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## **Appendices**

**Appendix A Papers and Presentations**

**Appendix B XRD refinement example**

**Appendix C Al-Pt-Ru Database (SGTE format)**

**Appendix D Thermo-Calc Binary and ternary TDB and POP files (on CD)**

**Appendix E XRD spectra in .wmf format (on CD)**

## Appendix A

### Papers and Conference Presentations

(Only copies of the abstracts and papers that are available have been attached in this section)

Papers and Conference Presentations related to this study:

- 1. A reassessment of the Al-Pt binary system**  
S.N. Prins, L.A. Cornish, W.E. Stumpf and B. Sundman  
Proceedings of CALPHAD XXXI Conference, 5-10 May 2002, Stockholm, Sweden.
- 2. Phases formed on solidification in the Al-Pt-Ru system**  
S.N. Prins and L.A. Cornish  
15<sup>th</sup> International Conference on Electron Microscopy, Volume 1, 695-696 (Paper No. 619).  
1-6 Sept 2002, Durban, South Africa
- 3. The Development of Platinum-based Alloys and their Thermodynamic Database**  
L.A. Cornish, J. Hohls, P.J. Hill, S.N. Prins, R. Süß and D.N. Compton  
34<sup>th</sup> International Conference on Mining and Metallurgy, 545-550, Bor Lake, Yugoslavia,  
30 September – 3 October 2002.
- 4. Thermodynamic Assessment of the Al-Ru System**  
S.N. Prins, L.A. Cornish, W.E. Stumpf and B. Sundman  
CALPHAD, 27 (2003) 79-90
- 5. Development of Platinum-based Alloys for High Temperature Applications**  
L.A. Cornish, S.N. Prins, R. Süß and D.N. Compton  
Oral presentation at the 7<sup>th</sup> Materials Modeling Meeting. 6 March 2003, Pietersburg, South  
Africa. (2003: <http://mmc.unorth.ac.za>).
- 6. Case Study: Comparison of experimentally determined and CALPHAD-method  
predicted liquidus surfaces of the Al-Pt-Ru system.**  
S.N. Prins and L.A. Cornish  
Oral presentation at the 7<sup>th</sup> Materials Modeling Meeting. 6 March 2003, Pietersburg, South  
Africa. (2003: <http://mmc.unorth.ac.za>).
- 7. Thermodynamic Assessment of the Al-Pt-Ru system.**  
S.N. Prins, B. Sundman, L.A. Cornish and W.E. Stumpf  
Accepted as oral presentation to the CALPHAD XXXII Conference, 25-30 May 2003,  
Quebec, Canada.
- 8. Thermodynamic Re-assessment of the Al-Pt System.**  
S.N. Prins, L.A. Cornish and B. Sundman  
Submitted to CALPHAD Journal.
- 9. Solidification of Al-Pt-Ru alloys (title to be confirmed)**  
S.N. Prins, L.A. Cornish, W.E. Stumpf and P.S. Boucher  
To be submitted to Journal of Alloys and Compounds.

10. **XRD study of phases in an investigation of the Al-Pt-Ru system**  
S.N. Prins, P.S. Boucher and L.A. Cornish  
21<sup>st</sup> European Crystallographic Meeting, 24-29 August 2003, Durban, South Africa.

Other publications and conference contributions submitted during this period, but not directly related to the thesis:

1. **High Al-content Ternary Phases in Al-Cr-Ni**  
Lesley Cornish, Sara Prins, Daven Compton and Michael Witcomb  
Proceedings CALPHAD XXX, May 2001, York, UK.
2. **Comparing Quantitative and Semi-Quantitative Energy Dispersive X-ray Spectroscopy**  
S.N. Prins  
Oral presentation and paper in proceedings, Metrology Workshop, August 2002, Roodevallei, Pretoria, South Africa (2003: <http://www.nla.org.za/workshops>).
3. **ILZRO Zinc Alloy Development Project**  
J.M. Benson, S.N. Prins and D. Hope  
15th International Congress on Electron Microscopy, Volume 1, 1 - 6 September 2002, Durban, South Africa.
4. **Thermodynamic Assessments of the Pt-Cr and Cr-Ru Systems with an Extrapolation into the Pt-Cr-Ru System.**  
U. Glatzel and S.N. Prins  
Accepted as a poster contribution to the CALPHAD XXXII Conference, 25-30 May 2003, Quebec, Canada.
5. **The study of the Al-Pt-Ru system at 600°C**  
S.N. Prins and L.A. Cornish  
Submitted to the Microscopy and Microanalysis 2003 Conference, 3- 7 August 2003, San Antonio, Texas.
6. **A Metrology Approach to Uncertainty in Quantitative EDS Analyses.**  
S.N. Prins, L.H. Adlem and M.E. Lee  
Submitted to the Microscopy and Microanalysis 2003 Conference, 3- August 2003, San Antonio, Texas, USA.

Additionally, two confidential reports were submitted at Mintek

1. **Experimental and Thermo-Calc work on the development of Pt-based superalloys 2<sup>nd</sup> Report**  
L.A. Cornish, R. Suss, L. Glaner, D. Compton and S. N. Prins  
Mintek Report C3466M, 16 September 2002
2. **Experimental and Thermo-Calc work on the development of Pt-based superalloys 3<sup>rd</sup> Report**  
R. Suss, L. Glaner, D. Compton, L.A. Cornish and S. N. Prins  
Mintek Report C3536M, 6 February 2003

## A reassessment of the Al-Pt binary system

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The Al-Pt system is important as it is similar to the Al-Ni system and also showing a  $\gamma/\gamma'$  (Pt)/Pt<sub>3</sub>Al phase relation. This phase relation in the Al-Pt system has been earmarked as the basis of potential high temperature alloys, replacing the Ni-based superalloys in applications where the Ni-based superalloys have reached their upper temperature limits [01Hil1].

A current study investigating the Al-Cr-Pt-Ru alloy system has lead to this reassessment of the Al-Pt binary system as in the CALPHAD assessment by Wu and Jin [00Wu], modelling of the L12 Pt<sub>3</sub>Al phase does not accommodate the ordering of the L12 phase, as reported by Mishima *et al.* [86Mis] and Bronger *et al.* [97Bro]. A low temperature martensitic transformation for the Pt<sub>3</sub>Al has also been reported [86Mis] and experimental observations of ternary Al-Pt-X alloys indicated that the ternary additions either stabilise the high temperature or the low temperature form of Pt<sub>3</sub>Al (L1<sub>2</sub> and DO<sub>c</sub> respectively) [01Hil2]. The previous assessment [00Wu] also did not include the  $\beta$  phase since there are some discrepancies about its existence [90Mas]. However, experimental analysis of some ternary alloys indicated a phase which is probably  $\beta$ .

The current reassessment allows for the ordering of the Pt<sub>3</sub>Al phase and the Pt<sub>2</sub>Al and  $\beta$  phases has been included and the phase diagram is in good agreement with experimental observations.

The assistance of the PDI and DACST is gratefully acknowledged.

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## PHASES FORMED ON SOLIDIFICATION IN THE Al-Pt-Ru SYSTEM

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Two-phase high Pt content alloys have been shown to exhibit a structure similar to that of  $\gamma/\gamma'$  (Ni)/ $\sim\text{Ni}_3\text{Al}$  in the Ni-based superalloys [1] and very good properties have been obtained, even at high temperatures [2]. High Pt content alloys in the Al-Pt-Ru system were studied after heat treatment at 1350°C to allow the two-phase structure to be optimised at the envisaged application temperature [3]. This work is part of a larger investigation in which the component phase diagrams of the Al-Cr-Pt-Ru system will be studied in detail, so that the phase relationships and phase compositions can serve as an input to Thermo-Calc<sup>TM</sup>. The solidification reactions were required, thus the alloys were studied in the as-cast condition.

Six alloy samples were manufactured by arc-melting the elements and were studied in the as-cast condition using a LEO 1525 FE-SEM with an Oxford Inca EDS. At least five analyses were made on each phase or area.

The highest Pt content alloy had a very similar structure to an alloy studied by Biggs *et al.* [3]. There were (Ru) needles in a eutectic comprising (Ru) needles and small (Pt) dendrites in a  $\sim\text{Pt}_3\text{Al}$  matrix. Figure 1 shows a ternary eutectic which was not reported before [3].

Results from three alloys indicated that the  $\sim\text{RuAl}$  phase was found to contain at least 20 at.% Pt. The  $\sim\text{PtAl}_2$  phase exhibited up to 11 at.% solubility for ruthenium. The  $\sim\text{Ru}_4\text{Al}_{13}$  and  $\sim\text{RuAl}_6$  phases were difficult to analyse accurately, since they were found together on a fine scale (Figure 2), but they both showed solubility of at least 10 at.% platinum. Most of the other phases showed a more limited solubility;  $\sim\text{RuAl}_2$ ,  $\sim\text{Pt}_2\text{Al}_3$  and  $\sim\text{PtAl}$  contained only about 2 at.% of the third component.

The liquidus surface was dominated by the  $\sim\text{RuAl}$  phase, which stretched to within 10 at.% of the Al-Pt binary system, and then by the (Ru) phase. This is not surprising since both of these phases have very high melting points and they often dominate the phase diagram in related systems [4]. The  $\sim\text{RuAl}$  phase was involved in a number of subsequent reactions in the different alloys. It was involved in at least three peritectic reactions, forming  $\sim\text{PtAl}$ ,  $\sim\text{PtAl}_2$  and a phase which was too fine to be analysed accurately, although it appears to have a composition close to the  $\beta$  phase of Al-Pt [5]. It was also involved in the ternary invariant reaction:

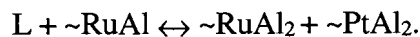


Figure 3 shows the remnants of  $\sim\text{RuAl}$  dendrites, appearing as fine particles, after the peritectic formation of  $\sim\text{Pt}_2\text{Al}$ . This reaction was followed by an eutectic reaction forming  $\sim\text{Pt}_2\text{Al}$  and  $\sim\text{Ru}_4\text{Al}_{13}$ . Figure 4 shows  $\sim\text{RuAl}$  dendrites surrounded by a thin two-phase

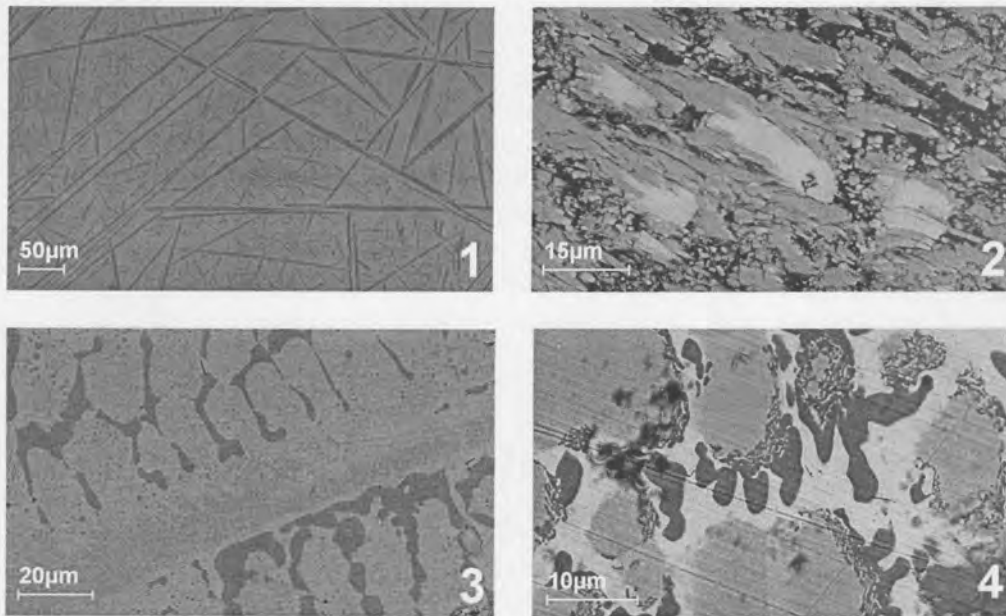
region (probably produced by subsequent solid state precipitation at much lower temperatures), then a  $\sim\text{RuAl}_2 + \sim\text{PtAl}_2$  eutectic. The binary eutectic reaction forming  $\sim\text{PtAl}$  and  $\sim\text{Pt}_2\text{Al}_3$  was also observed, very close to the Al-Pt binary. The other reactions were mainly peritectic in nature and tended to form more aluminium-rich phases. This is consistent with the Al-Ru and Al-Pt phase diagrams.

More alloys are being manufactured and the alloys are also being studied using XRD so that the phases can be confirmed.

The assistance of DACST and the PDI is gratefully acknowledged.

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**Figure 1.** BSE image of  $\text{Al}_{21}:\text{Pt}_{52}:\text{Ru}_{27}$  showing primary (Ru) needles in a ternary eutectic comprising (Ru) (smaller needles) + (Pt). **Figure 2.** BSE image of  $\text{Al}_{84}:\text{Pt}_{8.5}:\text{Ru}_{7.5}$  showing  $\sim\text{Pt}_5\text{Al}_{21}$  within a fine mixture of  $\sim\text{Ru}_4\text{Al}_{13}$  and  $\sim\text{RuAl}_6$ . **Figure 3.** BSE image of  $\text{Al}_{65}:\text{Pt}_{27}:\text{Ru}_8$  showing remnant dendrites of  $\sim\text{RuAl}$  (dark particles) within  $\sim\text{Pt}_2\text{Al}$  dendrites (light), surrounded by  $\sim\text{Pt}_2\text{Al} + \sim\text{Ru}_4\text{Al}_{13}$  eutectic. **Figure 4.** BSE image of  $\text{Al}_{54}:\text{Pt}_{14}:\text{Ru}_{32}$  showing  $\sim\text{RuAl}$  dendrites (medium) within  $\sim\text{Ru}_4\text{Al}_{13}$  (dark) +  $\sim\text{PtAl}_2$  eutectic (light). There are regions of solid state precipitation at the dendrite edges.



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0.506
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## THE DEVELOPMENT OF PLATINUM-BASED ALLOYS AND THEIR THERMODYNAMIC DATABASE

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### ABSTRACT

A series of quaternary platinum-based alloys have been demonstrated to exhibit the same two-phase structure as Ni-based superalloys and showed good mechanical properties. The properties of ternary alloys were a good indication that the quaternary alloys, with their better microstructure, will be even better. The quaternary alloy composition has been optimised at Pt<sub>42</sub>Al<sub>11</sub>Ru<sub>2</sub>Cr<sub>1</sub> for the best microstructure and hardness.

Work has begun on establishing a thermodynamic database for Pt-Al-Ru-Cr alloys, and further work will be done to enhance the mechanical and oxidation properties of the alloys by adding small amounts of other elements to the base composition of Pt<sub>42</sub>Al<sub>11</sub>Ru<sub>2</sub>Cr<sub>1</sub>.

Keywords: platinum-based alloys, thermodynamic database

### INTRODUCTION

Nickel-based superalloys have excellent mechanical properties because they have a microstructure comprising many small, strained-coherent, particles in a softer matrix [1987Sim]. The strengthening originates from dislocations being slowed down as they negotiate the small ordered particles. Additionally, there is solid solution strengthening in the (Ni) matrix. Although these alloys are used at relatively high temperatures, coarsening does not occur because the surface energy itself is very small. This is because the particle structure is very closely related to that of the matrix. Both are based on the face centred cubic structure: the matrix has a random fcc structure, and the particles have an L1<sub>2</sub> ordered structure. The lattice misfit between these structures is very small and renders the surface energy negligible [1987Sim].

The Ni-based superalloys have virtually reached their temperature limit for operation in turbine engines. However, there is a need to further increase the operational temperatures of these engines to achieve greater thrust, reduced fuel consumption and lower pollution. Thus, there is interest in developing a whole new suite of similar structured alloys based on a metal with higher melting point which can be used at temperatures of ~1300°C.

Platinum has been selected as the base material for these alloys because of its similarity to Ni in fcc structure and similar chemistry. Thus, similar phases to Ni<sub>3</sub>Al could be used to give similar mechanisms as found in the Ni-based superalloys. The important differences are the higher melting point (1769°C for platinum compared to 1455°C for nickel) and improved corrosion resistance. Although platinum-based alloys are unlikely to replace all Ni-based superalloys on account of both higher price and higher density, it is likely that they can be used for the highest application temperature components. Pt<sub>3</sub>Al has two forms, and the more desirable high temperature L1<sub>2</sub> form needs to be stabilised.

Experimental Pt-based alloys have been studied. It was found that successful Ni-based superalloy analogues could be manufactured with alloys of the approximate composition Pt<sub>42</sub>Al<sub>11</sub>X<sub>1</sub> where X was Cr, Ti and Ru [2001Hil1, 2001Hil2]. The best properties were exhibited by the Pt-Al-Cr and Pt-Al-Ru alloys, although the precipitate volume fraction was not as high as in the Ni-based superalloys. Although much heavier, the Pt-based alloys have the advantages of good mechanical properties and high temperature oxidation resistance [2000Hil1, 2001Sus1]. The ternary alloys have

mechanical properties which are better than those of the Ni- and Co-based superalloys, higher than conventional solid-solution strengthened Pt-based alloys, and comparable with mechanically alloyed ferritic ODS alloys [2002Sus].

### EXPERIMENTAL PROCEDURE

Several alloys were made up in order to ascertain whether the two-phase structure could be achieved in the quaternary system. Compositions were selected based on the results of the ternary Pt-Al-Cr and Pt-Al-Ru systems.

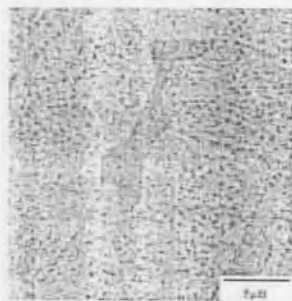
The alloys were prepared by arc-melting the pure elements several times to achieve homogeneity. The samples were then heat treated at 1350°C for 96 hours. The heat-treated samples were then cut in half, mounted and polished. The microstructure was examined using scanning electron microscopy (SEM) and, where possible, the phases were analysed using electron dispersive X-ray spectroscopy (EDS). The hardness of the alloys was measured using a Vickers hardness tester with a 10 kg load.

### RESULTS AND DISCUSSION

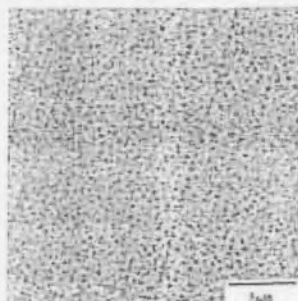
Three alloys were single-phase  $\sim$ Pt<sub>3</sub>Al, while three had two-phase microstructures. Two of these had large areas of  $\sim$ Pt<sub>3</sub>Al, together with a mixture of (Pt) and  $\sim$ Pt<sub>3</sub>Al (Figure 1a). The third (Pt<sub>84</sub>:Al<sub>11</sub>:Ru<sub>2</sub>:Cr<sub>3</sub>) was composed entirely of a fine two-phase mixture, which is the desired microstructure (Figure 1b). The EDS analyses of the overall and phase compositions are given in Table 1. Very fine phases were not analysed.

