



Thermodynamic Assessment of the Al-Ru System

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Abstract. The CALPHAD technique was used to calculate the Al-Ru binary phase diagram. The RuAl (B2) phase was described with the sublattice model (SL), also designated Compound Energy Formalism (CEF), as well as the Modified Sublattice Formalism (MSL), which describes the order disorder transformation with one Gibbs energy function. The RuAl₆ phase was described as a stoichiometric phase and the remaining intermetallic phases (Ru₄Al₁₃, RuAl₂ and Ru₂Al₃) were modelled with the sublattice model. The solubility of Ru in (Al) was considered negligible. Good agreement was obtained between the calculated and the experimental phase diagrams. © 2003 Published by Elsevier Science Ltd.

Introduction

The RuAl compound has an unusual combination of properties which have been exploited in high temperature and high wear environments such as spark plugs [1994Ste]. Fleischer and co-workers [1991Fle] first reported the excellent room temperature toughness, compared to other intermetallic compounds, and recommended its potential for structural applications because of its high melting point and good oxidation resistance. The improved toughness is due to five independent slip systems in the crystal.

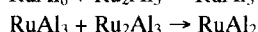
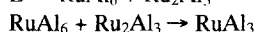
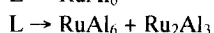
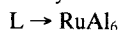
The excellent corrosion resistance of RuAl in hot, concentrated mineral acids was first reported by Wopersnow and Raub [1979Wop], and more recently, McEwan and Biggs [1996McE] demonstrated its capability as a coating in a range of aqueous media. They recognised that it has potential in corrosion-resistant coatings and electrochemical applications. The electrical conductivity of RuAl is high, almost metallic in value, and it exhibits good work function attributes [1995Smi]. This, and the good thermal conductivity [1998And] also renders the material suitable for spark-plug electrodes [1997Wol].

Although RuAl is difficult to manufacture by melting because of its high melting point, it can be manufactured by powder processing techniques, especially by reactive powder processing [1996Cor], or reactive hot isostatic processing (RHIP) [1996Wol].

Experimental Data

Phase Diagram Data

The crystal data for the phases of the Al-Ru system are listed in Table 1. Obrowski [1960Obr] reported the first phase diagram for the Al-Ru system and this was based on microscopic, X-ray and thermoanalytical observations. Six intermetallic phases were reported: RuAl₁₂ (although some uncertainty existed of the exact composition), RuAl₆, RuAl₃, RuAl₂, Ru₂Al₃ and RuAl, taking part in eight invariant reactions. The Ru-rich solid solution was reported to dissolve ~4 at. % Al at the eutectic temperature. No solubility of Ru in (Al) was detected and it was also concluded that all the Al-rich intermetallic compounds were line compounds. The RuAl phase was observed to melt at 2333 ± 20 K and the eutectic reaction between RuAl + (Ru) was at 2193 ± 20 K. Reactions were observed at 1573 and 1873 K and these were assigned to eutectic and peritectic reactions respectively. It was concluded, however, that some uncertainty existed of the solid-state reactions between 20 and 40 at. % Ru. Apart from Obrowski, no subsequent workers have reported the existence of RuAl₁₂. Other reactions reported by Obrowski, but not found by other workers were:



Schwomma [1963Sch] undertook X-ray work on a 33.3 at. % Ru sample, and found RuAl₂ and RuAl. The possibility of contamination by silicon and oxygen was, however, raised as a possibility by the author.

Edshammar determined the crystal structure for Ru₄Al₁₃ [1965Eds] (Obrowski's RuAl₃ [1960Obr]), and noted the similarity with Fe₄Al₁₃ because of the twinned prismatic structure and co-ordination numbers, although Ru₄Al₁₃ showed even better agreement with Os₄Al₁₃. He also found that Al atoms were absent from some of the sites which were partially occupied by Al in Fe₄Al₁₃ and Co₄Al₁₃. Ru₄Al₁₃ was, therefore, considered to be the ideal structure of RuAl₃ [1960Obr]. Subsequently with X-ray powder methods, Edshammar reported the crystal structures for five more intermetallic phases: RuAl, Ru₂Al₃, RuAl₂, RuAl_{-2.5} and RuAl₆ [1966Eds, 1968Eds]. The phase RuAl_{-2.5} was observed only in arc-melted samples. There were some additional CsCl-like phases reported around the composition RuAl, but no further details were given. No evidence of the RuAl₁₂ phase was found, and there were other inconsistencies with Obrowski's phase diagram [1960Obr] concerning the Ru₂Al₃ and RuAl₂ phases.

