

## New Pt-based alloys for high temperature application in aggressive environments: The next stage

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Mintek has been developing Pt-based alloys for high temperature applications in aggressive environments, for example, land-based turbine engines, to replace the currently used nickel-based superalloys (NBSAs). The Pt-based alloys have a similar structure to the NBSAs, and since Pt is more chemically inert and has a higher melting point, the Pt-based alloys can potentially be used at higher temperatures. The greater chemical inertness of the Pt-based alloys compared to the NBSAs means that coatings can be simpler, or perhaps not even used at all, depending on the environment. TEM work was done at NIMS, Japan, to investigate the changes in the microstructure of Pt-Al and Pt-Al-Ir alloys at elevated temperatures using *in-situ* heating up to 1100°C. Initial casting trials showed that work needs to be done to optimise casting parameters before commercialisation can take place. Room temperature tensile tests were performed and results were variable mainly due to microstructural differences. The alloy hardnesses were in the order of 300-350HV with ultimate tensile strengths of ~800 MPa and elongations of less than 10%. These results are comparable to other alloys used at high temperatures, which is very encouraging.

*Keywords: platinum, superalloys, hardness, tensile*

### Introduction

Mintek has been developing Pt-based alloys for high temperature applications in aggressive environments. The rationale for this is that some applications, for example, land-based turbine engines, are more efficient at higher temperatures. The current alloys in these are nickel-based super alloys (NBSAs), which are reaching their application temperature limit, as the temperatures approach the melting point of the alloys. Higher temperatures can be reached by intricate designs incorporating channels for air-cooling, or by using insulating coatings. The problem with the intricate designs is that they are very expensive to manufacture and can only be used under certain conditions. On the other hand, coatings also increase the manufacturing costs and can be difficult to tailor so that they fulfil their role. Challenges that have to be overcome include adhesion of the coating to the substrate, matching the coefficients of expansion between the different layers, and preventing spallation. The latter is a great problem, because once there has been a breach in the coating, the component can fail catastrophically because one part of it is not protected against either an aggressive environment or against heat. A replacement of bulk NBSAs would therefore be more preferable. Since Pt is more chemically inert and has a higher melting point (1769°C as opposed to 1455°C), Pt-based alloys can be used at higher temperatures than the NBSAs<sup>1</sup>. The greater chemical inertness compared to the NBSAs means that the coatings can be simpler, or perhaps not even used at all, depending on the environment. A cost of about twice that of a conventional NBSA turbine has been derived at the University of Bayreuth, based on the

higher Pt price and easier processing for the Pt-based alloys (which do not have to be single crystal).

The microstructure is of prime importance because the NBSAs derive their excellent properties from a very fine dispersion of precipitates based on Ni<sub>3</sub>Al in a Ni-rich matrix. The particles are ordered, and apart from the ordering their structure is effectively the same as the matrix: face centred cubic<sup>2</sup>. This means that there is a very low surface energy between the two phases, and thus a very limited driving force to reduce the surface area, which stabilises the precipitates against coarsening. Thus, the two-phase structure is very stable at high temperatures, and the precipitates keep their cuboid form. The stability is beneficial because it means that there is more interface area for the dislocations to interact with, which slows the dislocation movement down, thereby strengthening the alloys. The Pt-based alloys were designed to mimic the microstructure of the NBSAs. Additional elements were added to improve the strengthening, oxidation resistance and formability of the alloys. The Pt-based alloys have been characterised in terms of microstructure, oxidation resistance, creep and tensile strength and they have shown great promise.

### Previous work

The last major review of the development of Pt-based alloys<sup>3</sup> described the work leading to the selection of the main alloy system, Pt-Al-Cr-Ru, and covered the initial selection from potential binary alloys with ternary additions. This was done using the published phase diagram information and then manufacturing alloys by arc-melting

elemental constituents of at least 99.9% purity under an argon atmosphere. Testing was done to evaluate alloys for the presence of the two-phase microstructure, good mechanical properties (achieved by simple hardness tests and checking for ductility) and oxidation resistance<sup>4</sup>. From the initial study, alloys with aluminium additions exhibited the best oxidation resistance and further Pt-Al-X (where X is another metal) alloys were made and tested more rigorously<sup>5,6,7</sup>. Subsequently, it was found that there was a critical threshold of aluminium necessary for the formation of a stable oxide layer<sup>8,9</sup>. The best creep compression test properties were found for Pt-Al-Ta, Pt-Al-Cr and Pt-Al-Ru<sup>10</sup>. However, the oxidation resistance of the Ta-containing alloys was inferior, and so further work on Pt-Al-Ta alloys was not initiated<sup>7</sup>. A four-component alloy was selected on the basis that Cr additions gave good mechanical properties, and Ru was seen as a way to increase the volume fraction of the precipitates, as well as improving the strength of the matrix phase<sup>11</sup>.

The work had started at Mintek, initiated from discussion with NIMS workers in Japan, and the collaboration is still growing. Locally, collaborators include the University of the Witwatersrand, Nelson Mandela Metropolitan University, University of Cape Town and University of Limpopo. Another collaborating institution which is currently less involved is the CSIR. A new collaboration has started with the Universities of the Western Cape and Free State. A parallel programme is based at Bayreuth University and Jena Fachhochschule in Germany, and there are also co-workers at Leeds and Oxford Universities in the UK. Various other groups around the world are also working on high temperature replacements for NBSAs and the review<sup>12</sup> also compared the properties of the Pt-based alloys with those of their competitors. The advantages of the Pt-based alloys are their good strength and oxidation resistance, but their main disadvantages are price and density. Ceramics have good strength and excellent oxidation resistance, but are prone to brittleness. Various Nb-silicides demonstrate good mechanical properties and oxidation resistance, but not at the same compositions<sup>13</sup>.