Table 1. Compositions of the Pt-Al-Ru-Cr alloys after heat treatment at 1350°C for 96 hours.

Alloy Composition	Phase	Phase composition (at.%)			
		Pt	Al	Ru	Cr
Pt <sub>79</sub> :Al <sub>15</sub> :Ru <sub>2</sub> :Cr <sub>4</sub>	(Pt)	79.7±0.5	8.4±0.5	5.4±0.5	6.5±0.5
	$\sim$ Pt <sub>3</sub> Al	75.2±0.3	20.5±0.4	0.8±0.2	3.5±0.4
	$\gamma\gamma$	79.3±0.5	10.6±0.6	4.5±0.4	5.6±0.7
Pt <sub>87</sub> :Al <sub>11</sub> :Ru <sub>2</sub> :Cr <sub>2</sub>	$\sim$ Pt <sub>3</sub> Al	76.0±0.1	20.9±0.4	0.3±0.3	2.8±0.2
	$\gamma\gamma$	81.2±0.5	11.6±0.1	2.7±0.3	4.5±0.3
Pt <sub>84</sub> :Al <sub>11</sub> :Ru <sub>2</sub> :Cr <sub>3</sub>	$\gamma\gamma$	83.5±1.3	11.3±0.6	2.4±0.5	2.8±0.4



a) Pt<sub>81</sub>:Al<sub>13</sub>:Ru<sub>2</sub>:Cr<sub>4</sub>



b) Pt<sub>84</sub>:Al<sub>11</sub>:Ru<sub>2</sub>:Cr<sub>3</sub>

Figure 1. SEM micrographs, in back-scattered electron (BSE) mode, of the two types of two-phase alloys. a) With primary  $\sim$ Pt<sub>3</sub>Al (dark contrast) in a fine mixture of (Pt) and  $\sim$ Pt<sub>3</sub>Al; b) Fine mixture of (Pt) and  $\sim$ Pt<sub>3</sub>Al.

The hardness of the three Table 2. The alloys were small cracks on the edges.

Table 2. Vickers hard

Alloy Designation
Pt <sub>79</sub> :Al <sub>15</sub> :Ru <sub>2</sub> :Cr <sub>4</sub>
Pt <sub>87</sub> :Al <sub>11</sub> :Ru <sub>2</sub> :Cr <sub>2</sub>
Pt <sub>84</sub> :Al <sub>11</sub> :Ru <sub>2</sub> :Cr <sub>3</sub>

Table 3. Composition

Alloy Designation
Pt <sub>85</sub> :Al <sub>11</sub> :Ru <sub>2</sub> :Cr <sub>2</sub>
Pt <sub>84</sub> :Al <sub>11</sub> :Ru <sub>2</sub> :Cr <sub>3</sub>
Pt <sub>81</sub> :Al <sub>13</sub> :Ru <sub>2</sub> :Cr <sub>4</sub>
Pt <sub>80</sub> :Al <sub>12</sub> :Ru <sub>2</sub> :Cr <sub>2</sub>
Pt <sub>81</sub> :Al <sub>12</sub> :Ru <sub>2</sub> :Cr <sub>4</sub>

More alloys were pro be increased. Table 3 sh 1350°C in argon. Only th were also small areas of pr

The hardness of the alloys The hardness ranged from around the indentations.

Table 4. Vickers hard

Alloy Designation
Pt <sub>85</sub> :Al <sub>11</sub> :Ru <sub>2</sub> :Cr <sub>2</sub>
Pt <sub>84</sub> :Al <sub>11</sub> :Ru <sub>2</sub> :Cr <sub>3</sub>
Pt <sub>81</sub> :Al <sub>13</sub> :Ru <sub>2</sub> :Cr <sub>4</sub>
Pt <sub>80</sub> :Al <sub>12</sub> :Ru <sub>2</sub> :Cr <sub>2</sub>
Pt <sub>81</sub> :Al <sub>12</sub> :Ru <sub>2</sub> :Cr <sub>4</sub>
Pt <sub>79</sub> :Al <sub>15</sub> :Ru <sub>2</sub> :Cr <sub>4</sub>

in an attempt to imp treatment was conducted fo small size of the samples, t improvement. However, microstructure after this h There was no primary  $\sim$ Pt



Bor Lake, Yugoslavia

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ase microstructures. Two of -Pt<sub>3</sub>Al (Figure 1a). The third tecture, which is the desired re compositions are given in

ment at 1350°C for 96 hours.

Composition (at.%)		
	Ru	Cr
5	5.4±0.5	6.5±0.5
4	0.8±0.2	3.5±0.4
6	4.5±0.4	5.6±0.7
4	0.3±0.3	2.8±0.2
1	2.7±0.3	4.5±0.3
6	2.4±0.5	2.8±0.4

The hardness of the three two-phase heat treated alloys was measured and the results are given in Table 2. The alloys were reasonably ductile, although some of the hardness indentations exhibited small cracks on the edges.

Table 2. Vickers hardness of the two-phase quaternary alloys, using a 10 kg load

Alloy Designation	Hardness (HV <sub>10</sub> )
Pt <sub>70</sub> :Al <sub>15</sub> :Ru <sub>2</sub> :Cr <sub>13</sub>	438 ± 11
Pt <sub>61</sub> :Al <sub>11</sub> :Ru <sub>2</sub> :Cr <sub>26</sub>	453 ± 16
Pt <sub>67</sub> :Al <sub>11</sub> :Ru <sub>2</sub> :Cr <sub>20</sub>	472 ± 14

Table 3. Compositions of the Pt-Al-Ru-Cr alloys after heat treatment at 1350°C for 96 hours

Alloy Designation	Phase	Phase composition (at.%)			
		Pt	Al	Ru	Cr
Pt <sub>70</sub> :Al <sub>15</sub> :Ru <sub>2</sub> :Cr <sub>13</sub>	-Pt <sub>3</sub> Al	76.6±0.4	21.8±0.2	0.0±0.0	1.6±0.3
	γ/γ	85.3±0.3	10.1±0.7	2.2±0.1	2.4±0.3
Pt <sub>61</sub> :Al <sub>11</sub> :Ru <sub>2</sub> :Cr <sub>26</sub>	-Pt <sub>3</sub> Al	76.0±0.5	22.2±0.2	0.4±0.4	1.4±0.3
	γ/γ	84.9±0.6	10.1±1.4	2.3±1.1	2.7±0.9
Pt <sub>67</sub> :Al <sub>11</sub> :Ru <sub>2</sub> :Cr <sub>20</sub>	-Pt <sub>3</sub> Al	76.1±0.8	21.4±0.6	0.6±0.6	1.9±0.2
	γ/γ	84.9±0.4	9.5±0.2	2.4±0.3	3.2±0.3
Pt <sub>60</sub> :Al <sub>12</sub> :Ru <sub>2</sub> :Cr <sub>26</sub>	-Pt <sub>3</sub> Al	75.9±0.7	20.6±0.6	0.8±0.4	2.7±0.4
	γ/γ	81.6±1.0	9.2±1.2	3.9±1.7	5.3±0.7
Pt <sub>61</sub> :Al <sub>11</sub> :Ru <sub>2</sub> :Cr <sub>26</sub>	-Pt <sub>3</sub> Al	76.3±0.3	20.6±0.1	0.5±0.1	2.6±0.2
	γ/γ	83.0±0.8	9.2±0.4	3.1±0.1	4.7±0.4

More alloys were produced to ascertain if the volume fraction of the -Pt<sub>3</sub>Al precipitates could be increased. Table 3 shows the measured compositions after heat treatment for 96 hours at 1350°C in air. Only the Pt<sub>61</sub>:Al<sub>11</sub>:Ru<sub>2</sub>:Cr<sub>26</sub> alloy had a clear fine two-phase mixture, but there were also small areas of primary -Pt<sub>3</sub>Al.

The hardness of the alloys was measured after heat treatment and the results are given in Table 4. The hardness ranged from 417 to 430 HV<sub>10</sub>. The alloys showed good ductility, with no cracking around the indentations.

Table 4. Vickers hardness of the second batch of quaternary alloys, using a 10 kg load.

Alloy Designation	Hardness (HV <sub>10</sub> )
Pt <sub>70</sub> :Al <sub>11</sub> :Ru <sub>2</sub> :Cr <sub>20</sub>	430 ± 5
Pt <sub>61</sub> :Al <sub>11</sub> :Ru <sub>2</sub> :Cr <sub>26</sub>	425 ± 21
Pt <sub>67</sub> :Al <sub>11</sub> :Ru <sub>2</sub> :Cr <sub>20</sub>	421 ± 12
Pt <sub>60</sub> :Al <sub>12</sub> :Ru <sub>2</sub> :Cr <sub>26</sub>	419 ± 22
Pt <sub>61</sub> :Al <sub>11</sub> :Ru <sub>2</sub> :Cr <sub>26</sub>	425 ± 10
Pt <sub>67</sub> :Al <sub>11</sub> :Ru <sub>2</sub> :Cr <sub>26</sub>	417 ± 8

In an attempt to improve the microstructure of the second batch of alloys, a second heat treatment was conducted for 96 hours at 1350°C in air. Some oxidation took place, and due to the small size of the samples, this caused loss of aluminium. In all but one of the alloys, there was no improvement. However, alloy Pt<sub>61</sub>:Al<sub>11</sub>:Ru<sub>2</sub>:Cr<sub>26</sub> showed a clear, fine two-phase microstructure after this heat treatment, possibly due to the change in its overall composition. There was no primary -Pt<sub>3</sub>Al in evidence, so the overall composition is that of the two-phase



Cr<sub>1</sub>  
mode, of the two types of two-  
a fine mixture of (Pt) and

mixture:  $85.2 \pm 0.3$  at.% Pt,  $7.1 \pm 0.8$  at.% Al,  $3.1 \pm 0.8$  at.% Ru and  $4.6 \pm 0.1$  at.% Cr. Since the overall composition changed, the sample was redesignated as  $Pt_{85}:Al_7:Ru_3:Cr_5$ .

Figure 2 shows the microstructure of this alloy after the first and second heat treatments, and that of the  $Pt_{84}:Al_{11}:Ru_2:Cr_3$  alloy from the first batch. It can be seen that the precipitates in  $Pt_{84}:Al_{11}:Ru_2:Cr_3$  are approximately twice as large, but more well-defined than those of  $Pt_{85}:Al_7:Ru_3:Cr_5$ . The hardnesses were re-measured and are given in Table 7. They range from 396 to 415  $HV_{10}$ , and were less after the second anneal.

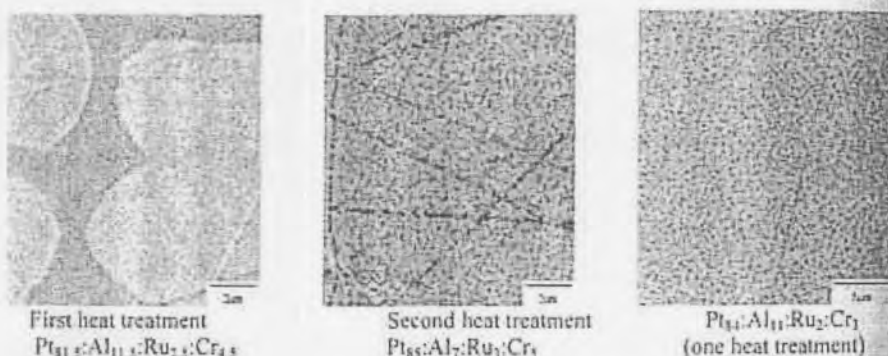


Figure 2. SEM BSE micrographs of alloy  $Pt_{81.5}:Al_{11.5}:Ru_{2.5}:Cr_{4.5}$  after one, and two heat treatments, and alloy  $Pt_{84}:Al_{11}:Ru_2:Cr_3$  after one heat treatment (Scratches can be seen.)

Table 2.7. Vickers hardness of the second batch of quaternary alloys after the second heat treatment, using a 10 kg load.

Alloy Designation	Hardness ( $HV_{10}$ )
$Pt_{84}:Al_{11}:Ru_2:Cr_3$	$403 \pm 20$
$Pt_{84}:Al_{11.5}:Ru_2:Cr_{2.5}$	$403 \pm 14$
$Pt_{83}:Al_{11}:Ru_2.5:Cr_{3.5}$	$405 \pm 8$
$Pt_{80.5}:Al_{17.5}:Ru_{2.5}:Cr_{4.5}$	$414 \pm 9$
$Pt_{81.5}:Al_{11.5}:Ru_{2.5}:Cr_{4.5}$	$396 \pm 6$
$Pt_{79.5}:Al_{10.5}:Ru_{4.5}:Cr_{5}$	$415 \pm 10$

## DISCUSSION

As has been shown before [2001Hil3], it is possible to obtain a (Pt) +  $\gamma$ -Pt<sub>3</sub>Al microstructure in the quaternary alloys. The volume fraction of  $\gamma$ -Pt<sub>3</sub>Al was estimated, using image analysis, to be approximately 25-30%. The highest hardness was found in the alloy without primary  $\gamma$ -Pt<sub>3</sub>Al. In the second batch of quaternary alloys, there was no clear relationship between the hardness and the composition or microstructure. The decrease in hardness after the second heat treatment is likely to be due to the changes in composition due to oxidation.

The best alloy to date is  $Pt_{84}:Al_{11}:Ru_2:Cr_3$  it has the required structure, no primary  $\gamma$ -Pt<sub>3</sub>Al and reasonable hardness. Other work has already shown that its oxidation resistance is better than the original ternary alloys [2001Sus2].

The other part of the project is the development of a thermodynamic database to facilitate the further development of these Pt alloys, while simultaneously developing the alloys further. This work will build on the information already gleaned from prior work, and will also extend the work to Pt alloys of higher order (i.e. alloys with more components, such as Ni).

The Parrot module is based on that of SGTE [1] the Al-Ru and Pt-Al system phase diagram for Al-Pt [2002Pri1] as Wu and Jin only described one form of this phase are important for

The Al-Ru system will be optimised and will be combined for the systems: Al-Cr-Ru [2002Sus2]. The Pt-Al-Cr also be studied. Results for phase or near single-phase optimisation.

Once the Pt-alloy data additions, added to improve optimisation.

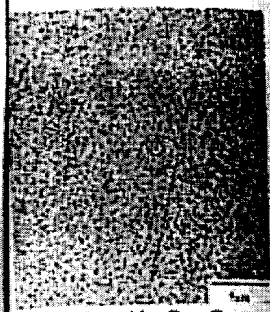
## CONCLUSION

It is possible to produce precipitates of similar shape.  $Pt_{84}:Al_{11}:Ru_2:Cr_3$  is the optimal Pt-Al-Ru-Cr thermodynamic. The assistance of DACST

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4.6±0.1 at.% Cr. Since the second heat treatments, and seen that the precipitates in well-defined than those of Table 7. They range from 396



Pt<sub>84</sub>Al<sub>11</sub>Ru<sub>2</sub>Cr<sub>3</sub>  
(one heat treatment)

after one, and two heat treatment (Scratches can be seen.)

alloys after the second heat

Hardness (HV <sub>10</sub> )
403 ± 20
403 ± 14
405 ± 8
414 ± 9
396 ± 6
415 ± 10

in a (Pt) + ~Pt<sub>3</sub>Al microstructure, using image analysis, to be alloy without primary ~Pt<sub>3</sub>Al. In ship between the hardness and the second heat treatment is likely to

structure, no primary ~Pt<sub>3</sub>Al oxidation resistance is better than

dynamic database to facilitate the developing the alloys further. This work, and will also extend the work on Ni).

The Parrot module in Thermo-Calc™ [1985Sun] that is being used to optimise the database is based on that of SGTE [1991Din] and Spencer's database [1998Spe]. The intermetallic phases in the Al-Ru and Pt-Al systems are not included in the current SGTE database. Although a calculated phase diagram for Al-Pt has been published by Wu and Jin [2000Wu], this was re-calculated [2002Pri1] as Wu and Jin's description did not exhibit any ordering in the Pt<sub>3</sub>Al phase. They also only described one form of the Pt<sub>3</sub>Al phase, and since both the cubic and tetragonal structures of this phase are important for this work, they must both be included.

The Al-Ru system has also been optimised by the group [2002Pri1]. Next, each ternary system will be optimised individually (already started for Al-Cr-Ru), and then once finalised, they will be combined for the quaternary. Experimental work has already commenced on the ternary systems: Al-Cr-Ru [2000Com1, 2000Com2, 2001Com], Pt-Al-Ru [2002Pri2] and Pt-Cr-Ru [2002Sus2]. The Pt-Al-Cr system will also be studied. Additionally, more quaternary alloys will also be studied. Results from the phase diagram work, together with enthalpies from the single-phase or near single-phase compositions from Leeds, UK will be input to Thermo-Calc™ for optimisation.

Once the Pt-alloy database has been optimised against some quaternary alloys, other small additions, added to improve the properties (as in nickel-based superalloys), will be included in the optimisation.

### CONCLUSION

It is possible to produce a fine two-phase  $\gamma/\gamma'$  structure in the Pt-Al-Ru-Cr system, with precipitates of similar shape to those in the nickel-based superalloy systems. The composition of Pt<sub>84</sub>Al<sub>11</sub>Ru<sub>2</sub>Cr<sub>3</sub> is the optimum composition because it has no primary phase. Development of the Pt-Al-Ru-Cr thermodynamic database has commenced. The assistance of DACST and the PDI is gratefully acknowledged.

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### 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 RuAl<sub>6</sub> phase was described as a stoichiometric phase and the remaining intermetallic phases (Ru<sub>4</sub>Al<sub>13</sub>, RuAl<sub>2</sub> and Ru<sub>2</sub>Al<sub>3</sub>) 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].

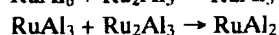
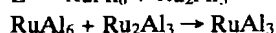
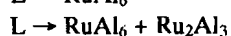
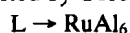
Although RuAl is difficult to manufacture by melting because of its high melting point, it can be manufactured by powder processing techniques, especially by reactive powder processing [1996Cor], or reactive hot isostatic processing (RHIP) [1996Wol].



