPSILON=FIXED 1
SET_CONDITION P=1E5 X(RE)=@1 T=@2
EXPERIMENT DGM(LIQUID)<-1E-3:1E-3
EXPERIMENT DGM(HCP_A3)<-1E-3:1E-3
EXPERIMENT DGM(BCC_A2)<-1E-3:1E-3
EXPERIMENT DGM(PHI)<-1E-3:1E-3
EXPERIMENT DGM(EPSILON)>-1E-3:1E-3
EXPERIMENT DGM(CHI)<-1E-3:1E-3

TABLE_VALUES
0.657 1037
0.655 1373
0.652 1749

TABLE_END

$$ CHI $$

TABLE 4400
CREATE_NEW_EQUILIBRIUM @@,1
LABEL A2C
CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE CHI=FIXED 1
SET_CONDITION P=1E5 X(RE)=@1 T=@2
EXPERIMENT DGM(LIQUID)<-1E-3:1E-3
EXPERIMENT DGM(HCP_A3)<-1E-3:1E-3
EXPERIMENT DGM(BCC_A2)<-1E-3:1E-3
EXPERIMENT DGM(PHI)<-1E-3:1E-3
EXPERIMENT DGM(EPSILON)<-1E-3:1E-3
EXPERIMENT DGM(CHI)>-1E-3:1E-3
TABLE VALUES
0.821 1028
0.818 1365
0.816 1740
TABLE_END

*****************************

$$ TWO PHASE 5100-5600 $$

*****************************

$$ HCP_A3 + BCC_A2 $$

TABLE 5100

CREATE_NEW_EQUILIBRIUM @@,1
LABEL A2HB

CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE HCP_A3=ENTERED 1
CHANGE_STATUS PHASE BCC_A2=ENTERED 1

SET_CONDITION P=1E5 N=1 X(RE)=@1 T=@2

EXPERIMENT DGM(LIQUID)<-1E-3:1E-3
EXPERIMENT DGM(HCP_A3)>-1E-3:1E-3
EXPERIMENT DGM(BCC_A2)>-1E-3:1E-3
EXPERIMENT DGM(PHI)<-1E-3:1E-3
EXPERIMENT DGM(EPSILON)<-1E-3:1E-3
EXPERIMENT DGM(CHI)<-1E-3:1E-3

TABLE_VALUES
0.041 1689
0.068 1689
0.104 1682
0.035 1768
0.068 1768
0.098 1768

TABLE_END

$$ HCP_A3 + PHI $$

TABLE 5200
CREATE_NEW_EQUILIBRIUM @@,1
LABEL A2HP
CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE HCP_A3=ENTERED 1
CHANGE_STATUS PHASE PHI=ENTERED 1
SET_CONDITION P=1E5 N=1 X(RE)=@1 T=@2
EXPERIMENT DGM(LIQUID)<-1E-3:1E-3
EXPERIMENT DGM(HCP_A3)>-1E-3:1E-3
EXPERIMENT DGM(BCC_A2)<-1E-3:1E-3
EXPERIMENT DGM(PHI)>-1E-3:1E-3
EXPERIMENT DGM(EPSILON)<-1E-3:1E-3
EXPERIMENT DGM(CHI)<-1E-3:1E-3

TABLE_VALUES
0.042 1076
0.073 1069
0.106 1062
0.195 1061
0.303 1060
$ BCC_A2 + PHI $ 

TABLE 5300 

CREATE_NEW_EQUILIBRIUM @@,1 

LABEL A2BP 

CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE BCC_A2=ENTERED 1
CHANGE_STATUS PHASE PHI=ENTERED 1
SET_CONDITION P=1E5 N=1 X(RE)=@1 T=@2
EXPERIMENT DGM(LIQUID)<-1E-3:1E-3
EXPERIMENT DGM(HCP_A3)<-1E-3:1E-3
EXPERIMENT DGM(BCC_A2)>-1E-3:1E-3
EXPERIMENT DGM(PHI)>-1E-3:1E-3
EXPERIMENT DGM(EPSILON)<-1E-3:1E-3
EXPERIMENT DGM(CHI)<-1E-3:1E-3

TABLE_VALUES
0.193 1681
0.190 1760
0.295 1759
0.314 1759
0.336 1765

TABLE_END

$$ PHI + EPSILON $$

TABLE 5400
CREATE_NEW_EQUILIBRIUM @@,1
LABEL A2PE
CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE PHI=ENTERED 1
CHANGE_STATUS PHASE EPSILON=ENTERED 1
SET_CONDITION P=1E5 N=1 X(RE)=@1 T=@2
EXPERIMENT DGM(LIQUID)<-1E-3:1E-3
EXPERIMENT DGM(HCP_A3)<-1E-3:1E-3
EXPERIMENT DGM(BCC_A2)<-1E-3:1E-3
EXPERIMENT DGM(PHI)>-1E-3:1E-3
EXPERIMENT DGM(EPSILON)>-1E-3:1E-3
EXPERIMENT DGM(CHI)<-1E-3:1E-3

