

Thermodynamic Assessment of the Ru-Zr Binary System

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The Ru-Zr system has been assessed by means of the Calphad approach. The solution phases (Liquid, (Ru), (α Zr) and (β Zr)) were modeled with the sublattice formalism and the excess term of the Gibbs energy with the Redlich-Kister equation. The intermetallic compounds Ru₂Zr and RuZr, which have homogeneity ranges, were treated as the formula (Ru,Zr)_{0.667}(Ru,Zr)_{0.333} and (Ru,Zr)_{0.5}(Ru,Zr)_{0.5} by a two-sublattice model with a mutual substitution of Ru and Zr on both sublattices. The calculated phase diagram and the thermodynamic properties of the system are in satisfactory agreement with the experimental data.

Keywords Calphad method, phase diagram, Ru-Zr system, thermodynamic assessment

1. Introduction

The phase diagram of the Ru-Zr system was investigated by Raub and Röschel^[1] then by Eremenko et al.^[2,3] using metallography, x-ray diffraction, and differential thermal analysis.

The recent evaluation performed by Okamoto^[4] is shown in Fig. 1.

The equilibrium phases include: (1) the liquid, L; (2) two intermediate phases Ru₂Zr and RuZr; and (3) the three terminal solid solutions (Ru), (α Zr) and (β Zr).

This present work deals with an assessment of the thermodynamic description of the Ru-Zr system using the CALPHAD technique^[5]. In this method, the thermodynamic models for the Gibbs energy of all the individual phases are studied using the Parrot module in the Thermo-Calc Software package^[6]. The thermodynamic parameters involved in the models are optimized from the experimental thermodynamic and phase diagram data.

2. Thermodynamic Data

Many authors determined the enthalpies of formation for the intermetallic compounds of the Ru-Zr system; the results are collected in Table 1. Topor and Kleppa^[8] measured the standard enthalpy of formation of RuZr using the solute-solvent drop method. Watson et al.^[10] employed the Linear

Augmented Slater-Type Orbitals (LASTO) band calculations. Furthermore de Boer et al.^[11] and Colinet et al.^[9] calculated by a semiempirical model the enthalpies of formation of RuZr and Ru₂Zr.

More recently, Mahdouk et al.^[7] measured the enthalpies of formation of RuZr and Ru₂Zr by a calorimetric method and attempted to assess the phase diagram using the software NancyUn elaborated by Charles^[14]. This routine is less powerful than the Thermocalc software because it took into account only the liquid and the intermetallic phases and the terminal solid solutions (Ru), (α Zr) and (β Zr) were not modeled. In the assessment by Mahdouk et al.^[7] no invariant reaction appears on the Zr rich side. In addition, the Ru₂Zr phase was considered as stoichiometric. It was therefore necessary to completely optimize the Ru-Zr system under a pressure $P = 10^5$ Pa.

The crystal structures of the various phases of the Ru-Zr system are reported in Table 2.

3. Thermodynamic Models

3.1 Unary Phases

The Gibbs energy function $G_i^\phi(T) = {}^0G_i^\phi - H_i^{\text{SER}}$ (298.15 K) for the element i (i =Ru, Zr) in the phase ϕ (ϕ = Liquid, BCC_A2, or HCP_A3) is described by an equation of the following form:

$$G_i^\phi(T) = a + bT + cT \ln T + dT^2 + eT^3 + fT^7 + gT^{-1} + hT^{-9} \quad (\text{Eq 1})$$

where H_i^{SER} (298.15 K) is the molar enthalpy of the element i at 298.15 K in its standard element reference (SER) state, HCP_A3 (hcp) for Ru and Zr.

In this paper, the Gibbs energy functions are taken from the SGTE compilation by Dinsdale^[15].

