Physical Properties and Application Performance of Platinum-Palladium-Rhodium Alloys Modified with Cerium

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The physical properties and some application performance parameters of a platinum-palladium-rhodium-cerium alloy (Pt-4Pd-3.5Rh-0.1Ce) (wt%) are reported. This alloy possesses finer grain size, higher recrystallisation temperature and better mechanical properties, including tensile strength, lasting strength and creep resistance, than traditional Pt-10Rh and Pt-4Pd-3.5Rh catalytic alloys. Catalytic gauzes made of the Pt-4Pd-3.5Rh-0.1Ce alloy also show a higher conversion rate of ammonia to oxides of nitrogen, lower Pt loss rate, improved resistance to corrosion, adhesion and poisoning, and longer service lifetime for nitric acid production than gauzes made of the traditional alloys.

1. Introduction
Nitric acid (HNO₃) is produced by ammonia (NH₃) oxidation through catalytic gauzes under pressures of 0.1–0.9 MPa and temperatures of 800–900°C. Pure Pt was originally selected as the catalyst due to its high catalytic activity and chemical stability (1). The operating life of catalytic gauzes strongly depends on the mechanical properties and grain size stability of the material from which they are made. The performance, lifetime and efficiency of gauzes used in the process of NH₃ oxidation are also determined by the rate of inactive surface growth which impedes the flow of gases through the gauzes, the methods used to process the alloys into wires and gauzes, the structural stability of the alloys and the stability of parameters of the NH₃ oxidation process (2, 3).

In order to improve the mechanical properties of Pt catalytic gauzes, Pt-Rh alloys with various Rh contents in the range 5–20 wt% Rh were developed. In the 1940s DuPont patented a Pt-Rh alloy containing 92.5–93% Pt and 7.0–7.5% Rh (4). In the 1950s the former USSR developed a Pt-4Pd-3.5Rh alloy catalyst by partial substitution of Pd for Rh in the formulation (5). After 25 years, another new catalyst alloy, consisting of 81% Pt, 15% Pd, 3.5% Rh and 0.5% Ru, was developed (5). Currently, Pt-Rh and Pt-Pd-Rh alloys are the
main catalyst materials used for production of HNO₃ through NH₃ oxidation.

Attempts have been made to improve the properties of these alloys by further modifications. A Pt-10Rh alloy modified with boron was found to have lower grain growth and similar catalytic properties to a ‘classical’ Pt-10Rh alloy. Its application in the nitric industry would enable the temperature of NH₃ oxidation to be increased, with subsequent improvements in process efficiency, while significantly reducing the emission of harmful nitrous oxide (N₂O) to the atmosphere and maintaining the operating lifetime of the gauzes (6). Iridium, zirconium, vanadium and rhenium may also be added to modify the alloy. The properties of Pt-5Rh-1Ir-0.1Zr, Pt-5Rh-1Ir-0.01V and Pt-5Rh-1Re alloys were found to be similar to those of Pt-10Rh (7, 8).

Research on the strengthening effect of rare earth (RE) metals on Pt and its alloys was performed at Kunming Institute of Precious Metals (KIPM) in China (9–11). As a result of this work, new Pt-Pd-Rh-RE catalytic alloys, containing 0–15 wt% Pd, 0–10 wt% Rh, 0–1.0 wt% single or mixed RE and the balance Pt, were developed and patented by KIPM (12). The present paper reviews the main properties of Pt-Pd-Rh catalytic alloys modified by Ce additions and their application in the production of HNO₃ in China.

2. Microstructure of the Alloys

In order to compare the Pt-10Rh binary alloy (‘PR-1’) and the Pt-4Pd-3.5Rh ternary alloy (‘PR-2’) with the Pt-4Pd-3.5Rh-0.1Ce quaternary alloy (‘PR-3’), a parallel study was carried out (13). X-Ray diffraction (XRD) patterns indicated that the three alloys are single solid solution structures (14). The microstructures of the PR-2 and PR-3 alloys annealed at 900ºC for 30 min are shown in Figure 1. It can be seen that the PR-3 alloy (Figure 1(b)) has a much finer grain size than the PR-2 alloy (Figure 1(a)). The recrystallisation softening curves of the PR-2 and PR-3 alloys are shown in Figure 2, indicating that the recrystallisation temperature of the PR-3 alloy is about 120ºC higher than that of the PR-2 alloy.

3. Physical Properties of the Alloys

3.1 Mechanical Properties

The mechanical properties of the three alloys after annealing at 900ºC for 1 h and after annealing continuously at 1000ºC at a rate of about 20 m min⁻¹ are indicated in Table I. Mechanical tests were carried out at room temperature. The tensile strength (σₜ) of the PR-3 alloy was significantly higher than that of the PR-1 and PR-2 alloys under both sets of annealing conditions. The tensile elongation (δ) in 100 mm of the PR-3 alloy was similar to those of the PR-1 and PR-2 alloys (13).