TABLE VALUES
0.596 1037
0.591 1367
0.591 1749

TABLE_END

$$ \text{ EPSILON + CHI } $$

TABLE 5500
CREATE_NEW_EQUILIBRIUM @ @,1
LABEL A2EC
CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE EPSILON=ENTERED 1
CHANGE_STATUS PHASE CHI=ENTERED 1
SET_CONDITION P=1E5 N=1 X(RE)=@1 T=@2
EXPERIMENT DGM(LIQUID)<-1E-3:1E-3
EXPERIMENT DGM(HCP_A3)<-1E-3:1E-3
EXPERIMENT DGM(BCC_A2)<-1E-3:1E-3
EXPERIMENT DGM(PHI)<-1E-3:1E-3
EXPERIMENT DGM(EPSILON)>-1E-3:1E-3
EXPERIMENT DGM(CHI)>-1E-3:1E-3

TABLE_VALUES
$\$ HCP_A3 + CHI $\$

TABLE 5600

CREATE_NEW_EQUILIBRIUM @@,1

LABEL A2HC

CHANGE_STATUS PHASE *=DORMANT

CHANGE_STATUS PHASE HCP_A3=ENTERED 1

CHANGE_STATUS PHASE CHI=ENTERED 1

SET_CONDITION P=1E5 N=1 X(RE)=@1 T=@2

EXPERIMENT DGM(LIQUID)<-1E-3:1E-3

EXPERIMENT DGM(HCP_A3)>-1E-3:1E-3

EXPERIMENT DGM(BCC_A2)<-1E-3:1E-3

EXPERIMENT DGM(PHI)<-1E-3:1E-3

EXPERIMENT DGM(EPSILON)<-1E-3:1E-3

EXPERIMENT DGM(CHI)>-1E-3:1E-3

TABLE_VALUES

0.937 1027
0.970 1027
0.935 1350

TABLE_END
$\text{INVARIANT EQUILIBRIA 41-46}$

$\text{HCP}_A3 + \text{BCC}_A2 + \text{PHI}$

CREATE_NEW_EQUILIBRIUM 41,1

LABEL A241

CHANGE_STATUS PHASE HCP_A3=FIXED 1
CHANGE_STATUS PHASE BCC_A2=FIXED 1
CHANGE_STATUS PHASE PHI=FIXED 1

SET_CONDITION P=1E5

EXPERIMENT T=1523:15

$\text{LIQUID} + \text{BCC}_A2 + \text{PHI}$

CREATE_NEW_EQUILIBRIUM 42,1

LABEL A242

CHANGE_STATUS PHASE LIQUID=FIXED 1
CHANGE_STATUS PHASE BCC_A2=FIXED 1
CHANGE_STATUS PHASE PHI=FIXED 1

SET_CONDITION P=1E5

EXPERIMENT T=2373:25
$$ \text{LIQUID + PHI + EPSILON} $$
CREATE_NEW_EQUILIBRIUM 43,1
LABEL A243
CHANGE_STATUS PHASE LIQUID=FIXED 1
CHANGE_STATUS PHASE PHI=FIXED 1
CHANGE_STATUS PHASE EPSILON=FIXED 1
SET_CONDITION P=1E5
EXPERIMENT T=2473:15

$$ \text{LIQUID + EPSILON + CHI} $$
CREATE_NEW_EQUILIBRIUM 45,1
LABEL A245
CHANGE_STATUS PHASE LIQUID=FIXED 1
CHANGE_STATUS PHASE EPSILON=FIXED 1
CHANGE_STATUS PHASE CHI=FIXED 1
SET_CONDITION P=1E5
EXPERIMENT T=3123:25

$$ \text{LIQUID + HCP_A3 + CHI} $$
CREATE_NEW_EQUILIBRIUM 46,1
LABEL A246
CHANGE_STATUS PHASE LIQUID=FIXED 1
CHANGE_STATUS PHASE HCP_A3=FIXED 1
CHANGE_STATUS PHASE CHI=FIXED 1
SET_CONDITION P=1E5
EXPERIMENT T=3248:15
$\text{====================}$

$\text{SAVITSKII 1969}$

$\text{====================}$

$\text{$HCP_A3$}$

$\text{TABLE 6100}$

$\text{CREATE\_NEW\_EQUILIBRIUM \_@@\_1}$
$\text{LABEL A9H}$
$\text{CHANGE\_STATUS PHASE *=DORMANT}$
$\text{CHANGE\_STATUS PHASE HCP\_A3=ENTERED 1}$
$\text{SET\_CONDITION P=1E5 X(RE)=\_@1 T=\_@2}$
$\text{EXPERIMENT DGM(LIQUID)<-1E-3:1E-3}$
$\text{EXPERIMENT DGM(HCP\_A3)>-1E-3:1E-3}$
$\text{EXPERIMENT DGM(BCC\_A2)<-1E-3:1E-3}$
$\text{EXPERIMENT DGM(PHI)<-1E-3:1E-3}$
$\text{EXPERIMENT DGM(EPSILON)<-1E-3:1E-3}$
$\text{EXPERIMENT DGM(CHI)<-1E-3:1E-3}$