3.2 Solution Phases

The solution phases (Liquid, (α Zr), (β Zr) and (Ru)), were modeled as substitutional solutions. The Gibbs energy

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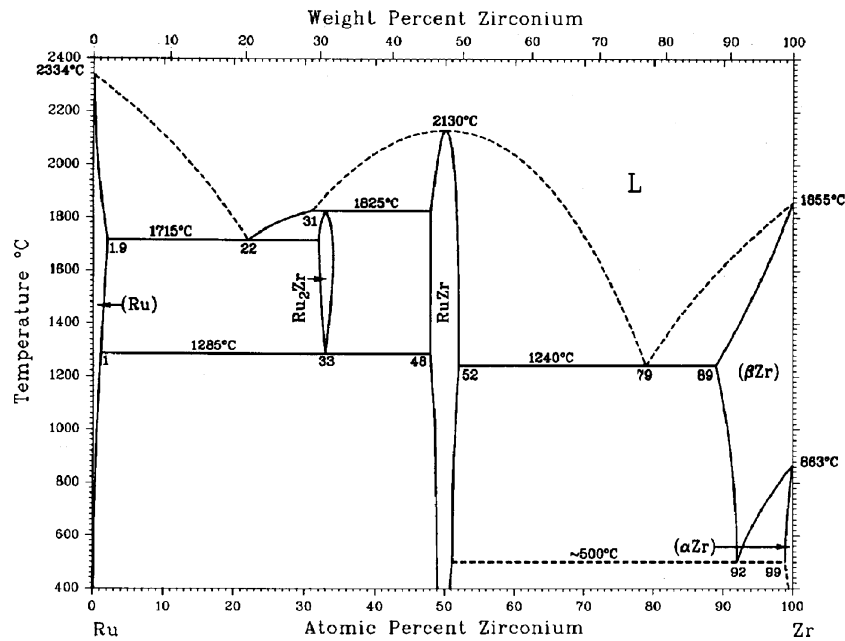


Fig. 1 The Ru-Zr phase diagram evaluated by Okamoto^[4]

Table 1 Calculated and measured enthalpies of formation of the intermetallic compounds

| Phase | Enthalpy of formation, kJ/mol.at | Technique used | T, K | Reference |
|--------------------|----------------------------------|---------------------------|------|-----------|
| RuZr | -55.8 ± 2.3 | Calorimetry | 1753 | [7] |
| | -68.65 ± 2.5 | Calorimetry | 298 | [8] |
| | -53 | Calculation | | [9] |
| | -61 | Calculation | | [10] |
| | -88 | Calculation | | [11] |
| | -68.7 | Calorimetry | 298 | [12] |
| | -88 | Calculation | | [13] |
| Ru ₂ Zr | -55.8 | Optimization | | [7] |
| | -55.95 | Optimization ^a | 1753 | This work |
| | -32 ± 0.9 | Calorimetry | 1743 | [7] |
| | -49 | Calculation | | [9] |
| | -78 | Calculation | | [11] |
| | -32.08 | Optimization | | [7] |
| | -31.97 | Optimization ^b | 1743 | This work |

The reference states were:

^aRu hcp_A3 T = 1753 K and Zr bcc_A2 T = 1753 K

^bRu hcp_A3 T = 1743 K and Zr bcc_A2 T = 1743 K

of one mole of formula unit of phase ϕ is expressed as the sum of the reference part ${}^{\text{ref}}G^\phi$, the ideal part ${}^{\text{id}}G^\phi$, and the excess part ${}^{\text{xs}}G^\phi$:

$$G_m^\phi = {}^{\text{ref}}G^\phi + {}^{\text{id}}G^\phi + {}^{\text{xs}}G^\phi \quad (\text{Eq 2})$$

As used in the Thermo-calc software:^[6]

$${}^{\text{ref}}G^\phi(T) = ({}^0G_{\text{Ru}}^\phi(T) - H_{\text{Ru}}^{\text{SER}}(298.15))x_{\text{Ru}} + ({}^0G_{\text{Zr}}^\phi(T) - H_{\text{Zr}}^{\text{SER}}(298.15))x_{\text{Zr}} \quad (\text{Eq 3})$$

$${}^{\text{id}}G^\phi = RT(x_{\text{Ru}} \ln x_{\text{Ru}} + x_{\text{Zr}} \ln x_{\text{Zr}}) \quad (\text{Eq 4})$$

where R is the gas constant; T is temperature, in Kelvin; x_{Ru} and x_{Zr} are the mole fraction of elements Ru and Zr, respectively.

