

THE DEVELOPMENT OF PLATINUM-BASED ALLOYS AND THEIR THERMODYNAMIC DATABASE

L. A. Cornish*, J. Hohls*, P. J. Hill*,
S. Prins****, R. Süß* and D. N. Compton*

**Physical Metallurgy Division, Mintek, Private Bag 3, Randburg, 2125, South Africa*

***CSIR-NML, P.O. Box 395, Pretoria, 0001, South Africa*

****Department of Metallurgical Engineering and Materials Science, University of Pretoria, Pretoria, 0002, South Africa*

(Received 26 September 2002; accepted 1 December 2002)

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 $Pt_{84}:Al_{11}:Ru_2:Cr_3$ 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 $Pt_{84}:Al_{11}:Ru_2:Cr_3$.

Keywords: platinum-based alloys, thermodynamic database

1. Introduction

Nickel-based superalloys have excellent mechanical properties because they have a microstructure comprising many small, strained-coherent, particles in a softer matrix [1]. 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 $L1_2$ ordered structure. The lattice misfit between these structures is very small and renders the surface energy negligible [1].

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 $\sim 1300^\circ\text{C}$.

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_3Al 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_3Al has two forms, and the more desirable high temperature $L1_2$ 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 $\text{Pt}_{82}:\text{Al}_{14}:\text{X}_4$ where X was Cr, Ti and Ru [2,3]. 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 [2,4]. 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 [5].

2. Experimental

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.

3. Results and discussion

Three alloys were single-phase $\sim\text{Pt}_3\text{Al}$, while three had two-phase microstructures. Two of these had large areas of $\sim\text{Pt}_3\text{Al}$, together with a mixture of (Pt) and $\sim\text{Pt}_3\text{Al}$ (Figure 1a). The third ($\text{Pt}_{84}:\text{Al}_{11}:\text{Ru}_2:\text{Cr}_3$) 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
$\text{Pt}_{78}:\text{Al}_{15.5}:\text{Ru}_2:\text{Cr}_{4.5}$	(Pt)	79.7±0.5	8.4±0.5	5.4±0.5	6.5±0.5
	$\sim\text{Pt}_3\text{Al}$	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
$\text{Pt}_{81.5}:\text{Al}_{11.5}:\text{Ru}_{2.5}:\text{Cr}_{4.5}$	$\sim\text{Pt}_3\text{Al}$	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
$\text{Pt}_{84}:\text{Al}_{11}:\text{Ru}_2:\text{Cr}_3$	$\gamma\gamma'$	83.5±1.3	11.3±0.6	2.4±0.5	2.8±0.4

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

Alloy Designation	Hardness (HV ₁₀)
$\text{Pt}_{78}:\text{Al}_{15.5}:\text{Ru}_2:\text{Cr}_{4.5}$	428 ± 11
$\text{Pt}_{81.5}:\text{Al}_{11.5}:\text{Ru}_{2.5}:\text{Cr}_{4.5}$	453 ± 16
$\text{Pt}_{84}:\text{Al}_{11}:\text{Ru}_2:\text{Cr}_3$	472 ± 14