$\text{TABLE\_VALUES}$
$\text{1.000 1372}$
$\text{1.000 1773}$
$\text{1.000 2381}$
$\text{1.000 3034}$

$\text{TABLE\_END}$

$\text{HCP_A3 + CHI}$

$\text{TABLE 6200}$
CREATE_NEW_EQUILIBRIUM @@,1
LABEL A9HC
CHANGE_STATUS PHASE *=DORMANT
CHANGE_STATUS PHASE HCP_A3=ENTERED 1
CHANGE_STATUS PHASE CHI=ENTERED 1
SET_CONDITION P=1E5 N=1 X(RE)=@1 T=@2
EXPERIMENT DGM(LIQUID)<-1E-3:1E-3
EXPERIMENT DGM(HCP_A3)>-1E-3:1E-3
EXPERIMENT DGM(BCC_A2)<-1E-3:1E-3
EXPERIMENT DGM(PHI)<-1E-3:1E-3
EXPERIMENT DGM(EPSILON)<-1E-3:1E-3
EXPERIMENT DGM(CHI)>-1E-3:1E-3

TABLE_VALUES
0.998 1372
0.996 1372
0.994 1376
0.990 1380
0.985 1383
0.980 1378
0.974 1368
0.958 1366
0.998 1773
0.996 1768
0.994 1772
0.990 1767
0.985 1771
0.980 1775
0.975 1774
0.959 1776
0.997 2363
0.993 2367
0.990 2371
0.985 2365
0.981 2369
0.975 2373
0.959 2375
0.997 3025
0.995 3029
0.991 3024
0.985 3014
0.979 3013
0.975 3026
0.959 3015

TABLE_END

$\textbf{\$\$ ENTHALPIES OF MIXING $\$\$}$

$\textbf{\$\$ ENTHALPIES OF MIXING $\$\$}$

ENTER-SYMBOL FUNCTION BMIX=HMR*0.001-X(RE)*16996.248*0.001
-(1-X(RE))*12373.979*0.001;

ENTER_SYMBOL FUNCTION HMIX=HMR*0.001-X(RE)*(-3.7516933)*0.001
-(1-X(RE))*(-3.8532314)*0.001;
TABLE_HEAD 7100
CREATE_NEW_EQUILIBRIUM @@,1
CHANGE_STATUS PHASE BCC_A2=FIXED 1
SET_CONDITION P=101325 T=298.15 X(BCC_A2,RE)=@1
EXPERIMENT BMIX=@2:10%
LABEL AHMB
TABLE_VALUES
  0.25  -9.820
  0.5   -24.550
  0.75  -25.400
TABLE_END

TABLE_HEAD 7200
CREATE_NEW_EQUILIBRIUM @@,1
CHANGE_STATUS PHASE HCP_A3=FIXED 1
SET_CONDITION P=101325 T=298.15 X(HCP_A3,RE)=@1
EXPERIMENT HMIX=@2:10%
LABEL AHMH
TABLE_VALUES
  0.25   20.350
  0.5    27.220
  0.75   20.800
TABLE_END

SAVE
A.3NI-HF-RE DATABASE FILE

$ Database file written 2011-4-7
$ From database: USER

ELEMENT /- ELECTRON_GAS  0.0000E+00  0.0000E+00  0.0000E+00!
ELEMENT VA  VACUUM  0.0000E+00  0.0000E+00  0.0000E+00!
ELEMENT HF  HCP_A3  1.7849E+02  5.8450E+03  4.3560E+01!
ELEMENT NI  FCC_A1  5.8690E+01  4.7870E+03  2.9796E+01!
ELEMENT RE  HCP_A3  1.8621E+02  5.3555E+03  3.6526E+01!

FUNCTION LIQV1  2.98150E+02 -78757.067; 6.00000E+03 N!
FUNCTION LIQV2  298.15 0.0; 6000.00 N!
FUNCTION LIQV3  2.98150E+02 -13329.186; 6.00000E+03 N!
FUNCTION LIQV4  298.15 0.0; 6000.00 N!
FUNCTION LIQV5  298.15 0.0; 6000.00 N!
FUNCTION LIQV6  298.15 0.0; 6000.00 N!
FUNCTION GHSERNI  2.98140E+02 -5179.159+117.854*T-22.096*T*LN(T)
    -.0048407*T**2; 1.72800E+03 Y
    -27840.655+279.135*T-43.1*T*LN(T)+1.12754E+31*T**(-9); 6.00000E+03 N!
FUNCTION BCCV11  2.98150E+02 -71541; 6.00000E+03 N!
FUNCTION BCCV12  298.15 0.0; 6000.00 N!
FUNCTION BCCV13  2.98150E+02 16011.428; 6.00000E+03 N!
FUNCTION BCCV14  298.15 0.0; 6000.00 N!
FUNCTION BCCV15  298.15 0.0; 6000.00 N!
FUNCTION BCCV16 298.15 0.0; 6000.00 N !