Anlage *et al.* [1988Anl] undertook experiments up to 26 at. % Ru using scanning electron microscopy, X-ray diffraction and thermal analysis (DSC). The RuAl₁₂ phase could not be confirmed, and Edshammar's [1965Eds] notation for the Ru₄Al₁₃ phase was used. It was also reported that both RuAl₆ and Ru₄Al₁₃ melt by peritectic reaction at 996 K and 1676 K respectively, and not congruently as suggested by Obrowski [1960Obr]. Some liquidus temperatures were provided. Problems with homogeneity of the alloys were reported, and also that the peritectic reaction forming RuAl₆ was sluggish. Under rapid solidification conditions, icosahedral phases were reported between 2.4 and 23.5 at. % Ru.

Table 1
The crystal data for the elements and compounds in the Al-Ru system.

Phase	Struktur-bericht	Pearson symbol	Prototype	Reference
Al	A1	<i>cF4</i>	Cu	
RuAl ₆		<i>oC28</i>	MnAl ₆	[1968Eds] [1982Cha]
Ru ₄ Al ₁₃		<i>mC102</i>	Fe ₄ Al ₁₃	[1965Eds]
RuAl ₂	C11α C54	<i>tI6</i> <i>oF24</i>	CaC ₂ TiSi ₂	[1960Obr] [1966Eds]
Ru ₂ Al ₃	D5 ₁₃	<i>hP5</i> <i>tI10</i>	Ni ₂ Al ₃ Os ₂ Al ₃	[1960Obr] [1966Eds]
RuAl	B2	<i>cP2</i>	CsCl	[1960Obr]
Ru	A3	<i>hP2</i>	Mg	

Table 2
Experimental, predicted and calculated thermodynamic data.

Phase	ΔH° [J/mole atoms]	Reference
RuAl ₆	-17 930 ± 10%	Estimated using Miedema's method [1998Wol]
	-22 286	Calculated – this work
Ru ₄ Al ₁₃	-30 030 ± 10%	Estimated using Miedema's method [1998Wol]
	-38 535	Calculated –this work
RuAl ₂	-38 260 ± 10%	Estimated using Miedema's method [1998Wol]
	-45 125	Calculated –this work
Ru ₂ Al ₃	-44 040 ± 10%	Estimated using Miedema's method [1998Wol]
	-43 946	Calculated –this work
RuAl	-47 320 ± 10%	Estimated using Miedema's method [1998Wol]
	-62 050 ± 3000	Experimental, calorimetry [1992Jun]
	-70 740	<i>Ab initio</i> [1992Lin]
	-58 150	<i>Ab initio</i> [1999Man]
	-95 510	<i>Ab initio</i> [2002Gar]
	-51 126	Calculated – this work (MSL)
	-51 057	Calculated - this work (SL)

Boniface and Cornish [1996Bon1] confirmed Anlage's results for the high-Al end of the phase diagram. No evidence of the L → Ru₂Al₃ + RuAl₆ eutectic reaction reported by Obrowski [1960Obr] was found and the presence of RuAl₂ in as-cast samples indicated stability at higher temperatures. The microstructures revealed that there was a peritectic cascade of reactions from the formation of Ru₂Al₃ to the formation of RuAl₆. A slight endothermic peak at 1733 K suggested the formation temperature for RuAl₂ [1996Bon2]. The Ru₂Al₃ phase was found to decompose at ~1223K.

Although Varich and Luykevich [1973Var] found a maximum solubility of Ru in (Al) of 3.23 at.% Ru by rapid solidification techniques, this solubility has not been reported at equilibrium conditions.

Thermodynamic data

The only reported experimental thermodynamic result for the Al-Ru system was determined by Jung and Kleppa [1992Jun] by dropping a mixed 1:1 powder mixture (atomic percent) of the elements into the calorimeter, which showed that RuAl (B2) has a high heat of formation, -124.1 kJ.mol⁻¹.

Miedema's method was used to estimate values for the heats of formation for the intermetallic phases [1998Wol], as no other data were available.

Several *ab initio* results have been reported for the enthalpy of formation of RuAl. However, the data are scattered, probably due to the different assumptions for defect formation in RuAl, which has been indicated to be vacancies [1987Fle] or anti-structure defects [1976Neu].

The thermodynamic data are listed in Table 2.

Thermodynamic modelling

Elements

The pure elements in their stable states at 298.15 K were chosen as the reference states for the system. Thermodynamic descriptions for the stable and metastable states of the pure elements were taken from the SGTE Database [1991Din].