The tensile strengths, stress-rupture curves and creep rupture times of the PR-1, PR-2 and PR-3 alloys at high temperature are shown in Figures 3–5. The tensile strength of the PR-3 alloy was higher than those of the PR-1 and PR-2 alloys even at high temperatures. The tensile strength of the PR-3 alloy at 1100ºC was similar to that of the PR-1 alloy and about 40% higher than that of the PR-2 alloy (see Figure 3), the lasting strength (defined as the stress to produce failure at a specified time and temperature) of the PR-3 alloy at 900ºC for 100 h was 1.7 times higher than that of the PR-1 alloy and about 3.5 times higher than that of the PR-2 alloy, respectively, and creep-rupture...
time of the PR-3 alloy was longer than those of both the PR-1 and PR-2 alloys (see Figure 4). The creep-rupture time of the PR-3 alloy at 900°C with a stress of 40 MPa was over 3 times longer than that of the PR-1 alloy and 10 times longer than that of the PR-2 alloy (see Figure 5).

3.2 Oxidation and Volatilisation of the Alloys

The volatilisation losses caused by oxidation of the three alloys during isothermal heating at 900°C in pure flowing oxygen were studied (15). The relationship between the weight loss per unit area (ΔW/S) and the heating time (t) shown in Figure 6 can be approximately expressed as in Equation (i):

$$\Delta W/S = K_1 t^{2/3}$$  (i)

Here $K_1$ is the weight loss rate constant for the alloy samples. The difference in $K_1$ is due to the effects of the Rh, Pd and RE components in the alloys on the formation rate of platinum oxide (PtO$_2$), as determined by Rubel et al. (16, 17). It can be seen from Figure 6 that the PR-3 alloy had the smallest $K_1$ value of the three alloys studied.

4. Performance of the Platinum Alloy Catalytic Gauzes

Parallel industrial experiments for HNO$_3$ production were carried out (18). Catalytic gauzes made from the PR-2 and PR-3 alloys were tested in an atmospheric pressure reactor, with an operating pressure of 0.1 MPa and temperatures of 820–840°C. Catalytic gauzes made from the PR-1, PR-2 and PR-3 alloys were tested in a medium pressure reactor, at an operating pressure of 0.5 MPa and temperatures of 860–880°C. The conversion rate of NH$_3$ to oxides of nitrogen, the weight loss rate of Pt and other parameters were determined in the same HNO$_3$ production plant.

4.1 Oxidation and Volatilisation of the Catalytic Gauzes

The rates of Pt loss from catalytic gauzes made from each of the three alloys were determined during parallel industrial experiments over a period of two years in an atmospheric pressure reactor (18). The relationship between the parameter $\psi$ ($\psi = \Delta W/W \times t$), which is the sum of the relative Pt loss per day for the PR-2 and PR-3 alloy gauzes, and the running time (t) is shown in Figure 7. It can be approximately written as Equation (ii):

$$\psi = K_2 t^{2/3}$$  (ii)

Here $K_2$ is the platinum loss rate constant for the Pt alloy catalytic gauzes. $K_2$ was $3.35 \times 10^{-4}$ $d^{-1}$ for the PR-2 alloy gauze and $2.95 \times 10^{-2}$ $d^{-1}$ for the PR-3 alloy gauze over the period studied. The Pt loss rate con-

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Table I

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition</th>
<th>Tensile strength, $\sigma_b$, MPa</th>
<th>Tensile elongation, $\delta$, %</th>
<th>Tensile strength, $\sigma_b$, MPa</th>
<th>Tensile elongation, $\delta$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PR-1</td>
<td>Pt-10Rh</td>
<td>260</td>
<td>16</td>
<td>350</td>
<td>12–16</td>
</tr>
<tr>
<td>PR-2</td>
<td>Pt-4Pd-3.5Rh</td>
<td>240</td>
<td>16</td>
<td>380</td>
<td>7–12</td>
</tr>
<tr>
<td>PR-3</td>
<td>Pt-4Pd-3.5Rh-0.1Ce</td>
<td>360</td>
<td>18</td>
<td>420</td>
<td>16–18</td>
</tr>
</tbody>
</table>

$^a$Temperature = 1000°C; rate = 20 m min$^{-1}$

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Fig. 3. Tensile strengths of the PR-1, PR-2 and PR-3 alloys at various temperatures
stant of the PR-3 alloy gauze was 25% lower than that of the PR-2 alloy gauze.

