Platinum-based alloys for high temperature and special applications

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Platinum-based alloys are being developed for high temperature and special applications for good corrosion and oxidation resistance. The microstructures are similar to those of nickel-based superalloys, and comprise ~Pt3Al particles in a Pt-based matrix. After assessing binary alloys, the best candidate system was found to be Pt-Al. Testing and selection of alloys based on Pt-Al were undertaken, where the ternary additions comprised Ru, Cr, Ta, Ir and Ti. As well as phase characterization work, mechanical and oxidation tests were undertaken. The best alloys were found to be Pt-Al-Cr and Pt-Al-Ru. However, the volume fraction of the ~Pt3Al was only around 40 per cent instead of the ~70 per cent found in Ni-based superalloys. To increase this, trials were conducted on a range of Pt-Al-Cr-Ru alloys, the optimum composition being Pt80:Al14:Cr3:Ru3. Currently, further additions are being made to the quaternary alloys to change selected properties.

As well as developing the alloys themselves, another part of the project is to compile a thermodynamic database using Thermo-Calc™. Phase diagram work has been undertaken so that the results can be input to Thermo-Calc™ so that the descriptions of the phases can be optimized. The final database will allow the phases and compositions of selected alloys to be derived, thus predicting the alloys’ components without necessarily undertaking further experimental work. This will aid the development of the alloys and will be a useful tool to the final developers of the alloys. Good agreement with experimental data has been observed, which is very encouraging for usefulness of the database.

Keywords: platinum-based alloys, intermetallic compounds, high temperature

Introduction

Nickel-based superalloys have excellent mechanical properties because they have a microstructure comprising many small, strained-coherent particles in a softer matrix. 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 L12 ordered structure. The lattice misfit between these structures is very small and renders the surface energy negligible.

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, a 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 Ni3Al 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. These facts inspired the proposal by Wolff that Pt-based analogues to Ni superalloys could be developed to serve in the most critical and demanding of high temperature applications. 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. Pt3Al has at least two forms, and the more desirable high temperature L12 form needs to be stabilized. The lowest temperature form has yet to be fully confirmed.

Work undertaken at Mintek

In a preliminary investigation by Hill et al., ternary Pt-X-Z compositions were selected to yield two-phase microstructures consisting of fcc (Pt) matrix and ordered fcc (L12) Pt3X precipitates. It was reported that two-phase microstructures, leading to a considerable precipitation-strengthening effect, could be achieved in Pt-Ti-Z and Pt-Al-Z systems, where Z = Ni, Ru and Re. Alloys in these systems have shown promising mechanical properties at room temperature, with hardness values higher than 400 HV1 and high resistance to crack initiation and propagation. The alloys containing Al exhibited considerably better...
oxidation behaviour than the other alloys—this was attributed to the formation of a protective Al-oxide scale. Internal oxidation was observed in alloys containing Ti instead of Al, and this was presumed to be the cause of their inferior properties. Al was regarded as the essential addition in order to develop an oxidation-resistant alloy, therefore further work focused on Pt-Al-Z alloys only.

Hill et al. did extensive work on the phase relations and room temperature mechanical properties of Pt-Al-Z alloys, with Z = Ru, Re, W, Mo, Ni, Ti, Ta and Cr. They have shown that microstructures similar to Ni- and Co-based superalloys can be achieved in the Pt-based alloy Pt86:Al10:Z4, consisting of cuboidal \( \sim \text{Pt}_3 \text{Al} \) precipitates in a (Pt) matrix. It was found that ternary alloying elements, and in particular Cr and Ru, conferred additional benefit. Cr stabilizes the cubic form of the \( \sim \text{Pt}_3 \text{Al} \) phase and Ru is added as solid solution strengthener.

However, the high-temperature properties of these alloys are of critical importance. The high-temperature oxidation behaviour of Pt-Al-Z alloys (Z= Re, Ta, Ti, Cr, Ir and Ru) has been studied by Hill et al. and Süss et al.