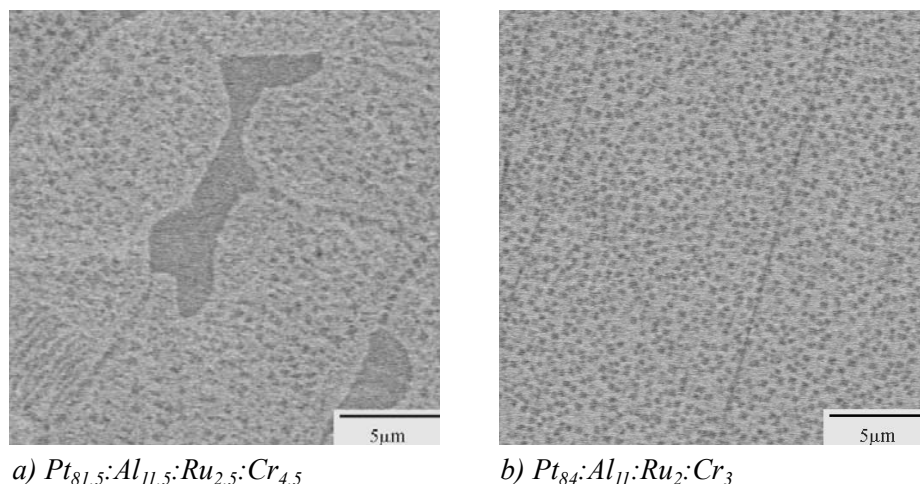


Figure 1. SEM micrographs, in back-scattered electron (BSE) mode, of the two types of twophase alloys. a) With primary $\sim Pt_3Al$ (dark contrast) in a fine mixture of (Pt) and $\sim Pt_3Al$; b) Fine mixture of (Pt) and $\sim Pt_3Al$.

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.

More alloys were produced to ascertain if the volume fraction of the $\sim Pt_3Al$ precipitates could be increased. Table 3 shows the measured compositions after heat treatment for 96 hours at 1350°C in argon. Only the $Pt_{85}:Al_{11}:Ru_2:Cr_2$ alloy had a clear fine two-phase mixture, but there were also small areas of primary $\sim Pt_3Al$.

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_{10} . The alloys showed good ductility, with no cracking around the indentations.

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 $Pt_{81.5}:Al_{11.5}:Ru_{2.5}:Cr_{4.5}$ showed a clear, fine two-phase microstructure after this heat treatment, possibly due to the change in its overall composition. There was no primary $\sim Pt_3Al$ in evidence, so the overall composition is that of the two-phase mixture: 85.2±0.3 at.% Pt, 7.1±0.8 at.% Al, 3.1±0.8 at.% Ru and 4.6±0.1 at.% Cr.

Since the overall composition changed, the sample was redesignated as Pt₈₅:Al₇:Ru₃:Cr₅.

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 ₈₅ :Al ₁₁ :Ru ₂ :Cr ₂	~Pt ₃ Al	76.6±0.4	21.8±0.2	0.0±0.0	1.6±0.3
	γγ'	85.3±0.3	10.1±0.7	2.2±0.1	2.4±0.3
Pt ₈₄ :Al _{11.5} :Ru ₂ :Cr _{2.5}	~Pt ₃ Al	76.0±0.5	22.2±0.2	0.4±0.4	1.4±0.3
	γγ'	84.9±0.6	10.1±1.4	2.3±1.1	2.7±0.9
Pt ₈₃ :Al ₁₁ :Ru _{2.5} :Cr _{3.5}	~Pt ₃ Al	76.1±0.8	21.4±0.6	0.6±0.6	1.9±0.2
	γγ'	84.9±0.4	9.5±0.2	2.4±0.3	3.2±0.3
Pt _{80.5} :Al _{12.5} :Ru _{2.5} :Cr _{4.5}	~Pt ₃ Al	75.9±0.7	20.6±0.6	0.8±0.4	2.7±0.4
	γγ'	81.6±1.0	9.2±1.2	3.9±1.5	5.3±0.7
Pt _{81.5} :Al _{11.5} :Ru _{2.5} :Cr _{4.5}	~Pt ₃ Al	76.3±0.3	20.6±0.1	0.5±0.1	2.6±0.2
	γγ'	83.0±0.8	9.2±0.4	3.1±0.1	4.7±0.4

Figure 2 shows the microstructure of this alloy after the first and second heat treatments, and that of the Pt₈₄:Al₁₁:Ru₂:Cr₃ alloy from the first batch. It can be seen that the precipitates in Pt₈₄:Al₁₁:Ru₂:Cr₃ are approximately twice as large, but more well-defined than those of Pt₈₅:Al₇:Ru₃:Cr₅. The hardnesses were re-measured and are given in Table 5. They range from 396 to 415 HV₁₀, and were less after the second anneal.

