



UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

The Al-Pt-Ru ternary phase diagram

Sara Natalia Prins

Submitted in partial fulfilment of the requirements for the degree Master of Science in the Faculty of Engineering, Built Environment and Information Technology, University of Pretoria

1 April 2003



Declaration

I declare that this dissertation is my own work. It is being submitted for the degree of Masters of Science in the Faculty of Engineering, Build Environment and Information Technology, University of Pretoria, South Africa. It has not been submitted before for any degree or examination at any other University.

A handwritten signature in black ink, appearing to be 'Sara Natalia Prins'.

Sara Natalia Prins
1 April 2004



Table of Contents

Chapter 1	Introduction	1
1.1	Introduction	1
1.2	Background	1
1.3	Motivation	3
Chapter 2	Literature Review – The Phase Diagrams	8
2.1	The Elements: Al, Pt and Ru	8
2.2	The Al-Pt Binary System	
2.2.1	Phase Diagram Data	9
2.2.2	Thermodynamic Data	14
2.3	The Al-Ru Binary System	15
2.2.1	Phase Diagram Data	15
2.2.2	Thermodynamic Data	19
2.2.3	Applications of Al-Ru Intermetallics	20
2.3	The Pt-Ru system	21
2.4	The Al-Pt-Ru Ternary System	22
Chapter 3	Experimental Investigation	23
3.1	Introduction	23
3.2	Sample Preparation	23
3.3	Analyses	24
3.3.1	Scanning Electron Microscopy and Energy Dispersive X-Ray Analysis	24
3.3.2	X-Ray Diffraction	25
3.4	Methodology to Determine a Solidification Sequence for a Ternary Alloy	27
3.4.1	Analyses of As-Cast Alloys	27
3.4.2	Fundamental and theoretical considerations	28
3.4.2.1	Phase diagram considerations	28
3.4.2.2	Liquid-solid interactions and transformations	30
3.4.2.3	Deriving the solidification sequence and liquidus surface projection	32
3.5	Syntax and Terminology	34
Chapter 4	Experimental Results and Discussion	35
4.1	Introduction	35
4.2	Microstructures and proposed solidification sequences	36
4.2.1	PAR 1 - Al ₈₆ :Pt ₇ :Ru ₇ alloy	36
4.2.2	PAR 2 - Al ₆₆ :Pt ₂₆ :Ru ₆ alloy	39
4.2.3	PAR 3 - Al ₅₇ :Pt ₁₂ :Ru ₃₁ alloy	41
4.2.4	PAR4 - Al ₅₄ :Pt ₃₈ :Ru ₈ alloy	43

4.2.5	PAR5 - Al ₅₀ :Pt ₂₅ :Ru ₂₅ alloy	45
4.2.6	PAR6 - Al ₂₅ :Pt ₅₅ :Ru ₂₀ alloy	46
4.2.7	PAR7 - Al ₇₃ :Pt ₂₂ :Ru ₅ alloy	49
4.2.8	PAR 8 – Al ₇₁ :Pt ₇ :Ru ₂₂ alloy	50
4.2.9	PAR 9 - Al ₅₉ :Pt ₃₃ :Ru ₈ alloy	52
4.2.10	PAR10 - Al ₃₄ :Pt ₄₆ :Ru ₂₆ alloy	54
4.2.11	PAR 11 - Al ₄₂ :Pt ₅₂ :6 alloy	56
4.2.12	PAR 12 - Al ₃₃ :Pt ₅₉ :Ru ₈ alloy	58
4.2.13	The PAR 13- Al ₈₅ :Pt ₁₀ :Ru ₅ alloy	59
4.2.14	The PAR14- Al ₆₆ :Pt ₁₃ :Ru ₂₁ alloy	61
4.2.15	The PAR 15- Al ₄₇ :Pt ₅₁ :Ru ₂ alloy	63
4.2.16	The PAR 16- Al ₇₄ :Pt ₈ :Ru ₁₈ alloy	65
4.3	XRD results	67
4.4	Solidification projection.	72
4.4.1	Liquidus surface projection	73
4.4.2	Solidification reaction sequence	75
4.5	Conclusions	76
Chapter 5 The CALPHAD Method		77
5.1	Introduction	77
5.2	History	77
5.3	Current Status	79
5.4	CALPHAD Methodology	80
5.5	CALPHAD Thermodynamics	84
5.5.1	Some basic principles	84
5.5.2	Thermodynamics of Pure Elements	84
5.5.3	Thermodynamics of solutions	85
5.5.3.1	Substitutional Solutions	86
5.5.3.2	Sublattice Model / Compound Energy Formalism	87
5.5.3.2.1	CEF applied to B2/A2 order/disorder transformation	90
5.5.3.2.2	CEF applied to fcc ordering	91
5.6	CALPHAD Optimisations	93
5.7	Prediction of higher order systems	94
5.8	Conclusions	95
Chapter 6 The Assessments – Results and Discussion		95
6.1	The Models	95
6.2	Some basic concepts	97
6.3	Assessment procedures	
6.3.1	Al-Ru	98
6.3.2	Al-Pt	100
6.3.3	Al-Pt-Ru	101
6.4	Results and discussion	
6.4.1	Al-Ru	102