## Ongoing research work

### Introduction

Much work has been done since the last review<sup>3</sup>, and the work is now moving from more fundamental research to concentrating on commercialisation. Additionally, corrosion resistance is being studied at the University of the Witwatersrand, and the results are very favourable compared to NBSAs and coated NBSAs. The underlying research is still very important and will still continue, but other factors which are more important to commercialisation are also being studied.

Although the main alloy is Pt<sub>86</sub>:Al<sub>11</sub>:Cr<sub>3</sub>:Ru<sub>2</sub>, the effect of other additions on mechanical properties has also been studied. Cobalt was found to be beneficial for formability, while palladium and nickel were substituted for platinum in an attempt to reduce the density and costs. However, the Ni and Pd additions were disappointing in that there was no beneficial effect - indeed, the strength was decreased. Collaborators at the University of Bayreuth and the Fachhochschule Jena in Germany had more favourable results with Ni, but did not use Ru<sup>14</sup>. To complement the study of the extra alloying elements, phase diagram work was also undertaken on the Pt-Ni-Ru<sup>15</sup>, Pt-Co-Ru, Pt-Co-Cr

and Pt-Cr-Ni<sup>16</sup> systems. More work has also been done on the Pt-Cr-Ru<sup>17,18</sup> and Pt-Al-Co<sup>19</sup> systems.

## Transmission Electron Microscopy

### Introduction

Since the interaction of dislocations in the matrix with the precipitates determines the mechanical properties, a rigorous transmission electron microscopy (TEM) study was made on a series of Pt<sub>86</sub>:Al<sub>10</sub>:X<sub>4</sub> alloys where X = Cr, Ru, Ti, Ir and Ta (at.%) to analyse the dislocation content, precipitation and microstructure of samples compressed at different temperatures (21, 800, 100 and 1300°C) [20]. Lattice parameters of the (Pt) matrix phase in Pt-Al-X (X = Ru, Cr and Ti) alloys were determined by using selected area electron diffraction (SAED). All patterns were of the <112>-zone type. The results differed slightly from those reported by Hill *et al.*<sup>11</sup>, which could be attributed to calibration problems with the microscope's camera. In addition, an unusual ordering phenomenon was found in the Pt<sub>3</sub>Al precipitates in binary Pt-Al alloys<sup>21</sup>.

### Pt-Al-Cr

There are indications that the precipitates were not cuboidal, but octahedral in nature. The density of small precipitates decreased with increasing compression temperature, while the dislocation density in the matrix increased. The structure of the dislocation system stayed the same - no other slip systems were activated at higher temperatures.

### Pt-Al-Ru

The morphology of these precipitates differed markedly from those of the Pt-Al-Cr sample. They were ogdoadically-diced (otherwise described as cruciform or Maltese Cross-shaped) as shown in Figure 1, generally consisting of four interconnected lobes. The precipitates showed twinned regions, suggesting that a martensitic transformation has occurred. Their edges were curved,

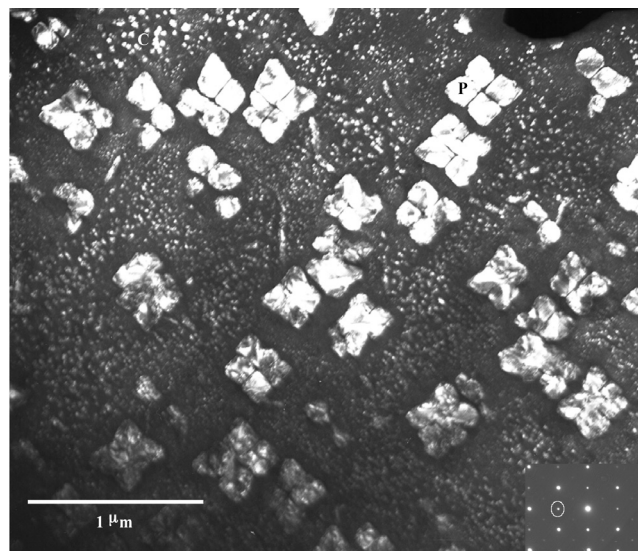


Figure 1. Dark field TEM micrograph of the microstructure of a typical room temperature compressed Pt<sub>86</sub>:Al<sub>10</sub>:Ir<sub>4</sub> alloy (insert: SAD pattern with reflection used to obtain image circled)

showing low surface energy for their boundaries, but became more regular at higher compression temperatures. The twin bands also became better developed at higher temperatures, with dislocations found in alternating twin bands. The dislocations occurred in pairs, indicative of superlattice dislocations, which are expected in the ordered structure of these precipitates (just as in the  $\gamma'$  phase of NBSAs). The long dislocations share the same Burger's vector as those in the Pt-Al-Cr system.

#### ***Pt-Al-Ti***

Compressed at 20°C, the precipitates had well-defined, straight borders. They contained no dislocations, although the matrix had a high density of dislocation tangles. With compression at 800°C, there were still no dislocations present within the precipitates, while the dislocation density in the matrix was significantly lower. There was also a high density of smaller precipitates in the matrix, which could add to strengthening of the matrix. Only when compression was done at 1100°C, were dislocations observed in the precipitates. They shared the same Burger's vector as the dislocations in the other alloys. The low density of dislocations in the matrix indicates significant recovery at elevated temperatures. At 1300°C, the precipitates were once again void of dislocations, possibly due to recovery at this elevated temperature.

#### ***Pt-Al-Ir***

The precipitates appeared similar to those in the Pt-Al-Ru sample. No dislocations were seen in the precipitates themselves, although some dislocations in the matrix extended to the precipitate/matrix interface. After compression at 800°C, the precipitate edges straightened (although their corners were still round) and the first dislocations appeared in the precipitate. Isolated dislocations traversed the matrix. At 1100°C, most of the octahedrally-diced (cruciform shaped) precipitates had become spherical. Twin bands were still visible, with dislocation pairs in some. Multiple twinning occurred in the precipitates. At 1300°C, the precipitates were more irregular again. The dislocation density was high, and they threaded through all twin bands, not only alternating bands, implying that a second slip system became operative at the higher temperature.

