Introduction

This is the second paper of a series of four on the work undertaken under the auspices of the Platinum Development Initiative (PDI), which was in operation from April 1997 until October 2007, comprising Anglo Platinum, Impala Platinum, Lonmin (previously Lonrho) and Mintek. The aim was to encourage new research into Pt-based alloys which would eventually lead to an increased use of Pt (1). Earlier reviews have already been published on the development of the thermodynamic database used to calculate phase diagrams, phases and...
phase proportions (2–4). It had been found that the addition of ternary alloying elements, and in particular chromium and ruthenium, was beneficial. 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 strengthener (5–7).

An extensive transmission electron microscopy (TEM) investigation was undertaken in order to try to understand the differences between the precipitates in the different alloys. Since the Pt-based alloys had been conceived as analogues of the nickel-based superalloys (NBSAs), the same terminology can be used here as for the NBSAs. Thus, the Pt-rich solid solution, (Pt), is γ and the ~Pt₃Al precipitates are γ'.

The reason why Pt₃Al was not chosen at the outset as the basis of the strengthening precipitate for the development of Pt-based alloys for high-temperature applications in aggressive environments is that it has at least two forms: a high-temperature cubic form which is identical to Ni₃Al, and at least one (8), if not two (9), 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 (9) has yet to be fully confirmed, although work at Mintek has found a transformation at the identified temperature (10). Thus, there are two conflicting phase diagrams regarding the transformation temperatures of γ', Pt₃Al. According to McAlister and Kahan (8), there is a transformation of the high-temperature Pt₃Al phase from L₁₂ to a tetragonal low-temperature variant (designated D₀₋₁) at ~ 1280°C. However, Oya et al. (9) report an additional transformation at a lower temperature. The transformation temperatures given by Oya et al. are γ' → γ₁ at ~ 340°C and γ₁ → γ₂ at 127°C (9).

Structure of Low-Temperature Pt₃Al in the Binary Alloys

It was necessary to ascertain the lower temperature structures of the Pt₃Al phases in a representative binary alloy before deriving the strengthening effects in the ternary alloys. As for all the alloys described here (11–19), the samples were made originally by arc-melting, then annealed for 96 h at 1350°C, before deformation to 0.2% proof stress, and then 3 mm diameter cylinders were cut by spark erosion. The TEM samples were sectioned as discs of 1 mm thickness, mechanically lapped to 100 μm and dimpled to 30 μm. Low angle (4°) argon ion milling was carried out at room temperature, using an acceleration voltage of 4 kV before perforation on a Gatan Inc 691 Precision Ion Polishing System (PIPS™) ion mill.

The atomic structure of the tetragonal (D₀₋₁) phase of Pt₃Al was constructed by using the atomic positions determined by Bronger et al. (20) for the space group P4/mmm. The unit cells were constructed using the JEMS software package from P. A. Stadelmann, CIME-EPFL, Lausanne, Switzerland, which was also used to simulate the diffraction patterns. The unit cell construction was repeated using the MacTempas software package from Total Resolution LLC, Berkeley, U.S.A., which gave the same results, and high resolution images were also simulated.

Figure 1 is a bright-field TEM image of a typical Pt₃Al precipitate in the Pt₈₆:Al₁₄ (at.%.) alloy, containing a number of stacked plates or laths (P)

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Fig. 1 Bright-field TEM image of a Pt₃Al precipitate in a Pt₈₆:Al₁₄ (at.%.) alloy (19). P = stacked plates or laths; M = (Pt) solid solution matrix. The arrows indicate individual platelets inside the plate of stacked platelets in the region below.
characteristic of alloys in which a martensitic transformation has occurred, in a (Pt) solid solution matrix (M). Electron diffraction analysis of the stacked plates revealed that they were in twin orientation to each other. The [001] directions (or c-axes) of the tetragonal D0’c unit cells are perpendicular to one another in adjacent plates, and the twin plane is \{112\}. These [001] directions were parallel to the <100> type directions in the cubic matrix, consistent with Khachaturyan and Shatalov (21). Comparison of the experimental primary spots in the [110] selected area diffraction (SAD) with the simulated D0’c diffraction pattern revealed some differences. There were no experimental <001> and <003>, reflections, and there were extra experimental spots with reciprocal lattice vectors \(\pm 1/3 [002]\) and \(\pm 2/3 [002]\). The reflections at \(\pm 1/3 [002]\) indicated that the precipitate phase had a tetragonal unit cell with a c-axis 1½ times that of the D0’c unit cell.

