An Overview: Platinum-Based Super-Alloys as Coating Material for Materials Operating in Extreme Environments

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MINTEK

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as at September 2014

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The Platinum Development Initiative (PDI) was officially started in April 1997 in South Africa, comprising SA companies such as Anglo Platinum, Impala Platinum, Lonmin and Mintek, with the aim to encourage new research into Pt-based alloys which would eventually lead to an increased use of Pt, by broadening the industrial base.

A range of platinum-based superalloys with promising properties were then developed by Mintek in collaboration with South African universities (mainly the University of the Witwatersrand (Wits)) under the PDI Program.

Due to the scarcity/lack of thermodynamic data-bases on this work, most of the work was heavily experimental

- Thermodynamic Database Development
Objectives

- Development of Pt-based alloys for high-temperature applications in aggressive environments
- Target use: in bulk and as coating
- Major elements: Pt, Al, Cr and Ru
- Microstructure improvement to the best possible of analogue Nickel-based superalloys (NBSA)
- First alloys (40 Vol. % of precipitates) vs 70 Vol.% for nickel-based superalloys
  - Lower precipitate volume means lower strength
Microstructure and Mechanical Properties

- Strengthening precipitates for nickel-based superalloys: dispersion of $\gamma'$-phase $[\text{Ni}_3(\text{Al, Ti, Nb})]$  
- Strengthening precipitates for platinum-based superalloys: $\text{Pt}_3\text{Al}$ [1-2]  
- Three structures of the $\text{Pt}_3\text{Al}$, the cubic high-temperature being the preferred one  
  - Stabilisation of the high-temperature by addition of Ti, Cr, and Ta [3]  
- Alloy type: $\text{Pt}-(11-14)\text{Al}-(3-6)\text{Cr}-(1-3)\text{Ru}$ (at.%)  
- Optimum composition around $\text{Pt}-11\text{Al}-3\text{Cr}-2\text{Ru}$ (at.%) on the basis of high volume of $\text{Pt}_3\text{Al}$ precipitates and increased hardness with an average size of 200 nm for the precipitates [Mintek]

<table>
<thead>
<tr>
<th>Alloy composition (at.%)</th>
<th>Mat./Strength. phase</th>
<th>Nano-hardness (GPa)</th>
<th>Elastic Modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-12Al-4Cr-2Ru</td>
<td>Pt/Pt$_3$Al</td>
<td>7.3 ± 0.6 /11.4±0.9</td>
<td>233.3 ± 21.8 /259.7 ±23.7</td>
</tr>
<tr>
<td>Pt-12Al-6Cr-5Ni-2Re</td>
<td>$\gamma / \gamma'$</td>
<td>7.5±0.3/11.5±0.3</td>
<td>282</td>
</tr>
<tr>
<td>CMSX-10 NBSAs</td>
<td>$\gamma / \gamma'$</td>
<td>7.2±0.2/7.5±0.1</td>
<td>231/255</td>
</tr>
</tbody>
</table>

SEM and TEM Micrograph

SEM micrographs in backscattered electron (BSE) mode:
(a) with primary $\sim \text{Pt}_3\text{Al}$ (dark contrast) in a fine mixture of (Pt) and $\sim \text{Pt}_3\text{Al}$;
(b) fine mixture of (Pt) and $\sim \text{Pt}_3\text{Al}$ [4]

Pt-11.5Al-4.5Cr-2.5Ru (at.%)  Pt-11Al-3Cr-2Ru (at.%)

TEM micrograph for nominal Pt-12Al-4Cr-2Ru (at.%) showing $\sim\text{Pt}_3\text{Al}$ (marked A) with channels of (Pt) matrix [5]

Mechanical Properties

Vickers Hardness of the Two-Phase quaternary Alloys, using a 10 kg Load, after Annealing at 1350°C [6]

<table>
<thead>
<tr>
<th>Alloy Composition</th>
<th>Hardness after first anneal, HV$_{10}$</th>
<th>Hardness after first anneal, HV$_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt$<em>{85}$:Al$</em>{11}$:Cr$_2$:Ru$_2$</td>
<td>430 ± 5</td>
<td>403 ± 20</td>
</tr>
<tr>
<td>Pt$<em>{84}$:Al$</em>{11.5}$:Cr$_{2.5}$:Ru$_2$</td>
<td>425 ± 21</td>
<td>403 ± 14</td>
</tr>
<tr>
<td>Pt$<em>{83}$:Al$</em>{11}$:Cr$<em>{3.5}$:Ru$</em>{2.5}$</td>
<td>421 ± 12</td>
<td>405 ± 8</td>
</tr>
<tr>
<td>Pt$<em>{80.5}$:Al$</em>{1.25}$:Cr$<em>{4.5}$:Ru$</em>{2.5}$</td>
<td>419 ± 22</td>
<td>414 ± 9</td>
</tr>
<tr>
<td>Pt$<em>{81.5}$:Al$</em>{11.5}$:Cr$<em>{4.5}$:Ru$</em>{2.5}$</td>
<td>423 ± 10</td>
<td>396 ± 6</td>
</tr>
<tr>
<td>Pt$<em>{79.5}$:Al$</em>{10.5}$:Cr$<em>{5.5}$:Ru$</em>{4.5}$</td>
<td>417 ± 8</td>
<td>415 ± 10</td>
</tr>
</tbody>
</table>