Figure 1 shows the increase in the thickness of the continuous layers with time for the different alloys. PM2000 was used as a benchmark alloy, and is an Fe-Cr-Al alloy with a fine dispersion of \( \text{Y}_2\text{O}_3 \) particles in a ferritic matrix, which exhibits dispersion strengthening. The Pt86:Al10:Ti4 and Pt86:Al10:Ru4 alloys showed similar parabolic oxidation behaviour to the benchmark alloy. The Pt86:Al10:Ir4 and Pt86:Al10:Cr4 alloys showed parabolic behaviour during the early stages of oxidation (with high initial oxidation rates), after which their continuous oxide layers grew at a logarithmic rate, giving these two alloys the thinnest continuous oxide layers after 800 hours' exposure.

It was found that an external alumina film formed after a transient period during which discontinuous alumina particles precipitated in a Pt matrix (Figure 2a). This is the result of the oxygen diffusion through the scale being quicker than Al diffusion in the alloy. Only when a critical volume of oxides is reached, does transition from internal oxidation to external scale formation occur. The continuous film appeared to provide protection for the alloy, since no internal oxidation occurred during long-term exposure (Figure 2a). However, the alloys were still outperformed by the PM2000, which formed a perfectly continuous oxide layer (Figure 2b). Further work was required in order to accelerate the formation of the continuous layer of the Pt alloys. It was likely that this could be achieved by increasing the Al content.

![Figure 1. Results of the isothermal oxidation tests conducted on Pt-Al-Z alloys at 1350°C, showing the specific mass changes with time over the first 100 hours.](image1)

![Figure 2. Secondary electron images of alloys isothermally oxidized at 1350°C for various times, showing (1) transient oxidation and (2) continuous oxidation.](image2)
Hill et al. also studied the effects of various ternary substitutional alloying additions on the high-temperature compressive strengths of Pt-Al-Z alloys (Z = Ti, Cr, Ru, Ta, and Re), although the microstructures and Pt:Al:Z ratios of the alloys varied. It was found that the Pt-Al-Z alloys had higher strengths above 1150°C than the commercial Ni-based superalloy MAR-M247. However, further work was necessary to elucidate the effects of the ternary alloying additions on the high-temperature mechanical properties of Pt-Al-Z alloys, because differences between the microstructures of the alloys tested made it difficult to isolate the influences of the ternary additions and high-temperature compressive strength does not equate to creep strength.

Süss et al. investigated the effects of various alloying additions on the creep properties of Pt-Al-Z alloys at 1300°C. The ternary elements (Z = Ti, Cr, Ru, Ta, and Ir) were selected to improve the high-temperature mechanical properties and phase stability of the alloys, in accordance with the findings of Hill et al. The Pt:Al:Z ratios of the alloys tested were standardized to eliminate effects of differing Al contents. The properties of the Pt-Al-Z alloys were once again compared to those of PM2000.

Figure 3 shows the stress-rupture curves of all the alloys tested. PM2000 has the highest strength of the alloys tested, but the shallow slope of the stress-rupture curve indicates high stress sensitivity and brittle creep behaviour. In practice this means that PM2000 structures are likely to fail in the presence of stress concentrations or short overloads during usage. Pt86:Al10:Cr4 possesses the highest strength of the investigated Pt-based alloys.

Figure 4 shows some selected creep curves (tested at 30 MPa) for the four alloys. No primary creep stage could be observed for any of the three Pt-based alloys within the measurement error of the creep test facility. After secondary creep, the Pt-based alloys undergo pronounced tertiary creep, leading to fracture strain values between 10 per cent and 50 per cent at 1300°C. For PM2000, it was not possible to resolve different stages of the creep curves because of very low creep rates together with fracture strains below 1 per cent (Figure 4).

Figure 5 shows the stress rupture lives of PM2000 and the most promising Pt-based alloy, Pt86:Al10:Cr4, together with 10-hour stress-rupture strength values at 1300°C of several conventional solid-solution strengthened Pt-based alloys according to Lupton et al., as well as that of Pt ZGS, an oxide dispersion strengthened Pt alloy from Johnson Matthey.

