The Platinum Development Initiative: Platinum-Based Alloys for High Temperature and Special Applications: Part I

By L. A. Cornish
DST/NRF Centre of Excellence in Strong Materials, Johannesburg 2050, South Africa,
and School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Private Bag 3, Johannesburg 2050, South Africa

R. Süß*
Advanced Materials Division, Mintek, Private Bag X3015, Randburg 2125, South Africa,
DST/NRF Centre of Excellence in Strong Materials, Johannesburg 2050, South Africa,
and School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Private Bag 3, Johannesburg 2050, South Africa;
*E-mail: rainers@mintek.co.za

A. Douglas**
Advanced Materials Division, Mintek, Private Bag X3015, Randburg 2125, South Africa,
and DST/NRF Centre of Excellence in Strong Materials, Johannesburg 2050, South Africa

L. H. Chown
Advanced Materials Division, Mintek, Private Bag X3015, Randburg 2125, South Africa,
and DST/NRF Centre of Excellence in Strong Materials, Johannesburg 2050, South Africa

and L. Glaner
Advanced Materials Division, Mintek, Private Bag X3015, Randburg 2125, South Africa,
DST/NRF Centre of Excellence in Strong Materials, Johannesburg 2050, South Africa,
and School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Private Bag 3, Johannesburg 2050, South Africa

Under the auspices of the Platinum Development Initiative, platinum-based alloys are being developed for high-temperature and special applications requiring good corrosion and oxidation resistance. The best candidate system was found to be platinum-aluminium, after reviewing binary systems and assessing experimental ternary alloys. Ternary alloys based on Pt-Al, where the ternary additions comprised chromium, iridium, molybdenum, nickel, rhenium, ruthenium, tantalum, titanium and tungsten were tested. As well as phase characterisation work, mechanical and oxidation tests were undertaken. The best alloys were found to be Pt-Al-Cr and Pt-Al-Ru. The microstructures were similar to those of nickel-based superalloys, and comprise ~ Pt3Al precipitates in a Pt-based matrix. However, the volume fraction of the ~ Pt3Al was only ~ 40% instead of the ~ 70% found in Ni-based superalloys.

Introduction

The Platinum Development Initiative (PDI) was officially started in April 1997, comprising Anglo Platinum, Impala Platinum, Lonmin (then Lonrho) and Mintek. The aim was to encourage new research into Pt-based alloys which would eventually lead to an increased use of Pt, by broadening the industrial base. It was hoped that further research would be spawned following publication of the PDI’s research, and the world network of Pt researchers would grow. The major topic was identified as the development of new alloys based on Pt which would probably have similar microstructures to the Ni-based superalloys (NBSAs) and
could be used at even higher temperatures, as well as in more aggressive environments. Pt alloys are well known for their use in aggressive environments (1–4), especially in the glass industry, but the present work was aimed at developing alloys that were similar to NBSAs. Since there are well recognised thermodynamic databases available for the NBSAs, it was decided that such a database would also be developed for the new alloys in parallel to developing the alloys themselves.

Additionally, material was loaned for other projects which were seen to be of interest. These included diffusion studies of selected platinum group metals (pgms) in NBSAs (5), work on Pt-based shape memory alloys, together with related work on the Pt-Ti phase diagram (6–10) and nanotechnology studies on Ru (11). Although the PDI ceased functioning as an entity in October 2007 due to changes in funding and research direction, the bulk alloy work is still ongoing in the DST/NRF Centre of Excellence in Strong Materials, and Mintek is focusing on the development of the pgm alloys as coatings and for powder metallurgy.

A parallel study was undertaken at the University of Cambridge, U.K., on the microstructure and properties of platinum-hafnium-rhodium and platinum-rhodium-zirconium alloys (12–15). The presence of the Pt$_8$Hf and Pt$_8$Zr phases did not allow a $\gamma$ (f.c.c.)-$\gamma'$ (L1$_2$) NBSA analogue in the Pt-Hf and Pt-Zr alloys, because these phases were between the $\gamma$ and $\gamma'$ phases. However, the Pt$_8$Hf and Pt$_8$Zr phases did not penetrate far into the Pt-Hf-Rh and Pt-Rh-Zr systems, and $\gamma$-$\gamma'$ regions were formed beyond their limits of penetration. Compressive proof stress results indicated better properties for Pt$_{45}$Hf$_{15}$ Rh$_{40}$ (at.%) than the alloys developed at Mintek, but the oxidation resistance was much poorer.

This is the first of a series of review articles which will cover the work done on the development of the Pt-based alloys. Two papers by this group have already been published in Platinum Metals Review on the development of the thermodynamic database (16, 17), together with a third paper from the group’s coworkers in Germany (18).