FUNCTION GHSERRE 2.98150E+02 -7695.279+128.421589*T-24.348*T*LN(T) -0.00253505*T**2+1.92818E-07*T**3+32915*T**(-1); 1.20000E+03 Y -15775.998+194.667426*T-33.586*T*LN(T)+.00224565*T**2-2.81835E-07*T**3 +1376270*T**(-1); 2.40000E+03 Y -70882.739+462.110749*T-67.956*T*LN(T)+.01184945*T**2-7.88955E-07*T**3 +18075200*T**(-1); 3.45800E+03 Y +346325.888-1211.37186*T+140.831655*T*LN(T)-.033764567*T**2 +1.053726E-06*T**3-1.34548866E+08*T**(-1); 5.00000E+03 Y -78564.296+346.997842*T-49.519*T*LN(T); 6.00000E+03 N !

FUNCTION GHSERH 2.98150E+02 -6987.297+110.744026*T-22.7075*T*LN(T) -0.004146145*T**2-4.77E-10*T**3-22590*T**(-1); 2.50600E+03 Y -1446776.33+6193.60999*T-787.536383*T*LN(T)+.1735215*T**2 -7.575759E-06*T**3+5.01742495E+08*T**(-1); 3.00000E+03 N !

FUNCTION CHIV61 2.98150E+02 -1568000; 6.00000E+03 N !

FUNCTION CHIV62 298.15 0.0; 6000.00 N !

FUNCTION CHIV65 2.98150E+02 -339900; 6.00000E+03 N !

FUNCTION CHIV66 298.15 0.0; 6000.00 N !

FUNCTION CHIV63 2.98150E+02 -1478000; 6.00000E+03 N !

FUNCTION CHIV64 2.98150E+02 46.764543; 6.00000E+03 N !

FUNCTION CHIV67 2.98150E+02 261100; 6.00000E+03 N !

FUNCTION CHIV68 298.15 0.0; 6000.00 N !

FUNCTION CHIV71 298.15 0.0; 6000.00 N !

FUNCTION CHIV72 298.15 0.0; 6000.00 N !

FUNCTION CHIV75 298.15 0.0; 6000.00 N !

FUNCTION CHIV76 298.15 0.0; 6000.00 N !
FUNCTION CHIV77  298.15 0.0; 6000.00  N !
FUNCTION CHIV78  298.15 0.0; 6000.00  N !
FUNCTION CHIV73  298.15 0.0; 6000.00  N !
FUNCTION CHIV74  298.15 0.0; 6000.00  N !
FUNCTION EPSV41  2.98150E+02  93420;   6.00000E+03   N !
FUNCTION EPSV42  298.15 0.0; 6000.00  N !
FUNCTION EPSV45  2.98150E+02  191400;   6.00000E+03   N !
FUNCTION EPSV46  298.15 0.0; 6000.00  N !
FUNCTION EPSV43  2.98150E+02 -118300;   6.00000E+03   N !
FUNCTION EPSV44  298.15 0.0; 6000.00  N !
FUNCTION EPSV47  2.98150E+02  77460;   6.00000E+03   N !
FUNCTION EPSV48  298.15 0.0; 6000.00  N !
FUNCTION EPSV51  298.15 0.0; 6000.00  N !
FUNCTION EPSV52  298.15 0.0; 6000.00  N !
FUNCTION EPSV55  298.15 0.0; 6000.00  N !
FUNCTION EPSV56  298.15 0.0; 6000.00  N !
FUNCTION EPSV57  298.15 0.0; 6000.00  N !
FUNCTION EPSV58  298.15 0.0; 6000.00  N !
FUNCTION EPSV53  298.15 0.0; 6000.00  N !
FUNCTION EPSV54  298.15 0.0; 6000.00  N !
FUNCTION HCPV21  2.98150E+02  109402.52;   6.00000E+03   N !
FUNCTION HCPV22  298.15 0.0; 6000.00  N !
FUNCTION HCPV23  298.15 0.0; 6000.00  N !
FUNCTION HCPV24  298.15 0.0; 6000.00  N !
FUNCTION HCPV25  298.15 0.0; 6000.00  N !
FUNCTION HCPV26  298.15 0.0; 6000.00  N !
FUNCTION PHIV31    2.98150E+02  -1848000;   6.00000E+03   N !
FUNCTION PHIV32    2.98150E+02  47.092318;   6.00000E+03   N !
function alpV81  298.15 -4e6; 6000 N!
function alpv82 298.15 0.0; 6000.00  N !
function betav91 298.15 -5e6; 6000 N!
function betav92 298.15 0.0; 6000.00  N !
FUNCTION UN_ASS 298.15 0; 300 N !

TYPE_DEFINITION % SEQ *!
DEFINE_SYSTEM_DEFAULT ELEMENT 2 !
DEFAULT_COMMAND DEF_SYS_ELEMENT VA /- !

PHASE LIQUID:L %  1 1.0 !

CONSTITUENT LIQUID:L :HF,NI,RE : !