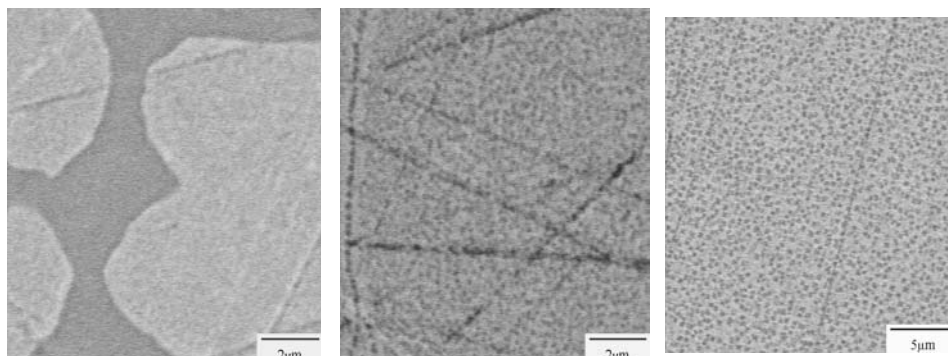
Table 4. Vickers hardness of the second batch of quaternary alloys, using a 10 kg load.

Alloy Designation	Hardness (HV ₁₀)
Pt ₈₅ :Al ₁₁ :Ru ₂ :Cr ₂	430 ± 5
Pt ₈₄ :Al _{11.5} :Ru ₂ :Cr _{2.5}	425 ± 21
Pt ₈₃ :Al ₁₁ :Ru _{2.5} :Cr _{3.5}	421 ± 12
Pt _{80.5} :Al _{12.5} :Ru _{2.5} :Cr _{4.5}	419 ± 22
Pt _{81.5} :Al _{11.5} :Ru _{2.5} :Cr _{4.5}	423 ± 10
Pt _{79.5} :Al _{10.5} :Ru _{4.5} :Cr _{5.5}	417 ± 8

4. Discussion

As has been shown before [6], it is possible to obtain a (Pt) + \sim Pt₃Al microstructure in the quaternary alloys. The volume fraction of \sim Pt₃Al was estimated, using image analysis, to be approximately 25-30%. The highest hardness was found in the alloy without primary \sim Pt₃Al. 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 Pt₈₄:Al₁₁:Ru₂:Cr₃ it has the required structure, no primary \sim Pt₃Al and reasonable hardness. Other work has already shown that its oxidation resistance is better than the original ternary alloys [7].



First heat treatment *Second heat treatment* *Pt84:Al11:Ru2:Cr3*
Pt81.5:Al11.5:Ru2.5:Cr4.5 *Pt85:Al7:Ru3:Cr5* *(one heat treatment)*

Figure 2. SEM BSE micrographs of alloy Pt81.5:Al11.5:Ru2.5:Cr4.5 after one, and two heat treatments, and alloy Pt84:Al11:Ru2:Cr3 after one heat treatment (Scratches can be seen.)

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 in Thermo-Calc™ [8] that is being used to optimise the database is based on that of SGTE [9] and Spencer's database [10]. 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 [11], this was re-calculated [12] as Wu and Jin's description did not exhibit any ordering in the Pt₃Al phase. They also only described one form of the Pt₃Al 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 [12]. 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 [13-15], Pt-Al-Ru [16] and Pt-Cr-Ru [17]. 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-CalcTM for optimisation.

Table 5. Vickers hardness of the second batch of quaternary alloys after the second heat treatment, using a 10 kg load.