The work of the PDI has allowed a number of Pt-based alloys to be identified, and much characterisation work has been done on these alloys. They have the potential to replace some of the NBSAs in the most extreme environments in terms of elevated temperatures, aggressive atmospheres and higher stresses (19–24). There was also the potential that either no coatings would be necessary, or at least simpler coatings could be employed than those currently used for NBSAs. Initial exploratory work was concerned with establishing potential systems on which to base the alloys. The systems were selected for potential two-phase microstructures, by studying the binary phase diagrams, and manufacturing a limited number of samples from possible ternary systems. These were then evaluated by microstructure, hardness testing and quick oxidation tests. Candidate systems which showed no potential, even allowing for the fact that the alloys might have unsuitable proportions, were eliminated. Those systems which showed promise became the basis for more in-depth studies, involving more alloys and phase diagram studies where necessary. The latter were required for the thermodynamic database.

It was realised that there was little or no information available on the required ternary systems, and even some of the binary systems had problems. Mechanical properties have been studied and some of the alloys are in the process of being optimised for further improvement. Oxidation and corrosion studies were done, and showed that the alloys had superior properties to the NBSAs, even for coated samples (25). Currently, there are two major ranges of Pt-based alloys which have been developed. One is more malleable but less resistant to extreme chemical environments, whereas the other has greater chemical resistance, but is less easy to form. Although neither alloy has been produced commercially, both are the subject of an ongoing project to develop them commercially as coatings, and also for powder metallurgy. The major problems in finding a suitable application are that the alloys are too dense for current designs of turbine engines, and also that their expense is restrictive. Thus, the alloys could have potential as coatings on other substrates.
NBSAs have excellent mechanical properties because they have a microstructure comprising many small, strained-coherent, precipitates in a softer matrix (26). 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 is limited because the surface energy itself is very small, thus reducing the driving force. This is because the precipitate structure is very closely related to that of the matrix. Both are based on the face centred cubic structure (f.c.c.): the matrix has a random f.c.c. structure, and the particles have an L12 structure, i.e. an ordered f.c.c. structure. The lattice misfit between these structures is very small and renders the surface energy negligible (26), thus reducing coarsening. The NBSAs have virtually reached their temperature limit for operation in turbine engines, which is \( \sim 1100^\circ C \). 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 \( \sim 1300^\circ C \).

Pt has been selected as the base material for these alloys because of its similarity to Ni in f.c.c. structure and its similar chemistry. Thus, similar phases to Ni3Al could be used to give similar mechanisms as found in the NBSAs. The important differences are the higher melting point (1769°C for Pt compared to 1455°C for Ni) and improved corrosion resistance. These facts inspired the proposal by Wolff and Hill that Pt-based analogues to Ni superalloys could be developed to serve in the most critical and demanding of high-temperature applications (27), especially given that work in Japan at NRIM (now NIMS) gave good properties for Ir- and Rh-based alloys (28–33). Although Pt-based alloys are unlikely to replace all NBSAs on account of both higher price and higher density, it is likely that they can be used for the highest application temperature components.

The reason why Pt3Al was not chosen at the outset as the basis for the strengthening precipitate is that it has at least two forms: a high temperature cubic form which is identical to Ni3Al, and at least one (34), if not two (35), lower temperature non-cubic forms. To be useful in service over a range of temperatures, the more desirable high-temperature L12 form needs to be stabilised, and transformations to the lower temperature form(s) stopped. The third and lowest temperature form (35) has yet to be fully confirmed, although work at Mintek and NIMS has found a transformation at the identified temperature.

**Mechanical Properties of the Ternary Alloys**

At the outset, it was decided that two commercial alloys would be used as comparators for the experimental alloys. They were MAR-M247 and PM2000. The first was selected as a NBSA, and therefore a representative of the alloys which the experimental alloys might replace. The second alloy is ferrous-based and is a mechanically alloyed oxide dispersion material; it was chosen as a comparator because of its advanced microstructure and high-temperature applications.

In the first investigations at Mintek and the University of the Witwatersrand (36–40), ternary Pt-X-Z compositions (where X is a component for strengthening precipitates, and Z is for solid solution strengthening and perhaps chemical resistance) were selected to yield two-phase microstructures consisting of f.c.c. (Pt) matrix and ordered f.c.c. (L12) Pt3X precipitates. The compositions were selected by studying the binary phase diagrams (41), and choosing alloys that could have ordered f.c.c. (cubic L12) phases. Potential systems identified in this way were: Pt-Al-Ni; Pt-Al-Re; Pt-Al-Ru; Pt-Nb-Ru; Pt-Ta-Re; Pt-Ta-Ru; Pt-Ti-Re; and Pt-Ti-Ru. Alloys were made by arc melting pressed powder components. Test specimens were prepared either by hot rolling or by machining. Depending on the specific requirement, the buttons at this stage varied between \( \sim 2 \) g and \( \sim 50 \) g. The alloys were characterised and hardness tests were done.
Large losses of niobium showed that the alloy was insufficiently stable, and the lath-like second phase Nb indicated that it was incoherent with the matrix. It was realised that rhenium additions must be limited to ~3 at.% in order to avoid precipitation of the Re-rich needle-like phase. Two-phase microstructures, leading to a considerable precipitation-strengthening effect, were achieved in Pt-Al-Z and Pt-Ti-Z systems (38), where Z = Ni, Re and Ru. Alloys in these systems showed promising mechanical properties at room temperature, with hardness values higher than 400 HV₁ and high resistance to crack initiation and propagation.