#### ***Pt-Al-Ta***

The precipitates had straight interfaces with a high density of interfacial dislocations, and a low density within the precipitates. Isolated tangles of mixed screw and edge dislocations were observed in the matrix. At 800°C in compression, irregular precipitates were observed with no dislocations, while the matrix had a high density of dislocations and small cubic precipitates were also evident. At 1100°C, the matrix dislocations disappeared, while the precipitates (which were now more regular) showed dislocations. At 1300°C, the interfaces of the precipitates were much better defined. However, the character of the dislocations inside the precipitates seemed to have changed. From a dislocation viewpoint, this alloy was the strongest, but earlier work<sup>3,7</sup> had showed that the oxidation resistance was insufficient.

#### ***High temperature TEM work***

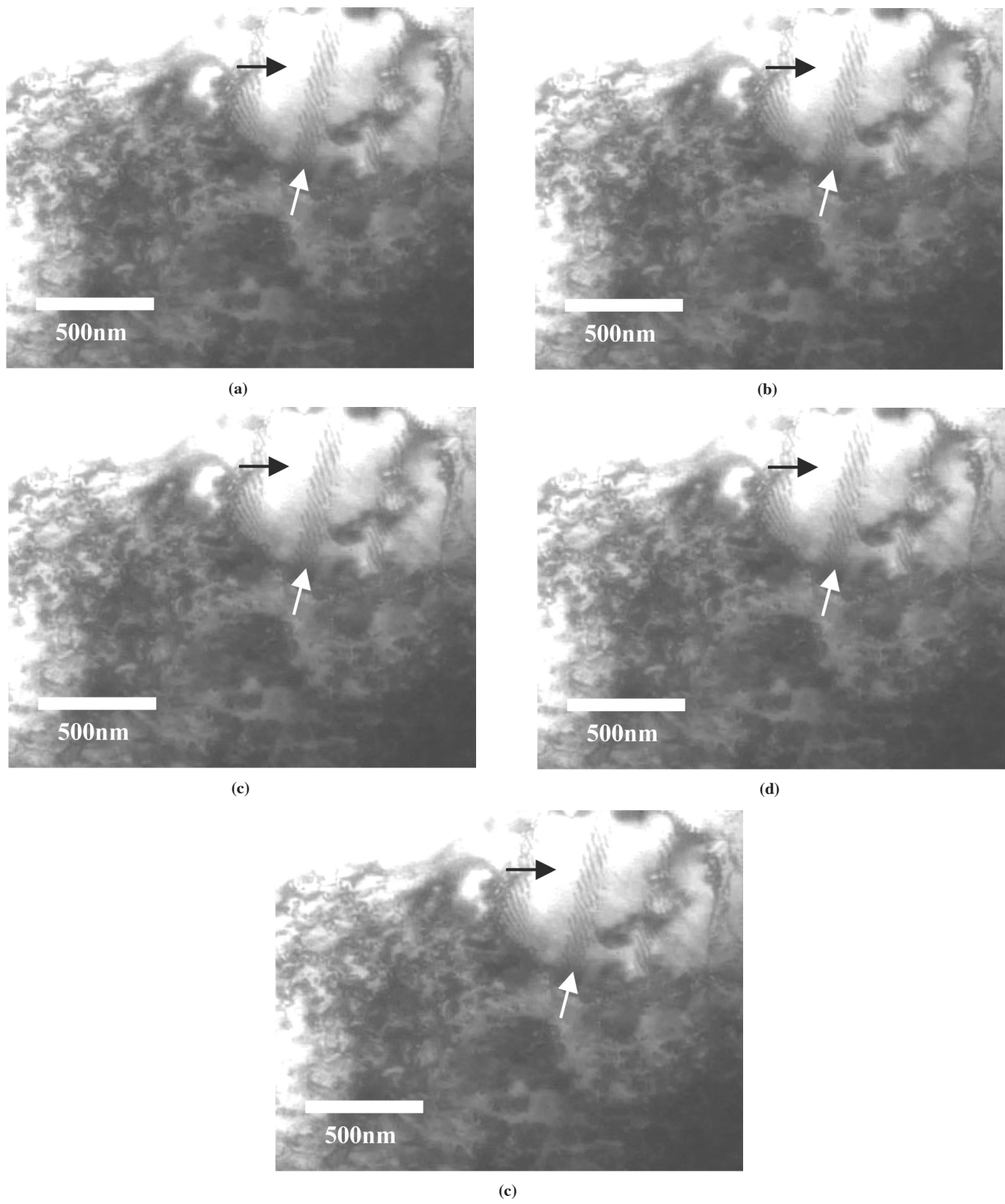
Recently, a visit was made to NIMS, Japan to undertake work that could not be done in South Africa. One aim was

to investigate the changes in the microstructure of a binary Pt-Al alloy and a ternary Pt-Al-Ir alloy at elevated temperatures using *in-situ* heating up to 1100°C in a JEOL 4000X TEM. The heating rate used was 10°C/min, with 5°C being used when more detailed changes were to be observed. It is important to be able to study the stability of the different Pt<sub>3</sub>Al phases because the higher temperature cubic form is preferred and is more ductile. Different alloying additions are known to stabilise the high temperature form: Cr, Ti, Ta<sup>11</sup> and Zr, Hf, Mn, Fe and Co<sup>22</sup>. The alloy studied was a binary Pt-Al alloy with the approximate composition Pt<sub>85</sub>:Al<sub>15</sub>. This is within the two-phase region consisting of the Pt solid solution phase (Pt) and a Pt<sub>3</sub>Al phase ( $\gamma'$ ). According to the phase diagram of McAlister and Kahan<sup>23</sup>, there is a transformation of the high temperature Pt<sub>3</sub>Al phase from L1<sub>2</sub> to a tetragonal low temperature variant (designated D0'c) at ~1280°C. However, there is a conflicting phase diagram presented by Oya *et al.*<sup>24</sup> that gives an additional transformation at a lower temperature. The transformation temperatures given by Oya *et al.* are  $\gamma' \rightarrow \gamma'_1$  at ~340°C and  $\gamma'_1 \rightarrow \gamma'_2$  at 127°C. Previous attempts to resolve this conundrum by SEM, XRD and DTA had been unsuccessful, which prompted the investigation of these transformation temperatures using *in-situ* heating of the alloy in a TEM.