The excess terms of all the solution phases were modeled by the Redlich-Kister^[16] formula.

$${}^{\text{xs}}G_m^\phi(T) = x_{\text{Ru}}x_{\text{Zr}}({}^0L_{\text{Ru,Zr}}^\phi(T) + {}^1L_{\text{Ru,Zr}}^\phi(T)(x_{\text{Ru}} - x_{\text{Zr}}) + {}^2L_{\text{Ru,Zr}}^\phi(T)(x_{\text{Ru}} - x_{\text{Zr}})^2 + \dots) \quad (\text{Eq 5})$$

$$\text{with } {}^iL_{\text{Ru,Zr}}^\phi(T) = a_i + b_iT \quad (\text{Eq 6})$$

Table 2 Symbols and crystal structures of the stable solid phases in the Ru-Zr binary system^[4]

| Diagram symbol | Composition at.% Zr | Pearson symbol | Strukturbericht designation | Symbol used in the Thermo-calc data file | Prototype |
|--------------------|---------------------|----------------|-----------------------------|--|-------------------|
| (Ru) | 0-1.9 | hP2 | A3 | HCP_A3 | Mg |
| (β Zr) | 89-100 | C12 | A2 | BCC_A2 | W |
| (α Zr) | 99-100 | hP2 | A3 | HCP_A3 | Mg |
| Ru ₂ Zr | 32-34 | hP12 | C14 | Ru ₂ Zr | MgZn ₂ |
| RuZr | 48-52 | cP2 | B2 | RuZr | CsCl |

where $iL_{Ru,Zr}^\phi(T)$ is the i th interaction parameter between the elements Ru and Zr, which is evaluated in the present work. The coefficients a_i and b_i are optimized using the PARROT module^[6].

3.3 Intermediate Phases with Homogeneity Ranges

The Ru₂Zr phase is a C14 Laves phase, isotypic with MgZn₂ while the RuZr phase is a B2 phase isotypic with CsCl. Both intermetallic compounds have homogeneity ranges, and were treated as (Ru%,Zr)_m(Ru,Zr%)_n by a two-sublattice model. The symbol % denotes the major component in the corresponding sublattice. The Gibbs energy function per mole (m) of the formula unit (Ru,%)_m(Zr,%)_n is the following:

$$G^{(Ru\%,Zr)_m(Ru,Zr\%)_n} - H_{(Ru\%,Zr)_m(Ru,Zr\%)_n}^{SER} = y_{Ru}^1 y_{Ru}^2 {}^0G^{Ru_mRu_n} + y_{Ru}^1 y_{Zr}^2 {}^0G^{Ru_mZr_n} + y_{Zr}^1 y_{Ru}^2 {}^0G^{Zr_mRu_n} + y_{Zr}^1 y_{Zr}^2 {}^0G^{Zr_mZr_n} + RT[(m(y_{Ru}^1 \ln y_{Ru}^1 + y_{Zr}^1 \ln y_{Zr}^1) + n(y_{Ru}^2 \ln y_{Ru}^2 + y_{Zr}^2 \ln y_{Zr}^2))] + {}^{xs}G_m^{Ru_mZr_n} \quad (Eq 7)$$

where y_{Ru}^1 and y_{Zr}^1 denote the site fractions of Ru and Zr in the first sublattice, y_{Ru}^2 and y_{Zr}^2 the site fractions of Ru and Zr in the second sublattice, ${}^0G^{Ru_mRu_n}$, ${}^0G^{Zr_mRu_n}$, and ${}^0G^{Zr_mZr_n}$

are the Gibbs energies of the hypothetical compounds Ru_mRu_n, Zr_mRu_n and Zr_mZr_n respectively. ${}^0G^{Ru_mZr_n}$ is the Gibbs energy of the stoichiometric compound Ru_mZr_n.

$$H_m^{SER} = (m y_{Ru}^1 + n y_{Ru}^2) H_{Ru}^{SER} + (m y_{Zr}^1 + n y_{Zr}^2) H_{Zr}^{SER} \quad (Eq 8)$$