Various modelling attempts were tried for the D0’c structure, and only one modification was successful. The atomic configuration of the D0’c structure is shown in Figure 2(a), and a modified tetragonal Pt3Al unit cell, with the c-axis equal to 1½ times that of the D0’c structure, is shown in Figure 2(b). The modified unit cell was constructed by repeating half of the D0’c structure, as shown in the dashed rectangles in Figure 2. The modified unit cell produced excellent agreement with both experimental and calculated electron diffraction patterns, and also with simulated high resolution (HR) TEM lattice images of the Pt3Al precipitates.

### Ternary Alloys

After studying the high-temperature compressive strengths of Pt-Al-Z alloys (where Z = chromium, iridium, ruthenium, tantalum or titanium) (1, 11, 22, 23), reasons for the different strengths were sought, and TEM was used to study the precipitate structures of the various alloys at the different testing temperatures. The samples had only a small amount of deformation (11). The precipitates showed at least a bimodal distribution, which could even be interpreted as a trimodal distribution (Figure 3(a)) (24). The elements Cr, Ta and Ti partitioned to \(\sim\) Pt3Al and stabilised the cubic L12 structure, giving precipitates of cuboid appearance with no discernable inner structure (Figure 3(a)). Conversely, Ir and Ru partitioned to the matrix, and the precipitates transformed to the D0’c structure (Figure 3(b)), with alternating contrast bands. These are acknowledged as being due to the twinning of the stacked plates and the modified D0’c structure (19), although the transformation had already been recognised as displacive (8, 9).

The lattice misfits between the matrix and precipitate phases were also measured at room temperature and at 800°C by X-ray diffraction (XRD) on a JEOL JDX-3500 diffractometer, with a copper source (11). The (220) peak was used to derive the (Pt) lattice parameters, (12) was used for tetragonal D0’c \(\sim\) Pt3Al, and (211) was used for cubic L12 \(\sim\) Pt3Al. Lattice misfits, \(\delta\), were then calculated from these measurements, using Equation (1) (25):

\[
\delta = 2 \left( \frac{a_{\text{ppt}} - a_{\text{matrix}}}{a_{\text{ppt}} + a_{\text{matrix}}} \right)
\]

**Fig. 2** (a) Unit cell of the D0’c structure of a typical Pt3Al precipitate in a Pt86-Al14 (at.%) alloy, B = [110]; (b) Unit cell of the modified tetragonal D0’c structure of a Pt3Al precipitate, B = [110] (19)
where \( a_{\text{ppt}} \) denotes the lattice parameter for the \( \sim \text{Pt}_3\text{Al} \) precipitate phase and \( a_{\text{matrix}} \) denotes the lattice parameter for the (Pt) matrix phase. The results are presented in Table I. There was little difference between the misfits at different temperatures, and they were all negative. With the exception of the Ru alloy, all the other alloys showed an increased misfit at the higher temperature. The misfits were lower for the \( \text{L1}_2 \) phases (Cr, Ta and Ti alloys) than for the lower temperature \( \text{D0}'_\text{c} \) structure (Ir and Ru alloys).

### Precipitates and Dislocation Interactions

Since the interaction of dislocations with the precipitates determines the mechanical properties, it was decided to study these interactions using TEM, and to compare the different effects of the ternary addition on the \( \sim \text{Pt}_3\text{Al} \) precipitates. Different alloying additions are known to stabilise the high-temperature form: Cr, Ta, Ti (11, 26) and cobalt, hafnium, iron, manganese and zirconium (26, 27). Compression samples had been used before (11, 22, 23), and new samples were made from these to study the dislocation content and precipitation characteristics. The samples had been compressed at different temperatures (21ºC, 800ºC, 1000ºC and 1300ºC) for Pt86:Al10:Z4 (at.%) alloys where \( Z = \text{Cr}, \text{Ir}, \text{Ru}, \text{Ta} \) and \( \text{Ti} \) (18). Lattice parameters of the (Pt) matrix phase in Pt-Al-Z (\( Z = \text{Cr}, \text{Ru} \) and \( \text{Ti} \)) alloys were derived from selected area electron diffraction (SAED), and all the patterns were <112>-zone type. The results were slightly different from those of Hill et al. (11); this was attributed to calibration differences in the microscope’s camera. Unlike NBSAs which have