A bright field image of the alloy is shown in Figure 2 (a - e), with the temperature increasing as indicated. The precipitate is characterised by martensite-type twin bands, and contains two types of bands: one with no dislocations (black arrow) and one that contains a high density of dislocations (white arrow). The number of dislocations decreases with increasing temperature (and time), which indicates that there is a transformation that takes place. The twin bands disappeared as atoms diffuse between the bands and as the crystal structure changes as the phase transformation takes place. However, this result only showed that a transformation did take place, but it does not say anything about the kinetics or transformation temperatures.

The transformation was also observed in diffraction mode and the diffraction patterns of the phases were different. Any changes in the crystal structure would manifest itself in a change in the selected area diffraction pattern of the  $\gamma'$  precipitate. The diffraction patterns were chosen at temperatures that were close to those postulated by Oya *et al.*<sup>24</sup> for the phase transformations. At ~339°C, which is above the temperature of 127°C that Oya *et al.*<sup>24</sup> gives for the  $\gamma'_1 \rightarrow \gamma'_2$  transformation, some of the additional spots had disappeared, indicating that some transformation has, in fact, taken place. Unfortunately, the exact temperature at which this happened could not be established. Another temperature was studied above the  $\gamma' \rightarrow \gamma'_1$  transformation temperature of 340°C as given by Oya *et al.*<sup>24</sup> indicated that the phase transformation had occurred. Based on these results, it appears as if the phase diagram of Oya *et al.*<sup>24</sup> for the Pt-Al system is more accurate than that of McAlister and Kahan<sup>23</sup>.

The strength of the alloy depends in part on the presence of small precipitates to act as a barrier to dislocation motion. This important function of the precipitates is vital, leading to the present study. Ideally, the precipitates should persist at high temperatures to provide strengthening under extreme temperature conditions, but this does not happen in the Pt-Al binary system under consideration. The experimental evidence is shown in Figure 3. The same precipitate is shown in the bright field TEM images, Figure



**Figure 2. Bright field TEM images of a Pt<sub>3</sub>Al precipitate with increasing temperatures.**

- (a) 54°C
- (b) 283°C
- (c) 477°C
- (d) 485°C
- (e) 512°C

3 (a) - (d). An identical area in the same field of view is chosen at different temperatures, as described in the figure caption above. There is a high density of small precipitates (with the exception of a precipitate free zone around the large precipitate) in the matrix surrounding the large precipitate at 580°C, as shown in Figure 3(a). At higher temperatures, the precipitates start to dissolve in the matrix, as seen by the lower density of precipitates in the image taken at 810°C in Figure 3(b). There appears to be some critical temperature between 810 and 870°C where precipitate dissolution occurs rapidly, since most of the small precipitates have disappeared at 870°C, as seen in Figure 3(c). All the small precipitates have disappeared by a temperature of 960°C, as seen in Figure 3(d). This implies that the binary alloy will have reduced precipitate strengthening at high temperatures. Additionally, interatomic diffusion occurs more rapidly at high temperatures, which leads to the dissolution of even the larger precipitates. The precipitate is noticeably smaller at 1170°C than at 1030°C, and the interfacial dislocation network has completely disappeared at the higher temperature.

The phase transformation temperatures in the Pt-Al system in the  $\gamma / \gamma'$  two-phase region was found to agree with the results of Oya *et al.*<sup>24</sup> instead of that of McAlister and Kahan<sup>23</sup>. Small precipitates in the Pt-Al system dissolve at higher temperatures and will not contribute to strengthening at high temperatures.

#### Diffusion

The alloys gain their strength from the alloying elements which form the precipitates or additionally help stabilise them. Since the alloys are designed for use at high temperatures and the precipitates need to retain their small size and shape, it is vital to understand the mechanisms that either allow or prevent the precipitates to be altered. These mechanisms have already been studied for the precipitates themselves, but the underlying mechanism that is the diffusion of the alloying elements needs to be studied. This is being studied by the manufacture of diffusion couples. Since the two most important phases are the Pt<sub>3</sub>Al precipitates and the (Pt) matrix, diffusion couples were manufactured to comprise two halves. These were the element of interest, and the particular phase. Thus two