6.4.2	Al-Pt	107
6.4.3	Al-Pt-Ru	115
6.5	Conclusions	119
Chapter 7 Comparison Experimental and Calculated		120
7.1	Introduction	120
7.2	Results and Discussion	120
7.3	Conclusions	124
Conclusions and Recommendations		125
References		127
<u>Appendices</u>		
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)		

List of Figures

Figure 2.1. The Al-Pt phase diagram after [1990Mas].	10
Figure 2.2. Revised Pt-rich portion of the Al-Pt phase diagram [1987Oya].	13
Figure 2.3. The calculated Al-Pt phase diagram by Wu and Jin [2000Wu].	14
Figure 2.4. The Al-Ru phase diagram after Massalski [1990Mas].	16
Figure 2.5. The modified Al-Ru phase diagram after Boniface and Cornish [1996Bon2].	16
Figure 2.6. The phase diagram of Anlage et al. [1988Anl] for the high-Al corner in the Al-Ru system.	18
Figure 2.7. The Pt-Ru phase diagram [1990Mas].	21
Figure 2.8. Calculated Pt-Ru phase diagram, from Spencer [1996Spe].	22
Figure 2.9. Isothermal section of the Al-Pt-Ru system at 1350°C [2001Big2].	22
Figure 3.1. Ternary plot showing the EDS phase analyses. The square indicates the overall composition, the triangles the phase analysis and the solid circle indicates a two-phase area.	27
Figure 3.2. Ternary invariant reactions, after West [1965Wes]	27
Figure 3.3. Phase diagram of two components showing the influence of solute diffusion on solidification, a phenomenon called coring [1990Tom]	31
Figure 3.4. Sample PAR14 on the liquidus surface.	33
Figure 4.1. Overall compositions of the Al-Pt-Ru alloys studied.	35
Figure 4.2. (a) and (b) show the two distinct different microstructure areas observed in the PAR1 alloy. (c) shows the detail of the finer (darker) microstructure and (d) shows the detail of the lighter, coarser microstructure area.	37
Figure 4.3. A ternary plot of the overall and phase compositions in the PAR 1 alloy.	38
Figure 4.4. (a) shows the dendrite structure of PAR 2 and (b) shows the remnants of primary T in the light PtAl ₂ dendrites.	40
Figure 4.5. A ternary plot of the overall and phase compositions in the PAR 2 alloy.	40
Figure 4.6. BSE images of PAR 3. (a) shows the overall microstructure. (b) shows the X phase as well as the two areas where Ru ₂ Al ₃ and T decomposed.	41
Figure 4.7 A ternary plot of the overall and phase compositions in the PAR 3 alloy.	42
Figure 4.8. BSE images of PAR 4. (a) shows dark primary ~RuAl dendrites, coated by a PtAl layer (the light phase) in a Pt ₂ Al ₃ matrix. (b) shows the detail of the PtAl coating layer.	43
Figure 4.9. A ternary plot of the overall and phase compositions in the PAR 4 alloy.	44
Figure 4.10. BSE image on the right showing dark ~RuAl dendrites in a light two-phase matrix. The light matrix consists of PtAl and Pt ₃ Al ₃ , which is the very light phase.	45
Figure 4.11. A ternary plot of the overall and phase compositions in the PAR 5 alloy.	46
Figure 4.12. (a) The BSE image of PAR 6. (a) shows the long dark (Ru) needles in the light ~Pt ₃ Al matrix, with a finer dark phase present between the long needles. (b) shows that the fine (Pt) blob-like phase, and the finer (Ru) needles which formed in the ternary eutectic.	47
Figure 4.13. A ternary plot of the overall and phase compositions in the PAR 6 alloy.	48