### 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: RuAl<sub>12</sub> (although some uncertainty existed of the exact composition), RuAl<sub>6</sub>, RuAl<sub>3</sub>, RuAl<sub>2</sub>, Ru<sub>2</sub>Al<sub>3</sub> 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 RuAl<sub>12</sub>. 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 RuAl<sub>2</sub> 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 Ru<sub>4</sub>Al<sub>13</sub> [1965Eds] (Obrowski's RuAl<sub>3</sub> [1960Obr]), and noted the similarity with Fe<sub>4</sub>Al<sub>13</sub> because of the twinned prismatic structure and co-ordination numbers, although Ru<sub>4</sub>Al<sub>13</sub> showed even better agreement with Os<sub>4</sub>Al<sub>13</sub>. He also found that Al atoms were absent from some of the sites which were partially occupied by Al in Fe<sub>4</sub>Al<sub>13</sub> and Co<sub>4</sub>Al<sub>13</sub>. Ru<sub>4</sub>Al<sub>13</sub> was, therefore, considered to be the ideal structure of RuAl<sub>3</sub> [1960Obr]. Subsequently with X-ray powder methods, Edshammar reported the crystal structures for five more intermetallic phases: RuAl, Ru<sub>2</sub>Al<sub>3</sub>, RuAl<sub>2</sub>, RuAl<sub>-2.5</sub> and RuAl<sub>6</sub> [1966Eds, 1968Eds]. The phase RuAl<sub>-2.5</sub> 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 RuAl<sub>12</sub> phase was found, and there were other inconsistencies with Obrowski's phase diagram [1960Obr] concerning the Ru<sub>2</sub>Al<sub>3</sub> and RuAl<sub>2</sub> phases.

Anlage *et al.* [1988Anl] undertook experiments up to 26 at. % Ru using scanning electron microscopy, X-ray diffraction and thermal analysis (DSC). The RuAl<sub>12</sub> phase could not be confirmed, and Edshammar's [1965Eds] notation for the Ru<sub>4</sub>Al<sub>13</sub> phase was used. It was also reported that both RuAl<sub>6</sub> and Ru<sub>4</sub>Al<sub>13</sub> 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 RuAl<sub>6</sub> 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>cF</i> 4	Cu	
RuAl <sub>6</sub>		<i>oC</i> 28	MnAl <sub>6</sub>	[1968Eds] [1982Cha]
Ru <sub>4</sub> Al <sub>13</sub>		<i>mC</i> 102	Fe <sub>4</sub> Al <sub>13</sub>	[1965Eds]
RuAl <sub>2</sub>	C11α C54	<i>tI</i> 6 <i>oF</i> 24	CaC <sub>2</sub> TiSi <sub>2</sub>	[1960Obr] [1966Eds]
Ru <sub>2</sub> Al <sub>3</sub>	D5 <sub>13</sub>	<i>hP</i> 5 <i>tI</i> 10	Ni <sub>2</sub> Al <sub>3</sub> Os <sub>2</sub> Al <sub>3</sub>	[1960Obr] [1966Eds]
RuAl	B2	<i>cP</i> 2	CsCl	[1960Obr]
Ru	A3	<i>hP</i> 2	Mg	

Table 2  
Experimental, predicted and calculated thermodynamic data.

Phase	$\Delta H^\circ$ [J/mole atoms]	Reference
RuAl <sub>6</sub>	-17 930 ± 10%	Estimated using Miedema's method [1998Wol]
	-22 286	Calculated – this work
Ru <sub>4</sub> Al <sub>13</sub>	-30 030 ± 10%	Estimated using Miedema's method [1998Wol]
	-38 535	Calculated –this work
RuAl <sub>2</sub>	-38 260 ± 10%	Estimated using Miedema's method [1998Wol]
	-45 125	Calculated –this work
Ru <sub>2</sub> Al <sub>3</sub>	-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  $L \rightarrow Ru_2Al_3 + RuAl_6$  eutectic reaction reported by Obrowski [1960Obr] was found and the presence of RuAl<sub>2</sub> in as-cast samples indicated stability at higher temperatures. The microstructures revealed that there was a peritectic cascade of reactions from the formation of Ru<sub>2</sub>Al<sub>3</sub> to the formation of RuAl<sub>6</sub>. A slight endothermic peak at 1733 K suggested the formation temperature for RuAl<sub>2</sub> [1996Bon2]. The Ru<sub>2</sub>Al<sub>3</sub> 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<sup>-1</sup>.

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

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

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  $\phi$  is expressed as

$$G_m^\phi = x_{Al} {}^\circ G_{Al}^\phi + x_{Ru} {}^\circ G_{Ru}^\phi + RT(x_{Al} \ln x_{Al} + x_{Ru} \ln x_{Ru}) + {}^{ex}G_m^\phi \quad (2)$$

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

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

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

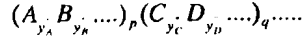
#### Intermetallic phases

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  $Ru_4Al_{13}$ ,  $RuAl_2$ ,  $Ru_2Al_3$  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  $L = a + b^*T$ .

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

$$\Delta_f G^{RuAl_6}(T) = {}^\circ G^{RuAl_6}(T) - 6 {}^\circ G_{Al}^{fcc-A1}(T) - {}^\circ G_{Ru}^{hcp-A3}(T) = a + bT \quad (8)$$

The models for  $Ru_4Al_{13}$ ,  $RuAl_2$  and  $Ru_2Al_3$  were based on models from previous assessments of similar phases in other systems. The  $Ru_4Al_{13}$  phase was modelled after the  $Fe_4Al_{13}$  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, (Al,Ru)(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, (Al,Ni)(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  $(Al,Ru,Va)_{0.5}(Al,Ru,Va)_{0.5}(Va)_3$ , the Gibbs energy is expressed as

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

where  $G_m^{dis}(x_i)$  is the molar Gibbs energy contribution from the disordered state (bcc-A2, modelled as a disordered solution phase) and  $(\Delta G_m^{ord*}(y_i', y_i'') - \Delta G^{ord*}(x_i, x_i))$  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

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

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

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

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  $120 \cdot T$  have been assigned to the interaction parameters  ${}^0L_{Al,Va:Va}^{bcc-A2}$  and  ${}^0L_{Ru,Va:Va}^{bcc-A2}$ .

In the SL model description of RuAl-B2, the interaction parameters for the two unstable end-members  $G_{Al:Va}^{B2}$  and  $G_{Ru:Va}^{B2}$  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  $L_{Al,Ru}^{bcc-A2}$  parameter. When the  $L_{Al,Ru}^{bcc-A2}$  parameter is made more negative, the solubility range for B2 becomes wider, whereas when the  $G_{Al,Ru}^{MSL,B2} = G_{Ru,Al}^{MSL,B2}$  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 Ru<sub>2</sub>Al<sub>3</sub> 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 Ru<sub>2</sub>Al<sub>3</sub> 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 <sub>6</sub> 0.1      0      14.8 0.1      0      14.3	923 922	[1988Anl] This work
L + Ru <sub>4</sub> Al <sub>13</sub> ↔ RuAl <sub>6</sub> 1.5      25      14.3 2.5      25.4      14.3	996 997	[1988Anl] This work
L + RuAl <sub>2</sub> ↔ Ru <sub>4</sub> Al <sub>13</sub> 17.6      33.6      25.8 18.1      31.1      26.7	1676 1725	[1988Anl] This work
L + Ru <sub>2</sub> Al <sub>3</sub> ↔ RuAl <sub>2</sub> 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 <sub>2</sub> Al <sub>3</sub> 33.5      42.5      42 27      42      41 35      45.9      39.9	1873 1973 1978	[1996Bon1] [2000Pri]* This work (MSL)
Ru <sub>2</sub> Al <sub>3</sub> ↔ RuAl + RuAl <sub>2</sub> 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  $\text{Ru}_2\text{Al}_3$  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  $\text{RuAl}_2$  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.

### Acknowledgements

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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)<sub>0.5</sub>

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

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

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

**bcc-A2** Disordered Solution Phase: (Al, Ru, Va)(Va)<sub>3</sub>

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

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

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

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

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

**RuAl<sub>6</sub>** Stoichiometric Phase: (Al)<sub>6</sub>(Ru)

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

**Ru<sub>4</sub>Al<sub>13</sub>** Sublattice Solution Phase: (Al)<sub>0.6275</sub>(Ru)<sub>0.235</sub>(Al, Va)<sub>0.1375</sub>

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

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

**RuAl<sub>2</sub>** Sublattice Solution Phase: (Al)<sub>2</sub>(Ru)(Al, Ru, Va)

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

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

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





**Ru<sub>2</sub>Al<sub>3</sub>**

Sublattice Solution Phase : (Al)<sub>3</sub>(Al,Ru)<sub>2</sub>(Ru,Va)

$$\begin{aligned} f G_{Al:Al:Va}^{Ru_2Al_3} &= 5^0 G_{Al}^{bcc-A2} \\ f G_{Al:Al:Ru}^{Ru_2Al_3} &= 5^0 G_{Al}^{bcc-A2} + {}^0 G_{Ru}^{bcc-A2} \\ f G_{Al:Ru:Va}^{Ru_2Al_3} &= 3^0 G_{Al}^{bcc-A2} + 2^0 G_{Ru}^{bcc-A2} - 312630 + 30.5 * T \\ f G_{Al:Ru:Ru}^{Ru_2Al_3} &= 3^0 G_{Al}^{bcc-A2} + 3^0 G_{Ru}^{bcc-A2} - 312630 + 30.5 * T \end{aligned}$$

**RuAl (B2)**

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

$$\begin{aligned} f G_{Al:Al}^{B2} &= 2^0 G_{Al}^{bcc-A2} \\ f G_{Al:Va}^{B2} &= {}^0 G_{Al}^{bcc-A2} + 60000 \\ f G_{Ru:Va}^{B2} &= {}^0 G_{Ru}^{bcc-A2} + 60000 \\ f G_{Ru:Al}^{B2} &= {}^0 G_{Ru}^{bcc-A2} + {}^0 G_{Al}^{bcc-A2} - 138700 + 15.5 * T \\ {}^0 L_{Al:Al:Va}^{B2} &= 49100 - 22.4 * T \\ {}^0 L_{Ru:Al:Va}^{B2} &= -51770 + 20 * T \\ {}^0 L_{Al:Ru:Al}^{B2} &= -30000 \\ {}^0 L_{Al:Ru:Va}^{B2} &= -30000 \end{aligned}$$

Modified Sublattice Model: (Al,Ru,Va)<sub>0.5</sub>(Al,Ru,Va)<sub>0.5</sub>(Va)<sub>3</sub>

$$\begin{aligned} f G_{Al:Ru:Va}^{MSL,B2} &= f G_{Ru:Al:Va}^{MSL,B2} = -87600 \\ {}^0 L_{Al:Ru:Al:Va}^{MSL,B2} &= {}^0 L_{Al:Al:Ru:Va}^{MSL,B2} = -73000 \end{aligned}$$

THERMODYNAMIC ASSESSMENT OF Al-Ru SYSTEM

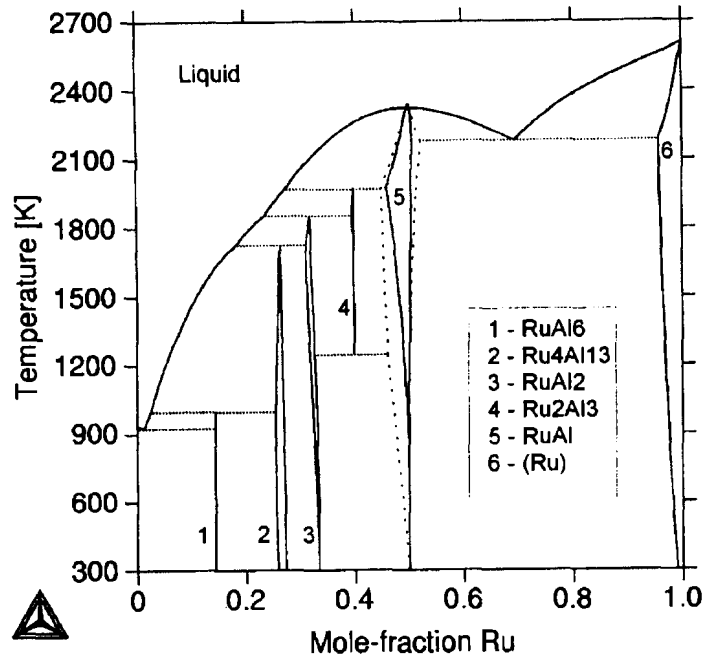


Figure 1. The calculated Al-Ru phase diagram showing B2 calculated using the SL (—) and MSL (---) models.

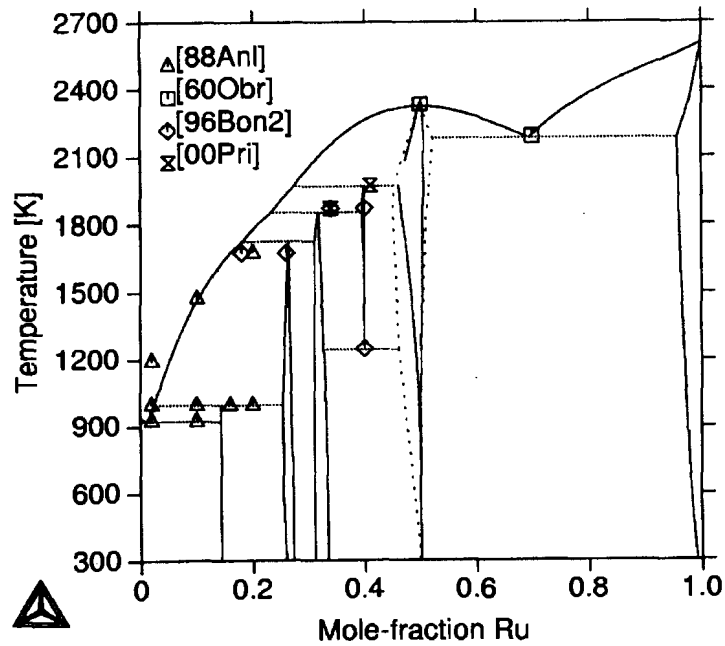
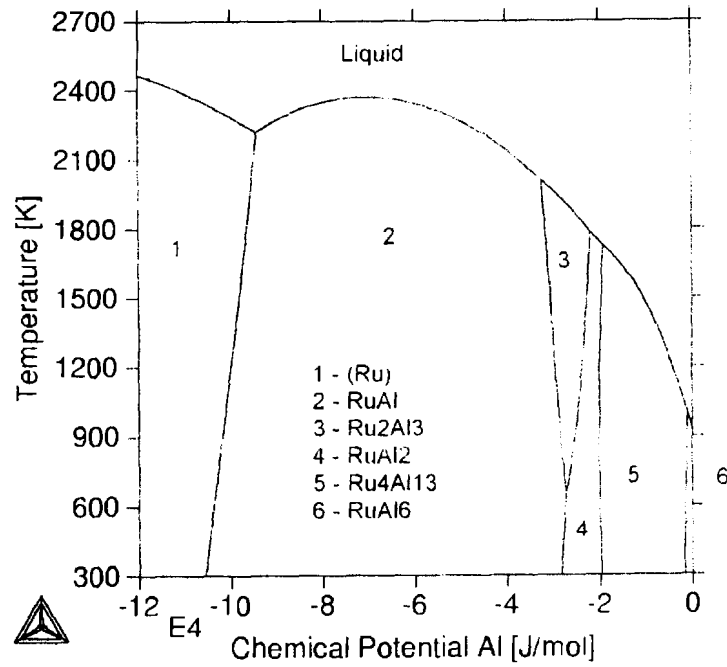
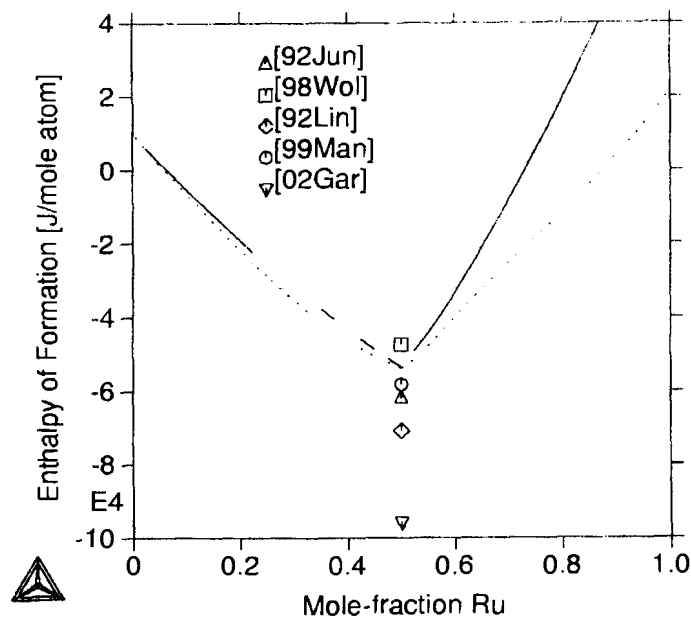


Figure 2. Comparison between the calculated phase diagram and experimental data.



**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.



## Case Study: Comparison of experimentally determined and CALPHAD-method predicted liquidus surfaces of the Al-Pt-Ru system.

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The Al-Pt-Ru ternary system has been studied experimentally. Sixteen samples were prepared by arc-melting. The samples were studied in the as-cast condition. The microstructures and compositions were analysed using scanning electron microscopy and energy dispersive X-ray spectroscopy, and the phases were confirmed by XRD. The solidification sequences of the alloys were derived from the as-cast microstructures and a liquidus surface projection was proposed. [2003Pri3]

Using the CALPHAD method, the Al-Ru and the Al- Pt systems have been calculated with the Parrot module in the Thermo-Calc software [2003Pri1, 2003Pri2]. The Pt-Ru system was calculated by Spencer [1996Spe]. The ternary system was extrapolated from these calculated binary systems to predict the liquidus surface projection. No ternary interaction parameters have been introduced and calculated for these predictions.

The experimental and calculated liquidus surface projections are in good agreement. The major differences arise from the fact that two new ternary phases were found in the experimental study. Since an extrapolation is based on the Gibbs energy functions for already entered phases, the software could not predict these new phases.

The good agreement between the experimental and calculated liquidus surface projections proves that thermodynamic modeling is powerful technique in the development of new alloy systems.

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## Thermodynamic Assessment of the Al-Pt-Ru System

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The Al-Pt-Ru system has been studied experimentally as part of a project to characterise and develop Pt-based superalloys [2002Pri2, 2003Pri2]. Pt-based superalloys have the potential to substitute Ni-based superalloys for high-temperature components in turbine engines, as they have a higher melting point and better corrosion resistance. The second part of the project involves building a thermodynamic database for Pt-based alloys.