The data [1991Din] are described as

$${}^{\circ}G_i^{\Phi} - H_i^{SER} = A_i^{\Phi} + B_i^{\Phi}T + C_i^{\Phi}T \ln T + D_i^{\Phi}T^2 + E_i^{\Phi}T^{-1} + F_i^{\Phi}T^3 + I_i^{\Phi}T^7 + J_i^{\Phi}T^{-9} \quad (1)$$

where H_i^{SER} (in which 'SER' stands for standard element reference) are the enthalpy values for the elements in their stable forms at 10^5 Pa and 298.15K.

Disordered solution phases: liquid, fcc, hcp and bcc

The solution phases were modelled as substitutional solution phases according to the polynomial Redlich-Kister Model. The Gibbs energy for a solution phase ϕ is expressed as

$$G_m^\phi = x_{Al} {}^oG_{Al}^\phi + x_{Ru} {}^oG_{Ru}^\phi + RT(x_{Al} \ln x_{Al} + x_{Ru} \ln x_{Ru}) + {}^{xs}G_m^\phi \quad (2)$$

where ${}^oG_i^\phi$ is the Gibbs energy of the pure element i with the structure ϕ (Eq. 1) and x_i is the mole fraction of the phase. The excess Gibbs energy is given by

$${}^{xs}G_m^\phi = x_{Al}x_{Ru} \sum_{v=1}^n {}^vL_{Al,Ru}^\phi (x_{Al} - x_{Ru})^v \quad (3)$$

where ${}^vL_{Al,Ru}^\phi$ is the interaction parameter expressed as $a + b \cdot T$. The a and b parameters are calculated with the CALPHAD method.

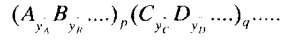
Intermetallic phases

There are five stable intermetallic phases in the Al-Ru binary system (Table 1). The intermetallic phases were modelled with the sublattice model, which is flexible enough to be applied to all of them. For $Ru_4Al_{1,3}$, $RuAl_2$, Ru_2Al_3 and $RuAl$ some defects have been introduced on the sublattices to model the solubility range, whereas $RuAl_6$ has been modelled without any solubility range. Furthermore, the $RuAl$ -B2 phase was also modelled with an alternative model, the modified sublattice model (MSL), which can describe both ordered B2 and disordered bcc-A2 with one single Gibbs energy function.

The Gibbs energy of mixing for a sublattice phase is given by

$$G_m = G^{ref} + G^{id} + G^{xs} \quad (4)$$

An intermetallic phase can schematically be described as follows [1981Sun]



where the species A, B... can be atoms or vacancies. p and q are the number of sites, y_i and y_j are the respective site fractions of species i and j in their respective sub-sublattices, designated by ' and ". When $p + q + \dots = 1$, the thermodynamic quantities are referred to as one mole of sites

The components of Eq. 4 are expanded as follows [1981Sun]:

$$G^{ref} = y_A' y_C'' G_{A:C}^{\circ} + y_A' y_D'' G_{A:D}^{\circ} + y_B' y_C'' G_{B:C}^{\circ} + y_B' y_D'' G_{B:D}^{\circ} \quad (5)$$

$$G^{id} = RT[p(y_A' \ln y_A' + y_B' \ln y_B') + q(y_C'' \ln y_C'' + y_D'' \ln y_D'')] \quad (6)$$

$$G^{xs} = y_A' y_B' [y_C'' L_{A,B:C} + y_D'' L_{A,B:D}] + y_C' y_D' [y_A'' L_{A:C,D} + y_B'' L_{B:C,D}] + y_A' y_B' y_C' y_D' L_{A,B,C,D} \quad (7)$$

$G_{A:B}^{\circ}$, $G_{A:D}^{\circ}$, $G_{B:C}^{\circ}$ and $G_{B:D}^{\circ}$ represent the Gibbs energy of formation of the stoichiometric compounds $A_p C_q$, $A_p D_q$, $B_p C_q$ and $B_p D_q$, which might be stable, metastable or even unstable in the system. y_i^s is the site fraction of element i on sublattice s . In Eq. 7, L is the interaction parameter and it is expressed as a function of temperature $L = a + b \cdot T$.