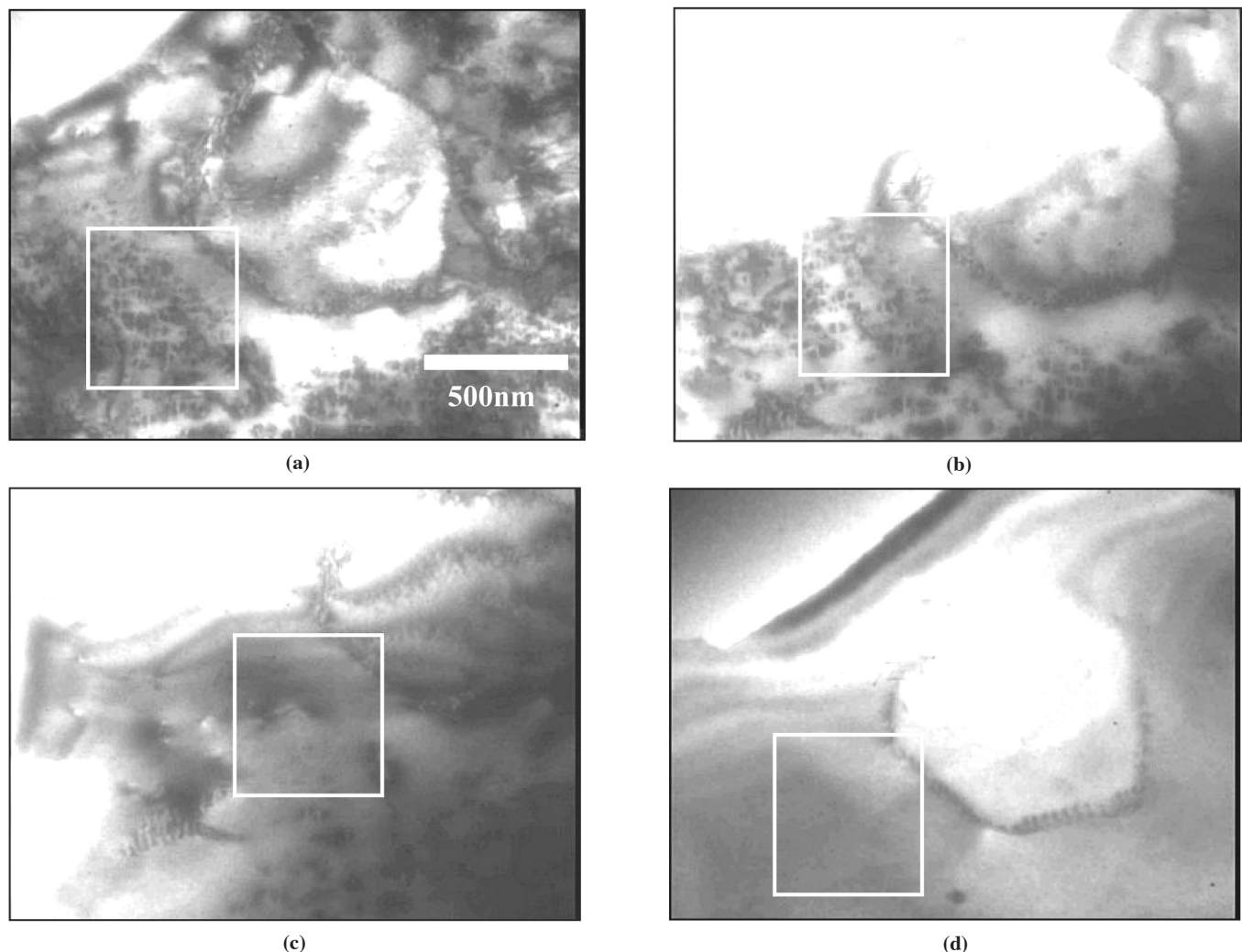


Figure 3. Bright field TEM micrographs showing the dissolution of small precipitates at increasing temperatures.

- (a) 580°C
- (b) 810°C
- (c) 870°C
- (d) 960°C

couples were manufactured for Co: Co/Pt<sub>3</sub>Al and Co/(Pt), and this was also done for other alloying additions: Ni, Ru, Cr, Ru and Al<sup>25</sup>.

Manufacture of the couples was problematic because of the lack of access to a hot isostatic press, but this problem was solved at NIMS using an elegant technique. The couple elements were put face-to-face in a Si<sub>3</sub>N<sub>4</sub> jig with two Si screws on either side, which were finger tightened. The assembly was placed in a furnace and heated to ~1300°C (except the couple comprising Al, which was heated to 700°C since the melting point of Al is 660.25°C). The difference in thermal expansion coefficient between the ceramic jig and the metal created a force on the couple to bond the units together. Figure 4 shows the diffusion couples.

#### Heat Treatment of Pt<sub>86</sub>:Al<sub>11</sub>:Cr<sub>3</sub>:Ru<sub>2</sub> and Pt<sub>79</sub>:Al<sub>11</sub>:Cr<sub>3</sub>:Ru<sub>2</sub>:Co<sub>5</sub>

The best ternary microstructures had been obtained by annealing either at 1350°C or 1400°C and quenching<sup>3,26,27</sup>. The effects of heat treatment temperatures and subsequent different cooling rates on the microstructure of the quaternary Pt-based superalloy have not been fully investigated yet, but this work is ongoing. Samples of the quaternary alloy Pt<sub>86</sub>:Al<sub>11</sub>:Cr<sub>3</sub>:Ru<sub>2</sub> as well as the quinary alloy Pt<sub>79</sub>:Al<sub>11</sub>:Cr<sub>3</sub>:Ru<sub>2</sub>:Co<sub>5</sub> were melted in a button arc furnace, sectioned and heat treated in a muffle furnace for 96 hours. The objective was also to determine the role played by the addition of Co. Both alloys were heat treated at 1350°C and 1400°C, and subsequently cooled down via three different methods: in the furnace (slow), in air when removed from the furnace (intermediate), and in water (fast).

The columnar solidification structure of the alloys could clearly be seen. There was no discernable difference between the two alloys in terms of the heat treatment temperature. High magnification SEM micrographs were also taken but, as expected, no second phase particles could be seen. The images appeared as if the alloys were single-phase, because the particles are too small to be seen on the microscope, and therefore the samples are being re-examined using Mintek's new high resolution Nova NanoSEM.