The Al-Pt-Ru ternary system has been optimised using the CALPHAD method. The ordered RuAl-B2 phase contains ~20 at. % Pt [2003Pri2] and has been modelled with the modified sublattice model (MSL) where the disorder contribution is given by the bcc-A2 phase. The ordered Pt<sub>3</sub>Al-L1<sub>2</sub> phase comprises ~3 at. % Ru [2001Big] and has been modelled with the four sublattice compound energy formalism (4SL CEF), which describes the Gibbs energy of the ordered L1<sub>2</sub> and disordered fcc-A1 phases with one energy function. The 4SL CEF allows for mixing on two sublattices, which gives a thermodynamic description for both short and long range order. The other Al-Pt and Al-Ru intermetallic phases were extrapolated from the optimised Al-Pt [2002Pri1] and Al-Ru [2003Pri1] binaries, without the addition of ternary parameters. Two new ternary phases have been found in the Al-Pt-Ru system, and these have been included in the assessment.

The calculations were done with the Thermo-Calc software. The calculated liquidus surface is in good agreement with the experimental results.

The financial assistance of the Department of Science and Technology and the PDI is gratefully acknowledged.

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## Reassessment of the Aluminum-Platinum Binary System

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**Abstract.** The Al-Pt binary system was assessed using the CALPHAD method. The four-sublattice compound energy formalism (4SL CEF) was used to describe the order-disorder relation between the Pt<sub>3</sub>Al-L1<sub>2</sub> and (Pt)-fcc phases. The model successfully describes both the long-range and the short-range order observed in PtAl<sub>3</sub>-L1<sub>2</sub> phase in this system. The optimization included the solution phases and the Pt<sub>5</sub>Al<sub>21</sub>, Pt<sub>8</sub>Al<sub>21</sub>, PtAl<sub>2</sub>, Pt<sub>3</sub>Al<sub>5</sub>, PtAl,  $\beta$ , Pt<sub>5</sub>Al<sub>3</sub>, PtAl<sub>2</sub> and PtAl<sub>3</sub> intermetallic phases. The low temperature polymorph of the Pt<sub>3</sub>Al phase has not been included in this optimisation.

### Introduction

Platinum based alloys are studied as potential alloys to replaced Ni-based superalloys (NBSA) in ultra-high temperature applications. The Pt-Al system exhibits the same  $\gamma/\gamma'$  relation as Ni-Al, which is the basis of the NBSA. The Pt-Al system is of further interest as Pt is used increasingly in the coating technology to increase the heat and corrosion resistance of NBSA turbine blades, since Pt promotes the formation of stable alumina oxide layers.

The Al-Pt system has been assessed using the CALPHAD method by Wu and Jin [2000Wu], but their assessment did not consider the ordering in the system. They have also not included the PtAl<sub>2</sub> or  $\beta$  phases, due to a lack of experimental data. A study of Pt-Al-X ternaries (X=Ru, Ti, Cr, Ni) confirmed the presence of the Pt<sub>2</sub>Al phase [2001Big]. Experimental work on Pt-Al-Ru ternary confirmed the presence of the  $\beta$  phase in the Al-Pt binary [2002Pri].

These experimental observations, and the need to include the ordering of the L1<sub>2</sub> phase, prompted the reassessment of the Al-Pt binary system.

### Experimental

#### Phase diagram data

McAlister and Kahan [McA1986] have reported nine stable intermetallic phases in the Al-Pt system, with two of the phases showing high and low temperature polymorphs (Figure 1). Six metastable phases have also been reported [1986McA, 2001Lab].

Pt<sub>5</sub>Al<sub>21</sub>, Pt<sub>8</sub>Al<sub>21</sub>, Pt<sub>2</sub>Al<sub>3</sub> and PtAl are stoichiometric phases, while PtAl<sub>2</sub>, Pt<sub>5</sub>Al<sub>3</sub>, Pt<sub>2</sub>Al and Pt<sub>3</sub>Al exist with a solubility range. A  $\beta$  phase exists at high temperatures and decomposes below 1533 K. The phase data for the stable phases are listed in Table 1. The existence of the  $\beta$  phase were not confirmed beyond doubt, but rather

Table 1.

The crystal data for the stable elements and phases in the Al-Pt system.

Phase	Composition (at. % Pt)		Pearson symbol	Space Group	Struktur- bericht	Prototype	Reference
(Al)	0		<i>cF4</i>	Fm3m	A1	Cu	
Pt <sub>5</sub> Al <sub>21</sub>	19.2		<i>c**</i>				[1964Huc] [1980Pia]
Pt <sub>8</sub> Al <sub>21</sub>	27		<i>tI116</i>	I4 <sub>1α</sub>			[1968Eds] [1982Eil]
PtAl <sub>2</sub>	31.5	33.5	<i>cF12</i>	Fm3m	C1	CaF <sub>2</sub>	[1937Zin] [1963Fer] [1982Eil]
Pt <sub>2</sub> Al <sub>3</sub>	40		<i>hP5</i>	P3m1			[1978Bah]
PtAl	50		<i>cP8</i>	P2 <sub>13</sub>	B20	FeSi	[1957Sch] [1963Fer] [1975Chs2]
	50.4	51.8					
β	52	56	<i>cP2</i>	Pm3m	B2	CsCl	[1975Cha] [1978Bha]
Pt <sub>5</sub> Al <sub>3</sub>	61.5	63	<i>oP16</i>	Pbam		Ge <sub>3</sub> Rh <sub>5</sub>	[1964Huc]
Pt <sub>2</sub> Al	66	67	<i>oP12</i>	Pnma	C23	PbCl <sub>2</sub>	[1975Cha1]
Pt <sub>2</sub> Al (LT)	66	67	<i>oP24</i>	Pmma		GaPt <sub>2</sub> (LT)	[1976Cha]
Pt <sub>3</sub> Al	67.3	77.7	<i>cP4</i>	Pm3m	L1 <sub>2</sub>	AuCu <sub>3</sub>	[1962Bro] [1964Huc] [1963Mag]
Pt <sub>3</sub> Al (LT)	73.5	100	<i>tP16</i>	P4/mbm	DO <sub>c</sub> '	GaPt <sub>3</sub> (LT)	[1975Cha1]
(Pt)	83.8	100	<i>cF4</i>	Fm3m	A1	Cu	

deduced from thermal arrest data. However, recent experimental results in the Al-Pt-Ru ternary system confirmed the presence of the β phase in the Al-Pt system.

There are discrepancies on the L12-DOc' transformation temperature of the Pt<sub>3</sub>Al phase.

### Thermochemical data

Ferro [1968] determined the enthalpies of formation by solution calorimetry. Worrel [1981] used an electrochemical cell technique to determine the Gibbs energy of mixing. Enthalpies of formation have been predicted using Miedema's method [1989deB]. The enthalpies of formation for PtAl and Pt<sub>3</sub>Al have been predicted using *ab initio* methods [2002Ngo]. The thermodynamic data are listed in Table 2.

## Thermodynamic Models

### The pure elements

The pure elements in their stable states at 298.15K were chosen as the reference states for the system (standard element reference SER). The Gibbs energies as a function of temperature for the stable elements were taken from the SGTE database [1991Din].

### The liquid phase

The liquid phase was modeled as a substitutional solution phase according to the polynomial Redlich-Kister model. The Gibbs energy for a solution phase is given by

$$G_m = \sum_i x_i^0 G_i + RT \sum_i x_i \ln(x_i) + {}^E G_m \quad (1)$$

Experimental, predicted and calculated enthalpies of formation for the stable phases in the Al-Pt system.

Phase	$\Delta H_f$ [J/mole atoms]	Method	Reference
Pt <sub>5</sub> Al <sub>21</sub>	-57 320	Solute solvent drop calorimetry	[1968Fer]
	-56 827	Calculated	This work
Pt <sub>8</sub> Al <sub>21</sub>	-71 130	Solute solvent drop calorimetry	[1968Fer]
	-81 751	Calculated	This work
PtAl <sub>2</sub>	-84 000	Solute solvent drop calorimetry	[1968Fer]
	-87 325	Calculated	This work
Pt <sub>2</sub> Al <sub>3</sub>	-94 980	Solute solvent drop calorimetry	[1968Fer]
	-79 000	Miedema semi-empirical method	[1989deB]
	-96 500	Direct Synthesis Calorimetry	[1993Mes]
	-89 839	Calculated	This work
PtAl	-100 420	Solute solvent drop calorimetry	[1968Fer]
	-100 000	Direct Synthesis Calorimetry	[1991Jun]
	-82 000	Miedema semi-empirical method	[1989deB]
	-67 440	<i>Ab initio</i>	[2002Ngo]
	-94 025	Calculated	This work
$\beta$	-91 300*	Calorimetry	[1968Fer]
	-92 913	Calculated	This work
Pt <sub>5</sub> Al <sub>3</sub>	-90 730	Miedema semi-empirical method	[1989deB]
	-87 213	Calculated	This work
Pt <sub>2</sub> Al	-88 280	Miedema semi-empirical method	[1989deB]
	-85 278	Calculated	This work
Pt <sub>3</sub> Al	-69 870	Solution Calorimetry	[1968Fer]
	-63 600	Direct Synthesis Calorimetry	[1993Mes]
	-50 990	Miedema semi-empirical method	[1989deB]
	-76 000**	Electrochemical	[1981Wor]
	-74 380	<i>Ab initio</i>	[2002Ngo]
	-51 668	Calculated	This work

\* estimated from the curve fitted to the enthalpies of formation experimentally determined by Ferro *et. al.* [1986Fer].

\*\* deduced from  $G = -76\,460 + 7.48 \cdot T$  [1981Wor]

where  $x_i$  is the mole fraction of the element  $i$  and  ${}^0G_i$  is the Gibbs energy of the element  $i$  in the liquid phase relative to its reference state. The second term is the ideal entropy of mixing, while the third term is excess Gibbs energy, which can be expressed as

$$G_m = x_{Al} x_{Pt} L_{AlPt} \quad (2)$$

$L_{AlPt}$  is the so-called interaction parameter and the composition dependence is expressed as a Redlich-Kister polynomial

$$L_{AlPt} = \sum_{\nu=0} (x_{Al} - x_{Pt})^{\nu} L_{AlPt}^{\nu} \quad (3)$$

where  $L_{AlPt}^{\nu}$  are obtained from the optimization and may or may not be temperature dependent.

### The fcc phases

The four-sublattice compound energy formalism (4SL CEF) [1998Sun] was used to model the fcc phases. The model is based on the four sublattices describing the four corners of a tetrahedron in an fcc unit cell, with all the nearest neighbours of an atom are on a different sublattice. The model can describe the fcc-A1, L1<sub>2</sub> and L1<sub>0</sub> phases, depending of the positions of the atoms on the tetrahedron. Not all the structures need to be stable in the alloy system [2001Kus].

The 4SL CEF describes the Gibbs energy of the A1, L1<sub>2</sub> and L1<sub>0</sub> structures with one function, which includes an ordered and a disordered energy contribution

$$G_m = G_m^{dis}(x_i) + \Delta G_m^{ord}(y_i^s)$$





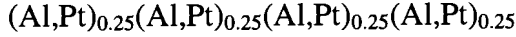
where  $G_m$  is the molar Gibbs energy of the phase,  $G_m^{4sl}$  is the molar ordering energy. The ordering energy, expressed as

$$\Delta G_m^{ord} = G_m^{4sl}(y_i^s) - G_m^{4sl}(y_i^s = x_i)$$

is zero when the phase is disordered.

The Pt<sub>3</sub>Al phase is an ordered structure (L1<sub>2</sub>) of the disordered fcc phase (A1), the latter in which the atoms are randomly distributed on the lattice. The associated other two ordered phases in this system, PtAl<sub>3</sub> (L1<sub>2</sub>) and PtAl (L1<sub>0</sub>), are unstable. The Pt<sub>3</sub>Al phase shows both long-range and short-range order (lro and sro respectively).

According to the 4SL CEF, the following model can be used to describe the fcc phases in this system



Physically, the sublattices describe the four corners of a tetrahedron in a unit cell. Due to the crystallographic symmetry of the unit cell, the sublattices must be identical, implying that all nearest neighbours of an atom is on a different sublattice. With 0.25 sites for each sublattice, the requirement of 1 mole of atoms in the model is met. For the disordered structure (fcc\_A1), all the sublattices are equivalent, which reduces this model to an equivalent (Al,Pt) substitutional model. When two sublattices have the same fractions, but different to the other two, which also have the same fractions, the model describes the PtAl phase (L1<sub>0</sub> structure). When three sublattices have the same fractions and the fourth sublattice a different fraction, the above model describes the Al<sub>3</sub>Pt and Pt<sub>3</sub>Al phases (L1<sub>2</sub> structure).

From the model, the following relationships hold

$$\sum_i y_i^s = 1 \quad (4)$$

$$x_i = 0.25 \sum_s y_i^s \quad (5)$$

with  $y_i^s$  the site fraction of each element  $i$  on each sublattice  $s$  and  $x_i$  the molar fraction of  $i$ .

The Gibbs energy expression describing the fcc phases of the 4SL CEF is

$$G_m = \sum_i \sum_j \sum_k \sum_l y_i^{(1)} y_j^{(2)} y_k^{(3)} y_l^{(4)} {}^o G_{ijkl} + 0.25 RT \sum_i y_i^{(s)} \ln(y_i^{(s)}) + {}^E G_m \quad (6)$$

where the first term describes the mechanical mixing of all the stoichiometric compounds defined by the model, with  ${}^o G_{ijkl}$  the Gibbs energy of the stoichiometric compound  $ijkl$  relative to the pure elements in the fcc state. The second term is the random mixing of all elements in each sublattice. The excess term  ${}^E G_m$  includes the first two interactions according to the CEF and is defined as

$${}^E G_m = \sum_{i_1} \sum_{i_2} \sum_j \sum_k \sum_l y_{i_1}^{(r)} y_{i_2}^{(r)} y_j^{(s)} y_k^{(t)} y_l^{(u)} L_{i_1, i_2; j, k, l} + \dots + \sum_{i_1} \sum_{i_2} \sum_{j_1} \sum_{j_2} \sum_k \sum_l y_{i_1}^{(r)} y_{i_2}^{(r)} y_{j_1}^{(s)} y_{j_2}^{(s)} y_k^{(t)} y_l^{(u)} L_{i_1, i_2; j_1, j_2; k, l} + \dots \quad (7)$$

The comma "," separate interacting constituents on the same sublattice, with ":" separating the sublattices. The first summation describes the regular interaction parameters,  $L_{i_1, i_2; j, k, l}$ , which represents interactions between  $i_1$  and  $i_2$  on sublattice  $r$ , when the other sublattices,  $s$ ,  $u$  and  $t$ , are occupied by constituents  $j$ ,  $k$  and  $l$ . This is the next nearest neighbour interactions.

The second summation is called the reciprocal parameters. They represent interaction on two sublattices,  $r$  and  $s$ , simultaneously while the other two sublattices,  $t$  and  $u$ , are occupied by constituents  $k$  and  $l$  respectively. This describes the nearest neighbour interactions, thus introduces a component to describe sro in the model.

As all the sublattices are equivalent, symmetry relations were applied to reduce the number of independent parameters.

## The intermetallic phases

The intermetallic compounds  $Pt_{21}Al_5$ ,  $Pt_{21}Al_8$ ,  $PtAl_2$ ,  $Pt_2Al_3$ ,  $PtAl$ ,  $Pt_5Al_3$  and  $Pt_2Al$  were treated as stoichiometric compounds. The  $\beta$  phase was assumed to be stoichiometric, since very little experimental information was available. The  $\beta$  phase was treated as  $Pt_{52}Al_{48}$ .

The Gibbs energy per formula unit  $Pt_mAl_n$  is expressed as

$${}^oG_m^{Pt_mAl_n} = m {}^oG_{Pt}^{fcc-Al} + n {}^oG_{Al}^{fcc-Al} + \Delta G_f^{Pt_mAl_n} \quad (8)$$

where  $\Delta G_f^{Pt_mAl_n}$  is the Gibbs energy of formation per mole of formula unit  $Pt_mAl_n$  and is given by the expression

$$\Delta G_f^{Pt_mAl_n} = a + b * T \quad (9)$$

The parameters  $a$  and  $b$  were evaluated in the present work.

## Optimisation

The optimization was carried out with the Parrot module [1984Jan] of the Thermo-Calc software [1985Sun]. With this module the Gibbs energy functions can be derived by fitting experimental data through a least square method. Different types of experimental data can be used and the weights can be assigned to the data based on the uncertainties associated with the original data.

In the initial optimization, the values from Wu and Jin [2000Wu] were used to calculate a basic set of data. The  $Pt_3Al$  phase was excluded. Once their phase diagram was reproduced, the fcc description was modified to the 4SL CEF formal. The ordered phases were introduced using the same Gibbs energy function as the disordered fcc. The results from Kuskofsky et al [2002Kus] were used to estimate starting values for the parameters. Conditions were set to ensure that  $PtAl_3$  and  $Pt_2Al_2$ , which are experimentally unstable in this system, were unstable in the thermodynamic description as well.

Both the  $Pt_2Al$  and  $\beta$  phases were introduced as a stoichiometric compounds. For the  $\beta$  phase, an initial metastable congruent melting formation was set. This could not be done for the  $Pt_2Al$  phase, since it forms in the solid state. The metastable congruent melting for the  $\beta$  phase was removed and the peritectic formation included. The decomposition of the  $\beta$  phase was introduced in the final set of optimisations.

## Results and Discussion

A self-consistent thermodynamic description has been obtained for the Al-Pt system. The 4SL CEF has been successfully applied in describing the order disorder transformation between the fcc and  $Pt_3Al$ . The calculated model parameters for the Al-Pt system are listed in Appendix I.

The calculated phase diagram is shown in Figure 1 and compared to the experimental data in Figure 2. The invariant temperatures and compositions are compared in Table 3. The calculated enthalpies of formation are compared to experimental, empirical and *ab initio* values in Table 2. The calculated enthalpy of formation for the  $Pt_3Al$  phase is compared with reported enthalpies of formation in Figure 4.

The calculated phase diagram is in good agreement with the experimental phase diagram of McAlister and Kahan [1986McA].

The calculated temperatures for the invariant reactions and compositions for the intermetallic phases are in good agreement with the experimental temperatures. The calculated eutectic temperature for the  $L \rightarrow \beta + Pt_5Al_3$  is ~ 50 degrees too high. This is not a well-defined area in the phase diagram from McAlister [1986McA], and could also be due to the estimation of the enthalpy of formation for the  $\beta$  phase.

The congruent formation of the  $Pt_3Al$  phase and  $L \rightarrow Pt_3Al + (Pt)$  eutectic reactions are not in very good agreement with the experimental diagram. The 4SL CEF model is of such that the formation composition of  $Pt_3Al$  is at 75 at. %, while it has been found to form congruently at 73.2 at. %. This off-stoichiometry formation cannot be reached with the model, and had an influence on the temperature as well as the enthalpy of formation



for the Pt<sub>3</sub>Al phase. The symmetry of the  $\beta$  phase is not possible to move the eutectic reaction to a lower Pt-contents.