For the pure stoichiometric phase $RuAl_6$, the sublattice model reduces to

$$\Delta_f G^{RuAl_6}(T) = {}^oG^{RuAl_6}(T) - 6 {}^oG_{Al}^{fcc-Al}(T) - {}^oG_{Ru}^{hcp-Al_3}(T) = a + bT \quad (8)$$

The models for $\text{Ru}_4\text{Al}_{13}$, RuAl_2 and Ru_2Al_3 were based on models from previous assessments of similar phases in other systems. The $\text{Ru}_4\text{Al}_{13}$ phase was modelled after the $\text{Fe}_4\text{Al}_{13}$ phase in the COST507 database, as these phases have been reported to have similar structures [1965Eds]. Several crystal structures have been reported for RuAl_2 and Ru_2Al_3 . RuAl_2 was finally modelled after the TiSi_2 prototype suggested by Edshammer [1966Eds]. In the COST507 database the TiSi_2 phase has been described as stoichiometric but to allow for the solubility range, an interstitial sublattice for defects was added since no information is available for the defect structures in RuAl_2 . This would be filled with vacancies at the ideal stoichiometry and both Al and Ru were allowed to enter this. To ensure compatibility with the Ni-Al system, Ru_2Al_3 was modelled after the reported Ni_2Al_3 prototype [1960Obr]. The model used in this assessment is based on the ordered model for Ni_2Al_3 by Ansara *et al.* [1997Ans].

The RuAl-B2 phase was expressed with the sublattice (SL) model with vacancies (Va) as the main defect, as found by Fleischer [1993Fle]. The model, $(\text{Al,Ru})(\text{Al,Va})$, allows for the phase extension to the Al-rich side rather than the Ru-rich side of the B2 phase. This SL model is different to the more frequently used form, $(\text{Al,Ni})(\text{Ni,Va})$ suggested by Ansara *et al.* [1997Ans], since RuAl decomposes eutectically on the Ru-rich side of the stoichiometric composition.

Applying the MSL formalism, the RuAl-B2 phase was described as suggested by Dupin and Ansara [1999Dup] as $(\text{Al,Ru,Va})_{0.5}(\text{Al,Ru,Va})_{0.5}(\text{Va})_3$, the Gibbs energy is expressed as

$$G_m = G_m^{\text{dis}}(x_i) + \Delta G^{\text{ord}*}(y_i^+, y_i^-) - \Delta G^{\text{ord}*}(x_i, x_i) \quad (9)$$

where $G_m^{\text{dis}}(x_i)$ is the molar Gibbs energy contribution from the disordered state (bcc-A2, modelled as a disordered solution phase) and $(\Delta G_m^{\text{ord}}(y_i^+, y_i^-) - \Delta G^{\text{ord}*}(x_i, x_i))$ is the ordering energy contribution, equal to zero in the disordered state. Though the value zero is now built in for the ordering energy, some constraints must still be introduced between the thermodynamic parameters of the function. Since the lattices are indistinguishable because of the crystallography, the following constraints in the model parameter must be met

$$G_{\text{Al,Ru:Va}}^{\text{MSL,B2}} = G_{\text{Ru:Al:Va}}^{\text{MSL,B2}} \quad (10)$$

$$L_{\text{Al,Ru:Ru}}^{\text{MSL,B2}} = L_{\text{Ru:Al,Ru}}^{\text{MSL,B2}} \quad (11)$$

$$L_{\text{Al,Ru:Al}}^{\text{MSL,B2}} = L_{\text{Al:Al,Ru}}^{\text{MSL,B2}} \quad (12)$$

The symmetrical MSL model description of RuAl-B2 introduces substitutional vacancies to the bcc-A2 disordered description. To ensure that the vacancy fraction in bcc-A2 is low at all temperatures, a high positive value of 120^*T have been assigned to the interaction parameters ${}^0L_{\text{Al,Va:Va}}^{\text{bcc-A2}}$ and ${}^0L_{\text{Ru,Va:Va}}^{\text{bcc-A2}}$.

In the SL model description of RuAl-B2, the interaction parameters for the two unstable end-members $G_{\text{Al:Va}}^{\text{B2}}$ and $G_{\text{Ru:Va}}^{\text{B2}}$ were fixed to 60 000 J/mole of atoms. This ensures that the unstable B2 structure, where half the sites are empty, does not become stable, as this will represent a simple cubic bcc structure with no ordering.

Optimisation

Some of the high Al-content data of Obrowski [1960Obr] were found to disagree with that of other workers [1966Eds, 1968Eds, 1988Anl, 1996Bon1, 1996Bon2], and only data that were consistent were, therefore, used. The diagram of Boniface and Cornish [1996Bon2] was modified raising the formation temperatures of the RuAl_2 and Ru_2Al_3 phases to give a more correct liquidus slope [2000Pri]. The invariant reactions used in the optimisation are listed in Table 3. Higher weights were given to reliable and consistent data. The experimental enthalpy value [1992Jun] was also assigned a higher weight than the enthalpies estimated with the Miedema method.