The strengthening effect achieved by precipitation of γ’ particles is clearly seen in a considerable increase of the stress-rupture strength, Rm/10h/1300°C, by a factor of 8 from 2.2 MPa for the pure Pt matrix to 17 MPa for Pt86:Al10:Cr4. The strength of Pt86:Al10:Cr4 alloy (which contains 97.2 per cent Pt by weight) is also higher than the solution strengthened Pt-based alloys, Pt-10 weight per cent Rh and Pt-20 weight per cent Rh. Alloying 30 weight per cent Rh is necessary to reach the strength of the alloy Pt86:Al10:Cr4, and the exceptionally high price of Rh and enormous machining problems limit the practical use of Pt-30 weight per cent Rh.

The creep strengths of the Pt-based alloys at the very high temperature of 1300°C are higher than those of the Ni- and Co-based superalloys, whose precipitates dissolve in this high-temperature regime, resulting in loss of strength. (No data are available to to show this, because this is well above the Ni- and Co-based superalloys application range.) The creep strength of the Pt86:Al10:Z4 system is comparable to mechanically alloyed ferritic ODS alloys, for example PM2000, as shown in Figure 5.
Since Pt$_{86}$:Al$_{10}$:Cr$_{4}$ was very promising with regard to high temperature strength and oxidation resistance, it was decided to test a quaternary alloy with Ru as addition. It was ultimately the objective to increase the volume fraction of γ ′ to enhance the alloy’s creep properties. More Al was added in an effort to accelerate oxide scale formation$^{14}$. After one hour at 1350°C, a thin continuous oxide layer had formed. After 10 hours’ exposure (Figure 6), the scale was already about three times as thick as that observed for Pt$_{86}$:Al$_{10}$:Cr$_{4}$ after the same time period (Figure 2). Neither a zone of discontinuous oxides, nor any other internal oxidation, was observed. The increased Al content of the alloys clearly accelerated the formation of a continuous layer and prevented mass loss due to volatilization. The main objective of the experiment was therefore achieved. However, in the long term the alloy’s oxidation might be too severe. The alloy should ideally form a continuous oxide layer quickly but then behave logarithmically with regard to mass increase.

The composition of the quaternary alloy needed to be optimized so that the maximum proportion of the second phase was achieved. Several alloys were therefore made up with this objective$^{15}$. 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 microstructures were subsequently 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.

Two alloys, Pt$_{78.5}$:Al$_{15.5}$:Ru$_{2.5}$:Cr$_{4.5}$ and Pt$_{81.5}$:Al$_{11.5}$:Ru$_{2.5}$:Cr$_{4.5}$, had large areas of ~Pt$_3$Al, together with a fine mixture of (Pt) and ~Pt$_3$Al (Figure 7a). Another, Pt$_{84}$:Al$_{11}$:Ru$_{2}$:Cr$_{3}$, was composed entirely of a fine two-phase mixture, which is the desired microstructure (Figure 7b).

More alloys were produced to ascertain if the volume fraction of the ~Pt$_3$Al precipitates could be increased. A 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. There was no improvement in the microstructure. The hardnesses of the alloys were measured and the results are given in Table I. The alloys were reasonably ductile, with no cracking around the indentations, as was found in some of the earlier single-phase quaternary alloys$^{15}$.

![Figure 6. SEM images of the transverse sections of the Pt$_{80}$:Al$_{14}$:Cr$_{3}$:Ru$_{3}$ alloy after exposure to air at 1350°C for an increasing amount of time]({figure6.png})

![Figure 7. SEM micrographs, in back-scattered electron (BSE) mode, of the two types of two-phase alloys. (a) With primary ~Pt$_3$Al (dark contrast) in a fine mixture of (Pt) and ~Pt$_3$Al; (b) Fine mixture of (Pt) and ~Pt$_3$Al]({figure7.png})
In an attempt to improve the microstructure of the alloys, a second heat treatment was conducted for 96 hours at 1350°C, after which alloy Pt\textsubscript{81.5}:Al\textsubscript{11.5}:Ru\textsubscript{2.5}:Cr\textsubscript{4.5} showed a clear, fine two-phase microstructure, possibly due to the change in its overall composition. There was no primary ~Pt\textsubscript{3}Al in evidence, so the overall composition is that of the two-phase mixture: 85.2 ±0.3 atomic per cent Pt, 7.1 ±0.8 atomic per cent Al, 3.1 ±0.8 atomic per cent Ru and 4.6 ±0.1 atomic per cent Cr. Since the overall composition changed, the sample was redesignated as Pt\textsubscript{85}:A1\textsubscript{17}:Ru\textsubscript{3}:Cr\textsubscript{5}. Figure 8 shows the microstructure of this alloy after the first and second heat treatments. It can be seen that the precipitates in Pt\textsubscript{84}:Al\textsubscript{11}:Ru\textsubscript{2}:Cr\textsubscript{3} (Figure 7b) are approximately twice as large, but more well-defined than those of Pt\textsubscript{85}:Al\textsubscript{17}:Ru\textsubscript{3}:Cr\textsubscript{5} (Figure 8a) and two heat treatments (Figure 8b)\textsuperscript{16}.