Although the phase area of the (Pt) solid solution is too narrow, especially at lower temperatures, the phase area for the Pt<sub>3</sub>Al phase is acceptable. The Pt<sub>3</sub>Al phase is ordered throughout its phase area and the unstable PtAl<sub>3</sub> and Pt<sub>2</sub>Al<sub>2</sub> phases, which are introduced through the 4SL CEF, are not stable at any composition or temperature in the phase diagram, which is correct.

The calculated solubility of Pt in (Al) is too high.

Table 3.  
Experimental and calculated invariant compositions and temperatures for the Al-Pt system.


Reaction and Compositions (at. % Pt)	Reaction Temperature [K]	Reference
L ↔ Pt <sub>3</sub> Al + (Pt) 79.5 76.4 85.7 83.7 99	1780 1748	[1986McA] This work
PtAl + L ↔ β 50.0 53.7 51.5 50.0 52.0	1783 1783	[1986McA] This work
L ↔ Pt <sub>2</sub> Al <sub>3</sub> + PtAl 44.47 40.0 50.0 46.7 40.0 50	1741 1773	[1986McA] This work
L + Pt <sub>3</sub> Al ↔ Pt <sub>5</sub> Al <sub>3</sub> 62.3 67.3 62.5 62.5	1738 1720	[1986McA] This work
Pt <sub>5</sub> Al <sub>3</sub> + Pt <sub>3</sub> Al ↔ Pt <sub>2</sub> Al 62.7 67.0 67.5 62.5	1703 1701	[1986McA] This work
L + Pt <sub>2</sub> Al <sub>3</sub> ↔ PtAl <sub>2</sub> 31.8 40.0 33.3 40.0 33.3	1679 1671	[1986McA] This work
L ↔ β + Pt <sub>5</sub> Al <sub>3</sub> 55.7 57.9 66.5 52.0 62.5	1670 1724	[1986McA] This work
β ↔ PtAl + Pt <sub>5</sub> Al <sub>3</sub> 54.2 50.0 61.5 52.0 50.0 62.5	1533 1533	[1986McA] This work
L + PtAl <sub>2</sub> ↔ Pt <sub>8</sub> Al <sub>21</sub> 18.8 32.6 27.5 33.3 27.5	1400 1404	[1986McA] This work
L + Pt <sub>8</sub> Al <sub>21</sub> ↔ Pt <sub>5</sub> Al <sub>21</sub> 3.1 27.5 19.2 27.5 19.2	1079 1097	[1986McA] This work
L ↔ (Al) + Pt <sub>5</sub> Al <sub>21</sub> 0.4 0.0 19.2 19.2	930 910	[1986McA] This work
L ↔ Pt <sub>3</sub> Al 73.2 73.2 75.3 75.3	1829 1877	[1986McA] This work
L ↔ PtAl 50.0 50.0 50.0 50.0	1827 1827	[1986McA] This work
L ↔ Pt <sub>2</sub> Al <sub>3</sub> 40.0 40.0 40.0 40.0	1800 1800	[1986McA] This work

A consistent set of thermodynamic parameters, taking into account the order-disorder relation between Pt<sub>3</sub>Al-L1<sub>2</sub> and (Pt)-fcc, was obtained for the Al-Pt system. The 4SL CEF successfully described the fcc phases. The calculated phase diagram is in good agreement with the experimental phase diagram.

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## Appendix I

### Thermodynamic parameters for the Al-Pt system [J/mol atoms]

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

<b>Liquid</b>	Disordered Solution Phase: (Al,Pt) ${}^0 G_{Al}^{liq}(T) - H_{Al}^{0, fcc-Al}(298.15) : [1991Din]$ ${}^0 G_{Pt}^{liq}(T) - H_{Pt}^{0, hcp-A3}(298.15) : [1991Din]$ ${}^0 L_{(Al,Pt)}^{Liq} = -352540 + 114.8 * T$ ${}^1 L_{(Al,Pt)}^{Liq} = 68570 - 53 * T$
<b>fcc-A1</b>	Disordered Solution Phase: (Al,Pt)(Va) ${}^0 G_{Al}^{fcc-A1}(T) - H_{Al}^{0, fcc-A1}(298.15) : [1991Din]$ ${}^0 G_{Pt}^{fcc-A1}(T) - H_{Pt}^{0, fcc-A1}(298.15) : [1991Din]$ ${}^0 L_{(Al,Pt)}^{fcc-A1} = ULDO + DGO + 1.5 * USRO$ ${}^1 L_{(Al,Pt)}^{fcc-A1} = ULD1 + DG1$ ${}^2 L_{(Al,Pt)}^{fcc-A1} = ULD2 + DG2 - 1.5 * USRO$
<b>Pt<sub>5</sub>Al<sub>21</sub></b>	Stoichiometric Phase: (Al) <sub>0.8077</sub> (Pt) <sub>0.1923</sub> ${}^f G_{Al:Pt}^{Pt_5Al_{21}} = 0.8077 {}^0 G_{Al}^{fcc-A1} + 0.1923 {}^0 G_{Pt}^{fcc-A1} - 56870 + 14.8 * T$
<b>Pt<sub>8</sub>Al<sub>21</sub></b>	Stoichiometric Phase: (Al) <sub>0.7242</sub> (Pt) <sub>0.2759</sub> ${}^f G_{Al:Pt}^{Pt_8Al_{21}} = 0.7242 {}^0 G_{Al}^{fcc-A1} + 0.2759 {}^0 G_{Pt}^{fcc-A1} - 81805 + 23.2 * T$
<b>PtAl<sub>2</sub></b>	Stoichiometric Phase: (Al) <sub>0.666</sub> (Pt) <sub>0.334</sub> ${}^f G_{Al:Pt}^{PtAl_2} = 0.666 {}^0 G_{Al}^{fcc-A1} + 0.334 {}^0 G_{Pt}^{fcc-A1} - 87371 + 22.1 * T$
<b>Pt<sub>2</sub>Al<sub>3</sub></b>	Stoichiometric Phase: (Al) <sub>0.6</sub> (Pt) <sub>0.4</sub> ${}^f G_{Al:Pt}^{Pt_2Al_3} = 0.6 {}^0 G_{Al}^{fcc-A1} + 0.4 {}^0 G_{Pt}^{fcc-A1} - 89885 + 21.5 * T$
<b>PtAl</b>	Stoichiometric Phase: (Al) <sub>0.5</sub> (Pt) <sub>0.5</sub> ${}^f G_{Al:Pt}^{PtAl} = 0.5 {}^0 G_{Al}^{fcc-A1} + 0.5 {}^0 G_{Pt}^{fcc-A1} - 94071 + 24.1 * T$
<b>Beta</b>	Stoichiometric Phase: (Al) <sub>0.48</sub> (Pt) <sub>0.52</sub> ${}^f G_{Al:Pt}^{Beta} = 0.48 {}^0 G_{Al}^{fcc-A1} + 0.52 {}^0 G_{Pt}^{fcc-A1} - 92959 + 24.1 * T$
<b>Pt<sub>5</sub>Al<sub>3</sub></b>	Stoichiometric Phase: (Al) <sub>0.375</sub> (Pt) <sub>0.625</sub> ${}^f G_{Al:Pt}^{Pt_5Al_3} = 0.375 {}^0 G_{Al}^{fcc-A1} + 0.625 {}^0 G_{Pt}^{fcc-A1} - 87260 + 24 * T$
<b>Pt<sub>2</sub>Al</b>	Stoichiometric Phase: (Al) <sub>0.334</sub> (Pt) <sub>0.666</sub> ${}^f G_{Al:Pt}^{Pt_2Al} = 0.334 {}^0 G_{Al}^{fcc-A1} + 0.666 {}^0 G_{Pt}^{fcc-A1} - 85325 + 24.9 * T$
<b>L1<sub>2</sub> (Pt<sub>3</sub>Al)</b>	4SL-CEF: (Al,Pt) <sub>0.25</sub> (Al,Pt) <sub>0.25</sub> (Al,Pt) <sub>0.25</sub> (Al,Pt) <sub>0.25</sub> ${}^f G_{Al:Al:Al:Pt}^{L1_2} = {}^f G_{Al:Al:Pt:Al}^{L1_2} = {}^f G_{Al:Pt:Al:Al}^{L1_2} = {}^f G_{Pt:Al:Al:Al}^{L1_2} = UPTAL3$



$${}^f G_{Al:Al:Pt:Pt}^{L1_2} = {}^f G_{Al:Al:Pt:Pt}^{L1_2} = UPTAL$$

$${}^f G_{Al:Pt:Pt:Pt}^{L1_2} = {}^f G_{Pt:Al:Pt:Pt}^{L1_2} = {}^f G_{Pt:Pt:Al:Pt}^{L1_2} = {}^f G_{Pt:Pt:Pt:Al}^{L1_2} = UPT3AL$$

$$L_{Al, Pt:*,*}^{L1_2} = L_{*, Al, Pt:*,*}^{L1_2} = L_{*,*, Al, Pt:*}^{L1_2} = L_{*,*,*, Al, Pt}^{L1_2} = ULO$$

$$L_{Al, Pt:Al, Pt:*,*}^{L1_2} = L_{*, Al, Pt:Al, Pt:*}^{L1_2} = L_{*,*, Al, Pt:Al, Pt}^{L1_2} = L_{*, Al, Pt:*, Al, Pt}^{L1_2} = L_{Al, Pt:*, Al, Pt:*}^{L1_2} = USRO$$

UAB	= -13595 + 8.3 * T
UPTAL	= 3 * UAB - 3913
UPTAL3	= 4 * UAB
UPT3AL	= 3 * UAB
USRO	= UAB
ULO	= 1412.8 + 5.7 * T
ULD0	= -110531 - 22.9 * T
ULD1	= -25094
ULD2	= 21475
DGO	= UPTAL3 + 1.5 * UPTAL + UPT3AL
DG1	= 2 * UPTAL3 - 2 * UPT3AL
DG2	= UPTAL3 - 1.5 * UPTAL + UPT3AL

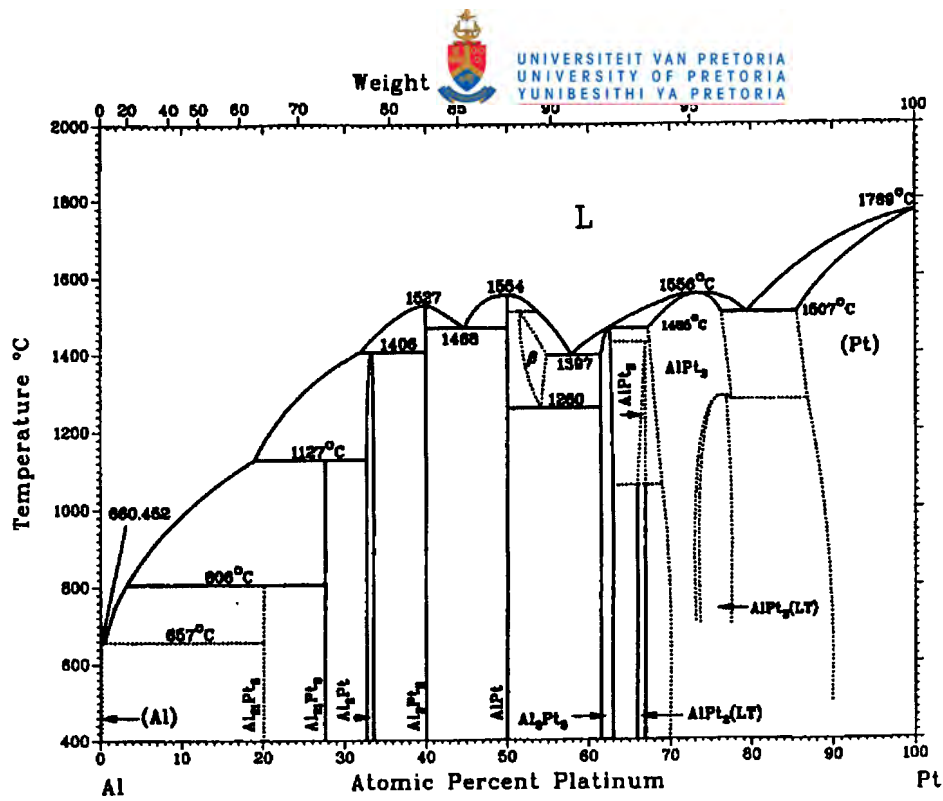


Figure 1. The Al-Pt phase diagram [1990Mas]

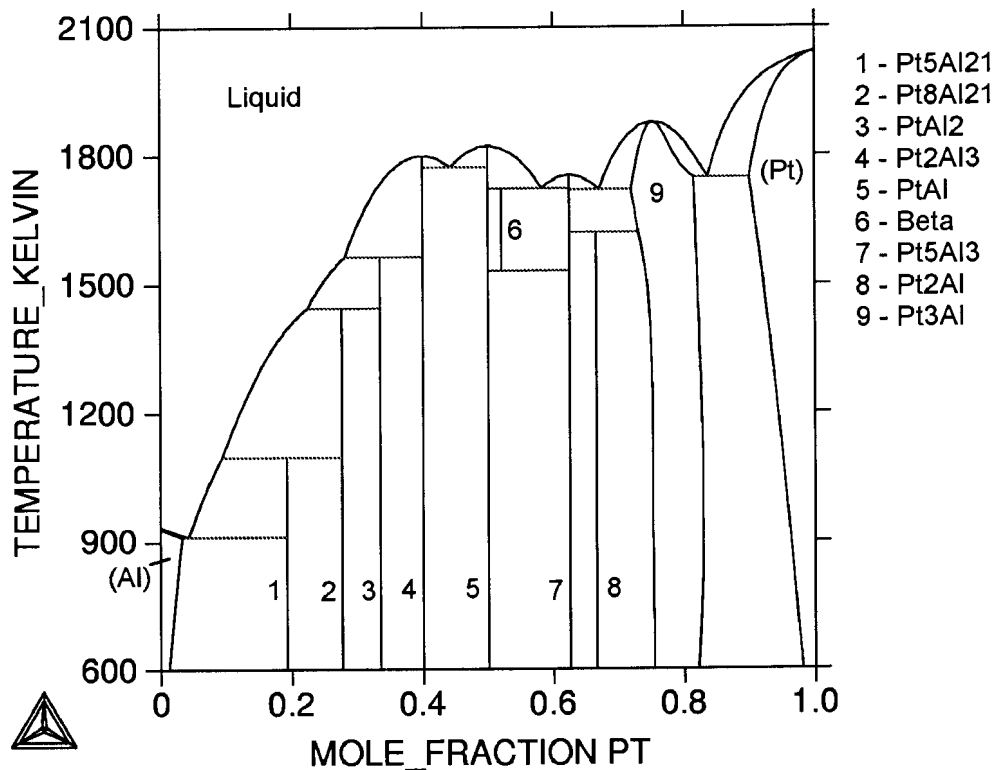


Figure 2. The calculated Al-Pt phase diagram.



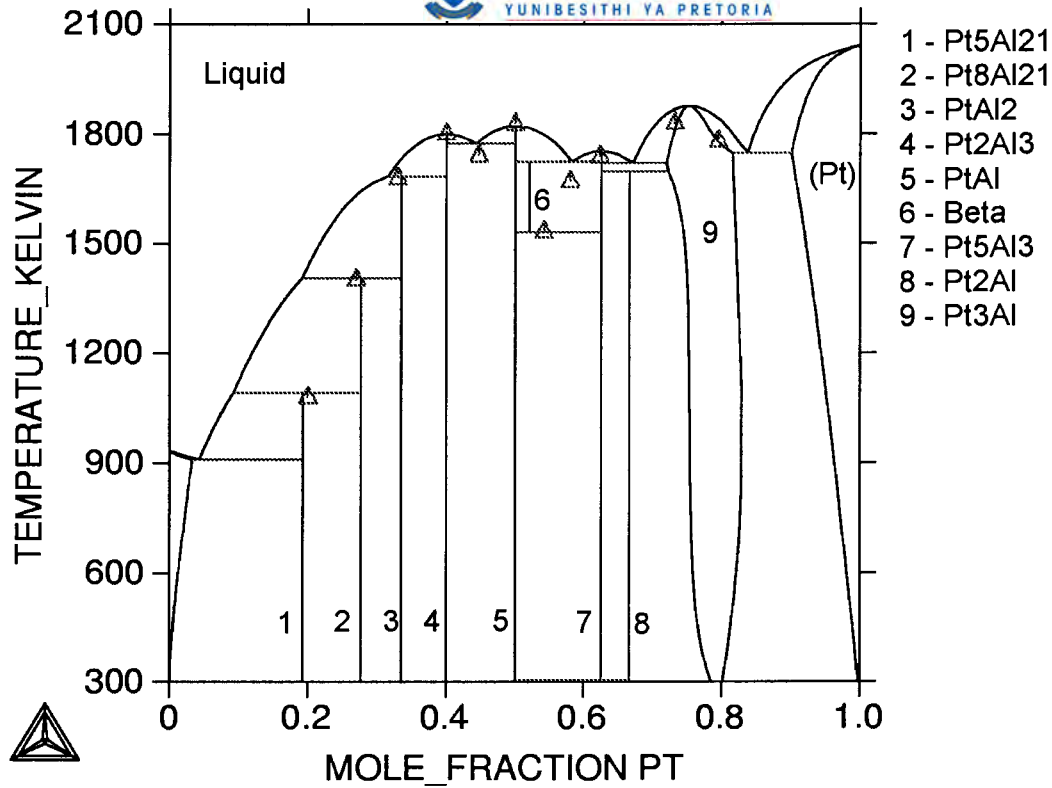


Figure 2. Comparison between the calculated phase diagram and experimental data [1986McA].

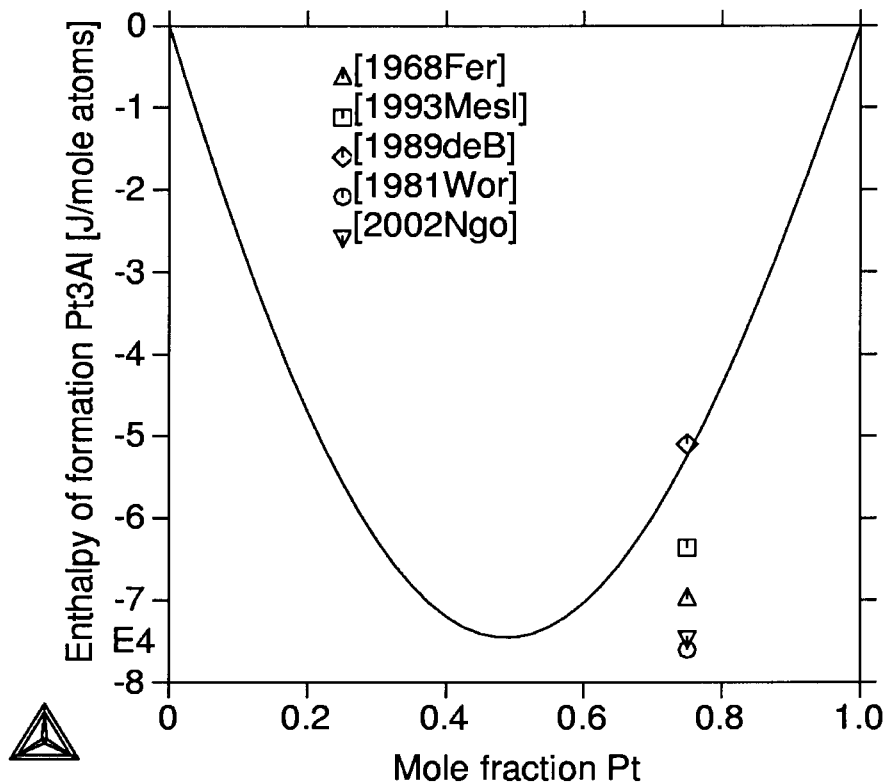


Figure 4. Comparison of the calculated, experimental [1968Fer, 1981Wor], Miedema estimated [1993Mes] and *ab initio* predicted [2002Ngo] enthalpy of formation at 298 K for the ordered  $Pt_3Al$  phase.