${}^{xs}G_m^{Ru_mZr_n}$ is the excess Gibbs energy expressed by the following expression:

$${}^{xs}G_m^{Ru_mZr_n} = y_{Ru}^1 y_{Zr}^1 (y_{Ru}^2 L_{Ru,Zr:Ru}^{Ru_mZr_n} + y_{Zr}^2 L_{Ru,Zr:Zr}^{Ru_mZr_n}) + y_{Ru}^2 y_{Zr}^2 (y_{Ru}^1 L_{Ru,Zr:Ru}^{Ru_mZr_n} + y_{Zr}^1 L_{Ru,Zr:Zr}^{Ru_mZr_n}) \quad (Eq 9)$$

where $L_{Ru,Zr:k}^{Ru_mZr_n}$ and $L_{k:Ru,Zr}^{Ru_mZr_n}$ represent the interaction parameters between the elements Ru and Zr in the related sublattice while the other sublattice is occupied only by the element k (k = Ru and Zr). These excess parameters are temperature dependent as:

$$a + bT. \quad (Eq 10)$$

For both intermetallic compounds, the Wagner-Schottky law^[17] was applied as follows:

$${}^0G^{Zr_mRu_n} = -{}^0G^{Ru_mZr_n} + {}^0G^{Ru_mRu_n} + {}^0G^{Zr_mZr_n} \quad (Eq 11)$$

In order that the hypothetical compounds Ru_mRu_n and Zr_mZr_n do not appear in the calculated phase diagram, the values +5000 and +20,000 J/mol of atoms, determined by trial and error, were added respectively to GHSERRu and GHSERZr for the RuZr compound:

Table 3 The optimized thermodynamic parameters of the Ru-Zr system

| Phase | Thermodynamic model | Parameters, J/mol.at |
|--------------------|--|---|
| Liquid | (Ru,Zr) | ${}^0L^{Liquid} = -192961.176 + 51.5461T$ ${}^1L^{Liquid} = -15154.6422 + 9.7998T$ ${}^2L^{Liquid} = -1813.2556$ |
| HCP_A3 | (Ru,Zr) ₁ (Va) [*] _{0.5} | ${}^0L^{HCP_A3} = -75308.0512 + 18.0703T$ ${}^1L^{HCP_A3} = -16666.7787 + 23.9292T$ |
| BCC_A2 | (Ru,Zr) (Va) ₃ (Ru) _{0.667} (Zr) _{0.333} (Ru) _{m=0.667} (Zr) _{n=0.333} | ${}^0L^{BCC_A2} = -166924.853 + 54.0292T$ |
| Ru ₂ Zr | | $G^{Ru_2Zr}_{Ru:Ru} - H^{HCP_A3}_{Ru} = 25000 + GHSER_{Ru}$ $G^{Ru_2Zr}_{Zr:Ru} - 0.333H^{HCP_A3}_{Ru} - 0.667H^{HCP_A3}_{Zr} = 100000 + 0.667 GHSER_{Zr} + 0.333 GHSER_{Ru} + 32060.9974 - 3.4010T$ $G^{Ru_2Zr}_{Ru:Zr} - 0.667H^{HCP_A3}_{Ru} - 0.333H^{HCP_A3}_{Zr} = +0.667 GHSER_{Ru} + 0.333 GHSER_{Zr} - 32060.9974 + 3.4010T$ $G^{Ru_2Zr}_{Zr:Zr} - H^{HCP_A3}_{Zr} = 75000 + GHSER_{Zr}$ ${}^0L^{Ru_2Zr}_{Ru:Ru,Zr} = -2324.1750T + 37.3348T$ ${}^0L^{Ru_2Zr}_{Ru,Zr:Ru} = -11790.5369$ |
| RuZr | (Ru) _{0.5} (Zr) _{0.5} (Ru) _{m=0.5} (Zr) _{n=0.5} | $G^{RuZr}_{Ru:Ru} - H^{HCP_A3}_{Ru} = 5000 + GHSER_{Ru}$ $G^{RuZr}_{Zr:Ru} - 0.5H^{HCP_A3}_{Ru} - 0.5H^{HCP_A3}_{Zr} = 25000 + .5G^{HSER}_{Zr} + .5G^{HSER}_{Ru} + 56149.5077 - 10.3112T$ $G^{RuZr}_{Ru:Zr} - 0.5H^{HCP_A3}_{Ru} - 0.5H^{HCP_A3}_{Zr} = +.5G^{HSER}_{Ru} + .5G^{HSER}_{Zr} - 56149.5077 + 10.3112T$ $G^{RuZr}_{Zr:Zr} - H^{HCP_A3}_{Zr} = 20000 + GHSER_{Zr}$ ${}^0L^{RuZr}_{Ru:Ru,Zr} = 250000$ ${}^0L^{RuZr}_{Ru,Zr:Ru} = -199.1429 + 10.6789T$ |