![Fig. 3 Typical TEM images of the \( \sim \text{Pt}_3\text{Al} \) precipitates in Pt-Al-Z alloys (\( Z = \text{Cr}, \text{Ir}, \text{Ru}, \text{Ta} \) or \( \text{Ti} \)), with letters indicating the different size ranges (where \( P = \text{primary}; I, T = \text{intermediate}; S = \text{secondary} \)): (a) \( \text{L1}_2 \) precipitates stabilised by Cr, Ta and Ti additions. The inset shows the selected area diffraction (SAD) pattern, confirming the \( \text{L1}_2 \) structure; (b) \( \text{D0}'_\text{c} \) precipitates stabilised by Ir and Ru additions (24).](image-url)
precipitates with \{100\} interfaces, the interfaces of the Pt-based alloys were not necessarily \{100\}, and this made the dislocations more complex, as did the different lower temperature structure. However, the dislocations were analysed to have a Burgers vector of \(\pm \frac{1}{2}<110>\), similar to those found for NBSAs.

**Platinum-Aluminium-Chromium**

The precipitates in the Pt-Al-Cr system were not cuboidal, but octahedral in shape. The density of small precipitates decreased with increasing compression temperature, while the dislocation density in the matrix increased, but the changes were not large in either. There were paired dislocations in all the large precipitates, and these were interpreted to be misfit dislocations because there were different types of dislocations at different parts of the precipitate, and networks around the edges. With increasing temperature, the structure of the dislocation system remained the same, and no other slip systems were activated.

**Platinum-Aluminium-Iridium**

The morphology of the precipitates in the Pt-Al-Ir alloys was different from those of the samples with Cr, Ta or Ti, as shown in Figure 4 (24). They were ‘ogdoadically-diced’ (28) (often described as cruciform or Maltese Cross-shaped), consisting of eight interconnected lobes (four in cross-section). At room temperature, there were no dislocations associated with the precipitates, although some matrix dislocations appeared to extend to the precipitate/matrix interface. After compression at 800°C, the precipitate edges straightened (although the corners were still rounded) and the first dislocations appeared in the precipitate. Isolated dislocations traversed the matrix. At 1100°C, the precipitates had become more spherical, with twin bands and multiple twinning. The dislocations associated with the large precipitates were in pairs. At 1300°C, the precipitates were more irregular, with a high dislocation density associated with all twin bands.

**Platinum-Aluminium-Ruthenium**

The precipitates in the Pt-Al-Ru alloys appeared similar to those in the Pt-Al-Ir sample, and showed twinned regions, confirming that there was a displacive transformation and a tetragonal structure. Their edges were curved, showing low surface energy for their boundaries, but were more regular at higher compression temperatures. The twin bands were better developed at higher temperatures, with dislocations observed in alternating twin bands. Once again, the dislocations occurred in pairs, indicative of dissociated dislocations.

**Platinum-Aluminium-Tantalum**

The precipitates in the Pt-Al-Ta system 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. After compression at 800°C, irregular precipitates with no dislocations were observed, while the matrix had a high dislocation density and small cubic precipitates. 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. Considering the dislocations, the Ta alloy was the strongest, but earlier work (29, 30) had showed that its oxidation resistance was insufficient for high-temperature and special applications.
Platinum-Aluminium-Titanium

After compression at 20°C, the precipitates had well-defined and straight edges, with no dislocations, although the matrix had a high density of dislocation tangles. After compression at 800°C, there were still no dislocations within the precipitates, although the matrix dislocation density was lower. There was also a high density of smaller precipitates in the matrix, which could add to strengthening of the matrix. Only after compression was carried out at 1100°C were dislocations observed in the precipitates (Figure 5) (24). It is not certain whether these were misfit dislocations at the interfaces between the precipitates and the matrix, or dislocations which penetrated through the precipitates, but they shared the same Burgers vector as the dislocations in the other alloys. The low matrix dislocation density indicated significant recovery at elevated temperatures. At 1300°C, the precipitates were again void of dislocations, also due to recovery.