**XRD study of phases in an investigation of the Al-Pt-Ru system.** S.N.Prins<sup>a</sup>, P.S. Boucher<sup>a</sup> and L.A. Cornish<sup>b</sup>, <sup>a</sup> CSIR-NML, PO Box 395, Pretoria 0001, RSA, <sup>b</sup> Physical Metallurgy Division, Mintek, Private Bag X3015, Randburg, 2125, RSA.

Keywords: Al-Pt-Ru, Pt-based alloys, XRD

As part of a study for the development of alloys based on Pt for high temperature applications [1], the Al-Pt-Ru phase diagram has been investigated. Both arc-melted and annealed samples have been characterised using scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) [2]. The samples were annealed in argon at 600°C for 160 hours. The phases were initially identified by their compositions and morphology, and X-ray diffraction was used to identify the structures and verify the phase identification.

Bulk polished halves of the as-cast and annealed button samples were scanned in a Philips XRD with Cu K $\alpha$  radiation using a continuous scan from 4 to 90° 2 $\theta$ .

Initially, it was thought that the experimentally recorded spectra could be matched with standard spectra from the ICDD database [3] for the expected phases. However, many phases were not yet included in the ICDD database. Even for the binary phases that were in the database, the presence of the third element shifted the diffraction patterns of the phases significantly, rendering identification difficult, especially for non-cubic structures.

A lattice parameter refinement procedure was followed to identify the phases, as well as to calculate the modified lattice parameters for the phases. Where prototypes for the phases were given in the literature, and the prototype was included in the ICDD, the prototype structure was used as a starting point.

A ternary phase of composition  $\sim$ Ru<sub>12</sub>Pt<sub>15</sub>Al<sub>73</sub> was observed to be stable to room temperature. By employing a search-and-match method, it was found that the ternary phase exhibited a primitive cubic structure and lattice parameter of  $\sim$ 0.7721 nm, and was of similar type to IrAl<sub>2.75</sub> and RhAl<sub>2.63</sub>.

XRD confirmed most of the phase identification from the SEM/EDS results, and also showed that the  $\sim$ Ru<sub>12</sub>Pt<sub>15</sub>Al<sub>73</sub> phase was a true ternary phase, and not an extension of Ru<sub>4</sub>Al<sub>13</sub> as initially thought.

The Platinum Development Initiative and Department of Science and Technology are acknowledged for supporting this work.

- [1] L.A. Cornish, J. Hohls, P.J. Hill, S.N. Prins, R. Süss and D.N. Compton, 34<sup>th</sup> International October Conference on Mining and Metallurgy Proceedings, Ed. Z.S. Markovic and D.T. Zivkovic, 545-550, 30 September – 3 October 2002, Bor Lake, Yugoslavia.
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- [3] International Center for Diffraction Data (ICDD). 'Powder Diffraction File', Pennsylvania, USA, 2001.



## Thermodynamic Assessments of the Pt-Cr and Cr-Ru Systems with an Extrapolation into the Pt-Cr-Ru

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A CALPHAD-like assessment of the Pt-Cr system has been carried out, starting with the data obtained from an assessment by Oikawa et al. [2001Oik]. The Pt<sub>3</sub>Cr phase was not included in their assessment. A four sublattice model has been incorporated in order to add the L1<sub>2</sub> ordered Pt<sub>3</sub>Cr phase. This phase shows an ordered-disordered transition from L1<sub>2</sub> to fcc at about 1403 K.

Within the Cr-Ru system a sigma phase (Strukturbericht D8b) has been modelled. The sigma model with 10:4:16 sites was used [2003Sun].

An extrapolation to the ternary system Pt-Cr-Ru has been made, with an emphasis on L1<sub>2</sub> ordered phases close to the Pt-rich side.

Financial assistance of the Department of Science and Technology, South Africa and the Platinum Development Initiative is gratefully acknowledged.

### References

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- [2003Sun] B. Sundman, private communication



## A STUDY OF THE Pt-Al-Ru SYSTEM AT 600°C

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The Pt-Al-Ru system is being studied as part of a larger project to develop and optimise Pt-based alloys for high temperature use [1]. These alloys are based on a two-phase microstructure of  $\sim\text{Pt}_3\text{Al}$  in a (Pt) matrix, analogous to the  $\gamma/\gamma'$  microstructure of Ni-based superalloys. Work has been done on the Pt-Al-Ru system [2,3] and the liquidus surface has been derived from as-cast alloys [3].

Six alloys were selected from the alloys so as to contain the phases of interest. The samples were sealed in silica tubes backfilled with argon and annealed at 600°C for 3 weeks. They were prepared metallographically and studied with a LEO 1525 SEM and Oxford INCA EDS. The phases were confirmed, as far as possible, using a Philips XRD with Cu K alpha radiation on solid samples.

The  $\sim\text{Pt}_{51}:\text{Al}_{21}:\text{Ru}_{28}$  sample comprised coarse needles of (Ru) in a binary eutectic of fine (Ru) needles and  $\sim\text{Pt}_3\text{Al}$ . Compared to the as-cast sample, the fine needles had coarsened, and there were no traces of the (Pt) component. Thus the heat treatment had removed the ternary eutectic which appeared due to non-equilibrium cooling. There was precipitation of  $\sim\text{Pt}_3\text{Al}$  in the coarse (Ru) needles; this indicated that the (Ru) solvus slopes to lower Ru contents at lower temperatures, and agrees with Obrowski's observations in the Al-Ru system [4].

The as-cast  $\sim\text{Pt}_{25}:\text{Al}_{46}:\text{Ru}_{29}$  sample comprised very cored  $\sim\text{RuAl}$  dendrites in a matrix of  $\sim\text{PtAl} + \text{Pt}_5\text{Al}_3$  which had originated from solid state decomposition of the high temperature beta phase. The heat treated sample showed much reduced coring (Fig. 1) and coarsening in the matrix phases.

The  $\sim\text{Pt}_{39}:\text{Al}_{52}:\text{Ru}_9$  sample in the as-cast condition had a complex structure that revealed primary formation of cored  $\sim\text{RuAl}$  followed by the formation of PtAl and  $\text{Pt}_2\text{Al}_3$ . The actual reactions were difficult to interpret since the PtAl and  $\text{Pt}_2\text{Al}_3$  phases were extremely fine. Annealing at 600°C reduced the coring in  $\sim\text{RuAl}$  and coarsened the microstructure so that a eutectic between  $\sim\text{RuAl}$  and  $\sim\text{PtAl}$  was revealed. The  $\sim\text{PtAl}$  within the eutectic had a higher Ru content, and so had a slightly darker contrast as indicated by the arrow in Fig. 2.

As-cast  $\sim\text{Pt}_{14}:\text{Al}_{54}:\text{Ru}_{32}$  was another complex sample and was not at equilibrium since it contained four phases:  $\sim\text{RuAl}$ ,  $\sim\text{RuAl}_2$ ,  $\sim\text{PtAl}_2$ , and  $\sim\text{Ru}_{12}\text{Pt}_{15}\text{Al}_{73}$ , a new ternary phase [3]. The annealed sample only had three phases:  $\sim\text{RuAl}$ ,  $\sim\text{RuAl}_2$  and  $\sim\text{PtAl}_2$ . In addition, there was precipitation of  $\sim\text{RuAl}_2$  within  $\sim\text{PtAl}_2$

The as-cast  $\sim\text{Pt}_{28}:\text{Al}_{64}:\text{Ru}_8$  specimen contained dendrites of  $\sim\text{Ru}_{12}\text{Pt}_{15}\text{Al}_{73}$  surrounded by  $\sim\text{PtAl}_2$ , in a eutectic comprising  $\sim\text{PtAl}_2$  and  $\sim\text{Ru}_{12}\text{Pt}_{15}\text{Al}_{73}$ . In the annealed condition, there was much less of the  $\sim\text{Ru}_{12}\text{Pt}_{15}\text{Al}_{73}$  phase and the eutectic had coarsened.

In the as-cast condition, the  $\sim\text{Pt}_8:\text{Al}_{85}:\text{Ru}_7$  alloy had two distinct microstructures locally and the primary phase was different in each:  $\sim\text{Ru}_{12}\text{Pt}_{15}\text{Al}_{73}$  and  $\sim\text{Pt}_5\text{Al}_{21}$  respectively. The other phases were



$\sim\text{RuAl}_6$  and (Al). Although the annealed sample contained regions which appeared different, the  $\sim\text{Pt}_5\text{Al}_{21}$  phase had disappeared, and the  $\sim\text{RuAl}_6$  phase was not discerned. However, since the  $\sim\text{Ru}_{12}\text{Pt}_{15}\text{Al}_{73}$  phase still showed coring, it is likely that the  $\sim\text{RuAl}_6$  phase was still present and was in local equilibrium with the less Pt-rich composition of  $\sim\text{Ru}_{12}\text{Pt}_{15}\text{Al}_{73}$ , but too fine to detect.

The phase and alloys' EDS analyses were plotted and compared to the as-cast values. The alloys suffered minimal aluminium loss on annealing.  $\text{Pt}_3\text{Al}$  had lost all discernible Ru, which agrees with other work [2]. Similarly,  $\text{RuAl}_2$  had negligible Pt after annealing, showing that the solubility for Pt decreases with temperature. The composition of  $\sim\text{Ru}_{12}\text{Pt}_{15}\text{Al}_{73}$  moved to slightly lower Pt contents at lower temperatures. Two samples exhibited a similar and a higher Ru composition for the  $\sim\text{PtAl}_2$  phase than in the as-cast samples, indicating that the solubility increased with temperature. Both the  $\text{PtAl}$  and  $\text{Pt}_2\text{Al}_3$  phase compositions shifted to more stoichiometric values after annealing, indicating a contraction in phase width at lower temperatures. At  $600^\circ\text{C}$ , the penetration of the  $\sim\text{RuAl}$  phase was reduced compared to the as-cast samples: from  $\sim 26$  at. % Pt to  $\sim 22$  at. % Pt. In addition, the phase width narrowed at lower temperatures.

Annealing the samples at  $600^\circ\text{C}$  equilibrated them to some degree; no sample had more than three phases, and the compositions had changed to more stoichiometric values. The only unexpected result was that the  $\sim\text{PtAl}_2$  phase extended to higher ruthenium contents.

## References

- [1] L.A. Cornish, J. Hohls, P.J. Hill, S.N. Prins, R. Süß and D.N. Compton, 34<sup>th</sup> International October Conference on Mining and Metallurgy Proceedings, Ed. Z.S. Markovic and D.T. Zivkovic, 545-550, 30 September - 3 October 2002, Bor Lake, Yugoslavia.
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- [4] W. Obrowski, *Metallwissenschaft und Technik* (Berlin), 17 (1960) 108-112.
- [5] This research was supported by the PDI and the DS&T, South Africa.

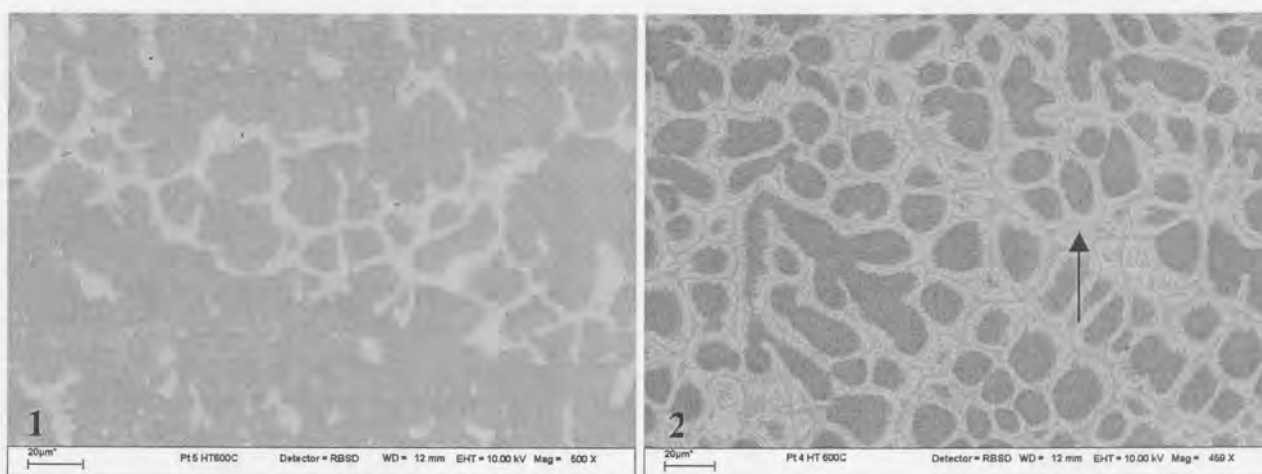


Fig. 1.  $\sim\text{Pt}_{25}:\text{Al}_{46}:\text{Ru}_{29}$ : BSE image showing  $\sim\text{RuAl}$  (dark) in a matrix of  $\sim\text{PtAl} + \text{Pt}_5\text{Al}_3$  (light).  
Fig. 2.  $\sim\text{Pt}_{39}:\text{Al}_{52}:\text{Ru}_9$ : BSE image showing  $\sim\text{RuAl}$  (dark),  $\sim\text{PtAl}$  (light) and  $\text{Pt}_2\text{Al}_3$  (medium grey).

## Appendix B

### XRD lattice parameter refinement on sample PAR4.

The XRD spectrum for sample PAR4 is shown in Figure 1, and the d-values and intensities of the spectrum as recorded on a Philips XRD are listed in Table 1.

From EDS analysis, it was proposed that the phases present in this sample are RuAl, PtAl and Pt<sub>2</sub>Al<sub>3</sub>. Initial XRD spectrum matching showed that PtAl<sub>2</sub> are possibly present in the sample. Furthermore, neither the PtAl nor Pt<sub>2</sub>Al<sub>3</sub> phases are included in the ICDD. However, PdAl and Pd<sub>2</sub>Al<sub>3</sub> are similar to PtAl and Pt<sub>2</sub>Al<sub>3</sub>, respectively, in crystal structure and lattice parameter and are included in the ICDD. The presence of the PtAl<sub>2</sub> phase found in the XRD is in contradiction to the EDS results. It was further found that it is difficult to distinguish between PtAl<sub>2</sub> and RuAl, since the standard diffraction patterns overlap almost completely.

For each of the four phases, a lattice refinement was done with the WinCell program [2000Raj]. To do the refinement, the hkl values for each phase and the observed corresponding two theta values (from Table 1) were entered into the program. WinCell does not take the peak intensities into account. An estimate of the lattice parameter is also entered.

The WinCell input screen for the PdAl phase is shown in Figure 2. The software then calculates through a non-linear regression the lattice parameter and the corresponding R<sup>2</sup> of the phase. The presence of a third element in the binary structures shifted the two theta values in some cases, and more than one attempt was then needed to identify the relevant two theta values to obtain the best R<sup>2</sup> value.

The WinCell output sheets for the four phases are attached. Output 2 is for PtAl<sub>2</sub>, which is actually NOT present in the sample, but it is interesting to note that both RuAl and PtAl<sub>2</sub> gave a good fit (factor R at the bottom of each output sheet). As can be seen from the input values listed in Table 2, RuAl overlaps completely with PtAl<sub>2</sub>. On closer investigation, comparing the input data with the ICDD standard reflections, the (311) reflection for PtAl<sub>2</sub> is absent. The (311) reflection for PtAl<sub>2</sub>, which appeared at 51.010 two theta, initially gave a bad fit in the refinement and was removed. The pattern then gave a much better R<sup>2</sup> value. However, since this is a major reflection for the PtAl<sub>2</sub> phase and the (311) reflection should not have been removed in the first place. Following the EDS analysis that suggested RuAl, a good fit was obtained for RuAl. It can be seen that there are many overlaps and that the relative intensities of the reflections should be considered where doubt exists.

This shows the power of using lattice refinement to confirm the presence of the phase. However, care should be taken since WinCell does not take into account the intensities of the reflections. It also be stated that WinCell does not ensure that space group conditions are met, and the operator must check the selected hkl values to make sure that they are not conflicting the space group rules.

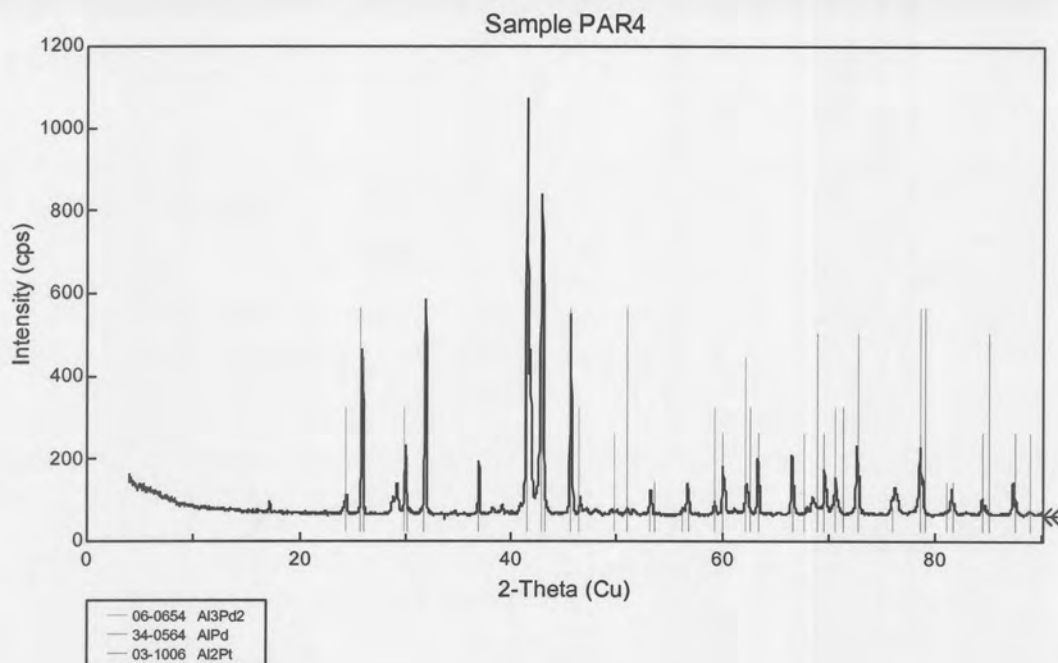


Figure 1. XRD spectrum for sample PAR4.