Extensive work was done on the phase relations and room temperature mechanical properties of Pt-Al-Z alloys, with Z = Cr, Mo, Ni, Re, Ru, Ta, Ti and W, after annealing the alloys at 1350°C for 96 hours (42). Microstructures similar to Ni- and cobalt-based superalloys were achieved in the Pt-based alloy Pt₈₆:Al₁₀:Z₄ (at.%), consisting of cuboidal ~Pt₃Al precipitates in a (Pt) matrix. It was found that ternary alloying elements, and in particular Cr and Ru, conferred additional benefits. More extensive work was carried out on the phase relations, and Cr was found to stabilise the cubic form of the ~ Pt₃Al phase, whereas Ru acted as a solid solution strengtheners (42–44). However, the 2 at.% Ru amount did not stabilise the high-temperature L₁₂ form of Pt₃Al. The lowest misfit between the (Pt) and ~Pt₃Al phases was found at between 3–5 at.% Ru and over 20 at.% Al (8). The tungsten-containing alloys also contained the lower temperature form of Pt₃Al, as did Ni-containing alloys. Coarse microstructures were produced in molybdenum-containing alloys and Mo substituted for Pt in Pt₈₆:Al₁₀:Z₄. All the Cr-, Ta- and Ti-containing alloys had favourable microstructures, and stabilised the favourable L₁₂ form of ~Pt₃Al.

The next stage (45–47) was to study the effects of various ternary substitutional alloying additions on the high-temperature compressive strengths of Pt-Al-Z alloys (where Z = Cr, Re, Ru, Ta and Ti). It was found that the Pt-Al-Z alloys had higher strengths above 1150°C than the commercial NBSA 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 and Pt:Al:Z ratios 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.

An investigation was therefore carried out on the effects of alloying additions on the creep properties of Pt-Al-Z alloys at 1300°C (48). The ternary elements (Z = Cr, Ir, Ru, Ta and Ti) were selected to improve the high-temperature mechanical properties and phase stability of the alloys, in accordance with the earlier findings (44–47). The Pt:Al:Z ratios of the alloys tested were standardised to eliminate the effects of differing Al contents. The properties of the Pt-Al-Z alloys were once again compared to those of PM2000. Figure 1 shows the stress-rupture curves of all the alloys tested. PM2000 had the highest strength of the alloys tested, but the shallow slope of the stress-rupture curve indicated high stress sensitivity and brittle creep behaviour. In practice, this means that PM2000 structures are more likely to fail in the presence of stress concentrations or short overloads during usage. The Pt₈₆:Al₁₀:Cr₄ alloy possessed the highest strength of the investigated Pt-based alloys.

Figure 2 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 experienced substantial tertiary creep leading to fracture strain values between 10% and 50% 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% (Figure 2).

Stress rupture curves of PM2000 and the most promising Pt-based alloy, Pt₈₆:Al₁₀:Cr₄, are shown in Figure 3, together with 10 hour stress-rupture strength values at 1300°C of several conventional solid-solution strengthened Pt-based alloys (49), as well as those of pure Pt and zirconia grain stabilised (ZGS) platinum, an oxide dispersion strengthened Pt alloy from Johnson Matthey.
Noble Metals (50). Strengthening was achieved by precipitation of $\gamma'$ particles, and gave considerably increased stress-rupture strength, $R_m/10 \, h/1300^\circ C$ (where m denotes maximum), by a factor of 8 from 2.2 MPa for the pure Pt matrix to 17 MPa for Pt$_{86}$Al$_{10}$Cr$_4$. The strength of the Pt$_{86}$Al$_{10}$Cr$_4$ alloy was also higher than the solution strengthened Pt-based alloys, Pt-10 wt.% Rh and Pt-20 wt.% Rh. Alloysing 30 wt.% Rh is necessary to reach the strength of the alloy Pt$_{86}$Al$_{10}$Cr$_4$, and the exceptionally volatile price of Rh and enormous machining problems limit the practical use of Pt-30 wt.% Rh. The creep strengths of the Pt-based alloys at 1300$^\circ$C were higher than those of the Ni- and Co-based superalloys, whose precipitates dissolve in this high-temperature regime, resulting in loss of strength. The creep strength of the Pt$_{86}$Al$_{10}$Cr$_4$ system is comparable to mechanically alloyed ferritic oxide dispersion strengthened alloys.