Alloy Designation	Hardness (HV₁₀)
Pt ₈₅ :Al ₁₁ :Ru ₂ :Cr ₂	403 ± 20
Pt ₈₄ :Al _{11.5} :Ru ₂ :Cr _{2.5}	403 ± 14
Pt ₈₃ :Al ₁₁ :Ru _{2.5} :Cr _{3.5}	405 ± 8
Pt _{80.5} :Al _{12.5} :Ru _{2.5} :Cr _{4.5}	414 ± 9
Pt _{81.5} :Al _{11.5} :Ru _{2.5} :Cr _{4.5}	396 ± 6
Pt _{79.5} :Al _{10.5} :Ru _{4.5} :Cr _{5.5}	415 ± 10

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.

5. Conclusion

It is possible to produce a fine two-phase γ/γ' structure in the Pt-Al-Ru-Cr system, with precipitates of similar shape to those in the nickel-based superalloy systems. The composition of Pt₈₄:Al₁₁:Ru₂:Cr₃ 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.

References

1. C.T. Sims, N.S. Stoloff, and W.C. Hagel, *Superalloys II*, Wiley Interscience, USA, 1987.
2. P.J. Hill, L.A. Cornish, M.J. Witcomb and P. Ellis *J. Alloys and Compounds*, 322 (2001) 166-175.
3. P.J. Hill, L.A. Cornish and M.J. Witcomb, *Proc. Microsc. Soc. South Afr.*, Volume 31, p. 22, Johannesburg, 5th-7th December 2001.
4. R. Süß, P.J. Hill, P. Ellis and I.M. Wolff, Proc. of the 7th European Conference on Advanced Materials and Processes, Rimini, Italy, 10th-14th June 2001.
5. R. Süß, L.A. Cornish, L. Glaner and D.N. Compton, ICEM 15, 15th International Congress on Electron Microscopy, 1st - 6th September 2002, Durban, South Africa, in press.
6. P.J. Hill, Y. Yamabe-Mitarai, H. Murakami, L.A. Cornish, M.J. Witcomb, I.M. Wolff and H. Harada, , TMS, 527-533. Snow King Resort, Jackson Hole, Wyoming, USA, Sept 2001. Rescheduled for 28th April - 1st May 2002.
7. R. Süß, P.J. Hill, P. Ellis and L.A. Cornish, *Proc. Microsc. Soc. South Afr.*, Volume 31, p. 21, Johannesburg, 5th-7th December 2001.
8. B. Sundman, B. Jansson and J.O. Andersson, *CALPHAD*, 9 (1985) 153.
9. A.T. Dinsdale, *Calphad*, 17 (1991) 319.
10. Noble Metal Database, The Spencer Group, 1995.
11. K. Wu and Z. Jon, *J. Phase Equilibria*, 21 (2000) 221.
12. S. Prins, L.A. Cornish, W. Stumpf and B. Sundman, *Calphad XXXI*, Stockholm May 5-10 2002, Programme and Abstracts.
13. D.N. Compton, L.A. Cornish and M.J. Witcomb, *Microscopy and Microanalysis 2000*, Volume 6, Supplement 2, 370-371, Philadelphia, Pennsylvania, USA, 13th-17th August 2000.
14. D.N. Compton, L.A. Cornish and M.J. Witcomb, *Proc. Microsc. Soc. South. Afr.*, Volume 30, p. 9, Grahamstown, 6th-8th December 2000.
15. D.N. Compton, L.A. Cornish and M.J. Witcomb *Microscopy and Microanalysis 2001*, Vol. 7, Supplement 2, 1248-1249. Pub. Springer-Verlag, NY, Inc., Long Beach, California, USA, 5th-9th August 2001.
16. S. Prins and L.A. Cornish, ICEM 15, 15th International Congress on Electron Microscopy, 1st - 6th September 2002, Durban, South Africa, in press.
17. R. Süß, D. Freund, R. Völkl, B. Fischer, P.J. Hill, P. Ellis and I.M. Wolff, *Materials Science and Engineering*, in press.