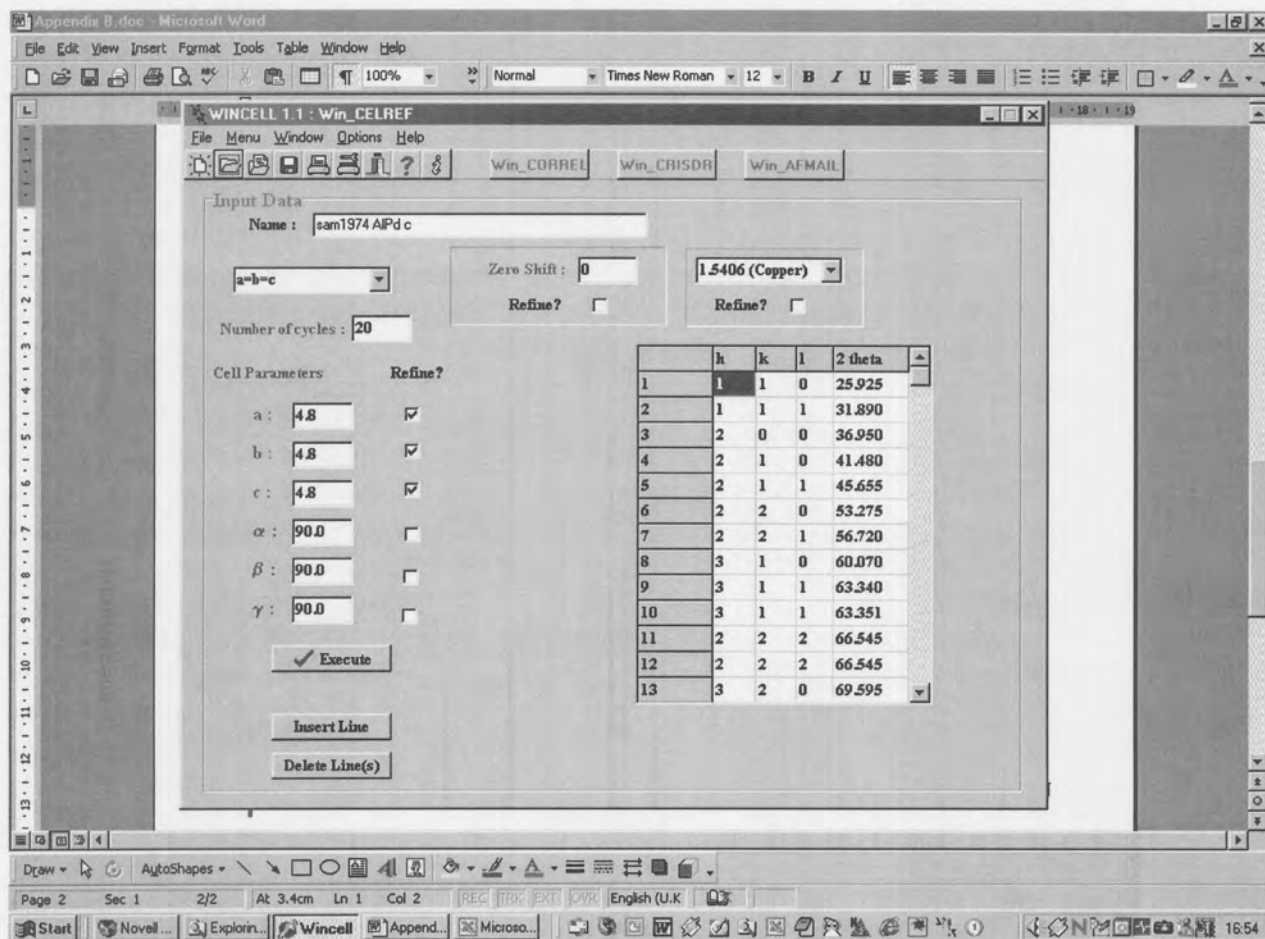


Figure 2. Input screen for the PdAl phase into WinCell.

Table 1. Comparison of WinCell input for RuAl and PtAl<sub>2</sub>.

RuAl				PtAl <sub>2</sub>			
h	k	l	2 theta	h	k	l	2 theta
1	0	0	30.000	1	1	1	25.925
1	1	0	42.965	2	0	0	30.000
1	1	1	53.275	2	2	0	42.965
2	0	0	62.260	2	2	2	53.275
2	1	0	70.260	4	0	0	62.260
2	1	1	78.595	3	3	1	68.515
2	1	0	78.579	4	2	0	70.675
				4	2	2	78.595
				4	2	2	78.579
				5	1	1	84.360



## Appendix C

### Thermodynamic database for Al-Pt-Ru



This database was extrapolated from the binaries, and no ternary parameters have been optimised yet.

The metastable parameters for Pt-bcc and Pt-hcp were added to the bcc and hcp phase descriptions. Due to the additions to the disorder descriptions, the ordered phases had to be stabilised. Pt was added as a third element to the B2 sublattices and Ru was added to the L12 sublattices to stabilise these two phases in the ternary, but no interaction parameters were included for these additions.

No ternary parameters were included for any phases.

```
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 AL FCC_A1            2.6982E+01 4.5773E+03 2.8322E+01!
ELEMENT PT FCC_A1            1.9508E+02 5.7237E+03 4.1631E+01!
ELEMENT RU HCP_A3            1.0107E+02 4.6024E+03 2.8535E+01!

FUNCTION GHSERPT  2.98150E+02 -7595.631+124.38828*T-24.5526*T*LN(T)
-.00248297*T**2-2.0138E-08*T**3+7974*T**(-1); 1.30000E+03 Y
-9253.174+161.52962*T-30.2527*T*LN(T)+.002321665*T**2-6.56947E-07*T**3
-272106*T**(-1); 2.04210E+03 Y
-222518.97+1021.2109*T-136.42269*T*LN(T)+.020501692*T**2
-7.60985E-07*T**3+71709819*T**(-1); 4.00000E+03 N!
FUNCTION GHSERRU  2.98150E+02 -7561.873+127.86623*T-22.914329*T*LN(T)
-.004062566*T**2+1.7641E-07*T**3+56377*T**(-1); 1.50000E+03 Y
-59448.103+489.51621*T-72.324122*T*LN(T)+.018726245*T**2
-1.952433E-06*T**3+11063885*T**(-1); 2.60700E+03 Y
-38588773+168610.52*T-21329.705*T*LN(T)+5.221639*T**2
-2.4024599E-04*T**3+1.3082993E+10*T**(-1); 2.74000E+03 Y
-55768.304+364.48231*T-51.8816*T*LN(T); 4.50000E+03 N!
FUNCTION GHSERAL  2.98140E+02 -7976.15+137.093038*T-24.3671976*T*LN(T)
-.001884662*T**2-8.77664E-07*T**3+74092*T**(-1); 7.00000E+02 Y
-11276.24+223.048446*T-38.5844296*T*LN(T)+.018531982*T**2
-5.764227E-06*T**3+74092*T**(-1); 9.33470E+02 Y
-11278.378+188.684153*T-31.748192*T*LN(T)-1.230524E+28*T**(-9);
2.90000E+03 N!
FUNCTION GHCPAL  2.98150E+02 +5481-1.799*T+GHSERAL#; 6.00000E+03 N!
FUNCTION GHCPPT  2.98150E+02 +2500+.1*T+GHSERPT#; 4.00000E+03 N!
FUNCTION GBCCPT  2.98150E+02 +15000-2.4*T+GHSERPT#; 4.00000E+03 N!
FUNCTION GBCCAL  2.98150E+02 +10083-4.813*T+GHSERAL#; 6.00000E+03 N
!
FUNCTION GBCCRU  2.98150E+02 +26500-6.2*T+GHSERRU#; 4.50000E+03 N!
FUNCTION GFCCRU  2.98150E+02 +12500-2.4*T+GHSERRU#; 4.50000E+03 N!
FUNCTION UAB     2.98150E+02 -13595+8.3*T; 6.00000E+03 N!
FUNCTION UPT3AL  2.98150E+02 +3*UAB#-3913; 6.00000E+03 N!
FUNCTION UPTAL   2.98150E+02 +4*UAB#; 6.00000E+03 N!
FUNCTION UPTAL3  2.98150E+02 +3*UAB#; 6.00000E+03 N!
FUNCTION UL0     2.98150E+02 +1412.8+5.7*T; 6.00000E+03 N!
```

FUNCTION USRO 2.98150E+02 +UAB#; 6.00000E+03 N!  
 FUNCTION ULD0 2.98150E+02 -110531-22.9\*T; 6.00000E+03 N!  
 FUNCTION ULD1 2.98150E+02 -25094; 6.00000E+03 N!  
 FUNCTION ULD2 2.98150E+02 21475; 6.00000E+03 N!  
 FUNCTION DG0 2.98150E+02 +UPTAL3#+1.5\*UPTAL#+UPT3AL#; 6.00000E+03  
 N!  
 FUNCTION DG1 2.98150E+02 +2\*UPTAL3#-2\*UPT3AL#; 6.00000E+03 N!  
 FUNCTION DG2 2.98150E+02 +UPTAL3#-1.5\*UPTAL#+UPT3AL#; 6.00000E+03  
 N!  
 FUNCTION UN\_ASS 2.98150E+02 0.0; 3.00000E+02 N!

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 DEFINE\_SYSTEM\_DEFAULT ELEMENT 2!  
 DEFAULT\_COMMAND DEF\_SYS\_ELEMENT VA!

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 CONSTITUENT LIQUID:L :AL,PT,RU : !

PARAMETER G(LIQUID,AL;0) 2.98140E+02 +11005.553-11.840873\*T  
 +7.9401E-20\*T\*\*7+GHSERAL#; 9.33600E+02 Y  
 +10481.974-11.252014\*T+1.234264E+28\*T\*\*(-9)+GHSERAL#; 2.90000E+03 N  
 REF0 !

PARAMETER G(LIQUID,PT;0) 2.98150E+02 +12520.614+115.11473\*T  
 -24.5526\*T\*LN(T)-.00248297\*T\*\*2-2.0138E-08\*T\*\*3+7974\*T\*\*(-1); 6.00000E+02  
 Y  
 +19019.913+33.017485\*T-12.351404\*T\*LN(T)-.011543133\*T\*\*2+9.30579E-07\*T\*\*3  
 -600885\*T\*\*(-1); 2.04210E+03 Y  
 +1404.968+205.86191\*T-36.5\*T\*LN(T); 4.00000E+03 N REF0 !

PARAMETER G(LIQUID,RU;0) 2.98140E+02 +19918.743+119.467485\*T  
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 8.00000E+02 Y  
 +50827.232-179.818561\*T+19.539341\*T\*LN(T)-.026524167\*T\*\*2  
 +1.667839E-06\*T\*\*3-3861125\*T\*\*(-1); 2.60700E+03 Y  
 -17161.807+349.673561\*T-51.8816\*T\*LN(T); 4.50000E+03 N REF0 !

PARAMETER G(LIQUID,AL,RU;0) 2.98150E+02 -73000-14\*T; 6.00000E+03 N  
 REF0 !

PARAMETER G(LIQUID,AL,RU;1) 2.98150E+02 -56000; 6.00000E+03 N REF0 !

PARAMETER G(LIQUID,AL,PT;0) 2.98150E+02 -352536+114.8\*T; 6.00000E+03  
 N REF0 !

PARAMETER G(LIQUID,AL,PT;1) 2.98150E+02 +68566-53\*T; 6.00000E+03 N  
 REF0 !

PARAMETER G(LIQUID,PT,RU;0) 2.98140E+02 -8000; 4.00000E+03 N REF0 !

\$ THIS PHASE HAS A DISORDERED CONTRIBUTION FROM BCC\_A2

PHASE B2 % 3 .5 .5 3 !

CONSTITUENT B2 :AL%,PT,RU,VA : AL,PT%,RU%,VA : VA% : !

PARAMETER G(B2,AL:AL:VA;0) 298.15 0; 6000 N!

PARAMETER G(B2,PT:AL:VA;0) 2.98150E+02 +V50#+V51#\*T; 6.00000E+03 N  
 REF0 !

PARAMETER G(B2,RU:AL:VA;0) 2.98150E+02 -87600; 6.00000E+03 N REF0 !

PARAMETER G(B2,VA:AL:VA;0) 298.15 0; 6000 N!

PARAMETER G(B2,AL:PT:VA;0) 2.98150E+02 +V50#+V51#\*T; 6.00000E+03 N

REF0 !

PARA G(B2,PT:PT:VA;0) 298.15 0; 6000 N!  
 PARA G(B2,RU:PT:VA;0) 298.15 0; 6000 N!  
 PARA G(B2,VA:PT:VA;0) 298.15 0; 6000 N!  
 PARAMETER G(B2,AL:RU:VA;0) 2.98150E+02 -87600; 6.00000E+03 N REF0 !  
 PARA G(B2,PT:RU:VA;0) 298.15 0; 6000 N!  
 PARA G(B2,RU:RU:VA;0) 298.15 0; 6000 N!  
 PARA G(B2,VA:RU:VA;0) 298.15 0; 6000 N!  
 PARA G(B2,AL:VA:VA;0) 298.15 0; 6000 N!  
 PARA G(B2,PT:VA:VA;0) 298.15 0; 6000 N!  
 PARA G(B2,RU:VA:VA;0) 298.15 0; 6000 N!  
 PARA G(B2,VA:VA:VA;0) 298.15 0; 6000 N!  
 PARAMETER G(B2,AL,RU:AL:VA;0) 2.98150E+02 -73000; 6.00000E+03 N

REF0 !

PARAMETER G(B2,AL,PT:AL:VA;0) 2.98150E+02 +V52#+V53#\*T; 6.00000E+03 N REF0 !

PARAMETER G(B2,AL,PT,RU:AL:VA;0) 2.98150E+02 +V54#+V55#\*T; 6.00000E+03 N REF0 !

PARAMETER G(B2,AL:AL,RU:VA;0) 2.98150E+02 -73000; 6.00000E+03 N REF0 !

PARAMETER G(B2,AL:AL,PT:VA;0) 2.98150E+02 +V52#+V53#\*T; 6.00000E+03 N REF0 !

PARAMETER G(B2,AL:AL,PT,RU:VA;0) 2.98150E+02 +V54#+V55#\*T; 6.00000E+03 N REF0 !

PARAMETER G(B2,VA:AL,RU:VA;0) 2.98150E+02 +80\*T; 6.00000E+03 N REF0 !

PARAMETER G(B2,VA:AL,PT:VA;0) 2.98150E+02 +80\*T; 6.00000E+03 N REF0 !

PARAMETER G(B2,VA:PT,RU:VA;0) 2.98150E+02 +80\*T; 6.00000E+03 N REF0 !

PARAMETER G(B2,AL,RU:VA:VA;0) 2.98150E+02 +80\*T; 6.00000E+03 N REF0 !

PARAMETER G(B2,AL,PT:VA:VA;0) 2.98150E+02 +80\*T; 6.00000E+03 N REF0 !

PARAMETER G(B2,PT,RU:VA:VA;0) 2.98150E+02 +80\*T; 6.00000E+03 N REF0 !

TYPE\_DEFINITION & GES AMEND\_PHASE\_DESCRIPTION B2 DIS\_PART BCC\_A2,,!

TYPE\_DEFINITION 'GES A\_P\_D BCC\_A2 MAGNETIC -1.0 4.00000E-01 !

PHASE BCC\_A2 %&' 2 1 3 !

CONSTITUENT BCC\_A2 :AL,PT,RU,VA : VA : !

PARAMETER G(BCC\_A2,AL:VA;0) 2.98140E+02 +GBCCAL#; 2.90000E+03 N REF0 !

PARAMETER G(BCC\_A2,PT:VA;0) 2.98140E+02 +GBCCPT#; 4.50000E+03 N REF0 !

PARAMETER G(BCC\_A2,RU:VA;0) 2.98140E+02 +GBCCRU#; 4.50000E+03 N REF0 !

PARA G(BCC\_A2,VA:VA;0) 298.15 0; 6000 N!

PARAMETER G(BCC\_A2,AL,RU:VA;0) 2.98150E+02 -176000+32\*T; 6.00000E+03 N REF0 !

PARAMETER G(BCC\_A2,AL,VA:VA;0) 2.98150E+02 +120\*T; 6.00000E+03 N REF0 !

PARAMETER G(BCC\_A2,PT,RU:VA;0) 2.98140E+02 0.0; 4.00000E+03 N REF0 !

PARAMETER G(BCC\_A2,PT,RU:VA;1) 2.98140E+02 0.0; 4.00000E+03 N REF0 !

PARAMETER G(BCC\_A2,PT,VA:VA;0) 2.98150E+02 +120\*T; 6.00000E+03 N REF0 !

PARAMETER G(BCC\_A2,RU,VA:VA;0) 2.98150E+02 +120\*T; 6.00000E+03 N REF0 !

PHASE BETA % 2.48 .52 !

CONSTITUENT BETA :AL : PT : !

PARAMETER G(BETA,AL:PT;0) 2.98150E+02 -92723+23.88\*T+.48\*GHSERAL#  
+.52\*GHSERPT#; 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 :AL,PT,RU : VA : !