#### Mechanical Testing and Analysis of Tensile Test Results

No tensile tests had been done on any of these Pt alloys before, and interested manufacturers represented at international conferences have asked for tensile data. The

**Table I**  
Nominal compositions of experimental alloys (wt %).

Alloy	at.% or wt%	Pt	Al	Cr	Ru
1	wt%	98.5	1.3	0.2	-
	at.%	86	10	4	-
2	wt%	96.2	1.5	-	2.3
	at.%	86	10	-	4
3	wt%	96.2	1.7	0.9	1.2
	at.%	84	11	3	2

first tests were done at Mintek. Since results become strain rate dependent very soon at high temperatures, it was decided to only evaluate the room temperature tensile properties of the best ternary alloys, compared with that of the quaternary alloy. Creep testing of the quaternary alloy will be done at high temperatures at a later stage. It has been shown that the high temperature compressive strength of Pt<sub>84</sub>:Al<sub>11</sub>:Ru<sub>2</sub>:Cr<sub>3</sub> is significantly higher than that of Pt<sub>86</sub>:Al<sub>10</sub>:Cr<sub>4</sub><sup>26</sup>.

Macro-scale tensile testing was excluded because of the high material cost. Smaller specimens than the sub-size specimen described by the ASTM standard for tension testing<sup>28</sup>, were used. Small specimen test technology has been an integral part of fusion materials development because of limited availability of effective irradiation volumes in test reactors, and has resulted in specimens that are miniaturised versions of their full-scale counterparts<sup>29</sup>. Yield stress is known to be thickness independent for thickness larger than a critical thickness  $t_{c,Y}$ , but is not affected by specimen width  $w$ , while ultimate stress is aspect ratio ( $t/w$ ) independent above a critical aspect ratio  $(t/w)_{c,U}$ <sup>30,31</sup>. From the literature<sup>29,32</sup>, it was decided that a specimen thickness of 3 mm and an aspect ratio of 1, i.e. a width of 3 mm, would ensure that the tensile properties should be independent on the specimen dimensions. The samples were 46mm in total length and 3mm thick, with gauge width and length 3 mm and 18 mm, respectively. Table I gives the nominal compositions of the experimental samples in atomic and weight percent.

Each 50g ingot was aged in air in a muffle furnace at 1250°C for 100 hours and quenched in water, to achieve a homogeneous two-phase microstructure without primary ~Pt<sub>3</sub>Al. Flat mini-tensile specimens were machined from each ingot by wire spark erosion. Tensile tests were performed with a cross-head speed of 5 mm/min. Due to the specific set-up of the test and imperfections of some of the



Figure 4. Diffusion couples

**Table II**  
**Room temperature mechanical properties of experimental alloys**  
**(summary).**

Alloy	Alloy composition (at.%)	Hardness (HV <sub>10</sub> )	Maximum ultimate tensile strength (MPa)	Elongation (%)
1	Pt <sub>86</sub> :Al <sub>10</sub> :Cr <sub>4</sub>	317 ± 13	836	~4
2	Pt <sub>86</sub> :Al <sub>10</sub> :Ru <sub>4</sub>	278 ± 14	814	~9
3	Pt <sub>84</sub> :Al <sub>11</sub> :Ru <sub>2</sub> :Cr <sub>3</sub>	361 ± 10	722	~1

specimens' shoulders, the extensometer was set up on a gauge length of 12.5 mm only. Elongation was estimated by measuring the length of the specimens before and after testing.

After testing, one half of each sample was prepared for metallography and Vickers hardness tests (20kg weight) were performed, followed by SEM analysis in backscattered electron (BSE) mode, as well as energy dispersive X-ray spectrometry (EDS). In general, there were no significant discrepancies between the nominal and actual compositions. One Ru alloy was contaminated by an insignificant amount of Ru (deduced to be ~0.01 wt%), while two Cr alloys were contaminated by an estimated ~0.05 wt% Cr. The contamination was probably the result of some minor sputtering in the button-arc furnace during melting. Subsequently, TEM specimens were also manufactured, and examined in a Philips CM200 TEM.

X-ray diffraction (XRD) analyses were conducted on the polished samples using Mo K $\alpha$  radiation. All samples except for the Ru alloy, which was just (Pt), comprised (Pt) and ~Pt<sub>3</sub>Al. The fracture surfaces of the other half of each sample were also examined using SEM in secondary electron (SE) mode.

It has been shown before that Ru is, in fact, a better solid solution strengthener in these alloys than Cr<sup>11</sup>, and therefore the fact that the Pt<sub>86</sub>:Al<sub>10</sub>:Cr<sub>4</sub> specimens were stronger than those of Pt<sub>86</sub>:Al<sub>10</sub>:Ru<sub>4</sub> could only be explained by a low volume fraction (~5%) of Pt<sub>3</sub>Al precipitates that were present in the Ru alloy. This was confirmed by both XRD and TEM, and implied that Pt<sub>86</sub>:Al<sub>10</sub>:Ru<sub>4</sub> had been annealed above its solvus, which was thought to be between 1250°C and 1300°C<sup>33</sup>. Thus, the higher ductility of this alloy was due to its single phase (Pt) nature.

The presence of ~Pt<sub>3</sub>Al in the Pt<sub>84</sub>:Al<sub>11</sub>:Ru<sub>2</sub>:Cr<sub>3</sub> specimens was confirmed by XRD and TEM. The volume fraction of precipitates varied from specimen to specimen. Some of the specimens failed outside the gauge length, and discarding these, the average hardnesses, maximum UTS and elongation for each alloy are given in Table II.

Pt<sub>86</sub>:Al<sub>10</sub>:Cr<sub>4</sub> was harder and also had a higher UTS than Pt<sub>86</sub>:Al<sub>10</sub>:Ru<sub>4</sub>. However, Pt<sub>84</sub>:Al<sub>11</sub>:Ru<sub>2</sub>:Cr<sub>3</sub>, with a significant volume fraction of ~Pt<sub>3</sub>Al, was the hardest, but had the lowest UTS of the three alloys. This was also the only alloy that failed intergranularly, while the others failed mainly by intragranular cleavage with some localised signs of dimpling. It is likely that the lower UTS was related to the intergranular failure mode, which correlates to its lower elongation.