* (Va) for vacancy

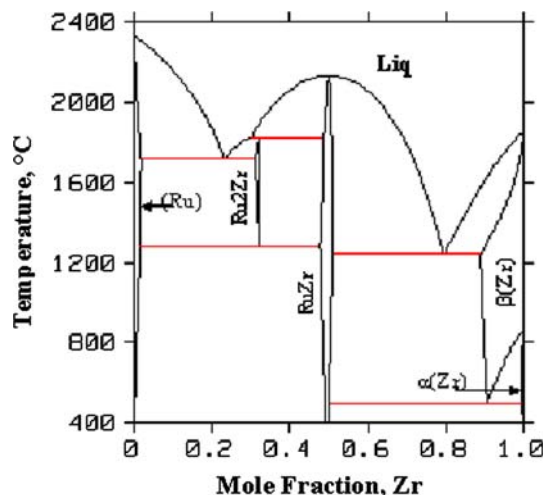


Fig. 2 Ru-Zr calculated phase diagram

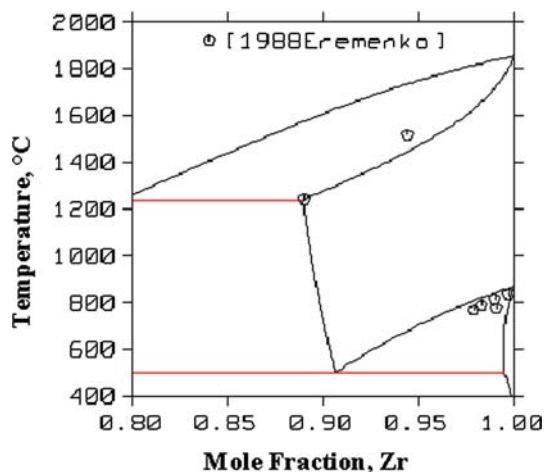


Fig. 5 Ru-Zr calculated phase diagram and data issued from literature in the Zr-rich side

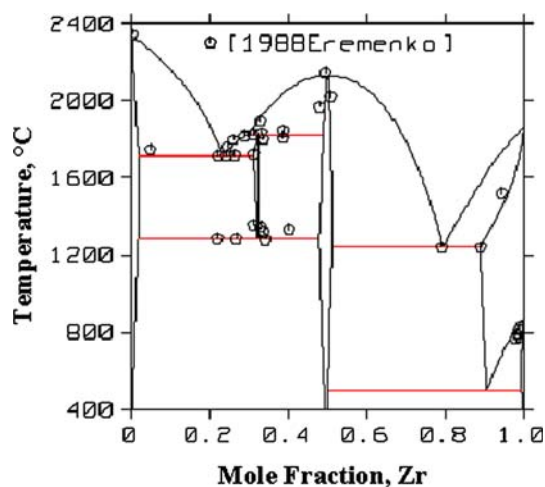


Fig. 3 Comparison of the Ru-Zr calculated phase diagram with the experimental data

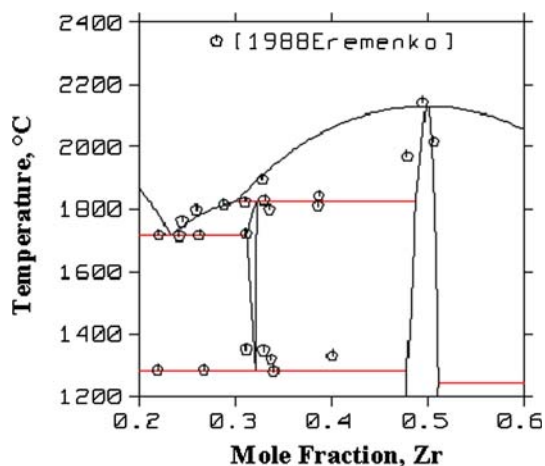


Fig. 4 Enlargement of the Ru-rich part of the phase diagram with the experimental data

$${}^0G^{\text{Ru}_m\text{Ru}_n} = \text{GHSERRu} + 5000 \text{ and } {}^0G^{\text{Zr}_m\text{Zr}_n} = \text{GHSERZr} + 20,000 \quad (\text{Eq 12})$$