The hardnesses after the first and second heat treatments are compared in Table I. The hardnesses were lower after the second anneal. As has been shown before, it is possible to obtain a (Pt) + ~Pt\textsubscript{3}Al microstructure in the quaternary alloys\textsuperscript{16}. The volume fraction of ~Pt\textsubscript{3}Al was estimated, using image analysis, to be approximately 25 to 30 per cent. The highest hardness was found in the alloy without primary ~Pt\textsubscript{3}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\textsubscript{84}:Al\textsubscript{11}:Ru\textsubscript{2}:Cr\textsubscript{3}. It has the required structure, no primary ~Pt\textsubscript{3}Al and reasonable hardness. Other work has already shown that its oxidation resistance is better than the original ternary alloys\textsuperscript{14}. 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 Thermo-Calc\textsuperscript{TM} program was chosen for the assessment of the phase diagrams to derive the database because it contains the Parrot module, which is the accepted verified optimization process for fitting phase diagrams to experimental data. The database comprises information on the different phases, which is stored as coefficients. Although other programs are available for calculating phase diagrams, currently only Thermo-Calc\textsuperscript{TM} can be used to optimize data. The Parrot module in Thermo-Calc\textsuperscript{TM} that is being used to optimize the database is based on that of SGTE\textsuperscript{18} and Spencer’s database\textsuperscript{19}. 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\textsuperscript{20}, this was re-calculated as Wu and Jin’s description did not exhibit any ordering in the Pt\textsubscript{3}Al phase\textsuperscript{21}. They also described only one form of the Pt\textsubscript{3}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 optimized by the group\textsuperscript{21}. Next, each ternary system will be optimized individually (already started for Al-Cr-Ru), and then once finalized, they will be combined for the quaternary. Experimental work was completed on the ternary systems: Al-Cr-Ru\textsuperscript{22–24}, Pt-Al-Ru\textsuperscript{25} and Pt-Cr-Ru\textsuperscript{26–28}, while Pt-Al-Cr is on the way\textsuperscript{29}.

Current and future work
The Pt-Al-Cr system is currently being studied and the experimental phase diagram is being derived. The Thermo-Calc\textsuperscript{TM} program has been used to derive liquidus projections for the Pt-Al-Ru and Pt-Cr-Ru systems by extrapolating from the calculated binary systems. The computer-calculated phase diagrams for the Pt-Al-Ru and Pt-Cr-Ru have shown good agreement with the experimental results considering that no ternary data were

Table I
Vickers hardness of the two-phase quaternary alloys, using a 10 kg load, after annealing at 1350°C\textsuperscript{15}

<table>
<thead>
<tr>
<th>Alloy Designation</th>
<th>Hardness after first anneal (HV\textsubscript{10})</th>
<th>Hardness after second anneal (HV\textsubscript{10})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt\textsubscript{82}:Al\textsubscript{11}:Ru\textsubscript{2}:Cr\textsubscript{3}</td>
<td>430 ± 5</td>
<td>403 ± 20</td>
</tr>
<tr>
<td>Pt\textsubscript{82}:Al\textsubscript{11.5}:Ru\textsubscript{2.5}:Cr\textsubscript{3.5}</td>
<td>425 ± 21</td>
<td>403 ± 14</td>
</tr>
<tr>
<td>Pt\textsubscript{82}:Al\textsubscript{11}:Ru\textsubscript{2}:Cr\textsubscript{3}</td>
<td>421 ± 12</td>
<td>405 ± 8</td>
</tr>
<tr>
<td>Pt\textsubscript{85}:Al\textsubscript{12.5}:Ru\textsubscript{2.5}:Cr\textsubscript{4.5}</td>
<td>419 ± 22</td>
<td>414 ± 9</td>
</tr>
<tr>
<td>Pt\textsubscript{84}:Al\textsubscript{11}:Ru\textsubscript{2.5}:Cr\textsubscript{3.5}</td>
<td>423 ± 10</td>
<td>396 ± 6</td>
</tr>
<tr>
<td>Pt\textsubscript{79}:Al\textsubscript{10.5}:Ru\textsubscript{4.5}:Cr\textsubscript{5.5}</td>
<td>417 ± 8</td>
<td>415 ± 10</td>
</tr>
</tbody>
</table>