The spread and inconsistencies in the results were disappointing. It would have been more ideal to test a wider range of specimens, but working with Pt always constrains the experimental matrix because of the expense.

One can safely say that these Pt-based alloys are in the order of 300-350 HV with a UTS of ~800MPa<sup>34,35</sup>. To put

it in perspective, this is significantly higher than the 40-50 HV of pure Pt in the soft state and its UTS of ~140 MPa<sup>36</sup>. Compared to other high-temperature alloys, such as the ferritic ODS alloy PM2000, which has a room temperature UTS of 720 MPa and elongation of 14% at room temperature<sup>37</sup>,  $\gamma$ -TiAl with UTS of 950 MPa and elongation of ~1%<sup>38</sup> and CMSX-4 with UTS 870 MPa<sup>39</sup> it is obvious that these Pt-based alloys are within range of these type of alloys, which is encouraging considering the as-yet unoptimised nature of their heat treatments and microstructures.

## Commercialisation phase

### Rationale

The ultimate target for the Pt-based alloys is the land-based turbine industry. However, as this is such a difficult market to penetrate, it has been decided to initially target other applications, thereby providing recognition for these alloys as useful industrial materials. The ultimate aim has not changed, and is still being actively pursued, but using the alloys in other applications could help speed up their acceptance in the turbine industry, whilst simultaneously increasing the overall use of platinum. Several niches have been identified, all of which require good strength at high temperatures in aggressive environments.

Four main directions are being targeted for the commercialisation interests. These are casting, development of alloys for the glass industry, coatings and powder metallurgy.

### Casting Trials

The primary objective of the casting trials was to test the castability of Mintek's alloys by using conventional investment casting. The casting trials were done with the help of Musuku Beneficiation Systems. It was decided to cast small turbine blades, which are very suitable for testing the casting behaviour of an alloy since it has abrupt changes from thick to thin sections, as well as casting grids, conventionally cast to test the form filling properties of an alloy.

A horizontal centrifugal casting system was used. All castings were done in exactly the same way Musuku casts other Pt alloys (albeit for jewellery), i.e. the spruing method, the same flask temperature (750°C), casting temperature (1850°C) and arm velocity. Prior to casting, the casting chamber was put under vacuum and purged with argon gas. Figures 5-6 show the respective castings at different angles.

The metal melted very easily with only a slight slag forming on top of the melt, which did not affect the casting and could not be seen afterwards. No oxidation occurred and the metal surface was perfectly clean after casting. The detail of the grids was very good, with almost perfect squares formed with very little distortion (Figures 5 and 6). Additionally, the corners and the thin sections of the blades came out very well.

However, there are casting parameters that need to be improved. No casting was filled completely (Figures 5-6). The size of the feeder buttons were fine, indicating that there was sufficient metal behind the casting, and that the problem was fluidity, which should be rectified by increasing the flask and/or casting temperature. The quaternary alloy was very brittle, and it cracked very easily

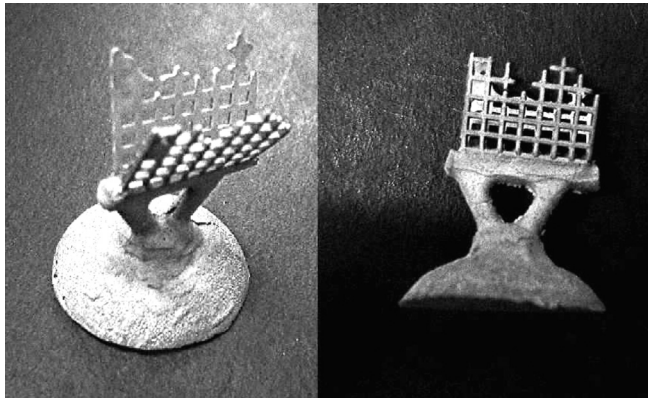


Figure 5. Pt<sub>84</sub>:Al<sub>11</sub>:Cr<sub>3</sub>:Ru<sub>2</sub> investment cast form-filling grids

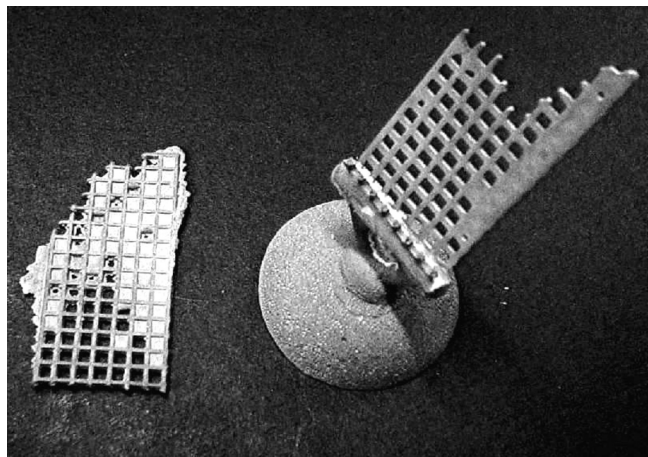


Figure 6. Pt<sub>82</sub>:Al<sub>15</sub>:Co<sub>3</sub> alloy investment cast form-filling grids

at the runners in the process of tapping the investment from the casting. The effect of cooling rates after casting needs to be investigated; the casting was air cooled for ~10 minutes, and then submerged in water. Air-cooling time could be extended, even overnight, or, in case the problem is excessive grain growth during air-cooling after casting, quenching directly after casting could be investigated. The investment cracked during casting, which was very unusual and this was possibly an investment defect, and unlikely to be due to the metal behaving differently from jewellery alloys in thermal shock or impact effects. Unfortunately, because of the cracking of the investment, there was some flashing which obscures some of the detail on the grids.