In the case of the Ru_2Zr compound having a different crystal structure compared to that of the RuZr compound, more positive additional values +25,000 and +75,000 J/mol of atoms were necessary to avoid the formation of the hypothetical compounds, see Table 2.

$${}^0G^{\text{Ru}_m\text{Ru}_n} = \text{GHSERRu} + 25,000 \text{ and } {}^0G^{\text{Zr}_m\text{Zr}_n} = \text{GHSERZr} + 75,000 \quad (\text{Eq 13})$$

4. Assessment Procedure

The thermodynamic optimization of the Gibbs energy parameters is an application of the CALPHAD method^[5] with the PARROT module of the Thermochemical software^[6].

This program is able to evaluate the thermochemical model parameters from experimental observations and quantities describing a set of equilibrium states of the system. Each of the selected data values is given a certain weight, which is chosen and adjusted based on the data uncertainties given experimentally. The criterion for the best optimization fit is the minimum in the sum of the square of weighted residuals.

Most of the experimental data mentioned in Section 2 were used for the optimization of the thermodynamic parameters. The compositions of the phases involved in the invariant reactions are mainly based on the phase diagram of the Ru-Zr system evaluated by Okamoto^[4]. For the intermetallic compounds (Ru_2Zr and RuZr), the interaction parameters of Eq 9 and ${}^0G^{\text{Ru}_m\text{Zr}_n}$ and ${}^0G^{\text{Zr}_m\text{Ru}_n}$, Eq 7 were adjusted according to the enthalpies of formation measured by Mahdoui et al.^[7] We chose the Mahdoui's data because he determined the values for both intermetallic compounds leading to an expectation of coherency. For the liquid and the solid solutions, the a_i and b_i parameters in Eq 6 were

determined by considering the phase diagram data evaluated by Okamoto^[4] and thermodynamic data. All the optimized parameters are given in Table 3.

5. Results and Discussion

The calculated phase diagram shown in Fig. 2 is compared with the experimental data in Fig. 3-5. A satisfactory general agreement is noted. The temperatures and the phase compositions involved in the invariant reactions in the Ru-Zr system, listed in Table 4, are compared with the experimental results from Okamoto's evaluation^[4] of published data. They are in very good agreement. The homogeneity range of the two intermetallic compounds fits well with the experimental data of Eremenko et al.^[3]. Indeed the homogeneity range of Ru₂Zr is slightly shifted to the Ru-rich side of the stoichiometry and the maximum of homogeneity range of RuZr is about

4 at.%. The congruent melting of RuZr calculated at 2131K and $x(\text{Zr}) = 0.5$ is in very good agreement with the experimental data of Eremenko et al.^[3] (2128 K and $x(\text{Zr}) = 0.494$). The measured and calculated enthalpies of formation of the intermetallic compounds, collected in Table 1, are also presented in Fig. 6. In the case of the RuZr compound, the agreement is good with the experimental data of Mahdouk et al.^[7] and with the calculation of Colinet et al.^[9]. For the Ru₂Zr compound, the data available in the literature are dispersed and our optimized value is in good agreement with the experimental data of Mahdouk^[7].