The calculations were carried out using the PARROT module [1984Jan] in the Thermo-Calc software [1985Sun].

As a first step, to ensure that the slope of the liquidus was correct at the melting point of the fcc phase, only the liquid, Al-fcc and Ru-hcp phases were optimised. A metastable eutectic reaction was created for this purpose. Once an acceptable liquidus slope was calculated, the RuAl-B2 phase, using the MSL description, was included in the optimisation as this was the only phase with experimental thermodynamic data. This gave the liquid phase a reference point.

Since one Gibbs energy function describes both the B2 and bcc-A2 phases in the MSL model, the parameters were selected so that the entropy contribution of the ordered B2 phase was described by the disordered A2 phase. This required that the coefficients of the B2 and A2 phases had to be tested for interdependence. This was done by calculating the solubility range of the B2 phase as a function of the $L_{Al,RuVa}^{bcc-A2}$ parameter. When the $L_{Al,RuVa}^{bcc-A2}$ parameter is made more negative, the solubility range for B2 becomes wider, whereas when the $G_{Al,RuVa}^{MSL,B2} = G_{RuAlVa}^{MSL,B2}$ parameter is made more negative, the solubility range becomes more narrow. Thus the parameters for the bcc-A2 phase were fixed to give a reasonable solubility range for the B2 phase and the RuAl-B2 parameters were used to adjust the solubility range.

The other phases, except for the Ru₂Al₃ phase, were introduced simultaneously. The liquid parameters were fixed while introducing the other phases into the calculation. The other phases were initially modelled to form by congruent melting. The peritectic invariant reactions were only introduced once the phases appeared in their correct composition ranges. Lastly, the Ru₂Al₃ phase was introduced in a similar fashion as the other phases.

All parameters were fixed and the MSL description of the B2 phase was changed to the sublattice format. Only these parameters were optimised during the second assessment.

Table 3
Invariant temperatures and compositions for the Al-Ru system.

Reaction (at. % Ru)	Reaction Temperature [K]	Reference
L ↔ (Al) + RuAl ₆ 0.1 0 14.8 0.1 0 14.3	923 922	[1988Anl] This work
L + Ru ₄ Al ₁₃ ↔ RuAl ₆ 1.5 25 14.3 2.5 25.4 14.3	996 997	[1988Anl] This work
L + RuAl ₂ ↔ Ru ₄ Al ₁₃ 17.6 33.6 25.8 18.1 31.1 26.7	1676 1725	[1988Anl] This work
L + Ru ₂ Al ₃ ↔ RuAl ₂ 26 36 33.4 23 36.1 33.9 23.4 39.6 31.8	1733 1873 1854	[1996Bon1] [2000Pri]* This work
L + RuAl ↔ Ru ₂ Al ₃ 33.5 42.5 42 27 42 41 35 45.9 39.9	1873 1973 1978	[1996Bon1] [2000Pri]* This work (MSL)
Ru ₂ Al ₃ ↔ RuAl + RuAl ₂ 395 46 35.9 40 49.5 32.9	1249 1243	[1996Bon1] This work (MSL)
L ↔ RuAl 50 50 50 50	2333 2342	[1960Obr] This work (MSL)
L ↔ RuAl + (Ru) 70 51 96 69.7 50.7 95.7	2193 2189	[1960Obr] This work (MSL)

*indicates the invariants which have been used in the optimisation

To ensure stability of the thermodynamic parameters of the intermetallic phases, a condition forcing the entropy of formation to be negative was set for all the intermetallic phases.

Results and discussion

Despite the lack of experimental thermodynamic data, the calculated phase diagram, as shown in Figure 1, is in good agreement with the later experimental phase diagrams [1988Anl, 1996Bon2]. The experimental and calculated invariant temperatures and compositions are given in Table 3 and the final set of thermodynamic parameters is listed in Appendix 1. The optimised diagram is compared to the experimental data in Figure 2.

The solubility range of the Ru_2Al_3 phase is too narrow [1996Bon1], but not enough experimental data were available to extend the solubility range in the calculations. However, this phase has been shown to have little extension into the ternary Al-Ru-X (where X = Ni, Cr, Ir, Pt) phase diagrams [1997Hor, 1999Hil, 2000Hoh, 2001Com1, 2002Com2, 2002Pri].

The B2 phase is also slightly narrower than in the experimental phase diagram, although it agrees with experimental findings of a larger solubility range towards the Al-rich side than the Ru-rich side. The MSL description gave a wider phase, and hence a better fit to the experimental RuAl-B2 phase.