It should be noted that Equation (ii) has the same form as Equation (i) because the same mechanism of Pt loss applies.

4.2 Conversion Rate of Ammonia to Oxides of Nitrogen

The mechanism of NH₃ oxidation over Pt, Pd and Rh wires has been reported (19). The overall reaction pathways to N₂O, nitrogen monoxide and nitrogen are equivalent on each of the three platinum group metals. NO is a primary reaction product, while N₂ and N₂O originate from consecutive NO transformations. The extent of the secondary reactions determines the net NO selectivity. Rh is the most active catalyst for the unwanted reduction of NO by NH₃, while Pt shows the lowest activity. This explains the superior NO selectivity attained over Pt. NO selectivity approaching 100% at complete NH₃ conversion can be equivalently attained over Pt, Pd and Rh by increasing the oxygen content in the feed. For a feed of O₂/NH₃ = 10, both N₂O and N₂ production are suppressed due to the impeded NO dissociation and favoured NO desorption at high O₂ coverage.

The conversion rate of NH₃ to oxides of nitrogen is one of the main performance indexes for catalytic gauzes. In an atmospheric pressure reactor, an NH₃ conversion rate of 96% or above is required for optimal operating efficiency. The average NH₃ conversion rate for the PR-2 alloy gauze in an atmospheric pressure reactor over a period of two years was 97%, and for the PR-3 alloy gauze it was 98.5%. In a medium pressure reactor, the NH₃ conversion rate for the PR-2 alloy gauze was about 1.0–1.5% higher than that of the PR-1 alloy gauze. This was attributed to the contribution of the Pd component (4). The NH₃ conversion rate for the PR-3 alloy gauze was about 1.0–2.0% higher than those of the PR-1 or PR-2 alloy.
gauzes. These results suggest that the addition of Ce to Pt-Pd-Rh alloys can further increase the conversion rate of NH₃ to oxides of nitrogen.

The catalytic activity of Pt alloys is related to the O₂ adsorptivity of Pt. High-resolution electron energy loss spectroscopy (HREELS) revealed two characteristic peaks at 700 cm⁻¹ and 870 cm⁻¹ due to O₂ adsorbed on Pt (111) at 92 K. This suggests that molecular oxygen may be attached on the surface of the Pt atoms. At higher temperatures, a dissociatively adsorbed O atom has a loss peak at 470 cm⁻¹, which may be assigned to a Pt-O stretching vibrational mode (4). This mode may promote the formation of active compounds and speed the NH₃ oxidation reaction. Pd metal has intrinsic catalytic activity for the NH₃ oxidation reaction, and the Pd component in the Pt alloy can also help to reduce PtO₂ to Pt and to prevent the formation of rhodium(III) oxide (Rh₂O₃) (20). Therefore adding or increasing the content of Pd in a Pt-Rh or Pt-Pd-Rh alloy would be expected to increase the NH₃ conversion rate.

The unfilled 4f electron shells of RE metals, especially elements such as cerium, lanthanum and praseodymium which have a variable valence, may be responsible for their catalytic activity. Under the conditions of the NH₃ oxidation reaction, Ce metal is oxidised to CeO₂ or Ce₂O₃ in a reversible oxidation-reduction reaction, Equation (iii):

\[ 2\text{CeO}_2 \rightarrow \text{Ce}_2\text{O}_3 + 1/2\text{O}_2 \]  

The Ce component has a large oxygen storage capacity. If the alloy has a Pd component, CeO₂ may be reduced and attached to Pd crystal surfaces (11). This can increase the oxygen storage capacity of the Pd lattice, and new active sites for NH₃ oxidation may be formed at the lattice interfaces between Pd atoms. This may explain the high NH₃ conversion rate of 98.5% observed for the PR-3 alloy catalyst in the atmospheric pressure reactor.

### 4.3 Platinum-Loss Rate of the Platinum Alloy Gauzes

During production of HNO₃, Pt is lost from catalytic gauzes, mainly due to PtO₂ volatilisation. The Pt loss rate can be measured as the weight loss of the catalytic gauze per tonne HNO₃ produced, and directly affects the production cost of HNO₃. The Pt loss rates for catalytic gauzes made from each of the three alloys were determined. The Pt loss rates for the PR-2 and PR-3 alloy gauzes running for 337 days in atmospheric pressure reactors are listed in Table II. The total Pt loss from the PR-3 alloy gauze was 861 g, and the Pt loss rate was 0.043 g Pt per tonne HNO₃. This was about 28% lower than that of the PR-2 alloy gauze.

It should be noted that these results may contain errors due to ignoring the increased weight of CeO₂. It is difficult to measure the CeO₂ weight increase, and as the alloy contains less than 0.1 wt% Ce evenly distributed throughout the alloy, only the small amount of Ce at the surface would become oxidised. Therefore this weight increase was ignored.