**Oxidation of the Ternary Alloys**

Although some alloys with potential for high-temperature applications had already been identified (40), more information was needed on the high-temperature properties, since they are of critical importance. Additionally, the oxidation resistance was ascertained by a stepped thermogravimetric regime in a Setaram TG-DTA 92.
analyser, with halts of 10,000 s at 900°C, 1100°C, 1300°C and 1400°C. There was internal grain boundary oxidation in the Pt-Ti-Ru alloys, and extensive internal oxidation in the Pt-Nb-Ru and Pt-Ta-Re alloys. 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 (38), therefore further work focused on Pt-Al-Z alloys only.

The high-temperature oxidation behaviour of Pt-Al-Z alloys (Z = Cr, Ir, Re, Ru, Ta and Ti) was studied (51, 52) by isothermal oxidation tests at 1200°C, 1280°C and 1350°C for at least 1000 hours. Figure 4 shows the increase in the thickness of the continuous layers with time for the different alloys tested. PM2000, a dispersion strengthened alloy, was used as a benchmark, and is iron-chromium-aluminium with a fine dispersion of yttrium oxide (Y₂O₃) particles in a ferritic matrix. The Pt₈₆:Al₁₀:Ti₄ and Pt₈₆:Al₁₀:Ru₄ alloys showed similar parabolic oxidation behaviour to the benchmark. The Pt₈₆:Al₁₀:Ir₄ and Pt₈₆:Al₁₀:Cr₄ alloys showed parabolic behaviour during the early stages of oxi-

![Fig. 4 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 1000 hours (52)](image-url)

![Fig. 3 Stress-rupture curves at 1300°C of PM2000, Pt, ZGS platinum and Pt₆₈:Al₁₀:Cr₄ compared with stress-rupture strength values, Rm/10 h/1300°C, of some conventional solid-solution strengthened Pt-based alloys (48)](image-url)
dation (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.

After a transient period, during which discontinuous alumina particles precipitated in a Pt matrix (Figure 5(a)), an external alumina film formed. This is formed because oxygen diffused through the scale more quickly than Al diffused in the alloy. Only when a critical volume of oxides was reached, did transition from internal oxidation to external scale formation occur (53). The continuous film appeared to provide protection for the alloy, since no internal oxidation occurred during long-term exposure (Figure 5(a)). However, the alloys were still outperformed by the PM2000 which formed a perfectly continuous oxide layer (Figure 5(b)). Further work was required in order to accelerate the formation of the continuous layer of the Pt-based alloys. It was deduced that this could be achieved by increasing the Al content.

Conclusions

A survey was undertaken on binary alloys which showed potential to give an f.c.c. solid solution (γ) and L1₂ (γ’) analogous to the NBSAs. Unsurprisingly, the Pt-Al system was identified as the most suitable base in terms of microstructure, mechanical properties and promising oxidation resistance. Experimental studies were done on Pt-Al-Z alloys (where Z = Cr, Ir, Mo, Ni, Re, Ru, Ta, Ti or W). Ultimately, the best alloys were Pt-Al-Cr and Pt-Al-Ru.

Part II of the present series will appear in a future issue of *Platinum Metals Review*.

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The Authors

Lesley Cornish is a Professor at the University of the Witwatersrand, South Africa, and is Director of the DST/NRF Centre of Excellence for Strong Materials, which is hosted by the University of the Witwatersrand. Her research interests include phase diagrams, platinum alloys and intermetallic compounds.

Rainer Süss is a Chief Engineer in the Physical Metallurgy Group in the Advanced Metals Division at Mintek, as well as the co-ordinator of the Strong Metallic Alloys Focus Area in the DST/NRF Centre of Excellence for Strong Materials. His research interests include phase diagrams, platinum alloys and jewellery alloys.

Alistair Douglas is currently Product Manager for FEI Electron Microscopes at Apollo Scientific, South Africa. He is responsible for sales and training of customers of high level electron microscopes. His research experience includes the study of platinum alloys for high-temperature use.

Lesley Chown is a Principal Engineer in the Physical Metallurgy Group in the Advanced Metals Division at Mintek. She has worked on continuously cast steels, platinum alloys and titanium alloys.

Lizelle Glaner is a Principal Technician in the Advanced Materials Division at Mintek, where she is in charge of the Nano Characterisation Laboratory. She has worked on gold catalysts, gold jewellery alloys and platinum alloys.

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