In order to check that the optimized thermodynamic parameters of the intermetallic compounds are satisfactory we verified that, when the liquid phase is suspended during the calculation of the Ru-Zr phase diagram, these two compounds are no more stable at very high temperatures. Due to the different crystal structure of the elements Ru (hcp) and Zr (bcc), the stable phases at these high temperatures, a single phase domain hcp_A3 (Ru) in the Ru rich side, then a two-phase domain (hcp_A3 (Ru) + bcc_A2 (Zr)) and a single domain bcc_A2 (Zr) in the Zr rich side are expected to be calculated when the mole fraction of Zr increases from 0 to unity. It will be noted that the power series in terms of temperature of the Gibbs energy, in the form of G-HSER, of the elements Ru and Zr are respectively defined up to 4500 and 4000 K in^[15]. If we calculate the Ru-Zr phase diagram at higher temperatures, from 4274 to 6000 K, for Ru the molar Gibbs energy of the bcc_A2 phase becomes a little bit more negative than the one of the hcp_A3 phase (for example at $T=4275$ K, GMR (bcc_A2) = -351927.55 J/mol of atoms while GMR (hcp_A3) = -351922.55 J/mol of atoms) and therefore the bcc_A2 phase becomes metastable. For Zr, from 2957 to 6000 K, the molar Gibbs energy of the hcp_A3 phase becomes a little bit more negative than the one of the bcc_A2 phase (for example at $T=2957$ K, GMR (hcp_A3) = -245164.14 J/mol of atoms while GMR (bcc_A2) = -245163.15 J/mol of atoms) and the hcp_A3 phase becomes metastable. When the temperature increases up to 6000 K, this difference $\Delta(\text{GMR})$ between the molar Gibbs energy of the two phases increases. This tendency is

Table 4 Invariant reactions in the Ru-Zr system

| Reaction | ^[4] | | Present work | |
|--|----------------|--|--------------|---|
| | T, °C | x(Zr) at.% | T, °C | x(Zr) at.% |
| Liq \rightleftharpoons (Ru) + Ru ₂ Zr | 1715 | Liq 22 (Ru) 1.9 Ru ₂ Zr 32 | 1715 | Liq 23.36 (Ru) 1.81 Ru ₂ Zr 31.11 |
| Ru ₂ Zr \rightleftharpoons Liq + RuZr | 1825 | Ru ₂ Zr 33 Liq 31 | 1825 | Ru ₂ Zr 32.23 Liq 30.13 |
| Liq \rightleftharpoons RuZr | 2130 | RuZr 48.5 Liq 50 | 2131 | RuZr 48.74 Liq 50 |
| RuZr + β (Zr) \rightleftharpoons Liq | 1240 | β (Zr) 89 RuZr 52 Liq 79 | 1241 | β (Zr) 88.92 RuZr 51.19 Liq 79.42 |
| β (Zr) \rightleftharpoons α (Zr) + RuZr | 500 | β (Zr) 92 α (Zr) 99 RuZr 51 | 499.6 | β (Zr) 90.64 α (Zr) 99.48 RuZr 50.10 |
| Ru ₂ Zr \rightleftharpoons (Ru) + RuZr | 1285 | Ru ₂ Zr 33 (Ru) 1 RuZr 48 | 1285 | Ru ₂ Zr 32.08 (Ru) 1.61 RuZr 47.80 |

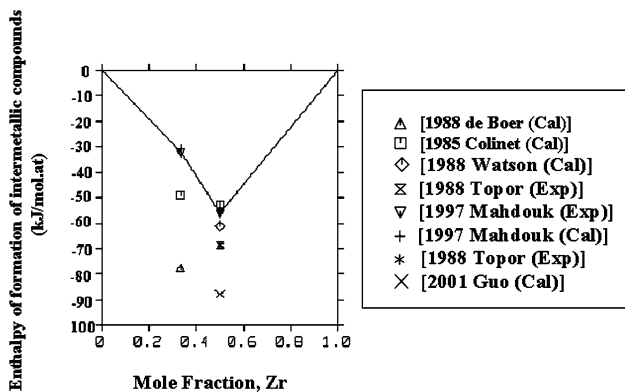


Fig. 6 Calculated (cal) and measured (exp.) enthalpies of formation of intermetallic compounds (kJ/mol.at)