PARAMETER G(LIQUID,HF;0)  2.98150E+02  +20414.959+99.790933*T
-22.7075*T*LN(T)-.004146145*T**2-4.77E-10*T**3-22590*T**(-1);  1.00000E+03
Y
+49731.499-149.91739*T+12.116812*T*LN(T)-.021262021*T**2
+1.376466E-06*T**3-4449699*T**(-1);  2.50600E+03  Y
-4247.217+265.470523*T-44*T*LN(T);  3.00000E+03  N REF1 !

PARAMETER G(LIQUID,NI;0)  2.98150E+02  +11235.527+108.457*T
-22.096*T*LN(T)-.0048407*T**2-3.82318E-21*T**7;  1.72800E+03  Y
-9549.775+268.598*T-43.1*T*LN(T);  3.00000E+03  N REF1 !

PARAMETER G(LIQUID,RE;0)  2.98150E+02  +16125.604+122.076209*T
\[-24.348 \times T \times \ln(T) - 0.00253505 \times T^2 + 1.92818 \times 10^{-7} \times T^3 + 32915 \times T^2 (-1)\]

1.20000E+03 Y

\[+8044.885 + 188.322047 \times T - 33.586 \times T \times \ln(T) + 0.00224565 \times T^2 - 2.81835 \times 10^{-7} \times T^3 + 1376270 \times T^2 (-1); \quad 2.00000E+03 Y\]

\[+568842.665 - 2527.83846 \times T + 314.178898 \times T \times \ln(T) - 0.08939817 \times T^2\]

+3.92854E-06 \times T^2 - 1.63100987 \times 10^{-7} \times T^3 + 1376270 \times T^2 (-1); \quad 3.45800E+03 Y

\[-39044.888 + 335.723691 \times T - 49.519 \times T \times \ln(T); \quad 6.00000E+03 N \text{ REF1} !\]

PARAMETER G(LIQUID,HF,NI;0) 2.98150E+02 -230010.19 +28.5962765 \times T;

6.00000E+03 N REF0 !

PARAMETER G(LIQUID,HF,NI;1) 2.98150E+02 +58890.2332 -29.5656474 \times T;

6.00000E+03 N REF0 !

PARAMETER G(LIQUID,HF,NI;2) 2.98150E+02 16038.6686; \quad 6.00000E+03 N REF0 !

PARAMETER G(LIQUID,HF,RE;0) 2.98150E+02 +LIQV1# +LIQV2# \times T;

6.00000E+03 N REF0 !

PARAMETER G(LIQUID,HF,RE;1) 2.98150E+02 +LIQV3# +LIQV4# \times T;

6.00000E+03 N REF0 !

PARAMETER G(LIQUID,HF,RE;2) 2.98150E+02 +LIQV5# +LIQV6# \times T;

6.00000E+03 N REF0 !

PARAMETER G(LIQUID,NI,RE;0) 2.98150E+02 16000; \quad 6.00000E+03 N REF0 !

PHASE ALPHA % 350 20 30 !

CONSTITUENT ALPHA : HF : RE : NI : !
PARAMETER G(ALPHA, HF: RE: NI; 0)  2.98150E+02
+50*GHSERHF# +20*GHSERRE#
+30*GHSERNI# + alpV81# + alpV82# * T;  6.00000E+03 N REF0 !

TYPE_DEFINITION & GES A_P_D BCC_A2 MAGNETIC -1.0  4.00000E-01 !
PHASE BCC_A2 %& 2 1 3 !
CONSTITUENT BCC_A2 : HF, NI, RE : VA : !

PARAMETER G(BCC_A2, HF: VA; 0)  2.98150E+02  + 5370.703 + 103.836026*T
-22.8995* T* LN(T) -.004206605*T**2 + 8.71923E-07*T**3 - 22590*T** (-1)
-1.446E-10*T**4; 2.50600E+03 Y
+1912456.77 - 8624.20573*T + 1087.61412*T*LN(T) -.286857065*T**2
+1.3427829E-05*T**3 - 6.10085091E+08*T**(-1); 3.00000E+03 N REF1 !

PARAMETER G(BCC_A2, NI: VA; 0)  2.98150E+02  + 8715.084
-3.556*T + GHSERNI#;
3.00000E+03 N REF0 !

PARAMETER TC(BCC_A2, NI: VA; 0)  2.98150E+02  575;  6.00000E+03 N REF0 !

PARAMETER BMAGN(BCC_A2, NI: VA; 0)  2.98150E+02  .85;  6.00000E+03 N REF0 !