Considering that it was the first time ever that the PDI alloys were investment cast, the exercise was rather successful and enough was learnt to build on for future castings. At this stage, there is no reason to believe that another casting method needs to be explored. Once the parameters are optimised, mechanical test specimens for creep and tensile testing will be cast for further rigorous testing.

### Alloys for the Glass Industry

One particular niche for strong alloys in an aggressive environment is the glass industry, which already uses Pt-based alloys. The glass manufacturers are always searching for more economical alloys - since the platinum content is very high and the platinum is a very high proportion of the

costs - and would like alloys which are cheaper, or which last longer. The glass industry uses a very high amount of platinum for the containment and processing of the molten glass. There are three major considerations: strength, corrosion resistance, and ease of shaping. From the properties measured so far, the PtBSAs are stronger at intermediate temperatures, up to 1300°C, than the conventional alloys.

The current industrial alloys are formed in a number of ways, and the more easily-formed alloys will be used in a larger number of devices. Any non-formable PtBSA could be cast, but this would limit the applications. However, it is thought that the alloys would be easily welded because they are polycrystalline. Single crystal alloys are problematic to weld because the single crystal structure is lost on solidification after melting. It would be prudent to undertake some welding trials, once some candidate alloys have been selected. The corrosion resistance is very important and needs to be tested, and there is already a recognised test that can be used as a standard [40].

Since platinum is so expensive, there might be a trend away from platinum alloys. However, since most of the newer applications use glass that is more aggressive, the use of platinum alloys in glass manufacture will actually increase, because ceramics cannot withstand the conditions. Most of the special glasses are also very aggressive in their manufacturing stages, especially when the oxides are first melted together. There is also an expansion in the manufacture of the special glasses, because they are used in items in rapidly expanding markets, such as LCD and plasma screens. The larger glass manufacturers have much platinum: some is their own, and some is leased. If the platinum alloys can be adapted to last longer, then the drive to replace them will be reduced.

### Powder Metallurgy

Another potential niche is powder metallurgy. This technique is used when the component is difficult (or impossible) to fabricate by cheaper methods, and excellent properties are needed. It can also be used to shape mixtures of powders. Since the targeted application is for high temperature in aggressive environments, it is likely that some of the components currently being targeted, such as valves and nozzles, might need to be made via powder methods. Many of these types of components are already being manufactured by powder methods in order to get the good properties required or because of their intricate shapes. Mintek is currently commissioning a high temperature version of a water atomiser that has already successfully produced a range of powder sizes and shapes, albeit for lower melting point alloys. The powders from the atomiser will be used for compacting experiments, and after much characterisation and testing, for the prototype components. After making the compacts, these have to be characterised and tested for strength, corrosion resistance, and where necessary, wear resistance.

A Mark III 'Atomijet-S' water atomiser has been designed and constructed by Mintek to atomise high melting temperature metals, specifically Pd and Pt and their alloys. The new design differs from the old in that there is a separate melting and pouring furnace, together with a pre-heated funnel or tundish. This design overcomes the material restrictions and geometric challenges associated with a combined melting and discharge furnace with a stopper rod, which restricts the maximum melting temperature. Differing ceramic materials are used for the

furnace crucibles according to the metal's melting temperature and associated materials performance that is required (e.g. alumina for Au and Ag, zirconia for Pd and Pt).

This combined research/pilot-scale atomiser has a melt capacity of approximately 250ml (max. 3kg Pd / 5kg Pt), and the molten metal stream is broken up from three sides in the atomisation chamber by three adjustable water jets, with the jets powered by high-pressure pumps with a capacity of 350 bar each. The two furnaces are housed in an insulated 'hot box', with a positive pressure of nitrogen maintained in the hot box and atomisation chamber to minimise oxidation. A unique feature of the atomiser is a number of toughened glass view ports that allows the pouring and atomisation processes to be safely viewed during operation. A bank of in-line filters ensures that minimal metal is lost in the water circuits.

For the targeted application, nozzles in the chemical and marine oil environments are being considered, while another niche is powder for different types of thermal spray coatings.

### Coatings

A third niche is using the alloys as coatings on a cheaper substrate, such as a stainless steel. Coatings are employed for a variety of reasons including attractiveness, corrosion resistance and/or wear resistance. Coatings can be preferable for cheaper components, or where the component is not needed to last so long. Thus, it is more economic to coat a cheaper substrate with a more expensive alloy than to have the whole component being made from the expensive alloy. Coatings can also be advantageous where low weight is important. The Pt-based alloys are dense, so using these alloys as coatings would provide the benefits thereof combined with the reduced density of a lighter substrate. This part of the project is complementary with powder metallurgy, because the powders can be a source for the coatings. Although coatings on NBSAs are being targeted initially, other niches include chemical plants (e.g. Sasol), marine environments, and the automotive industry.

### Conclusions

The latest research work on the original Pt-based alloys for high temperature applications in aggressive environments is progressing well, and some new alloying additions have been made, for example Ni, Co and Pd. Only the Co additions were beneficial. The first tensile tests of the alloys worldwide have been done. These tests were undertaken at ambient temperature, and were very encouraging because the results were comparable to those of other high temperature alloys used at high temperatures. TEM work has shown how the microstructure of the alloys changes at high temperature, and although encouraging, another the results suggest that further additions to stabilise the small precipitates would be beneficial above 1300°C, because small changes to the microstructure have been observed there.

Work has started for commercialisation and casting trials have begun. The alloys generally behaved well, but the casting parameters need to be optimised. Information has been gleaned for three other target niches, glass industry, powder metallurgy and coatings. Work is ongoing to develop a coating technique, and a water atomiser has been built to manufacture powders for both the powder metallurgy and coatings projects.

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