### 4.4 Corrosion Resistance of the Platinum Alloy Gauzes

The smooth surfaces of the original gauzes gradually became roughened during operation. It has been suggested that between 286°C and 374°C, adsorbate-enhanced surface diffusion of Pt can cause surface restructuring, well below the temperatures reported for significant Pt transport through the gas phase via volatile PtOₓ (21). Pt atoms, or rather PtO₂ particles, evaporating from a wire surface can lead to catalytic NH₃ oxidation taking place close to, but not at, the

### Table II

The Platinum Loss and Platinum Loss Rate of the PR-2 and PR-3 Alloy Gauzes in the Industrial Atmospheric Pressure Reactors

<table>
<thead>
<tr>
<th>Alloy gauze</th>
<th>Amount of Pt loss, g</th>
<th>Pt loss rate, g Pt⁻¹ HNO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>PR-2</td>
<td>1192</td>
<td>0.060</td>
</tr>
<tr>
<td>PR-3</td>
<td>861</td>
<td>0.043</td>
</tr>
</tbody>
</table>
gauze wire surface itself. Pt is then deposited on catalyst or catchment gauzes, forming deposits known as ‘Brussels sprouts’ or ‘cauliflowers’. These deposits have little catalytic activity. The Pt deposits on catalyst and catchment gauzes have a dense structure, with crystal-oriented flat subgrain walls (22, 23).

During the NH\textsubscript{3} oxidation process, each sheet of catalytic gauze becomes etched along the grain boundaries and defects of the alloys. A large number of corrosive pits, etching facets and cauliflower-like structures appear on the surfaces, causing surface structural reconstruction (24). The surface morphology of the PR-2 and PR-3 alloy catalytic gauzes after 6 months’ service in parallel atmospheric pressure reactors is shown in Figure 8. Cauliflower-like structures can be seen in the PR-2 alloy gauzes (Figure 8(a)); however, the PR-3 alloy gauzes (Figure 8(b)) do not show these cauliflower-like structures. It may be concluded that the PR-3 alloy gauzes showed less etching and therefore better corrosion resistance than the PR-2 alloy gauzes.

In addition, the PR-3 alloy gauzes showed higher resistance to adhesion and poisoning than the PR-2 alloy gauzes during service. The service lifetime of the PR-3 alloy gauzes was found to be about 1.5 to 2 times as long as those of the PR-1 and PR-2 alloy gauzes in atmospheric and medium pressure reactors (13). At 0.1 MPa, the service lifetime was 12 months for the PR-1 and PR-2 alloy gauzes, and 18 months for the PR-3 alloy gauze. At 0.5 MPa the service lifetimes were 3 months for the PR-2 alloy gauze and 6 months for the PR-3 alloy gauze.

5. Conclusions
The Pt-4Pd-3.5Rh-0.1Ce alloy has a finer grain size in both the as-cast and annealed form, higher recrystallisation temperature, greater tensile and lasting strengths, longer creep-rupture time at high temperature, and lower weight-loss rate constants than the traditional binary Pt-10Rh alloy and ternary Pt-4Pd-3.5Rh alloy. Catalytic gauzes manufactured from the quaternary Pt-4Pd-3.5Rh-0.1Ce alloy demonstrate a higher conversion rate for the oxidation of NH\textsubscript{3} to oxides of nitrogen, a lower Pt loss rate, better resistance to corrosion, adhesion and poisoning, and longer service life for the production of HNO\textsubscript{3} in industrial atmospheric and medium pressure reactors.

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Fig. 8. Surface of: (a) PR-2 alloy and (b) PR-3 alloy catalyst gauzes after 6 months’ service in parallel atmospheric pressure reactors (magnification × 200)
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Professor Yuan Tao Ning is a Professor of Physical Metallurgy at Kunming Institute of Precious Metals in China. His main research interests are related to principles of alloying and new materials based on precious metals, particularly platinum group metals and their alloys, including those modified by the rare earth metals. He has published around 200 papers in national and international periodicals and won national prizes for his scientific achievements.

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Professor Qingnan Shi is the Director of Educational Administration at Kunming University of Science and Technology in China. He has carried out important studies on nanomaterials by severe plastic deformation, mainly copper-, aluminium- and titanium-based alloys. He advises several research groups on topics including platinum-based superalloys, alloys for high-temperature applications and materials analysis.

Chaoguang Jia is a Senior Engineer at Kunming Metallurgy College in China. He has been engaged in editing, proofing and publishing of the Journal of Kunming Metallurgy College, and in collecting information on the platinum group metals.