Figure 4.14. The BSE images of PAR 7. (a) shows white PtAl ₂ dendrites in a darker X matrix. (b) shows precipitates of X in the PtAl ₂ dendrites.	49
Figure 4.15. A ternary plot of the overall and phase compositions in the PAR 7 alloy.	50
Figure 4.16. BSE images of PAR 8. (a) shows dark ~RuAl dendrites in a medium grey X phase. A very light phase ~PtAl ₂ is present in the medium grey phase. (b) shows the microstructure in more detail.	51
Figure 4.17. A ternary plot of the overall and phase compositions in the PAR 8 alloy.	51
Figure 4.18. BSE microstructure of PAR 9. (a) shows the dendritic structure. (b) shows the coring of the dark grey ~RuAl phase.	53
Figure 4.19. A ternary plot of the overall and phase compositions in the PAR 9 alloy.	53
Figure 4.20. BSE images of PAR10. (a) shows the 'feather-like' dendrite solidification structure, with some areas which appear 'cloudy'. In the close up, (b), the dark (Ru) needles, coated by a medium phase, ~RuAl in a light (Pt ₅ Al ₃ + PtAl) matrix. Between the dendrites, a fine eutectic structure is visible.	54
Figure 4.21 A ternary plot of the overall and phase compositions in the PAR 10 alloy.	54
Figure 4.22. BSE images of PAR 11. (a) shows the dendritic structure of the alloy. (b) clearly shows the presence of a fine phase in the dark dendrite phase as well as the area surrounding the dark dendrite.	56
Figure 4.23. A ternary plot of the overall and phase compositions in the PAR 11 alloy.	57
Figure 4.24. BSE images of PAR 12. (a) shows long thin and small fine (Ru) needles in a light Pt ₃ Al matrix. (b) shows the microstructure at a higher magnification.	58
Figure 4.25. A ternary plot of the overall and phase compositions in the PAR 12 alloy.	59
Figure 4.26. BSE images of PAR 13. (a) and (b) show the general microstructure. In (c) the ternary eutectic structure between the primary X dendrites can be seen. (d) shows the presence of another phase (lighter than dendrites) on the edges of the X dendrites.	60
Figure 4.27 A ternary plot of the overall and phase compositions in the PAR 13 alloy.	61
Figure 4.28. BSE images of PAR 14. (a) shows the dark RuAl ₂ dendrites surrounded by a medium X phase in a light ~PtAl ₂ matrix. (b) shows a higher magnification of the microstructure.	62
Figure 4.29. A ternary plot of the overall and phase compositions in the PAR 14 alloy.	62
Figure 4.30. (a) shows the overall microstructure of PAR 15. (b) shows the 'island'-like structure. (c) shows the solid state decomposition of a primary b grain while (d) shows the difference in decomposition microstructures.	63
Figure 4.31. A ternary plot of the overall and phase compositions in the PAR 15 alloy.	64
Figure 4.32. Schematic development of the solidification microstructure of the PAR15 alloy.	65
Figure 4.33. (a) shows the overall microstructure of PAR 16. (b) shows the medium primary RuAl ₂ dendrites coated by the black Ru ₄ Al ₁₃ phase. Small, very light areas of PtAl ₂ can be seen in the cored X phase.	65
Figure 4.34. A ternary plot of the overall and phase compositions in the PAR 16 alloy.	66
Figure 4.35. Summary of results for ternary Al-Pt-Ru alloys (square = overall composition, triangle = phase composition).	72