The B2 phase remains ordered throughout its stability range, which agrees with the available X-ray data [1963Sch, 1966Eds and 1994Bon] and the disordered bcc-A2 phase is unstable in the Al-Ru system at any composition.

The composition ranges of the $\text{Ru}_4\text{Al}_{13}$ and RuAl_2 phases are satisfactory, as both have been reported from stoichiometric compounds to having a 5 at. % composition range [1965Eds, 1988Anl, 1996Bon2]. The model description for $\text{Ru}_4\text{Al}_{13}$ is acceptable.

In Figure 3, the phase diagram is represented as a function of the chemical potential instead of composition. It indicates that, though the optimisation was performed with limited thermodynamic data, the entropy contributions in the calculated model parameters do not have excessive entropy contributions. The enthalpy of formation for the B2 phase at 298 K for the SL and MSL optimisations are compared with reported enthalpies of formation in Figure 4.

Conclusions

A consistent set of thermodynamic parameters, taking into account the ordered RuAl-B2 phase, was obtained for the Al-Ru binary system, and the resulting phase diagram agrees with a compiled diagram from experimental data. The results for the SL and MSL descriptions of the B2 phase compare well. The MSL description gave a better fit to the width of the experimental RuAl-B2 phase.

The MSL description is the preferred model to describe the ordered B2 phase with, and the description should be as simple as possible.

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Appendix I

Thermodynamic parameters for the Al-Ru system [J/mol]

The temperature range is $298.15 \leq T \leq 6000$, unless specified otherwise.
Parameters which are not listed are equal to zero.

Liquid Disordered Solution Phase: (Al,Ru)

$${}^0G_{Al}^{liq}(T) - H_{Al}^{0, fcc-A1}(298.15) : [1991Din]$$

$${}^0G_{Ru}^{liq}(T) - H_{Ru}^{0, hcp-A3}(298.15) : [1991Din]$$

$${}^0L_{(Al,Ru)}^{liq} = -73000 - 14T$$

$${}^1L_{(Al,Ru)}^{liq} = -56000$$

(Al) (fcc-A1) Disordered Solution Phase: (Al,Ru)(Va)

$${}^0G_{Al}^{fcc-A1}(T) - H_{Al}^{0, fcc-A1}(298.15) : [1991Din]$$

$${}^0G_{Ru}^{fcc-A1}(T) - H_{Ru}^{0, fcc-A1}(298.15) : [1991Din]$$

$${}^0L_{(Al,Ru)}^{fcc-A1} = -10000 - 10T$$

(Ru) (hcp-A3) Disordered Solution Phase: (Al, Ru)(Va)_{0.5}

$${}^0G_{Ru}^{hcp-A3}(T) - H_{Ru}^{0, hcp-A3}(298.15) : [1991Din]$$

$${}^0G_{Al}^{hcp-A3}(T) - H_{Al}^{0, hcp-A3}(298.15) : [1991Din]$$

$${}^0L_{(Al,Ru)}^{hcp-A3} = -105000 + 30T$$

bcc-A2 Disordered Solution Phase: (Al, Ru, Va)(Va)₃

$${}^0G_{Al}^{bcc-A2}(T) - H_{Al}^{0, bcc-A2}(298.15) : [1991Din]$$

$${}^0G_{Ru}^{bcc-A2}(T) - H_{Ru}^{0, bcc-A2}(298.15) : [1991Din]$$

$${}^0L_{Al,Ru,Va}^{bcc-A2} = -176000 + 32 * T$$

$${}^0L_{Al,Va,Va}^{bcc-A2} = 120 * T$$

$${}^0L_{Ru,Va,Va}^{bcc-A2} = 120 * T$$

RuAl₆ Stoichiometric Phase: (Al)₆ (Ru)

$${}^fG_{Al:Ru}^{RuAl_6} = 6{}^0G_{Al}^{fcc-A1} + {}^0G_{Ru}^{hcp-A3} - 156000 + 7 * T$$

Ru₄Al₁₃ Sublattice Solution Phase: (Al)_{0.6275}(Ru)_{0.235} (Al,Va)_{0.1375}

$${}^fG_{Al:Ru:Al}^{Ru_4Al_{13}} = 0.765{}^0G_{Al}^{fcc-A1} + 0.235{}^0G_{Ru}^{hcp-A3} - 35100 + 1.65 * T$$

$${}^fG_{Al:Ru:Va}^{Ru_4Al_{13}} = 0.6275{}^0G_{Al}^{fcc-A1} + 0.235{}^0G_{Ru}^{hcp-A3} - 35100 + 1.65 * T$$