PARAMETER G(BCC_A2, RE: VA; 0)  2.98150E+02  + 9304.721 + 124.721589*T
-24.348*T*LN(T) -.00253505*T**2 + 1.92818E-07*T**3 + 32915*T**(-1);
1.20000E+03 Y
+1224.002 + 190.967426*T - 33.586*T*LN(T) + .00224565*T**2 - 2.81835E-07*T**3
+1376270*T**(-1); 2.40000E+03 Y
-53882.739 + 458.410749*T - 67.956*T*LN(T) + .01184945*T**2 - 7.88955E-07*T**3
+18075200*T**(-1); 3.45800E+03 Y
+363325.888-1215.07186*T+140.831655*T*LN(T)-0.033764567*T**2
+1.053726E-06*T**3-1.34548866E+08*T**(-1); 5.00000E+03 Y
-61564.296+343.297842*T-49.519*T*LN(T); 6.00000E+03 N REF1!
PARAMETER G(BCC_A2, HF, NI; VA; 0) 2.98150E+02 -99329.7828+10.9654735*T;
6.00000E+03 N REF0!
PARAMETER G(BCC_A2, HF, NI; VA; 1) 2.98150E+02 -62642.8401+12.5916137*T;
6.00000E+03 N REF0!
PARAMETER G(BCC_A2, HF, RE; VA; 0) 2.98150E+02 +BCCV11#+BCCV12#*T;
6.00000E+03 N REF0!
PARAMETER G(BCC_A2, HF, RE; VA; 1) 2.98150E+02 +BCCV13#+BCCV14#*T;
6.00000E+03 N REF0!
PARAMETER G(BCC_A2, HF, RE; VA; 2) 2.98150E+02 +BCCV15#+BCCV16#*T;
6.00000E+03 N REF0!

PHASE BETA % 3 25 70 5 !
CONSTITUENT BETA : RE : HF : NI : !

PARAMETER G(BETA, RE: HF: NI; 0) 2.98150E+02
+70*GHSERHF#+25*GHSERRE#
+5*GHSERNI#+betaV91#+betaV92#*T; 6.00000E+03 N REF0!

PHASE CHI % 3 24 10 24 !
PARAMETER G(CHI,RE:HF:HF;0) 2.98150E+02
+24*GHSERRE#+10*GHSERHF#
+24*GHSERHF#+CHIV61#+CHIV62#*T; 6.00000E+03 N REF0!

PARAMETER G(CHI,RE:RE:HF;0) 2.98150E+02
+24*GHSERRE#+10*GHSERHF#
+24*GHSERHF#+CHIV65#+CHIV66#*T; 6.00000E+03 N REF0!

PARAMETER G(CHI,RE:HF:RE;0) 2.98150E+02
+24*GHSERRE#+10*GHSERHF#
+24*GHSERRE#+CHIV63#+CHIV64#*T; 6.00000E+03 N REF0!

PARAMETER G(CHI,RE:RE:RE;0) 2.98150E+02
+24*GHSERRE#+10*GHSERRE#
+24*GHSERRE#+CHIV67#+CHIV68#*T; 6.00000E+03 N REF0!

PARAMETER G(CHI,RE:HF,RE:HF;0) 2.98150E+02 +CHIV71#+CHIV72#*T;
6.00000E+03 N REF0!

PARAMETER G(CHI,RE:HF,RE:HF;0) 2.98150E+02 +CHIV75#+CHIV76#*T;
6.00000E+03 N REF0!

PARAMETER G(CHI,RE:RE:HF,RE;0) 2.98150E+02 +CHIV77#+CHIV78#*T;
6.00000E+03 N REF0!

PARAMETER G(CHI,RE:HF,RE:RE;0) 2.98150E+02 +CHIV73#+CHIV74#*T;
6.00000E+03 N REF0!

PHASE EPSILON % 2 1 2!

CONSTITUENT EPSILON :HF,RE :HF,RE:

PARAMETER G(EPSILON,HF:HF;0) 2.98150E+02
+GHSERHF#+2*GHSERHF#+EPSV41#
PARAMETER G(EPSILON,RE;HF) 2.98150E+02  +GHSERRE#+2*GHSERHF#+EPSV45#
+EPSV46#*T; 6.00000E+03   N REF0 !

PARAMETER G(EPSILON,HF;RE) 2.98150E+02  +GHSERHF#+2*GHSERRE#+EPSV43#
+EPSV44#*T; 6.00000E+03   N REF0 !

PARAMETER G(EPSILON,RE;RE) 2.98150E+02  +GHSERRE#+2*GHSERRE#+EPSV47#
+EPSV48#*T; 6.00000E+03   N REF0 !

PARAMETER G(EPSILON,HF,RE;HF) 2.98150E+02  +EPSV51#+EPSV52#*T;
6.00000E+03   N REF0 !

PARAMETER G(EPSILON,HF;HF,RE) 2.98150E+02  +EPSV55#+EPSV56#*T;
6.00000E+03   N REF0 !

PARAMETER G(EPSILON,RE;HF,RE) 2.98150E+02  +EPSV57#+EPSV58#*T;
6.00000E+03   N REF0 !

PARAMETER G(EPSILON,RE;RE) 2.98150E+02  +EPSV53#+EPSV54#*T;
6.00000E+03   N REF0 !

TYPE_DEFINITION 'GES_A_P_D FCC_A1 MAGNETIC -3.0  2.80000E-01 !
PHASE FCC_A1  %' 2 1 1 !

CONSTITUENT FCC_A1 :HF,NI,RE : VA : !