Figure 4.36. Proposed experimental liquidus surface projection.	74
Figure 4.37. Overall alloy compositions on the liquidus surface projection.	74
Figure 4.38. Experimental liquidus surface projection for the Al-Pt-Ru system, showing the solidification reactions.	75
Figure 5.1. Flowchart of the CALPHAD method, adapted from [2001Kum].	81
Figure 5.2. Phase diagram showing regions where only composition can be reliably measured at a given temperature and vice versa [2001Kum].	82
Figure 5.3. Composition space and reference energy surface for $(A,B)_1(C,D)_1$ [1998Sau].	87
Figure 5.4. Schematic crystallographic structure of the A2 and B2 phases. (a). A2, the disordered structure, where all the sites are equivalent. (b) B2, the ordered structure where the occupation of the site in the centre of the cube is different to the one on the corner.	89
Figure 5.5. The face-centred cubic (fcc) structure. The numbers indicate the four sublattices for ordering.	91
Figure 5.6. Extrapolation to higher order systems [1997Kat].	93
Figure 6.1. The calculated Al-Ru phase diagram showing B2 calculated using the SL (—) and MSL (---) models.	104
Figure 6.2. Comparison between the calculated Al-Ru phase diagram and experimental data	104
Figure 6.3. Phase diagram of temperature against chemical potential of Al.	106
Figure 6.4. Comparison of calculated enthalpy of formation for the SL (—) and MSL (---) RuAl-B2 models with experimental results [1992Jun] and ab initio [1992Lin, 1998Wol, 1999Man, 2002Gar] predictions.	106
Figure 6.5. The calculated Al-Pt phase diagram.	110
Figure 6.6. The calculated Al-Pt phase diagram compared with experimental invariant data points [1986McA].	110
Figure 6.7. Enlargement of the Al-Pt binary system to show the reactions for PtAl, β and the liquid phases	112
Figure 6.8 The Al-Pt phase diagram of temperature against chemical potential of Pt.	112
Figure 6.9. The Al-Pt phase diagram of temperature against chemical potential of Al.	113
Figure 6.10 Comparison of calculated enthalpy of formation for Pt_3Al ($L1_2$) phase with experimental results [1968Fer, 1981Wor, 1993Mes], Miedema estimations [1989deB] and ab initio predictions [2002Ngo].	113
Figure 6.11 Liquidus surface projection for Al-Pt-Ru, indicating liquidus surface areas for the phases.	115
Figure 6.12 Enlargement of the Al-corner of the Al-Pt-Ru liquidus projection.	116
Figure 6.13 Projection of temperature against composition to identify the reaction types.	118
Figure 6.14 Solidification reactions, as listed in Table 6.8.	118
Figure 6.15 Solidification reactions, as listed in Table 6.8 (enlargement of the Al-corner in Figure 6.14).	119
Figure 7.1. Experimental liquidus surface projection.	121
Figure 7.2. Predicted liquidus surface projection.	121

List of Tables

Table 1.1. Platinum demand and supply [2002Joh]	4
Table 2.1. Properties of the pure elements [1985Vil, 2001ICD].	9
Table 2.2. Crystal structure data for the stable phases in the Al-Pt binary system.	11
Table 2.3 Crystal structure data for the metastable phases in the Al-Pt binary system.	11
Table 2.4. Enthalpies of formation for the stable phases in the Al-Pt system.	15
Table 2.5. The compositions and crystal data for the elements and compounds in the Al-Ru system.	17
Table 2.6 Enthalpies of formation for the phases in the Al-Ru system.	20
Table 4.1. Targeted and analysed compositions for the experimental alloy samples.	36
Table 4.2. Summary of phase and composition analysis for the PAR1 alloy.	38
Table 4.3 Summary of the phase and composition analyses for the PAR 2 alloy.	40
Table 4.4. Summary of phase and composition analysis for the PAR 3 alloy.	42
Table 4.5. Summary of phase and composition analysis for the PAR4 alloy.	43
Table 4.6. Summary of phase and composition analysis for the PAR 5 alloy.	45
Table 4.7. Summary of phase and composition analysis for the PAR 6 alloy.	47
Table 4.8. Summary of phase and composition analysis for the PAR 7 alloy.	49
Table 4.9. Summary of phase and composition analysis for the PAR 8 alloy.	51
Table 4.10. Summary of phase and composition analysis for the PAR 9 alloy.	53
Table 4.11. Summary of phase and composition analysis for the PAR 10 alloy.	54
Table 4.12. Summary of phase and composition analysis for the PAR 11 alloy.	56
Table 4.13. Summary of phase and composition analysis for the PAR 12 alloy.	58
Table 4.14. Summary of phase and composition analysis for the PAR 13 alloy.	60
Table 4.15. Summary of phase and composition analysis for the PAR 14 alloy.	62
Table 4.16. Summary of phase and composition analysis for the PAR 15 alloy.	64
Table 4.17. Summary of phase and composition analysis for the PAR 16 alloy.	66
Table 4.18. The XRD results	69
Table 4.19. Solidification reactions for Al-Pt-Ru.	76
Table 5.1. Applications of the compound energy formalism.	88
Table 6.1. Thermodynamic models of the intermetallic phases in Al-Ru.	95
Table 6.2 Thermodynamic models of the intermetallic phases in Al-Pt.	95
Table 6.3 Calculated thermodynamic parameters for the Al-Ru system [J/mol]	102
Table 6.4 Calculated and Experimental invariant temperatures and compositions for the Al-Ru system.	105
Table 6.5. The calculated model parameters for Al-Pt [J/mole of atoms].	108
Table 6.6. Experimental and calculated invariant temperatures and compositions for the Al-Pt system.	111
Table 6.7. Experimental and calculated enthalpies of formation for the Al-Pt system.	114
Table 6.8. Solidification sequence for Al-Pt-Ru.	117
Table 7.1. Experimental solidification reactions for Al-Pt-Ru.	122
Table 7.2. Predicted solidification reactions for the calculated Al-Pt-Ru system.	123