Tensile testing results for Platinum-Aluminium derived ternary and quaternary alloys at room temperature [7]

<table>
<thead>
<tr>
<th>Alloy composition, (at. %)</th>
<th>Hardness after first anneal, HV$_{10}$</th>
<th>Maximum ultimate strength achieved MPa</th>
<th>Elongation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt$<em>{86}$:Al$</em>{10}$:Cr$_4$</td>
<td>317 ± 13</td>
<td>836</td>
<td>~4</td>
</tr>
<tr>
<td>Pt$<em>{86}$:Al$</em>{10}$:Ru$_4$</td>
<td>278 ± 14</td>
<td>814</td>
<td>~9</td>
</tr>
<tr>
<td>Pt$<em>{84}$:Al$</em>{11}$:Cr$_3$:Ru$_2$</td>
<td>430 ± 5</td>
<td>722</td>
<td>~1</td>
</tr>
</tbody>
</table>

Microstructure and Mechanical Properties

Tensile testing results for Platinum-Aluminium derived ternary and quaternary alloys at room temperature

<table>
<thead>
<tr>
<th>Alloy or Metal</th>
<th>Hardness range</th>
<th>Ultimate strength at room temperature, MPa</th>
<th>Elongation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-based alloys [8]</td>
<td>300–400</td>
<td>~ 800</td>
<td>-</td>
</tr>
<tr>
<td>Pure Pt [9]</td>
<td>~ 40</td>
<td>~140</td>
<td>-</td>
</tr>
<tr>
<td>Ferritic ODS alloy PM2000 [10]</td>
<td>-</td>
<td>720</td>
<td>14</td>
</tr>
<tr>
<td>γ-TiAl [11]</td>
<td>-</td>
<td>950</td>
<td>~1</td>
</tr>
<tr>
<td>CMSX-4 [12]</td>
<td>-</td>
<td>870</td>
<td>-</td>
</tr>
</tbody>
</table>

9. The PGM Database, Platinum: [link](http://www.platinummetalsreview.com/jmpgm/index.jsp)
High-Temperature Oxidation Behaviour - In Air

- Good alumina scale-forming capabilities of the Pt-Al-Cr and Pt-Al-Ru ternary alloys between 1150°C and 1350°C
- A continuous $\alpha$-$\text{Al}_2\text{O}_3$ scale with no zone of discontinuous oxide or any internal oxidation was formed on Pt-14Al-3Cr-2Ru (at.%) isothermally oxidized in air at 1350°C up to 500 hours
- Parabolic formation of alumina scale on a Pt-12Al-6Cr-5Ni (at.%) alloy when isothermally oxidized in air at temperature between 1100°C and 1300°C for up to 400 hours

Specific mass gain for water-quenched and air-cooled Pt-11Al-3Cr-2Ru (at.%) specimens after isothermal oxidation in air at 1350°C

SEM-BSE images of cross sections of Pt-11Al-3Cr-2Ru (at.%) specimens after 100 h oxidation in air at 1350°C (a) water-quenched (b) air-cooled


Pre-alloyed platinum sintered compact (left) and NBSA (right) specimens before and after oxidation test (After 10 cycles of 1 hour at 950°C in Na₂SO₄)

Alloy Development

High-temperature **Corrosion** Behaviour (in Na$_2$SO$_4$)

Nominal Chemical Compositions of Selected Platinum-Based Superalloys and Nickel-Based Superalloys Together with Their Corrosion Kinetics after Treatment in Na$_2$SO$_4$ at 950°C for 564 Hours [18]