PARAMETER G(FCC_A1,HF;VA) 2.98150E+02  +10000-2.2*T+GHSERHF#;
3.00000E+03   N REF0 !
PARAMETER G(FCC_A1,NI:VA;0) 2.98150E+02 +GHSERNI#; 3.00000E+03 N REF1 !
PARAMETER TC(FCC_A1,NI:VA;0) 2.98150E+02 633; 3.00000E+03 N REF0 !
PARAMETER BMAGN(FCC_A1,NI:VA;0) 2.98150E+02 .52; 3.00000E+03 N REF0 !
PARAMETER G(FCC_A1,RE:VA;0) 2.98150E+02 +3304.721+126.921589*T -24.348*T*LN(T) -.00253505*T**2+1.92818E-07*T**3+32915*T**(1);
1.20000E+03 Y
-4775.998+193.167426*T-33.586*T*LN(T)+.00224565*T**2-2.81835E-07*T**3 +1376270*T**(1); 2.40000E+03 Y
-59882.739+460.610749*T-67.956*T*LN(T)+.01184945*T**2-7.88955E-07*T**3 +18075200*T**(1); 3.45800E+03 Y
+357325.888-1212.87186*T+140.831655*T*LN(T)-.033764567*T**2 +1.053726E-06*T**3-1.34548866E+08*T**(1); 5.00000E+03 Y
-67564.296+345.497842*T-49.519*T*LN(T); 6.00000E+03 N REF1 !
PARAMETER G(FCC_A1,HF,NI:VA;0) 2.98150E+02 -113714.179+11.3117721*T;
6.00000E+03 N REF0 !
PARAMETER G(FCC_A1,HF,NI:VA;1) 2.98150E+02 36184.8998; 6.00000E+03 N REF0 !
PARAMETER G(FCC_A1,NI,RE:VA;0) 2.98150E+02 +27426.512-2.44*T;
6.00000E+03 N REF0 !
PARAMETER G(FCC_A1,NI,RE:VA;1) 2.98150E+02 -16906.701; 6.00000E+03 N REF0 !

TYPE_DEFINITION ( GES A_P_D HCP_A3 MAGNETIC -3.0 2.80000E-01 !
PHASE HCP_A3 % ( 2 1 .5 !

CONSTITUENT HCP_A3 : HF, NI, RE : VA : !

PARAMETER G(HCP_A3, HF: VA; 0) 2.98150E+02 + GHSERHF#; 3.00000E+03 N REF1 !

PARAMETER G(HCP_A3, NI: VA; 0) 2.98150E+02 - 4133.159 + 119.109*T
-22.096*T*LN(T) - 0.048407*T**2; 1.72800E+03 Y
-26794.655 + 280.39*T - 43.1*T*LN(T) + 1.12754E+31*T**(9); 3.00000E+03 N REF1 !

PARAMETER TC(HCP_A3, NI: VA; 0) 2.98150E+02 633; 3.00000E+03 N REF0 !

PARAMETER BMAGN(HCP_A3, NI: VA; 0) 2.98150E+02 .52; 3.00000E+03 N REF0 !

PARAMETER G(HCP_A3, RE: VA; 0) 2.98150E+02 + GHSERRE#; 6.00000E+03 N REF1 !

PARAMETER G(HCP_A3, HF, NI: VA; 0) 2.98150E+02 - 73978.6842; 6.00000E+03 N REF0 !

PARAMETER G(HCP_A3, HF, RE: VA; 0) 2.98150E+02 + HCPV21# + HCPV22#*T; 6.00000E+03 N REF0 !

PARAMETER G(HCP_A3, HF, RE: VA; 1) 2.98150E+02 + HCPV23# + HCPV24#*T; 6.00000E+03 N REF0 !

PARAMETER G(HCP_A3, HF, RE: VA; 2) 2.98150E+02 + HCPV25# + HCPV26#*T; 6.00000E+03 N REF0 !

PARAMETER G(HCP_A3, NI, RE: VA; 0) 2.98150E+02 + 12396.421 + 7.9925127*T; 6.00000E+03 N REF0 !
PHASE NI10HF7  %  2.588235 .411765 !

CONSTITUENT NI10HF7 :NI : HF : !

PARAMETER G(NI10HF7,NI;HF;0) 2.98150E+02 -50154.0373+.740813752*T
+.411765*GHSERHF#+.588235*GHSERNI#; 6.00000E+03 N REF0 !

PHASE NI11HF9  %  2.55 .45 !

CONSTITUENT NI11HF9 :NI : HF : !

PARAMETER G(NI11HF9,NI;HF;0) 2.98150E+02 -51243.393+.614729857*T
+.45*GHSERHF#+.55*GHSERNI#; 6.00000E+03 N REF0 !

PHASE NI1HF1  %  2.5 .5 !

CONSTITUENT NI1HF1 :NI : HF : !

PARAMETER G(NI1HF1,NI;HF;0) 2.98150E+02 -49117.6514-1.43327056*T
+.5*GHSERHF#+.5*GHSERNI#; 6.00000E+03 N REF0 !

PHASE NI1HF1L  %  2.5 .5 !

CONSTITUENT NI1HF1L :NI : HF : !

PARAMETER G(NI1HF1L,NI;HF;0) 2.98150E+02 -52117.6514+.67495151*T
+.5*GHSERHF#+.5*GHSERNI#; 6.00000E+03 N REF0 !
PHASE NI1HF2  %  2 1 2 !