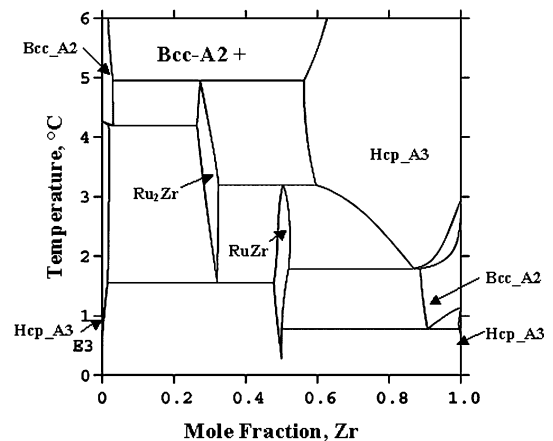


Fig. 7 Calculated Ru-Zr phase diagram when the liquid phase is suspended

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well illustrated in the graphs “Gibbs energy of phases Ru relative to hcp_A3” and “Zr relative to bcc_A2” published by^[15]. This gives account of the crystal structure of the phase domains calculated at very high temperature shown in Fig. 7: terminal solid solutions bcc_A2 (Ru) and hcp_A3 (Zr) and the two phase domain (bcc_A2 (Ru) + hcp_A3 (Zr)). In order to correct this fact, it will be necessary to extrapolate and refine the power series in terms of temperature of the Gibbs energy of the two elements Ru and Zr in the 4000-6000 K range.

6. Conclusion

A consistent set of thermodynamic parameters were optimized for the different phases of the Ru-Zr system. The

computed values are in satisfactory agreement with the experimental data for this system, phase diagram data as well as thermodynamic properties. Further experimental determinations, in particular the enthalpy of mixing of the liquid phase, will be necessary to refine the present assessment.

Appendix

The Gibbs free energies of the pure elements (solid and liquid) in the stable and metastable states, taken from SGTE database^[15]. The data are given in J/mol of atoms.

Ruthenium

GHSERu

$$\begin{aligned} &= -7561.873 + 127.866233T - 22.9143287T \ln(T) - 0.004062566T^2 + 1.7641 \cdot 10^{-7}T^3 \\ &\quad + 56377T^{-1} \quad (298.15 < T < 1500.00) \\ &= -59448.103 + 489.516214T - 72.3241219T \ln(T) + .018726245T^2 - 1.952433 \cdot 10^{-6}T^3 \\ &\quad + 11063885T^{-1} \quad (1500.00 < T < 2607.00) \\ &= -38588773 + 168610.517T - 21329.705T \ln(T) + 5.221639T^2 - 2.40245985 \cdot 10^{-4}T^3 \\ &\quad + 1.30829926 \cdot 10^{10}T^{-1} \quad (2607.00 < T < 2740.00) \\ &= -55768.304 + 364.482314T - 51.8816T \ln(T) \quad (2740.00 < T < 4500.00) \end{aligned}$$

GLIQRu

$$\begin{aligned} &= +27480.616 - 8.398748T + \text{GHSERu} \quad (298.15 < T < 800.00) \\ &= +50827.232 - 179.818561T + 19.539341T \ln(T) - 0.026524167T^2 + 1.667839 \cdot 10^{-6}T^3 \\ &\quad - 3861125T^{-1} \quad (800.00 < T < 2607.00) \\ &= -17161.807 + 349.673561T - 51.8816T \ln(T) \quad (2607.00 < T < 2740.00) \\ &= +38606.497 - 14.808753T + \text{GHSERu} \quad (2740.00 < T < 4500.00) \end{aligned}$$

Zirconium

GHSERZr

$$\begin{aligned} &= -7827.595 + 125.64905T - 24.1618T \ln(T) - 0.00437791T^2 + 34971T^{-1} \quad (130.00 < T < 2128.00) \\ &= -26085.921 + 262.724183T - 42.144T \ln(T) - 1.342896 \cdot 10^{31}T^{-9} \quad (2128.00 < T < 4000.00) \end{aligned}$$

GLIQZr

$$\begin{aligned} &= +18147.69 - 9.080812T + \text{GHSERZr} + 1.6275 \cdot 10^{-22}T^7 \quad (130.00 < T < 2128.00) \\ &= +17804.661 - 8.911574T + 1.342895 \cdot 10^{31}T^{-9} \quad (2128.00 < T < 4000.00) \end{aligned}$$

GBCCZr

$$\begin{aligned} &= -525.539 + 124.9457T - 25.607406T \ln(T) - 3.40084 \cdot 10^{-4}T^2 - 9.729E - 09T^3 + 25233T^{-1} \\ &\quad - 7.6143 \cdot 10^{-11}T^4 \quad (298.14 < T < 2128.00) \\ &= -30705.955 + 264.284163T - 42.144T \ln(T) + 1.276058E + 32T^{-9} \quad (2128.00 < T < 4000.00) \end{aligned}$$

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