First heat treatment Pt\textsubscript{81.5}:Al\textsubscript{11.5}:Ru\textsubscript{2.5}:Cr\textsubscript{4.5}  
Second heat treatment Pt\textsubscript{85}:Al\textsubscript{17}:Ru\textsubscript{3}:Cr\textsubscript{5}
input. These results are extremely encouraging because they show that higher order systems can be fairly accurately calculated from the lower order systems, and this bodes well for the development of the database for the Pt-based materials.

Additionally, more quaternary alloys will also be studied. Results from this phase diagram work, together with enthalpies from the single-phase or near single-phase compositions calculated by Leeds University, UK, will be input into Thermo-Calc™ for optimization.

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

Ni has already been added to improve the solution strengthening of the matrix and the results are encouraging, although less solution strengthening was achieved than hoped. A very fine mixture has been produced. Co is also being added for solid solution strengthening. Extensive phase diagram work has been undertaken on the Pt-Al-Co and Pt-Al-Ni systems. Additions have also been made that improve the formability.

The binary Pt75:Al25 (atomic per cent) alloy was studied using transmission electron microscopy (TEM) and the precipitate phase was found to have a different structure from that reported. It was a modified form of the D00c structure with a different unit cell than the usual D00′. Obtained for alloys based on Pt, Rh and Ir compared, and stable two-phase structures have been targeted materials for high temperature applications at high temperatures.

To assess the stability of the microstructure over long times, mobility of the different components within the alloys, and described above.

Mechanisms can be found, and also to compare these with will be done. A TEM investigation is underway on these alloys.

There were extensive hexagonal networks for the L12 precipitate/matrix interfaces. These networks were far less prominent for the modified D00c precipitate/matrix interfaces.

Preliminary tensile tests have been undertaken on the Pt-Al-Cr and Pt-Al-Ru and the best Pt-Al-Cr-Ru composition and the results are very encouraging. More tensile tests will be done. A TEM investigation is underway on these tensile test specimens so that the dislocations and their mechanisms can be found, and also to compare these with those of the high temperature-deformed specimens described above.

Diffusion studies are also being undertaken to assess the mobility of the different components within the alloys, and to assess the stability of the microstructure over long times at high temperatures.

Comparison of the PGM-based alloys with other targeted materials for high temperature applications

Some of the different PGM-based materials have been compared, and stable two-phase structures have been obtained for alloys based on Pt, Rh and Ir. The PGM-based alloys show excellent oxidation resistance with simple alloying, especially compared to other materials which are also being developed for high temperature applications (Figure 9) although the experiments were not undertaken under identical conditions. Although the strengths are comparable with other competitors, once the strength is normalized against density, the results appear less encouraging (Figure 10). However, before dismissing the PGM-based alloys, several other facts have to be taken into account. Firstly, there is the excellent corrosion resistance exhibited in Figure 9. It is highly likely that the PGM-based materials will need much less complex coatings, and they might not even require coatings at all. This is a great safety saving, as well as an expense saving. Additionally, the Pt-based alloys are formable, and thus a different component design could be developed to utilize the high strength but with less bulk of the material. Although the properties have not been measured, because of the fcc matrix structure and evidence from the hardness and tensile test results, the fracture toughness, impact resistance and fatigue resistance are likely to be high for the Pt-based alloys.

The other materials in Figures 9 and 10 have other limitations, which must also be considered. The silicon carbide composites have relatively low strengths, even on the density-normalized plot (Figure 9), although the impact...
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References


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