<table>
<thead>
<tr>
<th>Alloy name</th>
<th>Nominal composition, at%</th>
<th>Cumulative weight gain during corrosion, mg cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RS-1</td>
<td>Pt$<em>{86}$:Al$</em>{10}$:Cr$_4$</td>
<td>0.00004</td>
</tr>
<tr>
<td>RS-2</td>
<td>Pt$<em>{86}$:Al$</em>{10}$:Ru$_4$</td>
<td>0.00008</td>
</tr>
<tr>
<td>RS-3</td>
<td>Pt$<em>{84}$:Al$</em>{11}$:Cr$_3$:Ru$_2$</td>
<td>0.0001</td>
</tr>
<tr>
<td>P420</td>
<td>Pt$<em>{79}$:Al$</em>{15}$:Co$_6$</td>
<td>0.0001</td>
</tr>
<tr>
<td>P421</td>
<td>Pt$<em>{73}$:Al$</em>{15}$:Co$_{12}$</td>
<td>0.004</td>
</tr>
<tr>
<td>CMSX-4 (uncoated)</td>
<td>Ni$<em>{66.5}$:Cr$</em>{6.5}$:Co$<em>{11}$:Mo$</em>{0.3}$:W$<em>{1.7}$:Ta$</em>{1.8}$:Al$<em>{11.3}$:Ti$</em>{0.9}$</td>
<td>0.470</td>
</tr>
<tr>
<td>CMSX-4 (coated)</td>
<td>Ni$<em>{66.5}$:Cr$</em>{6.5}$:Co$<em>{11}$:Mo$</em>{0.3}$:W$<em>{1.7}$:Ta$</em>{1.8}$:Al$<em>{11.3}$:Ti$</em>{0.9}$</td>
<td>0.038</td>
</tr>
</tbody>
</table>

Objectives:
- Reduce the cost by taking out some of the Pt (Pt loading reduction)
- Reduce the density (Pt quite heavy/dense)

Facts:
- Solubility of V in Pt at 20 at.% V at 700°C to 7 at.% V at 1720°C (Ref 51)
- Potential for solid solution strengthening and melting temperature increase
- No reported data for Pt-Al-V
- Study of ternary phase diagram Pt-Al-V to define the compositions of developmental alloys in the Pt-Al-Cr-Ru-V system
- 9 alloys of the Pt-Al-V system investigated

Conclusions:
Typical microstructure components
- $\approx$Pt$_3$Al dendrites
- $\approx$Pt$_5$Al$_3$ needles
- A thin $\approx$Pt$_3$V layer on the dendrites
- A complex eutectic-like microstructure consisting of $\approx$PtAl + Pt$_5$Al$_3$ + $\approx$Pt$_5$Al$_3$
- With increasing V content: $\approx$V$_{27}$Pt$_{54}$Al$_{19}$ dendrites
- This ternary phase only appears at V contents higher than 17 at.%.

Alloying with Vanadium

As-cast Alloy 13, Pt-9Al-38V (at.%), showing dark ~PtV dendrites, in a sparse~V₃₇Pt₅₄Al₁₉ (light) + ~PtV (dark) eutectic, and porosity (black)

Pt-rich side of the Pt-Al-V phase diagram showing that the maximum V addition is around 15 at.%

SEM-BSE image of as-cast Alloy Pt-23Al-25V (at.%), showing light ~V₂₇Pt₅₄Al₁₉ dendrites, thin dark ~PtV and porosity (black)
Target alloy: Pt-11Al-3Cr-2Ru (at.%)

Via Mechanical Alloying route:

Microstructure of sintered pre-alloyed platinum compact (Sintered for 5 hours at 1450°C)
Powder Production

- Water atomisation
- Gas atomisation
- Mechanical alloying

Gas atomiser

Water atomiser

Retsch PM 100 milling machine
Powder Production

Plasma Technology

- Particle spherodisation
- Particle densification
- Coatings
- Nano particle production
Conclusions

- There is a huge potential of replacing the nickel-based superalloys (NBSAs) by the platinum-based alloys (PBAs) where temperatures higher than the current limit are needed.

- The microstructure of Platinum-based alloys (PBA: Pt, Al, Cr, Ru) consists of a platinum matrix and ~ Pt$_3$Al precipitates, which is roughly equivalent to the γ / γ′ nickel-based superalloys (NBSAs).

- Mechanical properties are very close to the Nickel-based Superalloys (NBSA).

- The PBAs have a potential of high operating temperatures than the NBSAs.

- The PBAs have better high-temperature oxidation and corrosion properties than the NBSAs.

- Alloying the PBAs with Vanadium (up to 15 at.% ) can increase the melting point and decrease the cost of the alloy while keeping the fundamental properties of the alloy.

- An optimum composition of the PBAs is around Pt-11Al-3Cr-2Ru (at.%).

- Pt-11Al-3Cr-2Ru (at.%) can be produced via powder metallurgy (mechanical alloying or atomisation).
Acknowledgements
Thank You
www.mintek.co.za