In Situ High-Temperature TEM

TEM studies of samples compressed at 0.2% proof stress at different temperatures (11, 22, 23) showed the differences between the conditions, and an opportunity arose to study samples in situ (31). This allowed the stability of the different PtAl phases to be studied, and the Al-Pt phase diagram to be verified, at least for the alloys used. McAlister and Kahan (8) give the L12 → D0′ transformation at ~1280°C, whereas Oya et al. (9) have two transformations: γ′ → γ′₁ at ~340°C and γ′₁ → γ′₂ at 127°C. Previous attempts to resolve this question by scanning electron microscopy (SEM), XRD and differential thermal analysis (DTA) have been unsuccessful. Therefore, in situ heating of the alloy in a transmission electron microscope was used in an attempt to find an answer. The alloys investigated were Pt₆₅:Al₁₅ (at.%) and Pt₆₅:Al₁₀:Ir₄, and the in situ study was undertaken using a heating stage up to 1100°C in a JEOL 4000EX transmission electron microscope. The heating rate used was 10°C min⁻¹, with 5°C min⁻¹ being used when more detailed changes were to be observed.

Bright-field TEM imaging as shown in Figure 6 (31) for the Pt₆₅:Al₁₅ (at.%) was used, with increasing temperature. At low temperature, the Pt₆₅Al precipitate was characterised by alternating twin bands, one with apparently no dislocations (black arrow) and the other with a high density of dislocations (white arrow). The number of dislocations decreased with increasing temperature (and time), which indicates that a transformation was occurring. The twin bands disappeared as atoms moved between the bands and as the crystal structure changed during the phase transformation, confirming that the transformation was displacive, and associated with dislocations. The transformation was also observed in diffraction mode as confirmation, since any changes in the crystal structure would also manifest in the γ′₁ diffraction patterns. The diffraction patterns were selected at temperatures close to the transformation temperatures of Oya et al. (9). In a diffraction pattern close to the <211> zone, there were extra spots in the fine structure, which is an indication of additional ordering in the crystal. Above 340°C, which is above the γ′₁ → γ′₂ transformation temperature of Oya et al. (9), the extra spots had almost completely disappeared, indicating a phase transformation. Thus, for the alloys used, this confirmed that the phase diagram of Oya et al. (9) for the Pt-Al system is more accurate than that of McAlister and Kahan (8). However, other workers using Pt from a different source achieved results...
which were in better agreement with a higher transformation temperature (32, 33). Thus, the transformation temperatures could be affected by minor impurities.

Since the strength of an alloy is partly dependent on the presence of small precipitates to act as a barrier to dislocation motion, the precipitates should persist at high temperatures to provide high-temperature strengthening. However, this did not occur in the Pt86:Al14 alloy. Figure 7 shows the same Pt3Al precipitate in bright-field TEM images (31). There is a high density of small precipitates (with the exception of one precipitate-free zone) in the matrix surrounding the large precipitate at 580°C (Figure 7(a)). At 810°C, the precipitates started to dissolve. Between 810°C and 870°C, precipitate dissolution became rapid, and most of the small precipitates had disappeared by 870°C (Figure 7(b)). All small precipitates had dissolved at 960°C. The loss of the small precipitates would be deleterious for strengthening at high temperatures, although the contributions of the different sized precipitates have not yet been ascertained. The large precipitate was noticeably smaller at 1170°C than at 1030°C, and the interfacial dislocation network had completely disappeared. However, the precipitates in the ternary alloy Pt86:Al10:Ir4 had better stability.

**Conclusions**

An in-depth TEM study was undertaken on selected binary and ternary (Pt) and ~Pt3Al alloys (roughly equivalent to the γ / γ’ nickel-based superalloys (NBSAs)) to ascertain how the ternary elements were substituting so that a greater understanding of the cubic L12 form of ~Pt3Al could be
gleaned. A modified form of the $\gamma'$ lower temperature Pt$_3$Al phase was identified by simulation and comparison with experimental data. The dislocations were studied and compared to those in NBSAs, mainly because of the presence of the lower temperature form of $\sim$ Pt$_3$Al ($\gamma'$) and the different misfits. In situ heating showed that for the binary alloy, the small precipitates disappeared at high temperatures, and the larger precipitates reduced in size. The ternary alloy Pt$_{86}$Al$_{10}$Ir$_4$ had more stable precipitates than the binary alloys.

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