RuAl₂ Sublattice Solution Phase: (Al)₂(Ru)(Al,Ru,Va)

$${}^fG_{Al:Ru:Va}^{RuAl_2} = 2{}^0G_{Al}^{fcc-A1} + {}^0G_{Ru}^{hcp-A3} - 136500 + 8 * T$$

$${}^fG_{Al:Ru:Al}^{RuAl_2} = 3{}^0G_{Al}^{fcc-A1} + {}^0G_{Ru}^{hcp-A3} - 138000 + 8 * T$$

$${}^fG_{Al:Ru:Ru}^{RuAl_2} = 2{}^0G_{Al}^{fcc-A1} + 2{}^0G_{Ru}^{hcp-A3} - 138000 + 8 * T$$

Ru₂Al₃Sublattice Solution Phase : (Al)₃(Al,Ru)₂(Ru,Va)

$${}^f G_{Al:Al:Va}^{Ru_2Al_3} = 5 {}^0 G_{Al}^{bcc-A2}$$

$${}^f G_{Al:Al:Ru}^{Ru_2Al_3} = 5 {}^0 G_{Al}^{bcc-A2} + {}^0 G_{Ru}^{bcc-A2}$$

$${}^f G_{Al:Ru:Va}^{Ru_2Al_3} = 3 {}^0 G_{Al}^{bcc-A2} + 2 {}^0 G_{Ru}^{bcc-A2} - 312630 + 30.5 * T$$

$${}^f G_{Al:Ru:Ru}^{Ru_2Al_3} = 3 {}^0 G_{Al}^{bcc-A2} + 3 {}^0 G_{Ru}^{bcc-A2} - 312630 + 30.5 * T$$

RuAl (B2)

Sublattice Solution Phase: (Al,Ru)(Al,Va)

$${}^f G_{Al:Al}^{B2} = 2 {}^0 G_{Al}^{bcc-A2}$$

$${}^f G_{Al:Va}^{B2} = {}^0 G_{Al}^{bcc-A2} + 60000$$

$${}^f G_{Ru:Va}^{B2} = {}^0 G_{Ru}^{bcc-A2} + 60000$$

$${}^f G_{Ru:Al}^{B2} = {}^0 G_{Ru}^{bcc-A2} + {}^0 G_{Al}^{bcc-A2} - 138700 + 15.5 * T$$

$${}^0 L_{Al:Al:Va}^{B2} = 49100 - 22.4 * T$$

$${}^0 L_{Ru:Al:Va}^{B2} = -51770 + 20 * T$$

$${}^0 L_{Al:Ru:Al}^{B2} = -30000$$

$${}^0 L_{Al:Ru:Va}^{B2} = -30000$$

Modified Sublattice Model: (Al,Ru,Va)_{0.5}(Al,Ru,Va)_{0.5}(Va)₃

$${}^f G_{Al:Ru:Va}^{MSL,B2} = {}^f G_{Ru:Al:Va}^{MSL,B2} = -87600$$

$${}^0 L_{Al:Ru:Al:Va}^{MSL,B2} = {}^0 L_{Al:Al:Ru:Va}^{MSL,B2} = -73000$$

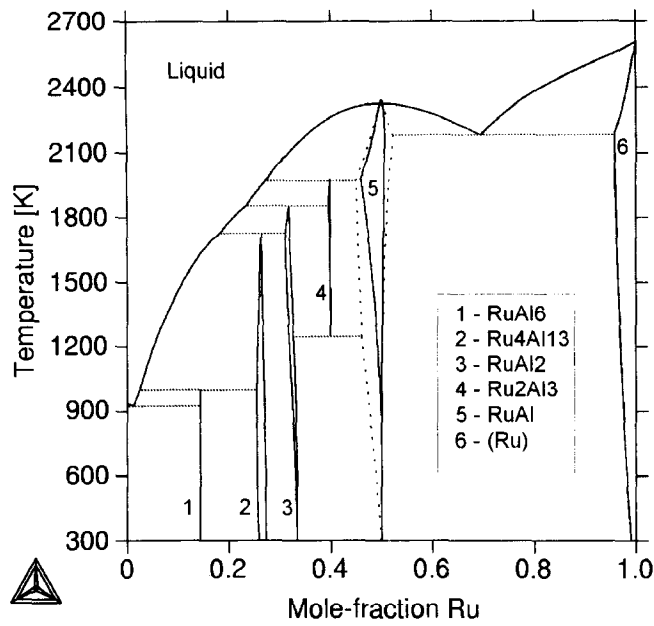


Figure 1. The calculated Al-Ru phase diagram showing B2 calculated using the SL (—) and MSL (---) models.