PARAMETER G(FCC\_A1,AL:VA;0) 2.98140E+02 +GHSERAL#; 2.90000E+03 N REF0 !  
PARAMETER G(FCC\_A1,PT:VA;0) 2.98150E+02 +GHSERPT#; 4.50000E+03 N REF0 !  
PARAMETER G(FCC\_A1,RU:VA;0) 2.98150E+02 +4938.127+125.46623\*T  
-22.914329\*T\*LN(T)-.004062566\*T\*\*2+1.7641E-07\*T\*\*3+56377\*T\*\*(-1);  
1.50000E+03 Y  
-46948.103+487.11621\*T-72.324122\*T\*LN(T)+.018726245\*T\*\*2  
-1.952433E-06\*T\*\*3+11063885\*T\*\*(-1); 2.60700E+03 Y  
-38576273+168608.12\*T-21329.705\*T\*LN(T)+5.221639\*T\*\*2-2.4024599E-04\*T\*\*3  
+1.3082993E+10\*T\*\*(-1); 2.74000E+03 Y  
-43268.304+362.08231\*T-51.8816\*T\*LN(T); 4.50000E+03 N REF0 !  
PARAMETER G(FCC\_A1,AL,PT:VA;0) 2.98150E+02 +ULD0#+DG0#+1.5\*USRO#;  
6.00000E+03 N REF0 !  
PARAMETER G(FCC\_A1,AL,PT:VA;1) 2.98150E+02 +ULD1#+DG1#; 6.00000E+03  
N REF0 !  
PARAMETER G(FCC\_A1,AL,PT:VA;2) 2.98150E+02 +ULD2#+DG2#-1.5\*USRO#;  
6.00000E+03 N REF0 !  
PARAMETER G(FCC\_A1,AL,PT,RU:VA;0) 2.98150E+02 +V10#+V11#\*T;  
6.00000E+03 N REF0 !  
PARAMETER G(FCC\_A1,AL,RU:VA;0) 2.98150E+02 -10000-10\*T; 6.00000E+03  
N REF0 !  
PARAMETER G(FCC\_A1,PT,RU:VA;0) 2.98140E+02 -17249.639-2.745999\*T;  
4.00000E+03 N REF0 !  
PARAMETER G(FCC\_A1,PT,RU:VA;1) 2.98140E+02 13184.597; 4.00000E+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 :AL,PT,RU : VA : !

PARAMETER G(HCP\_A3,AL:VA;0) 2.98140E+02 +GHCPAL#; 2.90000E+03 N REF0 !  
PARAMETER G(HCP\_A3,PT:VA;0) 2.98150E+02 -5095.631+124.48828\*T  
-24.5526\*T\*LN(T)-.00248297\*T\*\*2-2.0138E-08\*T\*\*3+7974\*T\*\*(-1); 1.30000E+03  
Y  
-6753.174+161.62962\*T-30.2527\*T\*LN(T)+.002321665\*T\*\*2-6.56947E-07\*T\*\*3  
-272106\*T\*\*(-1); 2.04210E+03 Y  
-220018.97+1021.3109\*T-136.42269\*T\*LN(T)+.020501692\*T\*\*2-7.60985E-07\*T\*\*3  
+71709819\*T\*\*(-1); 4.00000E+03 N REF0 !  
PARAMETER G(HCP\_A3,RU:VA;0) 2.98150E+02 +GHSERRU#; 4.50000E+03 N REF0 !  
PARAMETER G(HCP\_A3,AL,RU:VA;0) 2.98150E+02 -105000+30\*T; 6.00000E+03  
N REF0 !  
PARAMETER G(HCP\_A3,AL,PT:VA;0) 2.98150E+02 50000; 6.00000E+03 N  
REF0 !  
PARAMETER G(HCP\_A3,AL,PT,RU:VA;0) 2.98150E+02 +V15#+V16#\*T;  
6.00000E+03 N REF0 !  
PARAMETER G(HCP\_A3,PT,RU:VA;0) 2.98140E+02 +8629.8149-7.889606\*T;

4.00000E+03 N REF0 !

PARAMETER G(HCP\_A3,PT,RU:VA;1) 2.98140E+02 -5283.9355; 4.00000E+03 N  
REF0 !

\$ THIS PHASE HAS A DISORDERED CONTRIBUTION FROM FCC\_A1  
TYPE\_DEFINITION \* GES AMEND\_PHASE\_DESCRIPTION L12 DIS\_PART FCC\_A1,,,  
PHASE L12 %\* 5 .25 .25 .25 .25 1 !  
CONSTITUENT L12 :AL,PT,RU : AL,PT,RU : AL,PT,RU : AL,PT,RU : VA : !

PARAMETER G(L12,AL:AL:AL:AL:VA;0) 298.15 0; 6000 N!  
PARAMETER G(L12,PT:AL:AL:AL:VA;0) 2.98150E+02 +UPTAL3#; 3.00000E+03 N  
REF0 !

PARAMETER G(L12,RU:AL:AL:AL:VA;0) 298.15 0; 6000 N!  
PARAMETER G(L12,AL:PT:AL:AL:VA;0) 2.98150E+02 +UPTAL3#; 3.00000E+03 N  
REF0 !

PARAMETER G(L12,PT:PT:AL:AL:VA;0) 2.98150E+02 +UPTAL#; 3.00000E+03 N  
REF0 !

PARAMETER G(L12,RU:PT:AL:AL:VA;0) 298.15 0; 6000 N!  
PARAMETER G(L12,AL:RU:AL:AL:VA;0) 298.15 0; 6000 N!  
PARAMETER G(L12,PT:RU:AL:AL:VA;0) 298.15 0; 6000 N!  
PARAMETER G(L12,RU:RU:AL:AL:VA;0) 298.15 0; 6000 N!  
PARAMETER G(L12,AL:AL:PT:AL:VA;0) 2.98150E+02 +UPTAL3#; 3.00000E+03 N  
REF0 !

PARAMETER G(L12,PT:AL:PT:AL:VA;0) 2.98150E+02 +UPTAL#; 3.00000E+03 N  
REF0 !

PARAMETER G(L12,RU:AL:PT:AL:VA;0) 298.15 0; 6000 N!  
PARAMETER G(L12,AL:PT:PT:AL:VA;0) 2.98150E+02 +UPTAL#; 3.00000E+03 N  
REF0 !

PARAMETER G(L12,PT:PT:PT:AL:VA;0) 2.98150E+02 +UPT3AL#; 3.00000E+03 N  
REF0 !

PARAMETER G(L12,RU:PT:PT:AL:VA;0) 298.15 0; 6000 N!  
PARAMETER G(L12,AL:RU:PT:AL:VA;0) 298.15 0; 6000 N!  
PARAMETER G(L12,PT:RU:PT:AL:VA;0) 298.15 0; 6000 N!  
PARAMETER G(L12,RU:RU:PT:AL:VA;0) 298.15 0; 6000 N!  
PARAMETER G(L12,AL:AL:RU:AL:VA;0) 298.15 0; 6000 N!  
PARAMETER G(L12,PT:AL:RU:AL:VA;0) 298.15 0; 6000 N!  
PARAMETER G(L12,RU:AL:RU:AL:VA;0) 298.15 0; 6000 N!  
PARAMETER G(L12,AL:PT:RU:AL:VA;0) 298.15 0; 6000 N!  
PARAMETER G(L12,PT:PT:RU:AL:VA;0) 298.15 0; 6000 N!  
PARAMETER G(L12,RU:PT:RU:AL:VA;0) 298.15 0; 6000 N!  
PARAMETER G(L12,AL:RU:RU:AL:VA;0) 298.15 0; 6000 N!  
PARAMETER G(L12,PT:RU:RU:AL:VA;0) 298.15 0; 6000 N!  
PARAMETER G(L12,RU:RU:RU:AL:VA;0) 298.15 0; 6000 N!

PARAMETER G(L12,AL:AL:AL:PT:VA;0) 2.98150E+02 +UPTAL3#; 3.00000E+03 N  
REF0 !

PARAMETER G(L12,PT:AL:AL:PT:VA;0) 2.98150E+02 +UPTAL#; 3.00000E+03 N  
REF0 !

PARAMETER G(L12,RU:AL:AL:PT:VA;0) 298.15 0; 6000 N!  
PARAMETER G(L12,AL:PT:AL:PT:VA;0) 2.98150E+02 +UPTAL#; 3.00000E+03 N  
REF0 !

PARAMETER G(L12,PT:PT:AL:PT:VA;0) 2.98150E+02 +UPT3AL#; 3.00000E+03 N  
REF0 !

PARAMETER G(L12,RU:PT:AL:PT:VA;0) 298.15 0; 6000 N!  
PARAMETER G(L12,AL:RU:AL:PT:VA;0) 298.15 0; 6000 N!



PARA G(L12,PT:RU:AL:PT:VA;0) 298.15 0; 6000 N!  
PARA G(L12,RU:RU:AL:PT:VA;0) 298.15 0; 6000 N!  
PARAMETER G(L12,AL:AL:PT:PT:VA;0) 2.98150E+02 +UPTAL#; 3.00000E+03 N  
REF0 !  
PARAMETER G(L12,PT:AL:PT:PT:VA;0) 2.98150E+02 +UPT3AL#; 3.00000E+03 N  
REF0 !  
PARA G(L12,RU:AL:PT:PT:VA;0) 298.15 0; 6000 N!  
PARAMETER G(L12,AL:PT:PT:PT:VA;0) 2.98150E+02 +UPT3AL#; 3.00000E+03 N  
REF0 !  
PARA G(L12,PT:PT:PT:PT:VA;0) 298.15 0; 6000 N!  
PARA G(L12,RU:PT:PT:PT:VA;0) 298.15 0; 6000 N!  
PARA G(L12,AL:RU:PT:PT:VA;0) 298.15 0; 6000 N!  
PARA G(L12,PT:RU:PT:PT:VA;0) 298.15 0; 6000 N!  
PARA G(L12,RU:RU:PT:PT:VA;0) 298.15 0; 6000 N!  
PARA G(L12,AL:AL:RU:PT:VA;0) 298.15 0; 6000 N!  
PARA G(L12,PT:AL:RU:PT:VA;0) 298.15 0; 6000 N!  
PARA G(L12,RU:AL:RU:PT:VA;0) 298.15 0; 6000 N!  
PARA G(L12,AL:PT:RU:PT:VA;0) 298.15 0; 6000 N!  
PARA G(L12,PT:PT:RU:PT:VA;0) 298.15 0; 6000 N!  
PARA G(L12,RU:PT:RU:PT:VA;0) 298.15 0; 6000 N!  
PARA G(L12,AL:RU:RU:PT:VA;0) 298.15 0; 6000 N!  
PARA G(L12,PT:RU:RU:PT:VA;0) 298.15 0; 6000 N!  
PARA G(L12,RU:RU:RU:PT:VA;0) 298.15 0; 6000 N!  
PARA G(L12,AL:AL:AL:RU:VA;0) 298.15 0; 6000 N!  
PARA G(L12,PT:AL:AL:RU:VA;0) 298.15 0; 6000 N!  
PARA G(L12,RU:AL:AL:RU:VA;0) 298.15 0; 6000 N!  
PARA G(L12,AL:PT:AL:RU:VA;0) 298.15 0; 6000 N!  
PARA G(L12,PT:PT:AL:RU:VA;0) 298.15 0; 6000 N!  
PARA G(L12,RU:PT:AL:RU:VA;0) 298.15 0; 6000 N!  
PARA G(L12,AL:RU:AL:RU:VA;0) 298.15 0; 6000 N!  
PARA G(L12,PT:RU:AL:RU:VA;0) 298.15 0; 6000 N!  
PARA G(L12,RU:RU:AL:RU:VA;0) 298.15 0; 6000 N!  
PARA G(L12,AL:AL:PT:RU:VA;0) 298.15 0; 6000 N!  
PARA G(L12,PT:AL:PT:RU:VA;0) 298.15 0; 6000 N!  
PARA G(L12,RU:AL:PT:RU:VA;0) 298.15 0; 6000 N!  
PARA G(L12,AL:PT:PT:RU:VA;0) 298.15 0; 6000 N!  
PARA G(L12,PT:PT:PT:RU:VA;0) 298.15 0; 6000 N!  
PARA G(L12,RU:PT:PT:RU:VA;0) 298.15 0; 6000 N!  
PARA G(L12,AL:RU:PT:RU:VA;0) 298.15 0; 6000 N!  
PARA G(L12,PT:RU:PT:RU:VA;0) 298.15 0; 6000 N!  
PARA G(L12,RU:RU:PT:RU:VA;0) 298.15 0; 6000 N!  
PARA G(L12,AL:AL:RU:RU:VA;0) 298.15 0; 6000 N!  
PARA G(L12,PT:AL:RU:RU:VA;0) 298.15 0; 6000 N!  
PARA G(L12,RU:AL:RU:RU:VA;0) 298.15 0; 6000 N!  
PARA G(L12,AL:PT:RU:RU:VA;0) 298.15 0; 6000 N!  
PARA G(L12,PT:PT:RU:RU:VA;0) 298.15 0; 6000 N!  
PARA G(L12,RU:PT:RU:RU:VA;0) 298.15 0; 6000 N!  
PARA G(L12,AL:RU:RU:RU:VA;0) 298.15 0; 6000 N!  
PARA G(L12,PT:RU:RU:RU:VA;0) 298.15 0; 6000 N!  
PARA G(L12,RU:RU:RU:RU:VA;0) 298.15 0; 6000 N!  
PARAMETER G(L12,AL,PT:\*.\*:VA;0) 2.98150E+02 +UL0#; 3.00000E+03 N  
REF0 !  
PARAMETER G(L12,\*.AL,PT:\*.\*:VA;0) 2.98150E+02 +UL0#; 3.00000E+03 N  
REF0 !  
PARAMETER G(L12,\*.\*.AL,PT:\*.VA;0) 2.98150E+02 +UL0#; 3.00000E+03 N

REF0 !

PARAMETER G(L12,\*:\*:AL,PT:VA;0) 2.98150E+02 +UL0#; 3.00000E+03 N

REF0 !

PARAMETER G(L12,AL,PT:AL,PT:\*:\*:VA;0) 2.98150E+02 +USRO#; 3.00000E+03

N REF0 !

PARAMETER G(L12,AL,PT:\*:AL,PT:\*:VA;0) 2.98150E+02 +USRO#; 3.00000E+03

N REF0 !

PARAMETER G(L12,AL,PT:\*:\*:AL,PT:VA;0) 2.98150E+02 +USRO#; 3.00000E+03

N REF0 !

PARAMETER G(L12,\*:AL,PT:AL,PT:\*:VA;0) 2.98150E+02 +USRO#; 3.00000E+03

N REF0 !

PARAMETER G(L12,\*:AL,PT:\*:AL,PT:VA;0) 2.98150E+02 +USRO#; 3.00000E+03

N REF0 !

PARAMETER G(L12,\*:\*:AL,PT:AL,PT:VA;0) 2.98150E+02 +USRO#; 3.00000E+03

N REF0 !

PHASE PT2AL % 2.334 .666 !

CONSTITUENT PT2AL :AL : PT : !

PARAMETER G(P2AL,AL:PT;0) 2.98150E+02 -84989+24.9\*T+.334\*GHSERAL#  
+.666\*GHSERPT#; 6.00000E+03 N REF0 !

PHASE PT2AL3 % 2.6 .4 !

CONSTITUENT PT2AL3 :AL : PT : !

PARAMETER G(P2AL3,AL:PT;0) 2.98150E+02 -89885+21.5\*T+.6\*GHSERAL#  
+.4\*GHSERPT#; 6.00000E+03 N REF0 !

PHASE PT5AL21 % 2.8077 .1923 !

CONSTITUENT PT5AL21 :AL : PT : !

PARAMETER G(P5AL21,AL:PT;0) 2.98150E+02 -56873+14.8\*T+.8077\*GHSERAL#  
+.1923\*GHSERPT#; 6.00000E+03 N REF0 !

PHASE PT5AL3 % 2.375 .625 !

CONSTITUENT PT5AL3 :AL : PT : !

PARAMETER G(P5AL3,AL:PT;0) 2.98150E+02 -87260+24\*T+.375\*GHSERAL#  
+.625\*GHSERPT#; 6.00000E+03 N REF0 !

PHASE PT8AL21 % 2.7242 .2759 !

CONSTITUENT PT8AL21 :AL : PT : !

PARAMETER G(P8AL21,AL:PT;0) 2.98150E+02 -82342+23.7\*T+.7242\*GHSERAL#  
+.2759\*GHSERPT#; 6.00000E+03 N REF0 !

PHASE PTAL % 2.5 .5 !

CONSTITUENT PTAL :AL : PT : !

PARAMETER G(PTAL,AL:PT;0) 2.98150E+02 -94071+24.1\*T+.5\*GHSERAL#  
+.5\*GHSERP#; 6.00000E+03 N REF0 !

PHASE PTAL2 % 2.666 .334 !  
CONSTITUENT PTAL2 :AL : PT : !

PARAMETER G(PTAL2,AL:PT;0) 2.98150E+02 -87898+23.3\*T+.666\*GHSERAL#  
+.334\*GHSERP#; 6.00000E+03 N REF0 !

PHASE RU2AL3 % 3 3 2 1 !  
CONSTITUENT RU2AL3 :AL : AL,RU : RU,VA : !

PARAMETER G(RU2AL3,AL:AL:RU;0) 2.98150E+02 +V15#+5\*GBCCAL#+GBCCRU#;  
6.00000E+03 N REF0 !  
PARAMETER G(RU2AL3,AL:RU:RU;0) 2.98150E+02 -312631.26+30.5\*T+3\*GBCCAL#  
+3\*GBCCRU#; 6.00000E+03 N REF0 !  
PARAMETER G(RU2AL3,AL:AL:VA;0) 2.98150E+02 +5\*GBCCAL#; 6.00000E+03  
N REF0 !  
PARAMETER G(RU2AL3,AL:RU:VA;0) 2.98150E+02 -312631.26+30.5\*T+3\*GBCCAL#  
+2\*GBCCRU#; 6.00000E+03 N REF0 !

PHASE RU4AL13 % 3.6275 .235 .1375 !  
CONSTITUENT RU4AL13 :AL : RU : AL,VA : !

PARAMETER G(RU4AL13,AL:RU:AL;0) 2.98150E+02 -35100+1.65\*T+.765\*GHSERAL#  
+.235\*GHSERRU#; 6.00000E+03 N REF0 !  
PARAMETER G(RU4AL13,AL:RU:VA;0) 2.98150E+02 -35100+1.65\*T  
+.6275\*GHSERAL#+.235\*GHSERRU#; 6.00000E+03 N REF0 !

PHASE RUAL2 % 3 2 1 1 !  
CONSTITUENT RUAL2 :AL : RU : AL,RU,VA : !

PARAMETER G(RUAL2,AL:RU:AL;0) 2.98150E+02 -136500+8\*T-1368.28  
+3\*GHSERAL#+GHSERRU#; 6.00000E+03 N REF0 !  
PARAMETER G(RUAL2,AL:RU:RU;0) 2.98150E+02 -136500+8\*T-1412.41  
+2\*GHSERAL#+2\*GHSERRU#; 6.00000E+03 N REF0 !  
PARAMETER G(RUAL2,AL:RU:VA;0) 2.98150E+02 -136500+8\*T+2\*GHSERAL#  
+GHSERRU#; 6.00000E+03 N REF0 !

PHASE RUAL6 % 2 6 1 !  
CONSTITUENT RUAL6 :AL : RU : !

PARAMETER G(RUAL6,AL:RU;0) 2.98150E+02 -156000+7\*T+6\*GHSERAL#+GHSERRU#;  
6.00000E+03 N REF0 !

LIST\_OF\_REFERENCES  
NUMBER SOURCE  
REF0  
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