  CONSTITUENT NI1HF2 :NI%,VA : HF : !

PARAMETER G(NI1HF2,NI:HF;0)  2.98150E+02 -111302.197-5.81965736*T
+GHSERNI#+2*GHSERHF#;   6.00000E+03   N REF0 !
PARAMETER G(NI1HF2,VA:HF;0)  2.98150E+02 +2*GHSERHF#+39000-3.9*T;
6.00000E+03   N REF0 !
PARAMETER G(NI1HF2,NI,VA:HF;0)  2.98150E+02 -2104.49252;   6.00000E+03
N REF0 !

PHASE NI21HF8  %  2 .724138  .275862 !

  CONSTITUENT NI21HF8 :NI : HF : !

PARAMETER G(NI21HF8,NI:HF;0)  2.98150E+02 -42761.5317+.771832971*T
+.275862*GHSERHF#+.724138*GHSERNI#;   6.00000E+03   N REF0 !

PHASE NI3HF1  %  2 .75  .25 !

  CONSTITUENT NI3HF1 :NI : HF : !

PARAMETER G(NI3HF1,NI:HF;0)  2.98150E+02 -43001.1555+2.10098324*T
+.25*GHSERHF#+.75*GHSERNI#;   6.00000E+03   N REF0 !
PHASE NI3HF1L % 2.75 .25 !
CONSTITUENT NI3HF1L :NI : HF : !

PARAMETER G(NI3HF1L,NI:HF;0) 2.98150E+02 -46001.1555+4.13764312*T
+.25*GHSERHF#+.75*GHSERNI#;  6.00000E+03  N REF0 !

PHASE NI5HF1 % 2.833333 .166667 !
CONSTITUENT NI5HF1 :NI : HF : !

PARAMETER G(NI5HF1,NI:HF;0) 2.98150E+02 -38701.9491+6.49620875*T
+.166667*GHSERHF#+.833333*GHSERNI#;  6.00000E+03  N REF0 !

PHASE NI7HF2 % 2.777778 .222222 !
CONSTITUENT NI7HF2 :NI : HF : !

PARAMETER G(NI7HF2,NI:HF;0) 2.98150E+02 -43526.1566+3.7884212*T
+.222222*GHSERHF#+.777778*GHSERNI#;  6.00000E+03  N REF0 !

PHASE NI7HF3 % 2.7 .3 !
CONSTITUENT NI7HF3 :NI : HF : !

PARAMETER G(NI7HF3,NI:HF;0) 2.98150E+02 -44384.9972+.838752799*T
+0.3*GHSERHF#+.7*GHSERNI#; 6.00000E+03 N REF0!

PHASE PHI % 2 21 25!

CONSTITUENT PHI :HF :RE :!

PARAMETER G PHI,HF:RE;0) 2.98150E+02
+21*GHSERHF#+25*GHSERRE#+PHIV31#
+PHIV32#*T; 6.00000E+03 N REF0!

LIST_OF_REFERENCES

NUMBER SOURCE

REF1 'PURE4 - SGTE Pure Elements (Unary) Database (Version 4.6),
developed by SGTE (Scientific Group Thermodata Europe), 1991-2008,
and provided by TCSAB (Jan. 2008).'

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EDUCATION
Schreyer Honors College at Pennsylvania State University, University Park, PA
♦ M.S. in Materials Science and Engineering (Metallurgy) May 2011
♦ B.S. in Materials Science and Engineering (Metallurgy) May 2011
♦ Thesis title: “First-principles calculations and CALPHAD modeling of the Hf-Re-Ni ternary system”

INTERNSHIP EXPERIENCE
Allegheny Ludlum, Vandergrift, PA summer 2010
♦ Production quality of hot rolled and cold rolled anneal and pickle lines

RESEARCH EXPERIENCE
Phase Research Laboratory under Dr. Zi-Kui Liu, PSU 2007 – present
♦ First-principles calculations and CALPHAD modeling of Hf-Re-Ni for Ni-base superalloy database
Changsha, China summer 2009
♦ State Key Lab of Powder Metallurgy, Central South University (CSU)
♦ Thermodynamic modeling and first-principles calculations of Hf-Re
Shanghai, China fall 2008
♦ Shanghai Institute of Ceramics Chinese Academy of Sciences
♦ International Internship in Materials (IIM) program at
♦ Thin film deposition of storage phosphor on X-ray imaging plates for computed radiography

COMPUTER AND FOREIGN LANGUAGE SKILLS
Proficiency in Microsoft Office, ThermoCalc (thermodynamic modeling software), and SSH
Native speaker of Mandarin Chinese and Shanghainese (a dialect of Shanghai, China)

ACTIVITIES
Vice President of MatSE Student Advisory Committee 2009 – present
Keramos 2007 – present
Materials Advantage Club 2006 – present
Social Chair of Ballroom Dance Club 2006 – present
♦ Plan and coordinate social events
♦ Competes at the Silver level in five international standard dances and four Latin dances