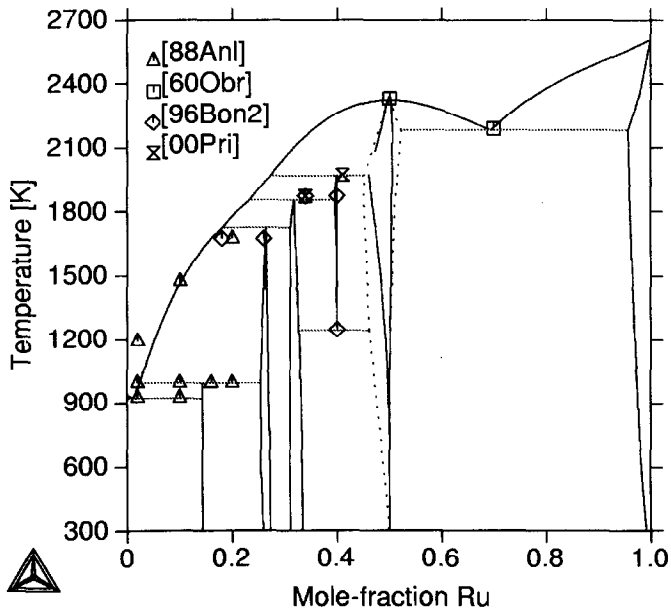


Figure 2. Comparison between the calculated phase diagram and experimental data.

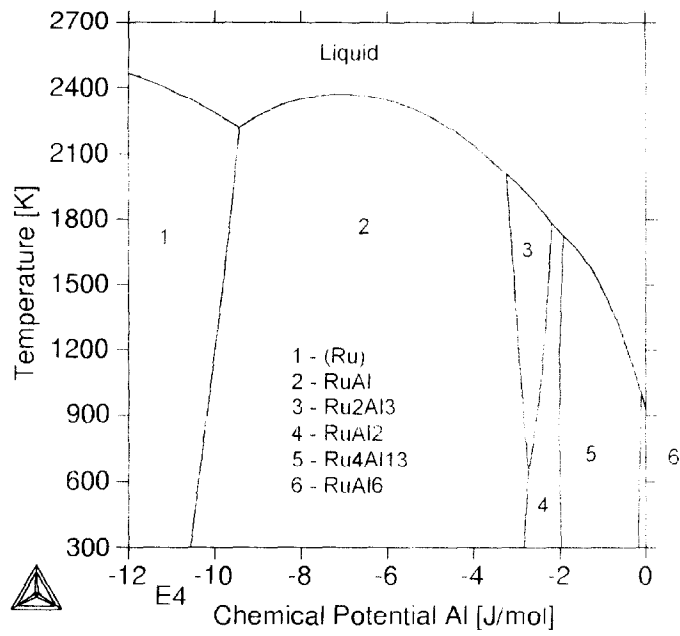


Figure 3. The phase diagram plotted as a function of chemical potential.

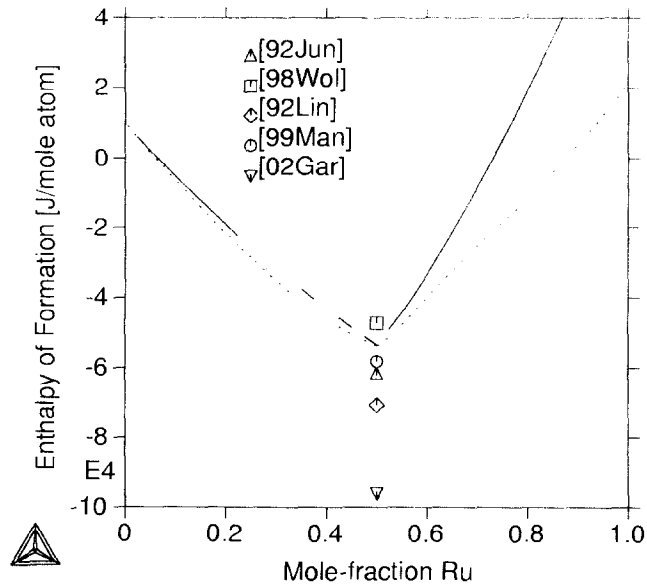


Figure 4. Comparison of the enthalpy of formation at 298 K for the SL (—) and MSL(---) RuAl-B2 descriptions with experimental [1992Jun], Miedema estimations [1998Wol] and *ab initio* [1992Lin, 1999Man, 2002Gar] values.